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Study of Vaporization Enthalpies and Vapor Pressures of Potential Environmental Pollutants by Correlation-Gas Chromatography

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Study of Vaporization Enthalpies and Vapor Pressures of Potential Environmental Pollutants by Correlation-Gas Chromatography

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Abstract

The focus of this dissertation is on the measurement and analysis of thermodynamic data, including vaporization, fusion, and sublimation enthalpies and vapor pressures of dialkyl phthalates, as well as aliphatic and aromatic primary and tertiary amines by correlation gas chromatography (CGC). These compounds are important industrial and pharmaceutical substances whose prolonged use and sometimes misuse with regards to their disposal has created an environmental concern. Thermodynamic properties, such as vaporization enthalpy and vapor pressure provide crucial information to numerous industries and fields of study that include the chemical and petrochemical industry, chemical engineering and environmental science.

Dialkyl phthalates are essential industrial products, with various commercial applications including their use as plasticizers in plastics used for packaging of consumer products, medical applications and waste disposal, as well as for applications in cosmetics. This work establishes a set of reasonably self-consistent experimental values for thermodynamic properties in an area that has been characterized by numerous inconsistent values over the years.

Many aliphatic and aromatic primary and tertiary amines are pharmaceutical compounds, often prescribed as ammonium salts for solubility reasons. This can lead to the production of the neutral parent species when unused portions are discarded in the environment. Widespread use of these materials has raised concerns over the environmental impact of improperly discarded medications. Prior to this work, the thermodynamic properties of many of the materials investigated in this study were simply unavailable.

Variants of some gas chromatographic methods have recently come under criticism and an additional focus of this thesis was to evaluate the limitations of the technique we employed for these measurements. Comparisons to other related methods were made in an effort to evaluate both the strengths and weaknesses of the current technique, correlation gas chromatography. During the course of these studies, some significant advances in the understanding of the applicability and versatility of this method have been achieved.

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Introduction

Thermodynamic properties, such as vaporization enthalpy and vapor pressure, are crucial to various significant fields of study, including the petrochemical industry and chemical and environmental engineering. Vaporization enthalpies provide important information about the magnitude of intermolecular forces and by inference, intramolecular forces. The interactions responsible for these enthalpies are normally weaker than chemical bonds. However, they are comparable to those forces responsible for the self-assembly that occurs in everything from biological systems to liquid crystals.[1] Vapor pressure measurements allow researchers the ability to determine the volatility of chemicals. This data is critical for environmental scientists, as the evaluation of the transport, distribution and fate of chemicals is highly dependent on their volatility and is of great importance.[2]

Thermodynamic data is extremely helpful to chemical engineers for the design of distillation columns, especially in terms of fractional distillation.[3] The risk of violent gas kickbacks during petroleum recovery is better predicted with the aid of critical thermodynamic data and is of vast significance to the petroleum industry.[4] The pharmaceutical industry is finding more and more use of thermodynamic models during different periods of process development and optimization procedures.[5] These are just some cases of the significance of this data to the industrial sector, but the influence of these properties are also evident in the environment.

Thermodynamic properties determine the atmospheric concentration of a compound. As has already been seen by the transport and deposit of pesticides in the polar ice caps, the volatility of certain compounds can lead to their dispersal into environments throughout the world. This buildup of chemicals can lead to the bioaccumulation of toxic substances in a species when the pollutant is released from the ice cap, or from another source of pollution. The pollutant is then biomagnified, as it moves from species to species along the food chain, until the toxin is consumed by human beings.[6] There is an increasing need to evaluate the impact of the many compounds in use and this requires thermochemical data. This need has been accompanied by an increase in environmental regulations throughout the world. Environmental engineers and chemists use this data to evaluate the dispersal rate of a chemical spill in the environment and to determine the best possible route for mitigation.[2] As has been shown, there are a variety of ways that thermodynamic data is used by researchers, but first these properties must be made available.

Numerous methods have been developed throughout the years to evaluate thermodynamic properties, including both direct and indirect methods. The methods that directly measure the vapor pressure of a compound or another parameter to which it is related, such as the gas saturation and effusion methods are referred to as direct methods. Indirect methods usually employ some form of chromatography and several variants have been developed. These include isothermal retention time gas chromatography, temperature gradient gas chromatography, and correlation gas chromatography. All require the use of standards with known thermodynamic properties for the determination of unknown compounds.

Some of the commonly used direct methods for measurement of vapor pressure and vaporization enthalpy analysis include:

1. Manometric Methods – These methods directly measure the pressure resulting from the vapor in equilibrium with the sample in liquid or solid phase. In a simple apparatus, the sample is sealed in a thermostated cell under vacuum and the pressure is measured with an appropriate device, such as a Pirani gauge, mercury manometer, thermocouple gauge, etc.[2]
2. Ebulliometry (Boiling Point Method) – Data is evaluated with the use of an ebulliometer, a device which is designed to correctly measure liquid boiling points by measuring the temperature of the vapor-liquid equilibrium. Saturated vapor pressure is analyzed at the boiling temperature.[2]
3. Effusion Methods – These methods measure the mass loss of a compound at constant temperature through a small orifice into a vacuum. The mass loss over a corresponding time is then used mathematically, along with area of the orifice, to determine the vapor pressure of compound.[2]
4. Gas Saturation (Transpiration Method) – Gas saturation is based on the production of a saturated vapor phase by passing an inert gas through a thermostated column packed with the powdered compound of interest. The setup employs a saturator containing the compound of interest under controlled temperature. Inert gas is then passed through the saturator at an adequately low enough rate to allow the equilibrium pressure of the substance to be maintained. The vaporized substance is then collected, weighed and determined using Dalton’s Law and the ideal gas law.[2]
5. Thermogravimetric Analysis (TGA) – TGA measures the rate of mass loss of a sample in a controlled atmosphere as a function of temperature or time as the temperature gradient increases at a consistent rate. Its basic setup requires a precision

pan loaded balance and a programmable furnace. The furnace can then be programmed to either heat at a constant rate or heat to obtain a constant mass loss over time.[7]

The direct methods are useful; however, more sample is required than when using an indirect method and the compound must also be pure for the analysis to be conducted.[8]

Indirect Methods

1. Relative Volatilization Rate – These methods measure the relative loss rates of different chemicals to obtain vapor pressure data provided that the vapor pressure of one of the compounds is known. An example of this technique is one which originates from the principle that, for compounds insoluble in water, the vapor pressure of the immiscible substance is largely unaffected by the addition of water. The vapor pressure of the compound can then be determined from the amount of water and compound volatilized after distillation.[2]
2. Chromatographic Methods – Gas chromatography is a common type of chromatography used for separating and analyzing compounds that can vaporize without decomposing. It employs the concept that the residence time of a sample on a column is inversely proportional to that compound's vapor pressure off the column.[9]

   The indirect methods are valuable due to the relative speed of the experiments, the small amount of sample required and their ability to analyze impure materials.[9]

As correlation gas chromatography (CGC) is the technique used by our laboratory, some of the most common gas chromatographic methods will be further discussed.

One of these methods, the gas chromatographic-retention time (GC-RT) method, was originally described by Hamilton.[10] While this technique has produced dependable data in many instances, this has not always been the situation.[11,12] Several adaptations of this method have been experimentally evaluated by Koutek et al.,[11] and Letcher and Naicker[13] have examined the theory. Letcher and Naicker found that the main sources of error associated with the GC-RT method were possible adsorption effects with the use of polar solutes and the lack of information regarding the values of the activity coefficients. If suitable reference compounds are chosen and one is careful that adsorption does not occur, errors in experimental vapor pressures could be as low as 10%.[13]

This method involves plotting $\ln[(t_r)_{tar}/(t_r)_{std}\ ]_T$ against $\ln(p_{std,,T})$ at different temperatures T, where $(t_r)_{tar}$ and $(\Delta_l{}^gH_m)_{tar}$ represent the relative retention time and vaporization enthalpy of the compound(s) of interest, respectively. The corresponding standard values are $(t_r)_{std}$ and $(\Delta_l{}^gH_m)_{std}$. The plot has been found to result in a linear relationship that can be described as follows:

$$\ln[(t_r)_{tar}/(t_r)_{std}]_T = [1-(\Delta_l{}^gH_m)_{tar}/(\Delta_l{}^gH_m)_{std}]\ln(p_{std,T}) - \mathrm{C} \qquad \text{(I-1)}$$

The resulting slope and intercept are characterized by $[1 - (\Delta_l{}^gH)_{tar}/(\Delta_l{}^gH)_{std}]$ and $-\mathrm{C}$. The vapor pressure of the compound(s) of interest at $T = 298.15$ K can then be extracted from:

$$\ln(p_{tar,298.15K}/\mathrm{Pa}) = [(\Delta_l{}^gH_m)_{tar}/(\Delta_l{}^gH_m)_{std}]\ln(p_{std,298.15K}/\mathrm{Pa}) + \mathrm{C} \qquad \text{(I-2)}$$

The vaporization enthalpy can also be calculated using the slope of the line and the vaporization enthalpy of the standard.[10]

Another method is the temperature gradient gas chromatography method and is one of the adaptations of the Hamilton technique. In this method the compound(s) of interest are analyzed, along with two or more standards with known vapor pressures, over a chosen temperature range using a temperature gradient. The experimentally observed retention times and the known vapor pressures of the standards are then used to determine the vapor pressures of the unknowns. While this method does allow for the analysis of larger compounds, it usually involves the use of only two standards with various functional groups to make these calculations.[8]

Correlation gas chromatography (CGC), the technique employed by our laboratory, is quick and can be a dependable method for analyzing vapor pressures and vaporization enthalpies given that appropriate standards with reliable thermodynamic data are chosen. The difficulty regarding activity coefficients is overcome by using standards containing the same functionality as the targets. The structure of the hydrocarbon portion of the molecule is apparently only of secondary importance and apparently does not appear to play an important role.

Three or more standard compounds with known thermodynamic properties are used. This approach has shown to be viable in numerous studies conducted in our laboratory.[14-23] In order to verify this approach, we also performed experiments using standard compounds with dissimilar functional groups to the target compound(s) and analyzed the data using both the CGC and GC-RT methods.[24] These results are discussed below.

The applicability of CGC is based on the following concepts. The residence time of each analyte on the column is measured by including a substance that passes directly through the column without being adsorbed and is referred to as the non-retained reference, t_{nr}. At the temperatures of most experiments this is frequently the solvent. The retention time of this analyte measures the time necessary to traverse the column. The adjusted retention time of each analyte, t_a, which measures the residence time of the analyte on the column, is equal to the retention time of the solute, t, minus the retention time of the non-retained reference.

$$t_a = t - t_{nr}. \qquad \text{(I-3)}$$

A key component to the GC methods is that the adjusted retention time, t_a, is inversely proportional to the given compound's vapor pressure above the condensed phase.

The experimental procedure for CGC is as follows. A small amount of the target compound(s) is combined with the standards whose vaporization enthalpies bracket the target compound(s) and then approximately 1 mL of a non-retained solvent such as methylene chloride, hexanes or methanol is added to the mixture. If the experiment is conducted at lower temperatures and the solvent is retained, methane can be bubbled into the solution and serve as the non-retained reference. After the solution is prepared, the mixture is injected into a gas chromatograph and the experiments are conducted in duplicate runs over a T/K = 30 temperature range at approximately T/K = 5 increments. The column temperature is maintained to T/K = 0.1 K between the two runs and helium is used as the carrier gas with a split ratio of approximately 100/1. The temperature of the column is maintained by the spectrometer, but is also monitored independently. The thermodynamic values of the unknowns can then be determined provided that the compounds are separated by chromatographic means.[9]

The vaporization enthalpy is calculated based on the adjusted retention time of the standards and the compound(s) of interest. A plot of $\ln(t_o/t_a)$ vs. $1/(T/\text{K})$, where t_o = 1 min, results in a straight line that gives the enthalpy of transfer from the column to gas phase, $\Delta_{sln}{}^{g}H_m$, for each compound when the slope of the line is multiplied by the gas constant, -

R. The enthalpy of transfer is related to the vaporization enthalpy, $\Delta_{l}{}^{g}H_{m}$, by eq I-4 where $\Delta_{intr}H_{m}$ (T_{m}) refers to the enthalpy of interaction of the analyte with the stationary phase of the column.[14]

$$\Delta_{sln}{}^{g}H_{m}\ (T_{m}) = \Delta_{l}{}^{g}H_{m}(T_{m}) + \Delta_{intr}H_{m}\ (T_{m}) \qquad \text{(I-4)}$$

With properly chosen standards, a second plot of $\Delta_{sln}{}^{g}H_{m}$ vs. the vaporization enthalpies of the standards from the literature, $\Delta_{l}{}^{g}H_{m}$(lit), results in a straight line giving an equation that is used to determine the vaporization enthalpy of the unknown.

It is frequently useful to have a rough idea of the vaporization enthalpy. Vaporization enthalpies have been estimated by the following equation:

$$\Delta_{l}{}^{g}H(298\ \text{K})/\ \text{kJ}\cdot\text{mol}^{-1} = 4.69(\text{n}_{\text{C}} - \text{n}_{\text{Q}}) + 1.3\cdot\text{n}_{\text{Q}} + \text{n}_{\text{i}}\Sigma\text{F}_{\text{i}}\cdot\text{b}_{\text{i}} + 3.0 + \text{C} \qquad \text{(I-5)}$$

where n_{C} represents the number of carbon atoms, n_{Q} represents the number of sp^{3} hybridized quaternary carbons and b stands for the contribution of the given functional group.[17] The additional terms vary depending on structure and are discussed below in more detail depending on the compounds being evaluated.

The adjusted retention time, t_{a}, can also be used to determine the unknown vapor pressures by plotting $\ln(t_{o}/t_{a})$ vs. the known literature vapor pressures in the form, $\ln(p/p_{o})$, resulting in a straight line whose parameters result in an equation used to determine the vapor pressure of the unknown.[9]

The fusion enthalpy must be measured for compounds that are solid at room temperature. This is because the vaporization enthalpy measured by gas chromatography is actually that of the sub-cooled liquid, so the fusion enthalpy must be measured to obtain the sublimation enthalpy of the compound. These three thermodynamic phenomena are related by the following equation, provided they have been adjusted to the same temperature, T:

$$\Delta_{cr}{}^{g}H(T) = \Delta_{l}{}^{g}H_{m}(T) + \Delta_{cr}{}^{l}H(T) \qquad \text{(I-6)}$$

Where $\Delta_{cr}{}^{g}H(T)$ is the sublimation enthalpy, $\Delta_{l}{}^{g}H_{m}(T)$ is the vaporization enthalpy and $\Delta_{cr}{}^{l}H(T)$ is the fusion enthalpy.

As previously stated, thermodynamic values must be adjusted to similar temperatures in order for their association to be allowed. Adjustment of the vaporization enthalpy to ambient temperature, T/K=298.15, is achieved using equation I-7:

$$\Delta_{l}{}^{g}H_{m}(298.15\text{ K})/(\text{kJ}\cdot\text{mol}^{-1}) =$$

$$\Delta_{l}{}^{g}H_{m}(T_{m}) + [(10.58 + 0.26\cdot C_{p}(\text{l})/(\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}))(T_{m}/\text{K} - 298.15\text{ K})]/1000 \qquad \text{(I-7)}$$

The term $\Delta_{l}{}^{g}H_{m}(T_{m})$ in this equation is representative of the vaporization enthalpy at the mean temperature of measurement, T_{m}, and $C_{p}(\text{l})$ represents the liquid heat capacity at T/K=298.15.[17]

Adjustment of the sublimation enthalpy to ambient temperature, T/K=298.15, is achieved using the equation:

$$\Delta_{cr}{}^{g}H_{m}(298.15\text{ K})/(\text{kJ}\cdot\text{mol}^{-1}) = \Delta_{cr}{}^{g}H_{m}(T_{m})/(\text{kJ}\cdot\text{mol}^{-1}) +$$

$$[(0.75 + 0.15\cdot C_{p}(\text{cr})/(\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}))(T_{m}/\text{K} - 298.15)]/1000 \qquad \text{(I-8)}$$

The term $\Delta_{cr}{}^{g}H_{m}(T_{m})$ in this equation is representative of the sublimation enthalpy at the mean temperature of measurement and $C_{p}(\text{cr})$ represents the heat capacity of the solid at T/K=298.15.[17]

Adjustment of the fusion enthalpy to ambient temperature, T/K=298.15, is achieved using the equation:

$$\Delta_{cr}{}^{l}H_{m}(298.15\text{ K})/(\text{kJ}\cdot\text{mol}^{-1}) = \Delta_{cr}{}^{l}H_{m}(T_{fus}) +$$

$$[(0.15C_p(\mathrm{cr}) - 0.26\cdot C_p(\mathrm{l})/(\mathrm{J\cdot mol^{-1}\cdot K^{-1}}) - 9.83)]\ [T_{\mathrm{fus}}/\mathrm{K} - 298.15\ \mathrm{K}]/1000 \qquad \text{(I-9)}$$

The term $\Delta_{\mathrm{cr}}{}^{\mathrm{l}}H_{\mathrm{m}}(T_{\mathrm{m}})$ in this equation is representative of the fusion enthalpy at the mean temperature of measurement.[17] These types of calculations are the manner in which final results are determined in our laboratory.

Correlation gas chromatography is a useful technique for evaluating the thermodynamic data of organic compounds, but it also has advantages compared to other methods. Experiments conducted by CGC are fast, taking just a few hours. It allows for small sample sizes since only a few milligrams are needed for analysis. This method also has the ability to examine impure materials since the thermodynamic properties are indirectly measured, unlike the direct methods.[9]

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Part 1: Dialkyl Phthalates

Chapter 1. Vapor Pressures and Vaporization Enthalpies of a Series of Dialkyl Phthalates by Correlation Gas Chromatography

1.1. Introduction

Dialkyl phthalates and their associated isomers are essential industrial products and many have been produced in sizeable quantities for a significant amount of time. Their significance ranges from their use as plasticizers in polymers to cosmetic applications.[1] These compounds are widespread in the environment due to their chemical properties and extensive usage. Throughout the years thermodynamic properties of some of these compounds have been frequently studied. Di-*n*-butyl phthalate and *bis* (2-ethylhexyl) phthalate were selected as reference compounds for vapor pressure measurements by the US EPA.[2]

The work herein determines the vapor pressures and vaporization enthalpies of a series of liquid dialkyl benzenedicarboxylates and the fusion, sublimation and vaporization enthalpies of three corresponding solids. This work aims to establish a set of self-consistent experimental values for thermodynamic data in an area that has been characterized by various inconsistent values[3,4] through the combination of recent experimental values from literature with results from correlation gas chromatography and transpiration measurements. A potential contributor to this inconsistency is the frequent use of the term octyl in reference to both 2-ethylhexyl as well as to the *n*-octyl group by suppliers and in the literature. The compounds investigated include dimethyl phthalate dimethyl terephthalate, dimethyl isophthalate, diethyl phthalate, di-*n*-butyl phthalate, benzyl butyl phthalate, dicyclohexyl phthalate, *bis* (2-ethylhexyl) phthalate, *bis* (2-

ethylhexyl) terephthalate and di-*n*-octyl phthalate. The structures of the dialkyl benzenedicarboxylates studied are provided in Figure 1-1.

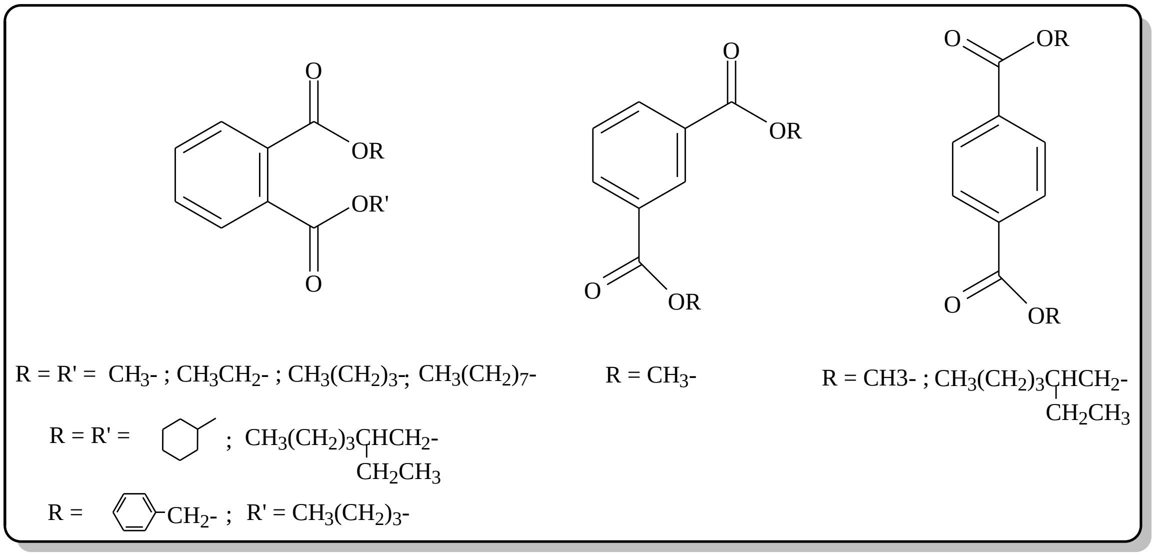

Figure 1-1. The structures of the dialkyl benzenedicarboxylates studied.

1.2. Experimental

1.2.1. Materials.

1.2.1.1. St. Louis. Analytical standards (0.99+ mass fraction) of dimethyl phthalate, diethyl phthalate, di-*n*-butyl phthalate, *bis* (2-ethylhexyl) phthalate and benzyl butyl phthalate were purchased as a mixture, 200 µg/mL in methanol (EPA 606-M Phthalate Ester Mix) from Supelco (48741). *bis* (2-Ethylhexyl) phthalate and *bis* (2-ethylhexyl) terephthalate were purchased as a mixture of two diasteriomers, a *meso* and *dl* pair. Individual samples of several of these materials were also purchased. These materials were used as purchased. Both the corresponding dioctyl phthalate and dioctyl terephthalate available from Sigma Aldrich correspond structurally to the *bis* (2-ethylhexyl) material. The structures were confirmed by ^{1}H NMR spectroscopy on a Bruker Avance 300 NMR Spectrometer.

1.2.1.2. Rostock. The liquid sample of di-*n*-butyl phthalate of 0.99 mass-fraction purity was purchased from Aldrich and further purified by repetitive distillation in vacuum. The degree of purity was determined by GC. No impurities (greater than mass fraction $3\cdot10^{-4}$) could be detected in the sample used for transpiration. Analysis was performed on a Hewlett Packard gas chromatograph 5890 Series II with a flame ionization detector. The dimensions of the capillary column HP-5 (stationary phase crosslinked 5% phenylmethyl silicone) were the following: the column length, inside diameter, and film thickness were 25 m, 0.32 mm and 0.25 μm, respectively.

1.2.2. Methods.

1.2.2.1. Transpiration Measurements (Rostock). Vapor pressures of di-*n*-butyl phthalate were measured by transpiration. Details of this method are provided in Appendix A. Additional details of these experiments are available elsewhere.[5,6] Table 1-1 reports results of the vapor pressure measurements.

TABLE 1-1. Vapor pressure of Di-*n*-butyl Phthalate by Transpiration

T/K [a]	m/mg [b]	V(N_2)/dm^3 [c]	Gas-flow dm^3 /h	p/Pa [d]	$u(p)$/% [e]
		Δ_l^gH(356 K)/kJ·mol^{-1} = (86.8 ± 0.4)[e]			
333.2	0.85	33.68	4.21	0.224	2.73
338.4	085	20.65	4.13	0.365	1.87
343.4	0.81	12.24	4.08	0.586	1.35
348.0	0.78	8.23	4.08	0.838	1.10
353.6	0.54	3.40	4.08	1.40	0.86
358.7	0.74	3.06	4.08	2.15	0.73
363.7	0.73	2.04	4.08	3.16	0.66
368.7	0.74	1.43	4.08	4.59	0.61
373.6	0.78	1.02	4.08	6.75	0.57
378.5	0.73	0.68	4.08	9.48	0.55

[a] Saturation temperature ($u(T)$ = 0.1 K). [b] Mass of transferred sample condensed at T = 243 K. [c] Volume of nitrogen ($u(V)$ = 0.005 dm^3) used to transfer m ($u(m)$ = 0.0001 g) of the sample. [d] Vapor pressure at temperature T, calculated from the m and the residual

vapour pressure at T = 243 K. [e]The uncertainty in the pressure measurements estimated by the expression u(p)) = 0.005(p/Pa) + 0.05 recommended in the ref. Ruzicka, K.; Fulem, M.; Ruzicka, V. Recommended vapor pressure of solid naphthalene. *J. Chem. Eng. Data* **2005**, *50*, 1956-1970.

The data was fit to eq 1-1 where the intercept (A' = (18.34 ± 0.13)) and slope (B' = (10444.6 ± 46.3)) were obtained by plotting $\ln(p/\ p_o)$ versus $1/T$ where p_o/Pa = 101325 and R is the gas constant, 8.314 $\mathrm{J{\cdot}mol^{-1}\ {\cdot}K^{-1}}$. The equation was characterized by a correlation coefficient of $r^2 = 0.9998$. The results are summarized in Table 1-2 discussed below. Additional details are included in Appendix A.

$$\ln(p/p_o) = A' - B'/RT \qquad (1\text{-}1)$$

TABLE 1-2. Literature Vaporization Enthalpies of Various Dialkyl Phthalates

	$\Delta_l^g H_m(T_m)$ $\mathrm{kJ{\cdot}mol^{-1}}$	T_m/K	Cp(l) $\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$	$\Delta C_p(l)\cdot\Delta T$ $\mathrm{kJ{\cdot}mol^{-1}}$	$\Delta_l^g H_m$(298.15 K) $\mathrm{kJ{\cdot}mol^{-1}}$	
					lit.	est (eq 1-6)
dimethyl phthalate[a]					77.0±1.2	73.8±5.9
diethyl phthalate[b]					82.1±0.5	77.5±6.2
di-*n*-butyl phthalate[c]					96.0±0.8	96.3±7.7
di-*n*-butyl phthalate[d]	86.8±0.4	356	505.4	8.2±1.7	95.0±1.7	
di-*n*-butyl phthalate[e]	89.2±0.1	333	505.4	4.9±1.0	94.1±1.0	
di-*n*-butyl phthalate[f]	83.6±0.2	452	505.4	21.8±4.5	105.4±4.5	
di-*n*-butyl phthalate[g]	89.1±0.3	303	505.4	0.7±0.1	89.8±0.3	
benzyl butyl phthalate[c]	89.0	466	531	24.9±2.7	113.9±2.7	108.4±8.7
benzyl butyl phthalate[h]	90.8	323	531	3.7±0.8	94.5±0.8	108.4±8.7
dicyclohexyl phthalate[c,i]	97.0	406	544.4	16.4±1.7	113.4±1.7	106±8.5[k]
bis (2-ethylhexyl) phthalate[g]	115.6±0.4	303	747.6	1.0±0.2	116.7±0.5	129.8±13.0
bis (2-ethylhexyl) phthalate[j]	113.2	333	747.6	7.1±1.4	120.3±1.4	
di-*n*-octyl phthalate[k]	107.5	408	760.6	22.9±4.5	130.4±4.5	133.8±13.0
di-*n*-octyl phthalate[c]	99.5	473	760.6	36.4±7.2	135.9±7.2	

[a]Ref 3. [b]Ref 4. [c]Ref 24. [d]This work. [e]Ref 18. [f]Ref 32. [g]Ref 2. [h]Ref 25. [i]Ref 26. [j]Ref *33*. [k]Ref 22.

1.2.2.2. Correlation Gas Chromatography (St. Louis). Correlation–gas chromatography experiments were conducted over a T/K = 30 temperature range at approximately T/K = 5 increments on an HP 5890 Gas Chromatograph running Chemstation and equipped with an FID detector using a Supelco 15 m x 0.32 mm SPB-5 capillary column (1.0 μm film thickness), helium as the carrier gas and a split ratio of approximately 100/1. A Vernier stainless steel temperature probe using a Go!Link USB interface running Logger Lite software was used to monitor the temperature that was maintained at ±0.1 K by the gas chromatography. At the temperature of the experiments, the solvent, either methanol or methylene chloride, was not retained by the column. The residence time of each analyte on the column, t_a, was calculated from its retention time and the retention time of the solvent by difference. Experimental retention times are provided in Appendix A. Plots of $\ln(t_o/t_a)$ versus $1/T$ of each analyte resulted in straight lines with correlation coefficients, $r^2 > 0.99$. The term t_o refers to the reference time, 60 s. The enthalpy of transfer of each analyte from the column to the gas phase, $\Delta H_{trn}(T_m)$, was calculated as the product of the slope of the line and the gas constant, - slope·R. The temperature T_m refers to the mean temperature of measurement. Results of a second plot of vaporization enthalpy, $\Delta_l{}^gH(298.15\text{ K})$ against $\Delta H_{trn}(T_m)$ are discussed below.

The slope of the line from plots of $\ln(t_o/t_a)$ versus $1/T$ measures the enthalpy of transfer from the condensed phase of the column to the gas phase, $\Delta H_{trn}(T_m)$ and is numerically equal to the sum of the vaporization enthalpy, $\Delta_l{}^gH(T_m)$, and the enthalpy of interaction (or solution) of the analyte with the stationary phase, $\Delta H_{intr}(T_m)$ at T_m.[7,8]

$$\Delta H_{trn}(T_m) = \Delta H_{vap}(T_m) + \Delta H_{intr}(T_m) \qquad (1\text{-}2)$$

The latter term has been found to be small in comparison to $\Delta_l{}^gH(T_m)$, a function of temperature, and at times endothermic.[9] Provided the standards are appropriately chosen and of comparable size, the vaporization enthalpy of the standards at any given temperature, T, has been found to correlate linearly with the enthalpy of transfer, $\Delta H_{trn}(T_m)$.[7-10] Proper selection of standards correct for heat capacity differences between

T_m and T and for the enthalpy of interaction with the column. While the hydrocarbon portion of the molecule may be varied, the type and number of functional groups are important criteria to be considered in selection of appropriate standards as are their retention times.

Correlation of $\ln(p/p_o)$ of the benzenedicarboxylates used as standards with their $\ln(t_o/t_a)$ values as a function of temperature, has also resulted in linear relationships characterized with correlation coefficients, $r^2 > 0.99$. These correlations were performed at $T/K = 10$ intervals over the temperature range $T/K = (298.15 \text{ to } 550)$. The vapor pressure - temperature dependence that was obtained was then fit to a third order polynomial also discussed below. The term p_o in this work refers to 101325 Pa.

1.2.3. Fusion Enthalpy Measurements. Dicyclohexyl phthalate is the only solid material examined whose fusion enthalpy has not been measured previously. Measurements were conducted on a Perkin Elmer DSC 7 instrument controlled by the Pyris Software. The instrument was standardized using indium metal with a mass fraction of 0.9999 supplied by the manufacturer, calorimetric grade benzoic acid supplied by Fisher and Gold Label scintillation grade naphthalene supplied by Aldrich ($w > 0.99$). The samples were hermetically sealed in 50 μL pans supplied by Perkin Elmer. A nitrogen flow rate of 0.3 $\text{mL}\cdot\text{s}^{-1}$ was passed over the cells. The samples were heated at a rate of 0.053 $\text{K}\cdot\text{s}^{-1}$. The resulting fusion enthalpy measured for dicyclohexyl phthalate is reported in Table 1-10 below. Additional details are available in the Appendix A.

1.2.4. Temperature adjustments. Temperature adjustments of enthalpy from the mean temperature of measurement to a common temperature was achieved using eqs 1-3 through 1-5.[11] These equations have been shown to provide reasonable temperature adjustments resulting from differences in the heat capacities of the two respective phases. The C_p(l) term refers to the liquid heat capacity at T/K = 298.15 and the C_p(cr) term refers to the solid heat capacity at T/K = 298.15. The heat capacities of both condensed phases were estimated by group additivity.[12] Experimental heat capacities of the liquid phase for dimethyl phthalate, diethyl phthalate, di-*n*-butyl phthalate and *bis* (2-ethylhexyl) phthalate and for the crystalline phase for dimethyl isophthalate and dimethyl terephthalate have been measured.[13-15] These values are compared to estimated values in Appendix A. Estimated values were used in the adjustment since eqs 1-3 through 1-5 were derived in this manner. The largest discrepancy between the experimental and estimated value was 6%.

$$\Delta_l{}^gH_m(298.15\ \mathrm{K})/(\mathrm{kJ{\cdot}mol^{-1}}) = \Delta_l{}^gH_m(T_m)\ /(\mathrm{kJ{\cdot}mol^{-1}}) + [(10.58 + 0.26{\cdot}C_p(\mathrm{l})/(\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}))(\ T_m/\mathrm{K} - 298.15)]/1000 \qquad (1\text{-}3)$$

$$\Delta_{cr}{}^lH\ (298.15\ \mathrm{K})/(\mathrm{kJ{\cdot}mol^{-1}})\ = \Delta_{cr}{}^lH\ (T_{fus})/\mathrm{kJ{\cdot}mol^{-1}}\ + [(0.15{\cdot}C_p(\mathrm{cr})-0.26{\cdot}C_p(\mathrm{l}))/(\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}})\ -9.83)]\ [T_{fus}/\mathrm{K}-298.15]/1000 \qquad (1\text{-}4)$$

$$\Delta_{cr}{}^gH_m(298.15\ \mathrm{K})/(\mathrm{kJ{\cdot}mol^{-1}}) = \Delta_{cr}{}^gH_m(T_m)\ /(\mathrm{kJ{\cdot}mol^{-1}}) + [(0.75 + 0.15{\cdot}C_p(\mathrm{l})/(\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}))(\ T_m/\mathrm{K} - 298.15)]/1000 \qquad (1\text{-}5)$$

1.2.5. Uncertainties. Uncertainties in temperature adjustments have been calculated using a standard deviation of ±16 $\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$ for C_p(l). This uncertainty was derived for substances with heat capacities averaging about 200-250 $\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$. Many of the substances in this study have much larger heat capacities and since a number of them have been measured experimentally, the following protocol was followed. Uncertainties were calculated using the difference between estimated and the experimental number if the difference exceeded ±16 $\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$ and ±16 if otherwise. The experimental uncertainty used is provided in Appendix A. Uncertainties in the temperature adjustment of fusion and sublimation enthalpies, eqs1-4 and 1-5, are estimates and amount to 30% of the total adjustment.[5] Uncertainties resulting from correlations and transpiration measurements are reported as standard deviations (u). Uncertainties associated with combined results were evaluated as $(u_1^2 + u_2^2 +..)^{0.5}$. Uncertainties in derived results were evaluated similarly unless noted otherwise.

1.2.6. Vaporization Enthalpy Estimations. Estimation of the vaporization enthalpies of the dialkyl phthalates reported below were calculated using eq 1-6.[16] The various terms in the equation are defined as follows: the n_C term refers to the number of carbon atoms; n_Q refers to the number of quaternary sp^3 hybridized carbon atoms; b_i refers to the group contribution of the functional groups, in this case an ester (10.5 kJ·mol^{-1}); n_i refers to the number of such groups (2); F_i refers to the substitution pattern of the carbons to which the function group is attached, calculated as an average if the two positions of attachment differ as is the case here (primary sp^3 carbon: F = 1.62, secondary sp^3 carbon, F = 1.08, quaternary sp^2 carbon, F = 0.85, tertiary sp^3 = 0.6); the C term includes an ortho substitution correction, and an alkyl branching correction if the branching occurs on an sp^3 carbon (-2.0 kJ·mol^{-1} for each correction). Average deviations in the use of the equation used in the estimations is typically 5% of the value for hydrocarbons and substances containing a single functional group and somewhat larger, 8% in this case, for compounds with more than one.[16]

$$\Delta_l^g H(298\text{ K})/\text{ kJ·mol}^{-1} = 4.69(n_C - n_Q) + 1.3 \cdot n_Q + n_i \Sigma F_i \cdot b_i + 3.0 + C \qquad (1\text{-}6)$$

1.3. Standards

1.3.1. Vapor Pressure Standards. Experimental vapor pressures for a variety of dialkyl phthalates have been reported using several different equations and formats. Recent values for dimethyl and diethyl phthalate have been reported in the form of the Cox equation, eq 1-7.[3,4] Liquid vapor pressures for dimethyl isophthalate have been reported in the form of the Wagner equation,[15] eq 1-8, and corresponding vapor pressures for di-*n*-butyl phthalate are available in the form of eqs 1-1 and 1-9. Both the Cox and Wagner equations are known to extrapolate well with temperature. How well eq 1-9 extrapolates, however, is not clear. The most extensive range of vapor pressures as a function of temperature for di-*n*-butyl phthalate was determined by Small *et al*. [17]. Since this study is a collection of older data though, concern arose in regards to the accuracy of the vapor pressures generated from this equation. As a means of confirming the dependability of this equation, the vapor pressures calculated were compared to those measured in this work by transpiration and those reported by Hales *et al*.[18] which were also fit to eq 1-9. Comparison of all three results plotted as $\ln(p/p_o)$ as a function of temperature where p_o/Pa = 101325 are illustrated in the lower curve of Figure 1-2 over the temperature range reported.

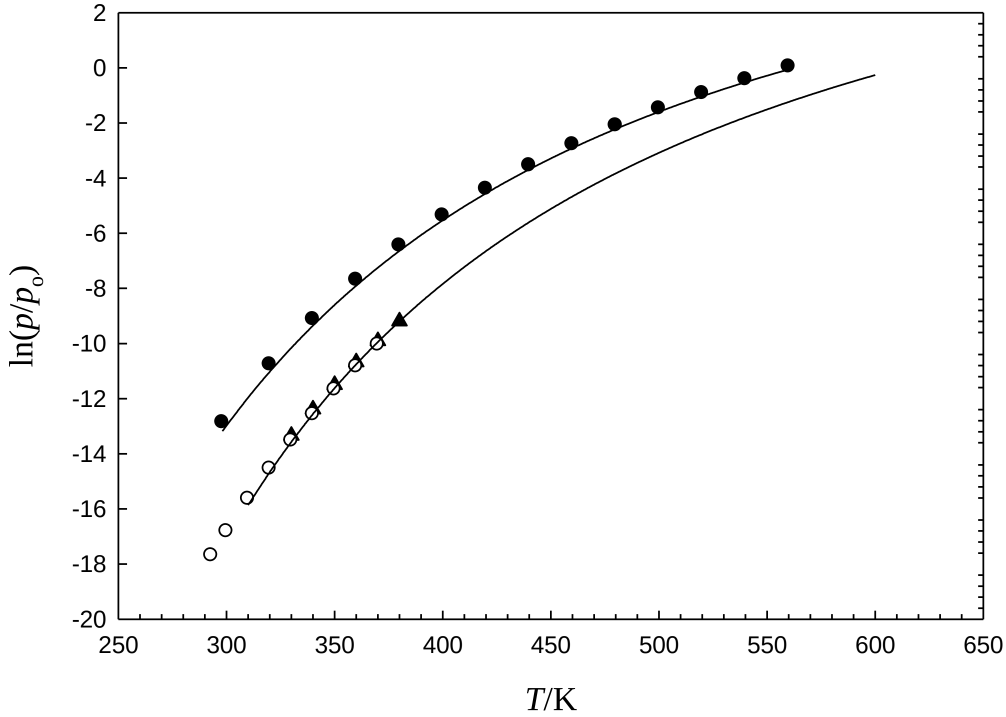

Figure 1-2. Bottom curve: A plot of $\ln(p/p_o)$ versus T/K for vapor pressures reported for dibutyl phthalate by Small *et al.*, (line),[17] Hales *et al.* (○),[18] and this work (▲). Top curve: A plot of $\ln(p/p_o)$ versus T/K for vapor pressures calculated by correlation for dimethyl isophthalate (line) and vapor pressures calculated using the Wagner eq (●).[15]

The data fits quite well. All three sets of vapor pressure were averaged and fit to the third order polynomial, eq 1-10, over the temperature range, T/K = (293 to 600). Equation 1-9 has also been found to extrapolate well with temperature.[9,10] The constants of eqs 1-1, and 1-7 through 1-10 are provided in Tables 1-3 through 1-7.

$$\ln (p/p_o) = (1-T_o/T)\exp[A_o + A_1(T/K) + A_2(T/K)^2] \qquad (1\text{-}7)$$

$$\ln (p/p_o) = 1/(T/T_c)\,[A(1 - T/T_c) + B(1 - T/T_c)^{1.5} + C(1 - T/T_c)^{2.5} + D(1 - T/T_c)^5] \qquad (1\text{-}8)$$

$$\ln(p/p_o) = a + b(T/K)^{-1} + c(T/K)^{-2} \qquad (1\text{-}9)$$

$$\ln(p/p_o) = A''(T/K)^{-3} + B''(T/K)^{-2} + C''(T/K)^{-1} + D'' \qquad (1\text{-}10)$$

TABLE 1-3. Parameters of the Cox Equation (1-7)

	A_o	$-10^3 \cdot A_1$/K	$10^6 \cdot A_2/K^2$	p_o/T_o/K	T_{range}/K
dimethyl phthalate[a]	3.076854	1.650657	1.171631	101.325 kPa /555.799	324-522
diethyl phthalate[b]	3.844479	0.9201487	0.5406641	0.0029Pa / 269.922	270-520

[a]Reference 3. [b]Reference 4.

TABLE 1-4. Parameters of the Wagner Equation (1-8)

	A	B	C	D	T_c/K	p_c/k Pa	T_{range} /K
dimethyl isophthalate[a]	-10.17884	4.62669	-6.96976	-2.77645	766	2650	350-607

[a]Reference 15.

TABLE 1-5. Parameters of Equation 1-9

	A	B	C	T_{range}/K
di-*n*-butyl phthalate[a]	15.992	-8739.43	-330691	293-373
di-*n*-butyl phthalate[b]	9.6344	-3836.11	-1261126	310-600

[a]Reference 18. [b]Reference 17.

TABLE 1-6. Parameters of the Clausius Clapeyron Equation (1-1)

	A’	B’	T_{range}/K
di-*n*-butyl phthalate[a]	18.34 ± 0.13	10444.6 ± 46.3	333-379
benzyl butyl phthalate[b]	9.54	10701	416-516
dicyclohexyl phthalate[b]	18.55	11671.8	391-475
di-*n*-octyl phthalate[b]	18.17	11967.5	423-523

[a]This work. [b]Reference 24.

TABLE 1-7. Parameters of Equation 1-10 Derived from the Work of Small *et al.*,[a] Hales *et al.*,[b] and Transpiration[c]

	A”’ $\cdot 10^{-6}/T^3$	B” $\cdot 10^{-4}/T^2$	C” $\cdot 10^{-2}/T^1$	D”	T_{range}/K
di-*n*-butyl phthalate	346.91	-362.407	14.3696	5.780	293-600

[a]Reference 17. [b]Reference 24. [c]This work.

Since references to the original literature were not available, the recommended vapor pressures from the EPA Product Properties Test Guidelines[2] reported in Table 1-8 were not used in these evaluations. The resulting vapor pressures calculated for di-*n*-butyl phthalate by eq 1-10, however, are well within the uncertainties proposed by the guidelines as described below. The pressures for di-*n*-butyl phthalate in all vapor pressure correlations were the values calculated using eq 1-10 and the constants provided in Table 1-7. The vapor pressures recommended by the EPA for *bis* (2-ethylhexyl) phthalate and the vaporization enthalpies calculated from this data are also included in Table 1-8. These values will be discussed below.

1.3.2. Vaporization Enthalpy Standards. Some of the most recent vaporization enthalpy values available in literature are summarized in Table 1-2. Temperature adjustments, including those for di-*n*-butyl phthalate measured by transpiration, are included in this table for measurements conducted at mean temperatures other than T/K = 298.15. Values estimated by eq 1-6 are also included in this table. The compounds used as standards initially in this work included dimethyl phthalate, diethyl phthalate and di-*n*-butyl phthalate. The vaporization enthalpies of two other compounds also involved in the evaluation of the vaporization enthalpies of *bis* (2-ethylhexyl) phthalate and di-*n*-octyl phthalate are values for dimethyl isophthalate and dimethyl terephthalate. Selection of values for these latter two compounds is discussed below. The values chosen as standards for dimethyl phthalate and diethyl phthalate are those reported by Rohac *et al*.[3,4]. Also accompanying the vaporization enthalpies they reported were the experimental vapor pressure measurements over a broad temperature range. The vaporization enthalpy chosen as the standard value for di-*n*-butyl phthalate is an average value of work reported by Hales *et al*.[18] (94.1±1.0), Verevkin *et al*.[19] (96.0±0.8) and the transpiration results from this work (95.0±1.7). This gives an average value of (95.0 ± 1.1) kJ·mol^{-1}. The vaporization enthalpy resultant of using vapor pressures calculated using eq 1-10 at a mean temperature of T/K = 350, the temperature common to measurements by Small *et al*.,[17] Hales *et al*.,[18] and this work resulted in a vaporization enthalpy of (96.5 ± 1.1) kJ·mol^{-1} at T/K = 298.15. This value is within experimental error of the standard value used. The value of (96.5 ± 1.1) kJ·mol^{-1}, and the vaporization enthalpy calculated from the vapor pressures reported in the EPA guidelines, (89.8 ± 0.3) kJ·mol^{-1}, were not included in calculating the standard value. The uncertainty in the EPA value reported in Table 1-8 only includes the standard deviation associated with the slope of the line using the vapor pressure values reported and the uncertainty associated with the temperature adjustment. It does not include any uncertainty associated with the range of vapor pressures reported in the table.

TABLE 1-8. EPA Product Properties Test Guidelines (OPPTS 830.7950) for Vapor Pressure[a]

	T/K	$10^4 \cdot p$/Pa EPA	$\Delta_l^g H_m$(303 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298.15 K) kJ·mol^{-1}
di-*n*-butyl phthalate	283.2	6.5±2.1		
	293.2	23±7		
	303.2	78±17	89.1±0.3	89.8±0.3
	313.2	240±90		
	323.2	700±80		
calculated[b]	298.15	43		
	T/K	$10^6 \cdot p$/Pa		
bis (2-ethylhexyl) phthalate	283.2	1.1		
	293.2	6		
	303.2	28	115.6±0.4	116.7±0.5
	313.2	120		
	323.2	490		
calculated[b]	298.15	13		

[a]Reference 2. [b]Calculated using eq 1-1.

1.3.3. Dimethyl Isophthalate and Dimethyl Terephthalate. An investigation of some of the recent thermodynamic measurements for dimethyl isophthalate and dimethyl terephthalate reveals some discrepancies in the values reported. Sublimation and fusion enthalpies for these two materials are available. Sublimation enthalpies at T/K = 298.15

are provided in Table 1-9. Two sublimation enthalpy values are available for both compounds[14,20] and both sets of values compare within their experimental uncertainties.

TABLE 1-9. Sublimation Enthalpies Adjusted to T/K = 298.15 for Dimethyl Isophthalate and Terephthalate

	$\Delta_{cr}{}^{g}H_m(T_m)$ kJ·mol^{-1}	T_m/K	C_p(cr) J·mol^{-1}·K^{-1}	ΔC_p(cr)·ΔT kJ·mol^{-1}	$\Delta_{cr}{}^{g}H_m$(298.15 K) kJ·mol^{-1}	Method[Ref]
dimethyl terephthalate	101.2±0.5	363.7	240.8	3.6±1.8	104.8±1.9	calorimetric[a]
	103.8±0.3	320.6		1.1±0.3	104.9±0.4	mass effusion[b]
dimethyl isophthalate	100.7±0.4	334.3	240.8	1.8±0.5	102.5±0.6	calorimetric[a]
	100.7±0.2	302		0.2±0.1	100.9±0.2[b]	mass effusion[b]

Fusion enthalpies reported in literature and their temperature adjustment to T/K = 298.15 are provided in Table 1-10.[21-23] Two of the three values available for dimethyl terephthalate are in good agreement and were averaged.

TABLE 1-10. Fusion Enthalpies of Dimethyl Isophthalate, Dimethyl Terephthalate and Dicyclohexyl Phthalate Adjusted to T/K = 298.15

	$\Delta_{cr}{}^{l}H_m(T_m)$ kJ·mol^{-1}	T_{fus}/K	C_p(l)/C_p(cr) J·mol^{-1}·K^{-1}	ΔC_p·ΔT kJ·mol^{-1}	$\Delta_{cr}{}^{l}H_m$(298.15 K) kJ·mol^{-1}
dimethyl terephthalate	34.87[a]	414.3	314/240.8	-6.4±1.9	28.4±1.9
	32.9±1.0[b,c]	413.8		-6.4±1.9	26.5±2.1
	31.63[d]	413.7		-6.4±1.9	25.2±1.9
dimethyl isophthalate	30.2±0.4[e]	341.5	314/240.8	-2.4±0.8	27.8±0.9
	25.3±0.8[b]	341.2		-2.4±0.8	22.9±1.1
dicyclohexyl phthalate[f]	32.3±1.4	336.5±0.3	544.4/437	-3.29±1.0	29.0±1.7

[a]Ref 21. [b]Ref 22. [c]Weight loss was observed. [d]Ref 23. [e]Ref 15. [f]This work, see Appendix A for details.

Two sets of vaporization enthalpies were calculated for both compounds from sublimation and fusion enthalpies by difference once the fusion enthalpies were adjusted to T/K = 298.15. Vaporization enthalpies of (76.5±2.2 and 79.0±2.3) and (73.9±1.0 and 78.8±1.2) kJ·mol^{-1}, were calculated for dimethyl terephthalate and dimethyl isophthalate, respectively. Even though the value of (78.8±1.2) kJ·mol^{-1}for dimethyl isophthalate is in good agreement with the value measured directly from vapor pressure measurements, (77.2±0.8),[15] this value at T/K = 298.15 is the result of vapor pressures extrapolated from measurements at T/K = (350-607). Due to the uncertainties in the fusion enthalpies of both compounds and the temperature extrapolation for dimethyl isophthalate, correlation gas chromatography experiments were conducted to identify the most likely vaporization enthalpy for each of the two compounds.

1.4. Results And Discussion

1.4.1. Vaporization Enthalpies at *T*/K = 298.15.

1.4.1.1. Dimethyl Terephthalate and Isophthalate. In order to determine the most likely vaporization enthalpies for dimethyl terephthalate and isophthalate a series of gas chromatography experiments were conducted. Although dependable vapor pressure data was available for dimethyl isophthalate, it was treated as an unknown in order to independently verify the validity of these correlations.[15] Dimethyl, diethyl, and di-*n*-butyl phthalate were used as reference standards. Separate runs were performed for dimethyl terephthalate and isophthalate due to their co-elution at some temperatures. Values of $\ln(t_o/t_a)$ for duplicate runs were first evaluated as a function of temperature over a T/K = 30 range at T/K = 5 intervals at a mean temperature of T/K = 500 for dimethyl terephthalate and T/K = 435 for dimethyl isophthalate and plotted against $1/T$ for both the standards and the targets. The resulting slopes and intercepts from runs 1/2 and 3/4, were used to evaluate an average value of (t_o/t_a), $(t_o/t_a)_{avg}$ as a function of temperature. This value was then correlated against the corresponding $\ln(p/p_o)$ of the standards. An example of the results of the correlation between $(t_o/t_a)_{avg,}$ and $\ln(p/p_o)$ is provided in Table 1-11 for the temperature, T/K = 298.15. Values of $\ln(p/p_o)$ of the standards were calculated using eqs 6, 7 and 9 with their corresponding constants from Tables 1-3 through 1-7. Equations 1-11 and 1-12, listed below Table 1-11, illustrate the linearity of the correlation for dimethyl terephthalate (runs 1/2) and dimethyl isophthalate (runs 3/4) at this temperature. In the final column of Table 1-11 the vapor pressures calculated from experimental values are compared to those acquired by correlation at T/K = 298.15. The vapor pressures of the standards are reproduced within 10% or less of their literature values. The vapor pressure for dimethyl isophthalate determined by correlation, p/Pa = 0. 192, is fairly smaller than the value, p/Pa = 0.263, extrapolated to T/K = 298.15 using the Wagner equation.[15]

Table 1-11. Correlations Between $\ln(t_o/t_a)_{avg}$ and liquid $\ln(p/p_o)_{exp}$ at T/K = 298.15 for Runs 1/2 and 3/4[a]

run 1/run 2	-slope/K	intercept	$\ln(t_o/t_a)_{avg}$	$\ln(p/p_o)_{exp}$	$\ln(p/p_o)_{calc}$	$p\cdot10^3$/Pa calc/lit
dimethyl	5262.39	11.549				
phthalate	5295.37	11.628	-6.117	-12.716	-12.667	319/304
dimethyl	5434.18	11.744				
terephthalate	5463.56	11.808	-6.506		-13.068	214/NA[b]
diethyl	5839.50	12.272				
phthalate	5862.46	12.331	-7.323	-13.840	-13.908	92.3/98.8
di-*n*-butyl	7248.39	13.936				
phthalate	7273.57	13.998	-10.386	-17.080	-17.061	3.9/4.3[c]
run 3/run 4						
dimethyl	5925.84	12.973				
phthalate	5884.79	12.883	-6.88	-12.7	-12.7	323/304
dimethyl	6165.75	13.267				
isophthalate	6160.71	13.258	-7.41		-13.2	192/263[d]
diethyl	6558.37	13.812				
phthalate	6550.36	13.797	-8.18	-13.8	-13.9	90.8/98.8
di-*n*-butyl	8087.86	15.727				
phthalate	8070.92	15.692	-11.4	-17.1	-17.1	4.0/4.3[c]

Run 1/2: $\ln(p/p_o) = (1.029\pm0.028) \ln(p/p_o) - (6.373\pm0.224)$ $r^2 = 0.9993$ (1-11)

Run 3/4: $\ln(p/p_o) = (0.975\pm0.032) \ln(p/p_o) - (5.95\pm0.29)$ $r^2 = 0.9989$ (1-12)

[a] Runs 1/2: slope and intercept measured at a mean temperature of T_m/K = 500; run 3/4; T_m/K = 435. [b] Not available. [c] EPA Guidelines. [d] Extrapolation of the Wagner eq, ref 15.

The resulting vapor pressures from correlations comparable to those in Table 1-11 repeated over the temperature range, T/K = (298.15 to 550), at T/K = 10 intervals were fit to eq 1-10 as a function of temperature. Table 1-12 summarizes the constants of eq 1-10 acquired for both the target compounds and standards. Column 6 of the table describes how well the experimental boiling temperatures were replicated using these constants. The boiling temperatures of the standards are reproduced within T/K = ±2 along with the value for dimethyl terephthalate. The boiling temperature of dimethyl isophthalate of T_b/K = 562 is reproduced within ΔT/K = 7 of the literature value (T_b/K = 555). In comparison, the Wagner eq predicts a boiling temperature of T_b/K = 558.[15] A comparison of the data evaluated by correlation using eq 1-10 for dimethyl isophthalate and those acquired using the Wagner eq over the temperature range T/K = (298.15 to 560) is provided by the upper curve in Figure 1-2.

TABLE 1-12. Constants for Eq 1-10, Boiling Temperatures and Vaporization Enthalpies for Dimethyl Terephthalate, Dimethyl Isophthalate and the Standards from Runs 1/2 and 3/4

Run 1/2	A”·10^{-6}	B”·10^{-4}	C” ·10^{-2}	D”	T_b/K calc/lit[3,4]	$\Delta_l^g H_m$ (298.15 K)[a] kJ·mol^{-1}
dimethyl phthalate	74.2963	-136.828	-26.2627	8.729	555/557	
dimethyl terephthalate	100.8643	-158.906	-22.0239	8.388	560/561	78.5 ± 0.3
diethyl phthalate	145.8162	-196.376	-15.9193	8.019	571/568	
di-*n*-butyl phthalate	100.8643	-357.347	13.4093	5.837	613/613	
Run 3/4						
dimethyl phthalate	76.08322	-138.330	-25.7508	8.671	555/557	
dimethyl isophthalate	106.3007	-163.485	-21.3244	8.358	562/555	78.9±0.3
diethyl phthalate	143.9568	-194.787	-16.5069	8.091	571/568	
di-*n*-butyl phthalate	339.4365	-357.435	13.4852	5.824	613/613	

[a] Calculated using the constants for eq 1-10 for runs 1/2 or 5/6 and eq 1 at T/K = 313 and adjusted to T/K = 298.15.

The vapor pressures evaluated for dimethyl terephthalate using the suitable constants for eq 1-10 over a T/K = 30 temperature range at T_m/K = 313.15 according to eq 1-1, result in a vaporization enthalpy of (77.1 ± 0.2) kJ·mol^{-1}. The temperature T_m/K = 313.15 was selected to lie within the temperature range of the correlations. Using eq 1-3 to adjust to T/K = 298.15 results in a vaporization enthalpy of (78.5 ± 0.3) kJ·mol^{-1}. This value compares very favorably with the value of (79.0±2.3) kJ·mol^{-1} calculated from the average fusion enthalpy of (25.9 ± 2.0) kJ·mol^{-1} and the average sublimation enthalpy of (104.9 ± 1.2) kJ·mol^{-1} both at T/K = 298.15 from Table 1-13. In subsequent correlations the literature value of (79.0 ± 2.0) kJ·mol^{-1} was chosen as the standard value used for dimethyl terephthalate.

Table 1-13. Vaporization Enthalpies at T/K = 298.15 from Sublimation and Fusion Enthalpies for Dimethyl Isophthalate and Terephthalate

	$\Delta_{cr}{}^{g}H_m$(298.15 K)[a] kJ·mol^{-1}	$\Delta_{cr}{}^{l}H_m$(298.15 K) kJ·mol^{-1}	$\Delta_{l}{}^{g}H_m$(298.15 K)[b] kJ·mol^{-1}
dimethyl terephthalate	104.9±1.2	28.4±1.9	76.5±2.2
		25.9±2.0[c]	79.0±2.3
dimethyl isophthalate	101.7±0.4	27.8±0.9	73.9±1.0
		22.9±1.1	78.8±1.2

[a]Average values from Table 1-2. [b] Calculated from the following equation: $\Delta_{l}{}^{g}H_m$(298.15 K) = $\Delta_{cr}{}^{g}H_m$(298.15 K - $\Delta_{cr}{}^{l}H_m$(298.15 K). [c]An average of (26.5±2.1) and (25.2±1.9) kJ·mol^{-1}.

Using suitable constants for eq 1-10 a similar evaluation of the vapor pressure data for dimethyl isophthalate at T/K = 313.15 resulted in a vaporization enthalpy of (77.6 ± 0.2) kJ·mol^{-1}. Adjustment to T/K = 298.15 gives a value of (78.9 ± 0.3) kJ·mol^{-1}. This value agrees favorably with the value of (78.8 ± 1.2) kJ·mol^{-1} calculated by difference between the sublimation and fusion enthalpies of (100.7±0.2) and (22.9±1.1) kJ·mol^{-1} listed in Table 1-13. The literature value of (78.8±1.2) kJ·mol^{-1} was used as the standard value for dimethyl isophthalate in subsequent correlations.

1.4.1.2. Dicyclohexyl phthalate, Benzyl Butyl Phthalate, *bis* (2-Ethylhexyl) Phthalate, *bis* (2-Ethylhexyl) Terephthalate and Di-*n*-octyl Phthalate. The vaporization enthalpies of benzyl butyl phthalate and *bis* (2-ethylhexyl) phthalate were calculated using the vaporization enthalpies of dimethyl, diethyl, and di-*n*-butyl phthalate and the most likely value for dimethyl isophthalate as standards. Results are reported as runs 5/6 in Table 1-14 and are characterized by equations 1-13 and 1-14 listed below the table. The vaporization enthalpy for *bis* (2-ethylhexyl) phthalate calculated by correlation in runs 5/6 of (115.8±3.9) kJ·mol^{-1} (see Table 1-17) is within experimental error of the EPA value of (116.7±0.5) kJ·mol^{-1} evaluated from the vapor pressures reported in Table 1-8. In subsequent calculations the EPA value of (116.7±0.5) kJ·mol^{-1} was used as the standard value for this compound. Results for benzyl butyl phthalate are discussed below.

Table 1-14. Evaluation of $\Delta_l^g H_m$(298 K) for Benzyl Butyl Phthalate and *bis* (2-Ethylhexyl) Phthalate

Run 5	- slope T/K	intercept	ΔH_{trn}(500 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298.15 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298.15 K) kJ·mol^{-1}(calc)
dimethyl phthalate	5206.7	10.782	43.29	77.0±1.2	76.6±2.8
dimethyl isophthalate	5506.9	11.201	45.78	78.8±1.2[a]	79.4±2.8
diethyl phthalate	5776.1	11.491	48.02	82.1±0.5	81.9±2.9
di-*n*-butyl phthalate	7173.5	13.136	59.64	95.0±1.1[b]	95.0±3.2
benzyl butyl phthalate	8346.5	14.276	69.39		105.9±3.6
bis (2-ethylhexyl) phthalate	9404.5	15.817	78.19		115.8±3.9

Run 5

$$\Delta_l^g H_m(298.15\ \mathrm{K})/\mathrm{kJ\cdot mol^{-1}} = (1.12\pm0.04)\Delta H_{trn}(500\ \mathrm{K}) - (28.0\pm2.1) \qquad r^2 = 0.9971 \qquad (1\text{-}13)$$

Run 6

$$\Delta_l^g H_m(298.15\ \mathrm{K})/\mathrm{kJ\cdot mol^{-1}} = (1.12\pm0.04)\Delta H_{trn}(500\ \mathrm{K}) - (28.1\pm2.1) \qquad r^2 = 0.9972 \qquad (1\text{-}14)$$

[a] From Table 1-11. [b] An average of (96.0±0.8), (95.0±1.1) and (94.1±1.0) kJ·mol^{-1}.

Runs 7/8 were also used to evaluate benzyl butyl phthalate and also included di-*n*-octyl phthalate as an unknown. The vaporization enthalpy for benzyl butyl phthalate and di-*n*-octyl phthalate in runs 7/8 calculated by correlation were (106.7±1.2) kJ·mol^{-1} and (122.6±1.4) kJ·mol^{-1}, respectively. Table 1-15 summarizes the results of run 7. Equations 1-15 and 1-16 listed below the table illustrate the linearity of both correlations.

Table 1-15. Evaluation of $\Delta_l^gH_m$(298 K) for Benzyl Butyl Phthalate and Di-*n*-octyl Phthalate

Run 7	Slope T/K	intercept	ΔH_{trn}(521 K) kJ·mol^{-1}	$\Delta_l^gH_m$(298.15 K) kJ·mol^{-1} (lit)	$\Delta_l^gH_m$(298.15 K) kJ·mol^{-1}(calc)
dimethyl phthalate	-4995.2	10.356	41.53	77.0±1.2	76.8±1.0
diethyl phthalate	-5543.3	11.023	46.08	82.1±0.5	82.1±1.0
di-*n*-butyl phthalate	-6898.5	12.585	57.35	95.0±1.1[a]	95.4±1.1
benzyl butyl phthalate	-8051.0	13.685	66.93		106.7±1.2
bis (2-ethylhexyl) phthalate	-9051.6	15.114	75.25	116.7±0.5	116.5±1.3
di-*n*-octyl phthalate	-9668.7	15.794	80.38		122.6±1.4

Run 7

$\Delta_l^gH_m$(298.15 K)/kJ·mol^{-1} = (1.18±0.014)ΔH_{trn}(521 K) - (27.8±0.8) $r^2 = 0.9997$ (1-15)

Run 8

$\Delta_l^gH_m$(298.15 K)/kJ·mol^{-1} = (1.19±0.014)ΔH_{trn}(521 K) - (25.3±0.84) $r^2 = 0.9997$ (1-16)

[a] An average of (96.0±0.8), (95.0±1.1) and (94.1±1.0) kJ·mol^{-1}.

Dicyclohexyl phthalate, *bis* (2-ethylhexyl) phthalate and *bis* (2-ethylhexyl) terephthalate were also included in runs 1/2 to evaluate the vapor pressure of dimethyl terephthalate described above. Vaporization enthalpies for dicyclohexyl phthalate and *bis* (2-ethylhexyl) terephthalate were evaluated using both *bis* (2-ethylhexyl) phthalate and the most likely value for dimethyl isophthalate. Dimethyl, diethyl, and di-*n*-butyl phthalate were also used as vaporization enthalpy standards. The results are listed in Table 1-16. Equations 1-17 and 1-18 describe the linearity of these correlations. Similar information for all duplicate runs is available in Appendix A. The results of all runs used to evaluate vaporization enthalpies are summarized in Table 1-17. This table also includes run averages and literature values of the standards.

Table 1-16. Evaluation of $\Delta_l^g H_m$(298 K) for Dicyclohexyl Phthalate, and *bis* (2-Ethylhexyl) Terephthalate

Run 1	- slope T/K	intercept	ΔH_{trn}(520 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298.15 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298.15 K) kJ·mol^{-1}(calc)
dimethyl phthalate	5262.4	11.549	43.75	77.0±1.2	76.9±1.1
dimethyl terephthalate	5438.2	11.744	45.21	79.0±2.0[a]	78.6±1.1
diethyl phthalate	5839.5	12.272	48.55	82.1±0.5	82.2±1.1
di-*n*-butyl phthalate	7248.4	13.936	60.26	95.0±1.1[b]	95.5±1.2
dicyclohexyl phthalate	8788.8	15.307	73.07		109.9±1.4
bis (2-ethylhexyl) phthalate	9487.3	16.624	78.87	116.7±0.5	116.4±1.4
bis (2-ethylhexyl) terephthalate	10212.0	17.478	84.9		123.2±1.5

Run 1

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.12±0.015)ΔH_{trn}(500 K) - (27.7±0.84) r^2 = 0.9995 (1-17)

Run 2

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.12±0.014)ΔH_{trn}(500 K) - (27.5±0.8) r^2 = 0.9995 (1-18)

[a]From Table 1-11. [b]An average of (96.0±0.8), (95.0±1.1) and (94.1±1.0) kJ·mol^{-1}.

Table 1-17. A Summary of the Vaporization Enthalpies (kJ·mol^{-1}) From Runs 1/2 and 5 to 8

	Run 1/2	Run 5/6	Run 7/8	Average	Lit
dimethyl phthalate	76.7±0.8/ 76.8±0.7	76.6±2.8/ 76.6±2.7	76.8±1.0/ 76.7±1.9	76.7±1.7	77.0±1.2
dimethyl terephthalate	78.6±1.0/ 78.6±1.1			78.6±1.1	79.0±2.0
dimethyl isophthalate		79.4±2.8/ 79.4±2.8		79.4±2.8	78.8±1.2
diethyl phthalate	82.2±0.8/ 82.1±0.7	81.9±2.9/ 81.9±2.9	82.1±1.0/ 82.1±1.1	82.1±1.6	82.1±0.5
di-*n*-butyl phthalate	95.4±0.9/ 95.4±0.8	95.0±3.2/ 95.0±3.2	95.4±1.1/ 95.2±1.2	95.2±1.7	95.0±1.0
dicyclohexyl phthalate	109.9±1.0/ 109.9±0.9			109.9±1.0	
benzyl butyl phthalate		105.9±3.6/ 105.9±3.6	106.7±1.2/ 106.1±1.3	106.2±2.4	
bis (2-ethylhexyl) phthalate	116.5±1.0/ 116.5±0.9	115.8±3.9/ 115.8±3.6	116.5±1.3/ 116.5±1.4	115.9±3.8[a]	116.7±0.5
bis (2-ethylhexyl) terephthalate	123.3±1.1/ 123.3±1.0			123.3±1.1	
di-*n*-octyl phthalate			122.6±1.4/ 122.6±1.4	122.6±1.4	

[a]Evaluated as an unknown only in runs 5 and 6.

The average vaporization enthalpy calculated in runs 5 through 8 for benzyl butyl phthalate is (106.2±2.4) kJ·mol^{-1}. Literature values range from (94.5 to 113.9±2.7)[24,25] kJ·mol^{-1}. As indicated in Table 1-2, the latter value necessitated a large temperature adjustment and this could be a cause of some of the inconsistency. The calculated value compares favorably to the estimated value of (108.4 ± 8.7) kJ·mol^{-1}. A vaporization enthalpy of (109.9±1.0) kJ·mol^{-1} was calculated by correlation for dicyclohexyl phthalate. This compares with a literature value of (113.4±1.7)[26] kJ·mol^{-1}and an estimated value of (106±8.5) kJ·mol^{-1}. The vaporization enthalpy of (122.6±1.4) kJ·mol^{-1} acquired in this work for di-*n*-octyl phthalate is also significantly smaller than the two literature values, (130.4±4.5[22] and 135.9±7.2[24]) kJ·mol^{-1}. Using literature values, a difference of about (14-19) kJ·mol^{-1} is evaluated between the vaporization enthalpies of di-*n*-octyl phthalate and *bis* (2-ethylhexyl) phthalate, two isomers that are structurally similar. This work measures a difference of (5.9 ± 1.5) kJ·mol^{-1} between the two isomers. This is a value more consistent with effects of branching observed in other systems (2 kJ·mol^{-1}·branch^{-1})[16]. Uncertainty in the large temperature adjustment of over 20% of the value may be partly responsible for the larger difference observed with the literature values.[24, 26]

A difference of (6.6 ± 1.2) kJ·mol^{-1} between *bis* (2-ethylhexyl) terephthalate (123.3±1.1 kJ·mol^{-1}) and the standard value for *bis* (2-ethylhexyl) phthalate (116.7±0.5 kJ·mol^{-1}) is calculated in this work. As previously stated, samples of both *bis* (2-ethylhexyl) phthalate and *bis* (2-ethylhexyl) terephthalate consist of a mixture of two diasteriomers that were unable to be separated by chromatography. The vaporization enthalpies calculated are for that of the mixture and also include contributions of the enthalpy of mixing, both for the diasteriomers and the enantiomers. Mixing effects are probably small though, given the structures are very similar.

1.4.2. Liquid Vapor Pressures. Vapor pressures were evaluated using, eqs 1-7 through 1-10, and the constants listed in Tables 1-3 and 1-7 for dimethyl, diethyl and di-*n*-butyl phthalate. The same procedure was followed for all vapor pressure correlations as explained above for dimethyl terephthalate. Vapor pressures were evaluated at T/K = 10 intervals over the temperature range T/K = (298.15 to 550). The correlation coefficients, r^2, were greater than 0.99 at all temperatures. The vapor pressures were then fit to eq 1-10 as a function of temperature. Table 1-18 lists the constants of eq 1-10 for compounds treated as unknown.

Table 1-18. Evaluation of the Constants of Eq 1-10, Normal Boiling Temperatures and Liquid Vapor Pressures

Runs 1/2	$A''' \cdot 10^{-6}$	$B'' \cdot 10^{-4}$	$C'' \cdot 10^{-2}$	D''	T_b/K calc/lit	$p \cdot 10^6$/Pa 298.15 K calc/lit
dicyclohexyl phthalate	635.470	-602.922	64.3113	1.319	490/497[a,b]	80/116[b]
bis (2-ethylhexyl) phthalate	638.697	-606.365	58.1740	2.577	677/657[b]	28/13[d]
bis (2-ethylhexyl) terephthalate	738.488	-689.358	73.3120	1.448	699/673[c]	5.4/173[c,e]
Runs 5/6						
benzyl butyl phthalate	542.368	-527.001	47.268	2.921	667/643[b,c]	200/666[g]
bis(2-ethylhexyl) phthalate	628.672	-600.317	56.198	2.765	677/657[b]	23/13[d]
Runs 7/8						
di-*n*-octyl phthalate	724.729	-680.153	71.484	1.548	700/663[c,f]	5.5/13.3[b]

[a] At p/kPa = 0.533 T_b/K = 497. [b] Ref 27. [c] Ref 28. [d] Ref 2. [e] Estimate. [f] Also T_b/K = 498 at p/Pa = 333, lit. (T_b/K = 501) ref 28. [g] Ref 34.

The vapor pressures of dimethyl, diethyl and di-*n*-butyl phthalate were used as standards in all correlations. Tables similar to Table 1-11 and 1-20 which contain all the compounds in the mixture for runs 1, 2 and 5 to 8 are available in Appendix A as are the Antoine constants discussed below.

1.4.2.1. Runs 1 and 2: Dicyclohexyl Phthalate, and *bis* (2-Ethylhexyl) Terephthalate.

The vapor pressures of dimethyl terephthalate, dicyclohexyl phthalate, *bis*(2-ethylhexyl) phthalate, and *bis* (2-ethylhexyl) terephthalate were evaluated as unknowns in runs 1/2. Results for dimethyl terephthalate discussed above are summarized in Table 1-12. Subcooled liquid vapor pressures for this compound are not available at T/K = 298.15 for comparison to the calculated value, p/Pa = $214 \cdot 10^{-3}$, as at this temperature the compound is a solid. *bis* (2-Ethylhexyl) phthalate was also treated as an unknown in runs 5/6 and thus results for this compound are discussed below.

Although the normal boiling temperature for dicyclohexyl phthalate is not available to compare, a boiling temperature at reduced pressure (T_b/K = 497 at p/kPa = 0.53) [27] is known. This value compares to T_b/K = 490, calculated using eq 1-10 at this pressure, Table 1-18. The vapor pressure evaluated for this compound at T/K = 298.15, p/Pa = $80 \cdot 10^{-6}$, compares to the literature value of p/Pa = $116 \cdot 10^{-6}$.[27] In addition, vapor pressures of p/Pa = (1.3 and 247) at T/K = (391 and 475), respectively, were evaluated from the constants listed in Table 1-6.[24] This data compares to vapor pressures of p/Pa = (1.63 and 268) evaluated at these two temperatures by eq 1-10.

In regards to *bis* (2-ethylhexyl) terephthalate, experimental vapor pressures at T/K = 298.15 do not appear to be known. An estimated value at T/K = 298.15[28] of p/Pa = $175 \cdot 10^{-6}$ can be compared to a vapor pressure of p/Pa = $5.4 \cdot 10^{-6}$ evaluated by eq 1-10. An experimental boiling temperature of T_b/K = 673[28] compares to a predicted boiling temperature of T_b/K = 699 using eq 1-10.

1.4.2.2. Runs 5 and 6: *bis* (2-Ethylhexyl) and Benzyl Butyl Phthalate. Vapor pressure correlations in runs 5/6 were evaluated using the Wagner eq for dimethyl isophthalate[15] as a standard and the vapor pressures of benzyl butyl phthalate and *bis* (2-ethylhexyl) phthalate were treated as unknowns. In runs 1/2 and 5/6, the normal boiling temperatures evaluated for *bis* (2-ethylhexyl) phthalate through correlation vary from the literature value by ΔT/K = 20. This observation implies that vapor pressures at elevated temperatures may not be very dependable. A boiling temperature of T_b/K = 502 at a reduced pressure of p/kPa = 0.67 has been reported[28]. This value is compared to a calculated temperature of T_b/K = 498 in runs 1/2 and T_b/K = 499 in runs 5/6. At T/K = 500 a vapor pressure of p/Pa = 799 is calculated. This value compares to vapor pressures of p/Pa = 729 in runs 1/2 and p/Pa = 697 in runs 5/6 evaluated from suitable constants of eq 1-10 at this temperature.[24] At T/K = 298.15 vapor pressures of p/Pa = $28\cdot10^{-6}$ in runs 1/2 and p/Pa = $23\cdot10^{-6}$ in runs 5/6 are calculated. This compares with the EPA recommended value of p/Pa = $13\cdot10^{-6}$. An earlier review of this material suggested a vapor pressure of p/Pa = $32\cdot10^{-6}$ at this temperature. [29]

A normal boiling temperature of T_b/K = 643 for benzyl butyl phthalate has been reported[27,28]. This value compares with a boiling temperature of T_b/K = 666 calculated in this work giving a difference of ΔT/K = 24. Using eq 1 and constants from Table 1-6 literature vapor pressures of p/Pa = 9.4 and 1380 are calculated at T/K = 416 and 515. These values can be compared to vapor pressures from this work of p/Pa = 18.0 and 2350, respectively. A vapor pressure of p/Pa = $2\cdot10^{-4}$ at T/K = 298.15 calculated in this work using eq 1-10 and suitable constants in Table 1-18 compares to a literature vapor pressure of p/Pa = $11\cdot10^{-4}$. [27,30]

1.4.2.3. Runs 7 and 8: Di-*n*-octyl Phthalate. Vapor pressures calculated from eq 1-10 and the constants for benzyl butyl phthalate and bis (2-ethylhexyl) phthalate evaluated in runs 5/6, listed in Table 1-18, were used as standards in this correlation. The experimental boiling temperature of di-*n*-octyl phthalate varies from the value evaluated using eq 1-10 by ΔT/K = 37. This implies that this vapor pressure may not be very dependable at near boiling temperatures. It appears predicted boiling temperatures at lower pressures are more dependable. A boiling temperature of T_b/K = 501 has been reported at *p*/Pa = 333.[28] A boiling temperature of T_b/K = 496.7 is predicted from eq 1-10 in runs 7/8. A boiling temperature of T_b/K = 487.2 has been reported at *p*/Pa = 266[28] while eq 1-10 predicts a value of T_b/K = 491.9. As reported by Stephenson and Malanowski [24], the vapor pressures for di-*n*-octyl phthalate calculated using eq 1-1 and the constants in Table 1-6 agree favorably over the temperature range specified in the table. Vapor pressures of *p*/Pa = 4.1 and 911, listed in Table 1-6, are calculated at the two experimental temperature limits of *T*/K = 423 and 523, respectively. Using eq 1-10 and constants from Table 1-18, vapor pressures of *p*/Pa = 4.6 and 1035 are calculated for runs 7/8 at these two temperatures, respectively.

1.4.3. Solid Vapor Pressures. At room temperature, dimethyl terephthalate and isophthalate and dicyclohexyl phthalate are crystalline solids. The vaporization enthalpies of these compounds were evaluated at the fusion temperature using eq 1-10 for all three materials and using the Wagner equation for dimethyl isophthalate since the vapor pressures of their liquid phase are available as a function of temperature from runs 1 and 2. The calculated vaporization and sublimation enthalpies at T_{fus} using the most likely fusion enthalpies for dimethyl terephthalate and isophthalate are listed in Table 1-19.

TABLE 1-19. Sublimation Enthalpies and Solid Vapor Pressures (p_{cr}/Pa) of Dimethyl terephthalate and Isophthalate and Dicyclohexyl Phthalate at T/K = 298.15

	$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}(T_{\mathrm{fus}})^a$ kJ·mol^{-1}	$\Delta_{\mathrm{cr}}{}^{\mathrm{l}}H_{\mathrm{m}}(T_{\mathrm{fus}})$ kJ·mol^{-1}	$\Delta_{\mathrm{cr}}{}^{\mathrm{g}}H_{\mathrm{m}}(T_{\mathrm{fus}})$ kJ·mol^{-1}	$\Delta_{\mathrm{cr}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K) kJ·mol^{-1} calc/lit	p_{cr}/Pa 298.15 K calc/lit
dimethyl terephthalate	67.5	32.9	100.4	104.1/104.9	0.009/0.01^c
dimethyl isophthalate	74.6	25.3	99.8	101.5/100.7	0.057/0.099^d
	73.2^b	25.3	98.5	100.0/100.7	0.077/0.099
dicyclohexyl phthalate	104.4	32.3±1.4	136.7±1.7	139.2/NA^e	$1.2{\cdot}10^{-6}$/NA^e

[a] Calculated using eq 1-10 unless indicated otherwise. [b] Calculated from vapor pressures using the Wagner eq. [c] Dimethyl terephthalate: p_{cr}/Pa from; log(p/Pa) = (16.2 ± 0.1) - (5423 ± 17)/T; p_{cr}/Pa = (0.01 ± 0.0012); ref 14. [d] Dimethyl isophthalate: p_{cr}/Pa from; log(p/Pa) = (16.6 ± 0.1) - (5249 ± 12)/T;. p_{cr}/Pa = (0.099 ± 0.009); ref 14. [e] Not available

With the assumption that the vapor pressures at T_{fus} are common to both the solid and liquid phases, the vapor pressures of the three solids, p_{cr}/Pa, were evaluated at a mean temperature of T/K = 298.15 using the integrated form of the Clausius-Clapeyron equation altered by inclusion of a heat capacity term for the temperature adjustment, eq 1-19.[31] The vapor pressures of the solids were then used to evaluate the sublimation enthalpy at the mean temperature of T/K = 298.15. The last two columns of Table 1-19 compare the resulting sublimation enthalpies and vapor pressures at this temperature to their literature values. Agreement with vapor pressures directly measured for both compounds is within a factor of two of the literature values. The sublimation enthalpies agree favorably with the literature values.

$$\ln(p_{\mathrm{cr}}/\mathrm{Pa}) \;=\; [\Delta_{\mathrm{cr}}{}^{\mathrm{g}}H\,(T_{\mathrm{fus}}) + \Delta_{\mathrm{cr}}{}^{\mathrm{g}}C_p{\cdot}\Delta T]\,[\,1/T_{\mathrm{fus}}/\mathrm{K} - 1/298.15]/\mathrm{R} + \ln(p_{(\mathrm{Tfus}}/\mathrm{Pa}_{)}) \qquad (1\text{-}19)$$

where: $\Delta_{\mathrm{cr}}{}^{\mathrm{g}}C_p{\cdot}\Delta T = [0.75 + 0.15{\cdot}C_p(\mathrm{cr})][(T_{\mathrm{fus}}/\mathrm{K} - 298.15)/2]$

TABLE 1-20. A Summary of Literature Vaporization, Fusion, and Sublimation Enthalpies Consistent With the Results of this Study

	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}(298.15)$ kJ·mol^{-1}	$\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}(T_{\mathrm{fus}})$ kJ·mol^{-1}	$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}(298.15\ )$ kJ·mol^{-1}	$p\cdot 10^4$/Pa 298.15 K
dimethyl phthalate	77.0 ± 1.2			p_{l} : 3040
dimethyl terephthalate	79.0 ± 2.0	32.3 ± 1.0	104.9 ± 1.2	p_{cr}: 85
dimethyl isophthalate	78.8 ± 1.2	25.3 ± 0.8	101.7 ± 0.4	p_{l}: 2631; p_{cr}:: 568
diethyl phthalate	82.1 ± 0.5			p_{l}: 988
di-*n*-butyl phthalate				p_{l}: 43
bis (2-ethylhexyl) phthalate	116.7 ± 0.5			p_{l}: 0.13

TABLE 1-21. A Summary of New Values From This Work

	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}(298.15)$ kJ·mol^{-1}	$\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}(T_{\mathrm{fus}})$ kJ·mol^{-1}	$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}(298.15\ )$ kJ·mol^{-1}	$(p)\cdot 10^4$/Pa 298.15 K
dimethyl terephthalate				p_{l}: 2140
di-*n*-butyl phthalate	95.0 ± 1.1^{a}			
benzyl butyl phthalate	106.2 ± 2.4			p_{l}: 2.0
dicyclohexyl phthalate	109.9 ± 1.0	32.3±1.4	138.3±1.7	p_{l}: 0.80; p_{cr}: 0.012
bis (2-ethylhexyl) terephthalate	123.3 ± 1.1			p_{l}: 0.054
di-*n*-octyl phthalate	122.6 ± 1.4			p_{l}: 0.055

^{a}An average between literature values and this work.

1.5. Summary

This work has established a set of reasonably self-consistent values for vapor pressure, vaporization and fusion enthalpies for dimethyl isophthalate and terephthalate using literature vapor pressures and vaporizations enthalpies for dimethyl, diethyl and di-*n*-butyl phthalate along with some additional experimental vapor pressure measurements by transpiration for di-*n*-butyl phthalate. Independent verification of the recommended vapor pressure for di-*n*-butyl phthalate has been performed and a vaporization enthalpy for this compound has been proposed. The recommended vapor pressure and vaporization enthalpy for *bis* (2-ethylhexyl) phthalate has also been independently verified. In addition, the vapor pressures and vaporization enthalpies for benzyl butyl, dicyclohexyl and di-*n*-octyl phthalate have been determined. The sublimation and fusion enthalpies for dicyclohexyl phthalate have also been calculated along with vapor pressures for both the liquid and solid phases at T/K = 298.15. Vapor pressures for the liquid phase have been calculated over a wide range of temperatures. The thermodynamic data from literature most in line with the results of this work and the data evaluated in this study are listed in Tables 1-20 and 1-21.

1.6. Some Additional Vaporization Enthalpies and Vapor Pressures of Dialkyl Phthalates by Correlation Gas Chromatography

Once our laboratory was able to establish a set of reasonably self-consistent values for the dialkyl phthalates it became of interest to evaluate another set of these compounds with questionable literature values. The work reported herein investigates the vaporization enthalpies and vapor pressures of five additional dialkyl phthalates. The compounds evaluated in this work include di-*n*-pentyl phthalate, di-*n*-hexyl phthalate and di-*n*-nonyl phthalate, along with previously unreported values for diisobutyl phthalate and *bis*(4-methyl-2-pentyl) phthalate. All were analytical standards. The structures of these compounds are illustrated in Figure 1-3.

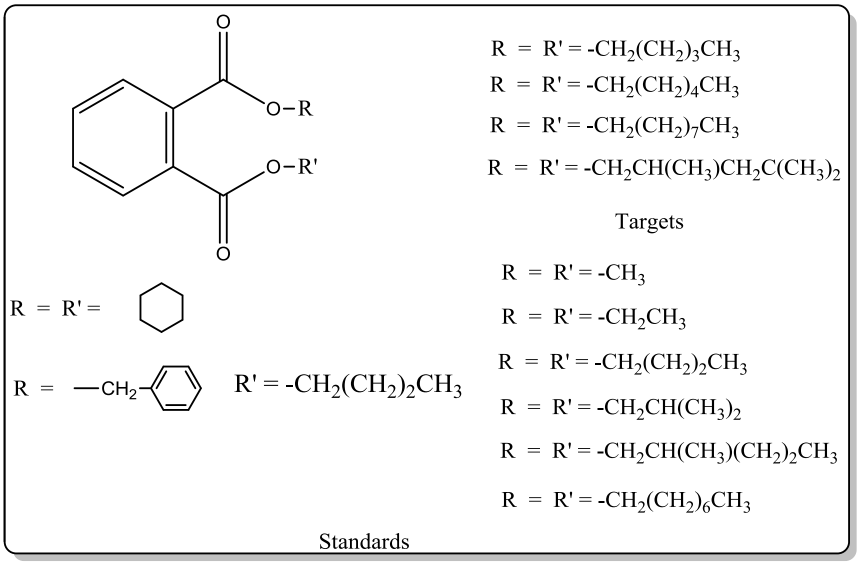

Figure 1-3. Structures of the the targets and standards of this investigation.

1.7. Experimental

1.7.1. Materials. Analytical standards (0.99+ mass fraction) of dimethyl phthalate, diethyl phthalate, di-*n*-butyl phthalate, *bis* (2-ethylhexyl) phthalate, benzyl butyl phthalate and di-*n*-octyl phthalate were purchased as a mixture, 200 µg/mL in methanol from Supelco (48741). Individual samples of several of these compounds were also purchased. Diisobutyl phthalate, *bis*(4-methyl-2-pentyl) phthalate, di-*n*-pentyl phthalate, di-*n*-hexyl phthalate and di-*n*-nonyl phthalate were also purchased as a mixture, 1000 µg/mL in hexane : acetone (80:20) from Restek (33227). According to the suppliers the alkyl substituents were the normal isomers and were used as purchased. *bis* (2-ethylhexyl) phthalate and *bis* (4-methyl-2-pentyl) phthalate are a mixture of diastereoisomers; the two diastereoisomers of the former were not separated by the chromatography under the conditions used but two peaks were observed for *bis*(4-methyl-2-pentyl) phthalate at the lower temperatures studied. Which of the two forms eluted first, the *meso* or *dl* form was not identified.

1.7.2. Methods. Correlation-gas chromatography experiments were conducted in the same manner as previously described in Section 1.2.2.2. Each plot was characterized by a correlation coefficient of $r^2 > 0.99$. The only differences were that this time the column temperature was maintained to T/K = 0.1 as monitored by a Fluke digital thermometer and hexanes/acetone served as the non-retained reference. All retention times are provided in Appendix A.

1.7.3. Uncertainties. All uncertainties reported in the tables below refer to one standard deviation unless noted otherwise and are equivalent to the standards uncertainties as defined by the Guide to the Expression of Uncertainty in Measurement.[37] Uncertainties resulting from correlations are reported as standard deviations (u_i). These were evaluated from both the uncertainty in the slope and intercept evaluated as $(u_1^2+u_2^2+\ ...)^{0.5}$. Uncertainties in derived results were evaluated similarly unless noted otherwise. Uncertainties associated with logarithmic terms are reported as an average. Uncertainties in boiling temperatures were calculated from the uncertainties associated from equations used to fit vapor pressures using Sigma Plot and Mathcad. Additional information is available in Appendix A.

1.7.4. Vaporization Enthalpy Estimations. Vaporization enthalpy estimations were conducted in the same manner as previously described in Section 1.2.6., again calculated using equation 1-6.

1.7.5. Temperature Adjustments. Adjustments from the mean temperature of measurement, T_m , to a common temperature, T/K = 298.15, were achieved in the same way as described in Section 1.2.4. using only equation 1-3.

1.8. Standards

1.8.1. Vapor Pressure Standards. Experimental vapor pressures for a number of dialkyl phthalates have been reported using different equations and formats. Recent values for dimethyl and diethyl phthalate have been reported in the form of the Cox equation, eq 1-7.[3,4] Vapor pressures for di-*n*-butyl phthalate were evaluated by combining vapor pressures from the work of Small et al.,[17] Hales et al.[18] and Gobble et al.[38] and fit to eq 1-10. Previous work by our group also provided constants for benzyl butyl phthalate, dicyclohexyl phthalate, *bis*(2-ethylhexyl) phthalate and di-*n*-octyl phthalate, by a process of correlation similar to the one described below.[38] All these results have been fit to the third order polynomial, eq 1-10. Once analyzed, some of the compounds investigated in this study were also used as standards in subsequent correlations. Provided vapor pressure data over a broad temperature range is available, both eqs 1-7 and 1-10 have been found to extrapolate well with temperature. The constants of eqs 1-7 and 1-10 are listed in Tables 1-22 and 1-23.

TABLE 1-22. Parameters of the Cox Equation (1-7)

	A_o	$-10^{-3}\cdot A_1/K$	$10^{-6}\cdot A_2/K^2$	$p_o/T_o/K$	T_{range}/K
dimethyl phthalate[a]	3.076854	1.650657	1.171631	101.325 kPa / 555.799	324-522
diethyl phthalate[b]	3.844479	0.9201487	0.5406641	0.0029Pa / 269.922	270-520

[a]Ref 3. [b]Ref 4.

TABLE 1-23. Parameters of Equation 1-10 Derived from Previous Work[a]

	$A(K^3)\cdot10^{-6}$	$B(K^2)\cdot10^{-4}$	$C(K)\cdot10^{-2}$	D
di-*n*-butyl phthalate	346.91±4.62	-362.407±34.82	14.370±8.54	5.780±0.683
benzyl butyl phthalate	542.368±4.59	-527.001±3.53	47.268±0.89	2.921±0.073
dicyclohexyl phthalate	635.470±8.89	-602.922±6.84	64.3113±1.72	1.319±0.14
bis(2-ethylhexyl) phthalate	638.697±2.78	-606.356±2.14	58.174±0.53	2.577±0.045
di-*n*-octyl phthalate	724.729±0.17	-680.153±0.128	71.484±0.032	1.548±0.003

[a] Ref 48.

1.8.2. Vaporization Enthalpy Standards. The compounds used as standards initially in this work included dimethyl phthalate, diethyl phthalate, di-*n*-butyl phthalate, benzyl butyl phthalate, dicyclohexyl phthalate, *bis*(2-ethylhexyl) phthalate and di-*n*-octyl phthalate. The values chosen as standards for dimethyl phthalate and diethyl phthalate are also those reported by Rohac *et al.*[3,4] The vaporization enthalpy chosen as the standard value for di-*n*-butyl phthalate is an average value of work reported by Hales *et al.*[18] (94.1±1.0) kJ·mol^{-1}, Small *et al.*[36] (96.0±0.8) kJ·mol^{-1} and the transpiration results from our previous work[38] (95.0±1.7) kJ·mol^{-1}, an average of (95.0 ± 1.1) kJ·mol^{-1}. The vaporization enthalpies used for standards benzyl butyl phthalate, dicyclohexyl phthalate, *bis*(2-ethylhexyl) phthalate and di-*n*-octyl phthalate are those previously reported by our group.[38] Duplicate values were also found for di-*n*-pentyl phthalate and di-*n*-hexyl phthalate at elevated temperatures. These values, at *T*/K = 298.15, were not used as standards in part because the duplicate values are not in good mutual agreement and are fairly old. The value for di-*n*-hexyl phthalate also required temperature adjustments of more than 10 kJ·mol^{-1}. Temperature adjustments for both are are provided in Appendix A and their values are discussed below. Values for all the compounds discussed at T/K =298.15 are provided in Table 1-24.

TABLE 1-24. Literature Vaporization Enthalpies and Vapor Pressures at T/K = 298.15 of Phthalate Ester Standards; p_o/Pa = 101325

	$\Delta_l^g H_m$(298.15 K) kJ·mol^{-1}		$10^4 \cdot p_l$/Pa[a] 298.15 K	
	Literature	Estimated		Reference
Dimethyl phthalate	77.0±1.2	73.8±6.0	3040	3
Diethyl phthalate	82.1±0.5	77.5±6.2	990	4
Di-isobutyl phthalate		92.3±7.4	63	41,42
Di-*n*-butyl phthalate	95.0±1.1	96.3±7.7	39	38, 17, 18
	93.7±0.7,[c]	105.7±8.5	5.7[d]	36, 24
Di-*n*-pentyl phthalate[b]	106.5±0.8[c]			
Benzyl butyl phthalate	106.2±2.4	110.4±8.8	2.0	48
Di-*n*-hexyl phthalate[b]	121.8,[c]113.5[c]	115±9.2	1.1[d]. 1.9[e]	18,49
Dicyclohexyl phthalate	109.9±1.0	110.0±8.8	0.8	48
bis (2-Ethylhexyl) phthalate	116.7±0.5	129±10.4	0.28	48,39
Di-*n*-octyl phthalate	122.6±1.4	133.8±10.7	0.055	48
Di-*n*-nonyl phthalate	120.1±0.9[c]	143.2±11.5	0.028[d]	49

[a] Reference 16. [b] Calculated using the constants from Table 1-23 unless noted otherwise. [c] Value not used as a standard; adjusted to T/K = 298.15 K from the mean temperature of measurement; uncertainties cited are associated with only the temperature adjustments, see Appendix A. [d] Vapor pressure extrapolated from: T/K ≈ 317 (di-*n*-pentyl phthalate); T/K ≈ 344 (di-*n*-hexyl phthalate) ; T/K = 333 (di-*n*-nonyl phthalate): ref 24. [e] Reference 41, 30.

1.9. Results

1.9.1. Vaporization Enthalpies at *T*/K = 298.15.

1.9.1.1. Diisobutyl Phthalate, Di-*n*-pentyl Phthalate and Di-*n*-hexyl Phthalate. The vaporization enthalpies of diisobutyl, di-*n*-pentyl and di-*n*-hexyl phthalate were evaluated using dimethyl, diethyl, di-*n*-butyl, benzyl butyl, dicyclohexyl and *bis*(2-ethylhexyl) phthalate as reference standards in runs 1/2. The results for run 1 are reported in Table 1-25. Equations 1-20 and 1-21 listed below the table summarize the linearity of both correlations evaluated in runs 1 and 2. Similar details for run 2 and all duplicate runs are available in Appendix A.

TABLE 1-25. Evaluation of $\Delta_l^g H_m$(298 K) for Diisobutyl Phthalate, Di-*n*-pentyl Phthalate and Di-*n*-hexyl Phthalate; p_o/Pa = 101325[a]

Run 1	- slope T/K	intercept	ΔH_{trn}(493 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298.15 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298.15 K) kJ·mol^{-1} (calc)
Dimethyl phthalate	5432.59	11.637	45.16	77.0±1.2	76.8±0.6
Diethyl phthalate	6004.05	12.342	49.92	82.1±0.5	82.1±0.6
Diisobutyl phthalate	7051.07	13.572	58.62		92.0±0.7
Di-*n*-butyl phthalate	7406.19	13.988	61.57	95.0±1.1	95.3±0.7
Di-*n*-pentyl phthalate	8132.24	14.855	67.61		102.1±0.7
Di-*n*-hexyl phthalate	8864.34	15.734	73.69		109.0±0.8
Benzyl *n*-butyl phthalate	8581.46	15.131	71.34	106.2±2.4	106.4±0.7
Dicyclohexyl phthalate	8935.95	15.342	74.29	109.9±1.0	109.7±0.8
bis (2-Ethylhexyl) phthalate	9671.45	16.736	80.40	116.7±0.5	116.6±0.8

Run 1

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.13±0.01)ΔH_{trn}(493 K) - (25.8±0.5) $r^2 = 0.9998$ (1-20)

Run 2

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.13±0.01)ΔH_{trn}(493 K) - (25.4±0.5) $r^2 = 0.9997$ (1-21)

[a] All uncertainties represent one standard deviation.

1.9.1.2. *meso* and *dl bis*(4-Methyl-2-pentyl) phthalate. Vaporization enthalpies of the two diastereoisomers, *meso* and *dl* of *bis*(4-methyl-2-pentyl) phthalate were evaluated in runs 3/4 over the temperatures T/K = (444 to 473.6) using dimethyl, diethyl, diisobutyl, di-*n*-butyl, and di-*n*-pentyl phthalate as reference standards. The vaporization enthalpies used for diisobutyl and di-*n*-pentyl phthalate are those evaluated in this work in runs 1/2. The results for run 3 are reported in Table 1-26. Equations 1-22 and 1-23 listed below the table summarize the linearity of both runs 3/4. While the two *bis*-(4-methyl-2-pentyl) phthalate began to co-elute around T/K = 493, separation was achieved at lower temperatures. Since *bis* (2-ethylhexyl) phthalate, an EPA test compound[39], is also likely a mixture of two diastereoisomers that previously were evaluated together, *bis*-(4-methyl-2-pentyl) phthalate seemed like a good test case to determine what effect co-elution of the two diastereoisomers would have on the vaporization enthalpies evaluated. Therefore *bis*-

(4-methyl-2-pentyl) phthalate was also evaluated under conditions of temperature in runs 5/6 in which both diastereoisomers co-eluted over the entire temperature range.

TABLE 1-26. Evaluation of $\Delta_l^g H_m$(298 K) at T/K = 298.15 for *bis*-(4-Methyl-2-pentyl) Phthalate Isomers; p_o/Pa = 101325[a]

Run 3	- slope T/K	intercept	ΔH_{trn}(459 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298.15 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298.15 K) kJ·mol^{-1}(calc)
Dimethyl phthalate	5780.53	12.324	48.06	77.0±1.2	76.9±0.8
Diethyl phthalate	6382.60	13.091	53.06	82.1±0.5	82.2±0.8
Diisobutyl phthalate	7484.06	14.431	62.22	92.0±0.8[b]	91.9±0.9
Di-*n*-butyl phthalate	7857.18	14.884	65.32	95.0±1.0	95.2±0.9
bis(4-Methyl-2-pentyl) phthalate[c]	8343.74	15.497	69.37		99.5±0.9
bis(4-Methyl-2-pentyl) phthalate[d]	8377.57	15.555	69.65		99.8±0.9
Di-*n*-pentyl phthalate	8626.00	15.839	71.71	102.2±0.8[b]	102.0±1.0

Run 3

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.06±0.01)ΔH_{trn}(459 K) - (25.8±0.6) $r^2 = 0.9997$ (1-22)

Run 4

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.06±0.01)ΔH_{trn}(459 K) - (25.1±0.6) $r^2 = 0.9997$ (1-23)

[a] All uncertainties represent on standard deviation. [b] Average value from runs 1/2 used as a standard. [c] 1st isomer through from column. [d] 2nd isomer through column.

1.9.1.3. Di-*n*-nonyl Phthalate and *bis*-(4-Methyl-2-pentyl) Phthalate. The vaporization enthalpy of di-*n*-nonyl phthalate and the two co-eluting *bis*-(4-methyl-2-pentyl) phthalate isomers were evaluated in runs 5/6 using dimethyl, diethyl, diisobutyl, di-*n*-butyl, di-*n*-pentyl, di-*n*-hexyl, benzyl butyl, and di-*n*-octyl phthalate as reference standards. Vaporization enthalpies for diisobutyl, di-*n*-pentyl, and di-*n*-hexyl phthalate are those evaluated from previous runs. Results for run 5 are reported in Table 1-27.

TABLE 1-27. Evaluation of $\Delta_l^gH_m$(298.15 K) for *bis*(4-Methyl-2-pentyl) Phthalate and Di-*n*-nonyl Phthalate; p_o/Pa = 101325[a]

Run 5	- slope T/K	intercept	ΔH_{trn}(523 K) kJ·mol^{-1}	$\Delta_l^gH_m$(298.15 K) kJ·mol^{-1} (lit)	$\Delta_l^gH_m$(298.15 K) kJ·mol^{-1}(calc)
Dimethyl phthalate	5343.16	11.425	44.42	77.0±1.2	77.0±0.4
Diethyl phthalate	5853.86	12.006	48.67	82.1±0.5	82.2±0.4
Diisobutyl phthalate	6807.68	13.048	56.60	92.0±0.8[c]	91.9±0.4
Di-*n*-butyl phthalate	7135.34	13.409	59.32	95.0±1.0	95.2±0.5
bis(4-Methyl-2-pentyl) phthalate[b]	7577.26	13.926	62.99		99.7±0.5
Di-*n*-pentyl phthalate	7804.95	14.164	64.89	102.2±0.8[c]	102.0±0.5
Di-*n*-hexyl phthalate	8483.43	14.937	70.53	109.0±0.9[c]	108.9±0.5
Benzyl butyl phthalate	8240.60	14.410	68.51	106.2±2.4	106.4±0.5
Di-*n*-octyl phthalate	9846.15	16.498	81.86	122.6±1.4	122.7±0.5
Di-*n*-nonyl phthalate	10526.52	17.279	87.51		129.6±0.9

Run 5

$\Delta_l^gH_m$(298.15 K)/kJ·mol^{-1} = (1.22±0.01)ΔH_{trn}(523 K) - (22.8±0.3) $r^2 = 0.9999$ (1-24)

Run 6

$\Delta_l^gH_m$(298.15 K)/kJ·mol^{-1} = (1.21±0.003)ΔH_{trn}(523 K) - (23.6±0.21) $r^2 = 0.9999$ (1-25)

[a] Uncertainties represent 1 standard deviation. [b] Only one peak observed. [c] Average value from runs 1/2.

Equations 1-24 and 1-25 listed below the table summarize the linearity of both of these correlations. Results from all six runs are summarized in Table 1-28. Appendix A also includes similar results for all the compounds used as standards.

TABLE 1-28. A Summary of the Vaporization Enthalpies (kJ·mol^{-1}) at T/K = 298.15 of Runs 1 to 6 Evaluated in This Work, p/p_o = 101325 Pa

Targets	Run 1/2	Run 3/4	Run 5/6	Average	Lit.
diisobutyl phthalate	92.0±0.7/92.0±0.8			92.0±0.8[a]	NA[e]
dipentyl phthalate	102.1±0.7/102.2±0.9			102.2±0.8[a]	93.7±0.7[f]; 106.5±0.8[g]
di-*n*-hexyl phthalate	109.0±0.8/109.00.9			109.0±0.9[a]	121.8±3.1[h]; 113.5±[i]
bis(4-methyl-2-pentyl) phthalate		99.5±0.9/99.5±0.9		99.5±0.9[b]	NA[e]
bis(4-methyl-2-pentyl) phthalate		99.8±0.9/99.8±0.9		99.8±0.9[c]	NA[e]
bis(4-methyl-2-pentyl) phthalate			99.7±0.5/99.6±0.5	99.7±0.5[d]	NA[e]
di-*n*-nonyl phthalate			129.6±0.9/129.4±0.5	129.5±0.7	120.1±0.9[j]

[a]Evaluated in runs 1and 2 only; used as a standard when used in subsequent runs. [b]1st diasterioisomer through the column. [c]2nd diasterioisomer through the column. [d]Analyzed as a mixture of diasterioisomers. [e]NA: not available. [f]Reference 24. [g]Reference 18. [h]Reference 49.

1.9.2. Liquid Vapor Pressures. Vapor pressures of the standards were calculated using eqs 1-7 and 1-10 using the appropriate constants from Tables 1-22 and 1-23. Since duplicate runs were run under similar conditions, the resulting slopes and intercepts from runs 1/2, 3/4, and 5/6 were used to evaluate average values of (t_o/t_a), $(t_o/t_a)_{avg}$. This term, as $\ln(t_o/t_a)_{avg}$, was then correlated against the corresponding $\ln(p/p_o)$ values of the standards. Examples of the results of these correlations for runs 1/2, 3/4 and 5/6 at T/K = 298.15 are provided in Tables 1-30 through 1-32. Equations 1-26 through 1-28 listed below each of these tables provide a measure of the linearity of the correlations at this temperature. The last column in Tables 1-30 through 1-32 compares the vapor pressures calculated from literature values to those obtained by correlation at this temperature. This process was then repeated from T/K = (310 to 500) at 10 K intervals. The correlation coefficients, r^2, exceeded 0.999 at all temperatures. The resulting $\ln(p/p_o)$ values as a function of temperature were then fit to eq 1-10 where p_o/Pa = 101325. Table 1-29 includes the constants of eq 1-10 for all the compounds evaluated in this study. Tables similar to Table 1-29 that include the constants for both standards and targets are available in Appendix A.

TABLE 1-29. Evaluation of the Constants of Eq 1-10 and Estimated Boiling Temperatures of The Compounds Evaluated in Runs 1 to 6 at p_o/Pa = 101325

Runs 1/2	$A(K^3)\cdot10^{-6}$	$B(K^2)\cdot10^{-4}$	$C(K)\cdot10^{-2}$	D	T_b/K calc/lit
Diisobutyl phthalate	302.085±1.09	-326.273±0.87	8.569±0.228	6.153±0.020	604±0.2/ 602.2[a]
Di-*n*-pentyl phthalate	448.865±1.26	-448.432±1.01	30.71±0.260	4.518±0.023	635.7±0.3/ 615.2[b]
Di-*n*-hexyl phthalate	547.152±1.45	-530.237±1.16	45.46±0.304	3.441±0.260	656.7±0.4/ 657.7[c]
Runs 3/4					
bis(4-Methyl-2-pentyl) phthalate (1)	406.879±0.86	-413.533±0.68	23.994±0.18	5.043±0.016	626.8±0.2/ NA[d]
bis(4-Methyl-2-pentyl) phthalate (2)	408.918±1.03	-415.201±0.82	24.077±0.22	5.068±0.019	626.7±0.2/ NA[d]
Runs 5/6					
Diisobutyl phthalate	299.551±0.74	-324.163±0.59	8.038±0.15	6.199±0.013	603.8±0.1/ 602.2[b]
bis (4-Methyl-2-pentyl) phthalate (*dl* + *meso*)	409.542±0.890	-416.189±0.711	24.685±0.187	4.967±0.016	628.1±0.2/ NA[d]
Di-*n*-nonyl phthalate	830.026±0.979	-767.452±0.782	87.536±0.206	0.392±0.018	722±3.0/ 686[b]

[a] Reference 43, 44. [b] Reference 41. [c] Reference 39. [d] Not available.

1.9.2.1. Diisobutyl Phthalate, Di-*n*-pentyl Phthalate and Di-*n*-hexyl Phthalate. Diisobutyl phthalate was treated as an unknown in runs 1/2 and 5/6 while the compound's ln(p/p_o) value at each temperature was used as a standard in runs 3/4. Similarly, di-*n*-pentyl phthalate was evaluated in runs 1/2 and used as a standard in the remaining runs. Di-*n*-hexyl phthalate, also evaluated in runs 1/2 was used as a standard only in runs 5/6. The other compounds used as standards for each run are reported in

Tables 1-30 through 1-32. The vapor pressures of the targets evaluated at each temperature from T/K = (298.15 to 500) and their uncertainties are available in Appendix A.

TABLE 1-30. Correlations Between $\ln(t_o/t_a)_{avg}$ and $\ln(p/p_o)_{exp}$ at T/K = 298.15 for Runs 1/2[a]

Run 1/Run 2	-slope/K	intercept	$\ln(t_o/t_a)_{avg}$	$\ln(p/p_o)_{exp}$	$\ln(p/p_o)_{calc}$	$p\cdot 10^4$/Pa Calc/Lit.[b]
dimethyl phthalate	5432.59	11.637	-6.622	-12.716	-12.67±0.11	3200±350/3040
	5483.86	11.730				
diethyl phthalate	6004.05	12.342	-7.837	-13.841	-13.92±0.11	910±100/990
	6059.75	12.445				
diisobutyl phthalate	7051.07	13.572	-10.124		-16.28±0.12	86±10/0.32
	7115.12	13.692				
di-*n*-butyl phthalate	7406.19	13.988	-10.897	-17.080	-17.07±0.12	39±5.0/43
	7470.61	14.109				
di-*n*-pentyl phthalate	8132.24	14.855	-12.467		-18.69±0.13	7.7±1.0/5.7
	8197.82	14.978				
benzyl *n*-butyl phthalate	8581.5	15.131	-13.705	-20.046	-19.97±0.14	2.2±0.3/2.0
	8658.5	15.28				
di-*n*-hexyl phthalate	8864.34	15.734	-14.043		-20.32±0.14	1.5±0.21/1.1
	8929.75	15.858				
dicyclohexyl phthalate	8935.95	15.342	-14.684	-20.964	-20.98±0.15	0.8±0.12/0.8
	9013.61	15.490				
bis(2-ethylhexyl) phthalate	9671.45	16.736	-15.739	-22.198	-22.06±0.15	0.27±0.04/0.13
	9721.58	16.829				

Run 1/2: $\ln(p/p_o) = (1.03\pm0.007)\ln(p/p^o) - (5.84\pm0.092)$ $r^2 = 0.9998$ (1-26)

[a] p_o/Pa = 101325; uncertainties are one standard deviation. [b] Vapor pressure references for the standards are provided in Table 1-24; references for the target are provided in Table 13.

1.9.2.2. *bis*(4-Methyl-2-pentyl) Phthalate Isomers. At low enough temperatures (T/K = 443 to 473) the *meso* and *dl* isomers of *bis*(4-methyl-2-pentyl) phthalate are able to be separated by gas chromatography. The results listed in Table 1-31 and Appendix A are discussed below. The constants of eq 1-10 for standards diisobutyl and di-*n*-pentyl phthalate used to evaluate the vapor pressure of the two isomers of *bis*(4-methyl-2-pentyl) phthalate are those previously calculated in runs 1/2. *bis*(4-methyl-2-pentyl) phthalate was also evaluated as an unknown in runs 5/6.

TABLE 1-31. Correlations Between $\ln(t_o/t_a)_{avg}$ and $\ln(p/p_o)_{exp}$ at T/K = 298.15 for Runs 3/4[a]

Run 3/Run 4	-slope/K	intercept	$\ln(t_o/t_a)_{avg}$	$\ln(p/p_o)_{exp}$	$\ln(p/p_o)_{calc}$	$p \cdot 10^4$/Pa Calc/Lit.[b]
dimethyl phthalate	5780.5	12.32				
	5865.0	12.49	-7.12	-12.716	-12.66	3200±430/3040
diethyl phthalate	6382.6	13.09				
	6465.7	13.26	-8.37	-13.840	-13.911	920±130/990
diisobutyl phthalate	7484.1	14.43				
	7573.0	14.61	-10.73	-16.270[b]	-16.268	87±14/0.32[c]
di-*n*-butyl phthalate	7857.2	14.88				
	7944.7	15.06	-11.53	-17.080	-17.067	39±6/43
bis(4-methyl-2-	8343.7	15.60				
pentyl) phthalate[d]	8427.56	15.67	-12.49		-18.023	15±3/0.19
bis(4-methyl-2-	8377.6	15.5				
pentyl) phthalate[e]	8467.3	15.74	-12.59		-18.135	13±2/0.19
di-*n*-pentyl phthalate	8626.0	15.84				
	8714.9	16.02	-13.15	-18.692	-18.687	7.8±1.4/5.7

Run 3/4: $\ln(p/p_o) = (1.002\pm0.011)\ln(p/p_o) - (5.5307\pm0.116)$ $r^2 = 0.9996$ (1-27)

[a] p_o/Pa = 101325; uncertainties are one standard deviation. [b] Vapor pressure references for the standards are provided in Table 1-24; references for the target are provided in Table 13. [c] Estimate. [d] 1st isomer through from column. [e] 2nd isomer through column.

1.9.2.3. Di-*n*-nonyl Phthalate. The standards used to evaluate the vapor pressure of di-*n*-nonyl phthalate are those from literature as well as the compounds analyzed in runs 1/2 and 3/4. The constants of eq 1-10 used for diisobutyl and di-*n*-pentyl phthalate are the average of the constants calculated in runs 1/2 and 3/4. The vapor pressure of di-*n*-nonyl phthalate was treated as an unknown in runs 5/6. The results listed in Table 1-32 and Appendix A are discussed below.

TABLE 1-32. Correlations Between $\ln(t_o/t_a)_{avg}$ and $\ln(p/p_o)_{exp}$ at T/K = 298.15 for Runs 5/6[a]

Run 5/Run 6	-slope/K	intercept	$\ln(t_o/t_a)_{avg}$	$\ln(p/p_o)_{exp}$	$\ln(p/p_o)_{calc}$	$p\cdot10^4$/Pa Calc/Lit.[b]
dimethyl phthalate	5343.16	11.425				
	5297.62	11.329	-6.468	-12.716	-12.665	(3200±420)/3040
diethyl phthalate	5853.86	12.006				
	5819.55	11.933	-7.607	-13.840	-13.904	(930±60)/990
diisobutyl phthalate	6807.68	13.048				
	6776.05	12.981	-9.765		-16.261	(88±6)
di-*n*-butyl phthalate	7135.34	13.409				
	7105.93	13.347	-10.504	-17.080	-17.068	(39±3)/43
bis(4-methyl-2-pentyl) phthalate	7577.26	13.926				
	7545.19	13.859	-11.468		-18.121	(14±1)
dipentyl phthalate	7804.95	14.164				
	7780.35	14.112	-11.998	-18.691	-18.700	(7.8±0.6)
di-*n*-hexyl phthalate	8483.43	14.937				
	8463.57	14.895	-13.504	-20.315	-20.344	(1.5±0.1)/1.1
benzyl butyl phthalate	8240.60	14.410				
	8221.96	14.372	-13.216	-20.046	-20.040	(2±0.2)/11
di-*n*-octyl phthalate	9846.15	16.498				
	9825.14	16.456	-16.512	-23.645	-23.629	(0.055±0.005)/ 0.055
di-*n*-nonyl phthalate	10526.52	17.279				
	10501.76	17.231	-18.010		-25.264	(0.011±0.001)

Run 5/6: $\ln(p/p_o) = (1.093\pm0.004)\ln(p/p_o) - (5.5973\pm0.045)$ $r^2 = 0.9999$ (1-28)

[a] p_o/Pa = 101325; uncertainties are one standard deviation. [b] Vapor pressure references for the standards are provided in Table 1-24.

1.10. Discussion

1.10.1. Vaporization Enthalpies at *T*/K = 298.15. The vaporization enthalpy for diisobutyl phthalate evaluated by correlation in runs 1/2, (92.0±0.8) kJ·mol^{-1} (Table 1-28), compares well with estimated value of (92.3±7.4) kJ·mol^{-1} (Table 1-24). Vaporization enthalpies of (102.2±0.8) kJ·mol^{-1} for di-*n*-pentyl phthalate and (109.0±0.9) kJ·mol^{-1}for di-*n*-hexyl phthalate (Table 1-28) also evaluated by correlation in runs 1/2 do not compare as well with the closest experimental values of (106.5 and 113.5) kJ·mol^{-1} (Table 1-24), respectively. The estimated values are in agreement with the values determined within the experimental uncertainties. As expected, the vaporization enthalpies of the *meso* and *dl*-bis-(4-methyl-2-pentyl) phthalate evaluated under conditions where the two diasterioisomers separate, runs 3/4 (Table 1-26), are very similar resulting in values of (99.5±0.9) and (99.8±0.9) kJ·mol^{-1}. These are reported in order of their elution off the column. At the higher temperatures where the two diastereoisomers co-elute, runs 5/6 (Table 1-27), the vaporization enthalpy evaluated of (99.7±0.5) kJ·mol^{-1} (Table 8) appears very close to an average value of the two diastereoisomers. Finally, the vaporization enthalpy of di-*n*-nonyl phthalate evaluated in this work of (129.5±0.5) kJ·mol^{-1}, falls roughly midway between the literature value and the value estimated.

Comparison of the vaporization enthalpies of the di-*n*-alkyl phthalates from di-*n*-butyl to di-*n*-nonyl phthalate evaluated in this and previous work,[38] results in a fairly constant methylene increment of (3.46±0.1) kJ·mol^{-1}. A methylene increment of (4.74±0.07) kJ·mol^{-1} is observed in the vaporization enthalpies of the methyl esters of butanoic acid inclusive to eicosanoic acid.[40] The smaller methylene increment observed for the diesters is probably reflective of a smaller accessible surface area for the phthalate esters. A larger methylene increment might be expected for the di-*n*-alkyl terephthalates, most of which have not been reported. A comparison of the vaporization enthalpies of 2-ethylhexyl phthalate (116.7±0.5 kJ·mol^{-1}) to the corresponding terephthalate (123.2±0.5 kJ·mol^{-1}) supports this conclusion.

1.10.2. Vapor Pressures at *T*/K = 298.15.

1.10.2.1. Diisobutyl Phthalate, Di-*n*-pentyl Phthalate and Di-*n*-hexyl Phthalate. The constants of eq 1-10 evaluated from correlations between $\ln(p/p_o)$ and $\ln(t_o/t_a)$ as a function of temperature are summarized in Table 1-29. Vapor pressures were calculated from the correlation observed at T/K = 298.15, eq 1-26, and the boiling temperature by extrapolation of eq 1-10 using the appropriate constants from Table 1-29. The vapor pressure evaluated for diisobutyl phthalate from runs 1/2 at T/K = 298.15, p/Pa = $(86\cdot\pm10)\cdot10^{-4}$, compares to literature values of p/Pa = $(63\cdot10^{-4})$[41,42]. For comparison, the recommended vapor pressure for di-*n*-butyl phthalate is somewhat smaller, p/Pa = 43. A calculated normal boiling temperature of T_b/K = (604±0.2) from the same runs can be compared to a reported value of T_b/K = 602[43,44] The corresponding vapor pressure and normal boiling temperature for di-*n*-pentyl phthalate from runs 1/2 are evaluated as p/Pa = $(7.7\pm1.04)\cdot10^{-4}$ at T/K = 298.15 and T_b/K = 635.7 and compare to reported values of p/Pa = $5.7\cdot10^{-4}$ and T_b/K = 615.2[41], At a reduced pressure of p/Pa = 533, the boiling temperatures are nearly identical (Table 1-29). For di-*n*-hexyl phthalate also evaluated in runs 1/2, a normal boiling temperature of T_b/K = 656.7±0.4) compares to a literature value of T_b/K = 657.7. The boiling temperatures at reduced pressure also compare well (Table 1-29).

1.10.2.2. *bis*(4-Methyl-2-pentyl) Phthalate Isomers. Vapor pressures for the two diasterioisomers of *bis* (4-methyl-2-pentyl) phthalate evaluated either individually or combined are not available but the reported boiling temperature of the two combined at a reduced pressure of p/p_o = 0.0079 of in order of their elution off the column.T_b/K = 447.2[45] compares to a calculated value of T_b/K= 466. The normal boiling temperature of the two individual diasterioisomers in order of their elution off the column are virtually identical, T_b = (626.8±0.2 and 626.7±0.2). They compare to a value of T_b/K = (628.1±0.2) evaluated at higher temperatures with a slightly different set of standards (runs 3/4 vs runs 5/6). Comparison of the vapor pressures and predicted boiling temperatures of the two diasterioisomers summarized in Tables 1-31 and 1-32 for runs 3/4 and 5/6 appears that co-elution plays a minor role in affecting these properties evaluated in this manner. Similarly behavior would be expected for the two diasterioisomers of *bis* 2-ethylhexyl phthalate. In the case where an alkane and a phthalate diester also co-eluted over the entire 30 K temperature range, the vaporization enthalpies and vapor pressures of the two different analytes were also not noticeably affected by the co-elution. In this latter case the two different analytes were correlated separately with their respective homologues in the mixture.[46] In both cases, the results were reproducible well within the experimental uncertainty.

1.10.2.3. Di-*n*-nonyl Phthalate. The vapor pressure evaluated for di-*n*-nonyl phthalate from runs 5/6 at T/K = 298.15, p/Pa = (0.011±0.001), compares to the literature value of p/Pa = (0.028).[24] The literature vapor pressure for di-*n*-nonyl phthalate was extrapolated from T/K = 333.[24] The boiling temperature at a reduced pressure of 0.041 kPa for di-*n*-nonyl phthalate is T_b/K = 458.2[43,47] which compares to a calculated value of T_b/K= 468.7.

TABLE 1-33. A Summary of Vaporization Enthalpies, Vapor Pressures at T/K = 298.15, and Boiling Temperatures from This Work and Comparisons With Available Literature Data

	$\Delta_l^g H_m$(298.15) kJ·mol^{-1}	$10^4 \cdot p$/Pa (298.15K) This Work[a] / Lit	(p/kPa): ($T_{B\ calc}$/K)/($T_{B\ lit}$/K)
Diisobutyl phthalate	92.0±0.8	(88±6)/63[e]	101.3 kPa: 603.9/600.2[k]
Di-*n*-pentyl phthalate	102.2±0.8	(7.7±1.0)/5.7[f]	0.53 kPa: 463/465[l]
bis(4-Methyl-2-pentyl) phthalate[b]	99.5±0.9	(15±3)/NA[g]	0.8 kPa: 465.7/447.2[m]
bis(4-Methyl-2-pentyl) phthalate[c]	99.8±0.9	(13±2)/NA[g]	0.8 kPa: 465.9/447.2[m]
bis(4-Methyl-2-pentyl) phthalate[d]	99.7±0.5	(14±1)/NA[g]	0.8 kPa: 466.3/447.2[m]
Di-*n*-hexyl phthalate	109.9±0.9	(1.5±0.21)/1.1[h], (19±12)[i]	0.67 kPa: 483/483.2[n]
Di-*n*-nonyl phthalate	129.5±0.7	(0.011±0.001)/ 0.028[j]	0.041 kPa: 468.7/458.2[o]

[a]The vapor pressures reported are those in which each compound was evaluated as a target; p_o/Pa = 101325. [b]1st isomer through column. [c]2nd isomer through column. [d]Both diastereoisomers eluting as one peak. [e]Ref 41,42. [f]Extrapolated from T/K ≈ 317 using the constants reported in ref 24. [g]Not Available. [h]Extrapolated from T/K ≈ 344 using the constants reported in ref 24. [i]Ref 30; analysis of a mixture of dipentyl isomers. [j]Extrapolated from T/K ≈ 313 using the constants reported in ref 24. [k]Ref 43,44. [l]Ref 43,50. [m]Ref 43,45. [n]Ref 41,50. [o]At p/kPa = 0.041; ref 43,47.

1.11. Summary

The vaporization enthalpies and vapor pressures of a series of dialkyl phthalates were analyzed by correlation gas-chromatography. Table 1-29 lists the constants of eq 1-10 obtained by fitting vapor pressures as a function of temperature over the temperature range T/K = (298.15 to 500). Also included in this table are the boiling temperatures obtained by extrapolation of eq 1-10. These values are compared to experimental boiling temperatures. Table 1-33 summarizes the thermodynamic properties evaluated for the target dialkyl phthalates of this study. Also included in this table is a comparison of calculated and experimental vapor pressures and boiling temperatures at various reduced pressures.

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Part 2: Primary Amines

Chapter 2. The Vaporization Enthalpies and Vapor Pressures of Some Primary Amines of Pharmaceutical Importance by Correlation Gas Chromatography

2.1. Introduction

Numerous simple primary amines have been of significant pharmaceutical interest. These compounds are often primarily prescribed in their ammonium salt form. Amantadine (1-aminoadamantane), has been used for treatment of dementia, and other disorders of the central nervous system,[1,2] for the prevention of influenza A,[1] and as a possible treatment for hepatitis C when combined with other substances.[3,4] Rimantadine (1-adamantylethanamine) has also been used to prevent influenza A.[5] Both rimantadine and amantadine, however, are no longer recommended.[6] Another simple amine, phentermine (α, α-dimethylphenethylamine), is prescribed as an appetite suppressant for patients suffering from obesity.[7] This compound is also pharmacologically similar to amphetamine. A monoamine oxidase inhibitor called Tranylcypromine (*trans*-1-phenylcyclopropylamine) was developed as an analog of amphetamine and has been used to treat mood and anxiety disorders.[8] The structures of these compounds are displayed in Figure 2-1. Although these compounds are widely used, information about the physical properties of many of these compounds in literature is fairly limited. This work evaluates the vapor pressures and vaporization enthalpies of the amines as their free base. As some of these materials are solid at room temperature, the vapor pressure of the solid phase and that of the sub-cooled liquid as investigated by correlation gas chromatography and differential scanning calorimetry are also reported.

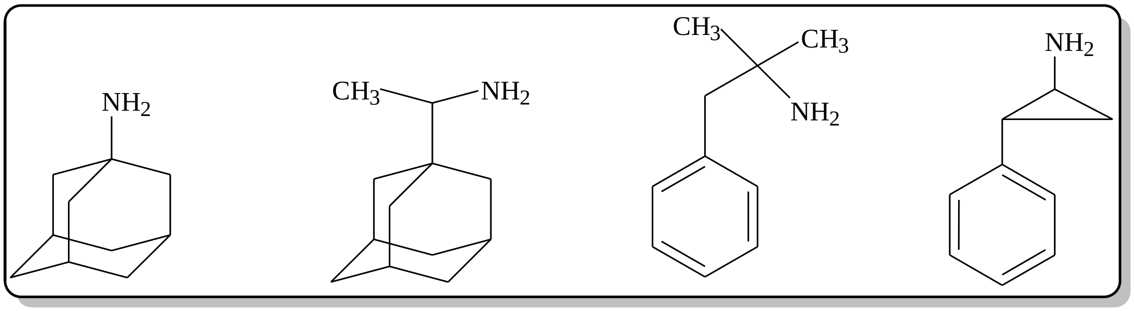

Figure 2-1. From left to right: amantadine; (*dl*)-rimantadine; phentermine; tranylcypromine.

The vapor pressures and vaporization enthalpies of a set of primary *n*-alkylamines have recently been reported, including that of amphetamine.[9] Transpiration experiments were performed in order to measure these *n*-alkylamines and the properties of amphetamine were acquired through correlation gas chromatography. The data evaluated in this previous study combined with some additional data from literature triggered a similar evaluation of rimantidine, phentermine, and tranylcypromine. These compounds are all functionally similar to previously used or studied materials. Using a series of 1-alkanamine standards, the vapor pressures and vaporization enthalpies of these materials are evaluated. When available, the vapor pressure data is compared to literature values and boiling temperatures. The vapor pressures and sublimation enthalpies of 1-dodecanamine and 1-tetradecanamine are also reported using available fusion enthalpies or those that have been measured.

Previously, Bazyleva *et al.*[10] have reported the thermochemical information for amantadine (1-adamantylamine). The structural similarity of amantadine to rimantidine is what prompted our initial interest in using this compound as a standard for our measurements. Upon examination of the properties of amantadine, however, we were surprised by the size of its sublimation enthalpy. A thorough investigation of the vapor pressure of amantadine as a function of temperature provided a sublimation enthalpy of just (61.7 ± 0.6) kJ·mol^{-1}.[10] At first glance, this value seemed extremely small for a crystalline solid melting at T/K = (479-481). Particularly because a vaporization enthalpy of about 60 kJ·mol^{-1} is estimated by a simple equation used to estimate vaporization enthalpy.[11] The estimation details are explained in the experimental section. Due to the sublimation enthalpy being lower than expected, the vaporization enthalpy and vapor pressure of liquid amantadine were also investigated by correlation gas chromatography. The vapor pressure and sublimation enthalpy of both the solid and sub-cooled liquid were also investigated and the values of the solid are compared to existing values.[10]

2.2. Experimental

2.2.1. Materials. Table 2-1 lists the source of the amines used in this study and their composition. (*dl*)-Rimantadine was supplied as the hydrochloride salt which was neutralized with 1M NaOH and extracted with hexane before use. The remainder of the amines were added to the hexane solution until comparable concentrations of all the amines were achieved. Analytical grade phentermine was purchased as a solution in methylene chloride and in the experiments where this substance was included, used as provided. The purity of this material was evaluated by gas chromatography. The retention time of each amine was also measured independently for identification purposes.

TABLE 2-1. Origin of the Standards and Targets and Their Analysis

Compound	CAS RN	Supplier	Mass fraction	GC
Benzylamine	[100-46-9]	MCB[a]	0.96	
1-heptanamine	[111-68-2]	Sigma Aldrich	0.99	
(*dl*) α-methylbenzylamine	[618-36-0]	Sigma Aldrich	0.99	>0.99
2-phenethylamine	[64-04-0]	Fluka	AS[b]	>0.99
1-octanamine	[111-86-4]	Sigma Aldrich	0.99	
(*dl*)-tranlcypromine (*trans* 2-phenylcyclopropylamine)	[155-09-9]	Sigma	0.97	
phentermine[c] (α,α-dimethylphenethylamine)	[122-09-8]	Supleco	0.99+	
amantadine (1-adamantylamine)	[768-94-5]	Sigma Aldrich	0.97	
1-decanamine	[2016-57-1]	Sigma Aldrich	0.95	
(*dl*)-rimantadine[d] (1-(1-adamantyl)ethylamine)	[13392-28-4]	Sigma Aldrich	0.99	
1-dodecanamine	[124-22-1]	Sigma Aldrich	0.98	
1-tetradecanamine	[2016-42-4]	Sigma Aldrich	0.95	

[a] Matheson, Coleman and Bell. [b] Analytical Standard. [c] Supplied in methylene chloride. [d] Available as the hydrochloride.

2.2.2. Fusion Enthalpies. The fusion enthalpy of 1-adamanylamine (amantadine) was measured on a Perkin Elmer DSC 7 instrument using the Pyris Series Thermal Analysis software at a heating rate of rate of 5 K/60s under a flow of nitrogen. The instrument was calibrated using high purity indium and tin samples provided by the manufacturer. The measurements of 1-adamanylamine (amantadine) were performed on samples as received from the supplier and also on material that was vacuum sublimed. As noted by Bazyleva *et al.*,[8] 1-adamanylamine in contact with air reacts with either carbon dioxide or water vapor since the commercial sample exhibited broad peaks at approximately *T*/K = 333, 410 and 435. Only the peak due to fusion was found to be totally reproducible. Samples that were hermetically sealed in aluminum pans, examined after fusion exhibited some pan distortion likely due to the buildup of internal pressure. This distortion was probably responsible for some peak abnormalities observed near the fusion temperature. These abnormalities were avoided by using of high pressure sealable stainless steel capsules, (Perkin Elmer, Product number: B0182902) capable of withstanding pressures up to 150 atm. Following sublimation of the sample, only a single peak at T/K = 477 was observed. The area of the fusion peak at T/K = 477 was sharp and no additional peaks were observed. Experimental results recorded on both sets of sealed cells are summarized in Table 2-2. In addition to the fusion enthalpy exhibited by 1-adamanylamine, solid-solid phase transitions below room temperature at T_{trs1}/K = 241.4 (1.72±0.01) kJ·mol^{-1} and T_{trs2}/K = 284.6 (5.31±0.01) kJ·mol^{-1}have also been reported.[8]

TABLE 2-2. Fusion Enthalpies of 1-Adamantylamine (sublimed)

mass	T_{fus}/K onset	$\Delta_{\text{cr}}{}^{\text{l}}H_{\text{m}}(T_{\text{fus}})$ J·g^{-1}	$\Delta_{\text{cr}}{}^{\text{l}}H_{\text{m}}(T_{\text{fus}})$ kJ·mol^{-1}
13.92	476.5	47.83	7.23
22.59	478.2	49.33	7.46
12.36	477.4	47.18	7.14
avg	477.4±0.9	48.1±1.1	7.3±0.2

2.2.3. Powder Pattern: 1-Adamanylamine. Efforts to obtain a crystal structure of 1-adamantylamine at room temperature were unsuccessful. The material was not observed to diffract. The powder pattern of 1-adamantylamine at T/K =298.15 indicated approximately 50% crystallinity. Details regarding the powder pattern are included in the supplementary material. Powder XRD data were collected using a Rigaku Ultima IV powder diffractometer with Cu radiation. Scans were collected in 2theta-theta scanning mode at 40KV/44mA power settings. JADE 9.3 software was used for data analysis.

2.2.4. Methods. Correlation-gas chromatography experiments were conducted in the same manner as previously described in Section 1.2.2.2. Each plot was characterized by a correlation coefficient of $r^2 > 0.99$. The only differences were that this time the column used was a 0.32 mm, 30 m DB5 column, the temperature was maintained to T/K = 0.1 as monitored by a Fluke digital thermometer and hexanes and methylene chloride served as the non-retained reference. All retention times are provided in Appendix B.

2.2.5. Estimation. Vaporization enthalpy estimations were conducted in the same manner as previously described in Section 1.2.6., again calculated using equation 1-6. Here though, the contribution of the functional group (b) is that of a primary amine (14.8 kJ·mol^{-1}).[11] The carbon bearing the nitrogen was treated as a quaternary carbon (n_Q). For amantadine, $C_{10}H_{17}N$, a vaporization enthalpy of 61.3 kJ·mol^{-1} is estimated.

2.2.6. Standards. The vaporization enthalpies used for the standards are summarized in Table 2-3. The values in bold are the average values used in the correlations. Additional details on their selection can be found in reference 9.

TABLE 2-3. Thermodynamic Properties of the Primary Amines Used As Standards.[9]

Compounds	T/K Range	$\Delta_l^g H_m(T_m)(T_m/K)$ kJ·mol^{-1}	C_p^l J·mol^{-1}·K^{-1}	$\Delta_l^g C \Delta T$ kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}	p/Pa[a] 298.15 K	Ref.
Benzylamine	293 - 363	52.7 ± 0.3 (328)	215.6	1.9 ± 0.5	54.6 ± 0.6	95	13
	302 - 458	48.96 (380)	215.6	5.4 ± 1.3	54.4 ± 1.3	110	14, 15
	276 - 313	54.5 ± 0.3 (295)	215.6	-0.2	54.3 ± 0.3	88	9
	277 - 316	54.4 ± 0.3 (297)			54.4 ± 0.3	87	9
				(avg)	**54.4 ± 0.6**	95±10	
1-heptanamine	298.15				50.0 ± 0.1		16
	327 - 430	43.4 ± 0.6 (379)	285.7	6.8 ± 1.3	50.2 ± 1.4	288	17
	280 - 306	50.2 ± 0.4 (293)	285.7	-0.4	49.8 ± 0.4	291	9
				(avg)	**50.0 ± 0.2**	**288**[17]	
(*dl*) α-methyl-Benzylamine	283 - 318	54.7 ± 0.3 (301)			55.0 ± 0.3	1.2	18
	284 - 323	54.9	241		55.3 ± 0.3	82	9
				(avg)	**55.2 ± 0.4**	82	
2-phenethyl-Amine	273 - 352	55.7 ± 0.2 (313)			56.8 ± 0.2	44	13
	285 - 323		247.5		57.5 ± 0.3	43	9
				(avg)	**57.2 ± 0.3**	44±1	
1-octanamine	308 - 453	47.8 ± 0.4 (381)	317.6		55.5 ± 2.3	136	17
	344 - 494	43.5 ± 0.4 (419)			54.6 ± 0.5	122	19
	274 - 313	55.3 ± 0.3 (294)			55.1 ± 0.3	108	9
				(avg)	**55.1 ± 0.5**	**122**[19]	
1-decanamine	329 - 431	56.1± 0.6 (380)	381		65.1 ± 0.6	11	17
	299 - 343	64.9 (321)			64.9 ± 0.3	12	9
				(avg)	**65.0 ± 0.2**	**11**[17]	
1-dodecanamine	367- 444	61.3 ± 0.4 (406)	445.2		74.8 ± 1.8	2	17
	356 - 455	62.8 ± 0.7 (399)			75.5 ± 1.8	3	15
					75.2 ± 1.8	**2**[17]	
1-tetradecanamine	382-455	64.5 ± 1.0 (409)	509	15.9 ± 1.8	**85.4 ± 2.0**	0.03	17

[a] Extrapolated to T/K = 298.15 if necessary from the temperature range noted in column 2, reference 9; only the values in bold were used in subsequent correlations.

Vapor pressures for the all of the standards are also available but some are available only over a limited temperature range. Vapor pressures over a larger temperature range have been reported for 1-octanamine by Steele *et al.* [19] and for 1-heptanamine, 1-octanamine, 1-decanamine, 1-dodecanamine and 1-tetradecanamine by Ralston *et al.*[17] as noted in Table 2-3. Since the results from Ralston *et al.* are quite old, the vapor pressures for 1-octanamine reported by Ralston *et al.* were compared to those reported by Steele *et al.*

and found to compare quite favorably. A visual comparison is available in the supplementary material. Consequently, the vapor pressures measured for 1-heptanamine, 1-decanamine, and 1-dodecanamine by Ralston *et al.*[17] and those reported by Steele *et al.* for 1-octanamine were used as standards in subsequent correlations. Only the vapor pressures for 1-tetradecanamine reported by Ralston *et al.* did not correlate well with the other 1-alkanamines at the lower temperatures, perhaps because of the large temperature extrapolation required. The vapor pressures of 1-tetradecanamine were not used as standards in the initial correlations. This compound's vapor pressures were treated as a target and evaluated by correlation for comparative purposes at the higher temperatures. The vapor pressures for 1-tetradecanamine evaluated in this work were used as a standard in one subsequent set of correlations. The experimental vaporization enthalpy of 1-tetradecanamine, evaluated at a mean temperature of T/K = 409 from literature vapor pressure measurements reported over the temperature range T/K = (382-454) and adjusted to T/K = 298.15, did correlate well with the other 1-alkanamines as determined in the trial runs described below and was used as a vaporization enthalpy standard. The literature vapor pressures reported for the C_7, C_8 C_{10} and C_{12} 1-alkanamines,[17, 19] reported over the temperature ranges cited in Table 2-3 were all fit to a third order polynomial, eq 1-10, found to extrapolate well with temperature.[9,12] The constants of eq 1-10, A-D are summarized in Table 2-4; p represents the vapor pressure and p_o refers to 101325 Pa. Equation 1-10 was then used to predict the normal boiling temperature of the C_7, C_8 C_{10} and C_{12} 1-alkanamines which are also reported in Table 2-4. As noted in the last two columns of this table, the predicted boiling temperatures reproduce the experimental values within few degrees. As a consequence of this agreement, the vapor pressures calculated using eq 1-10 were used as standards.

TABLE 2-4. Constants for Equation 1-10 Generated from Experimental Vapor Pressure - Temperature Data

	$A \cdot 10^{-8}$ /K^3	$B \cdot 10^{-6}$ /K^2	$C \cdot 10^{-3}$/K	D	T_b/K[a] Calc	T_b /K[a] lit
1-heptanamine[17]	-10.395	7.611	-23.498	26.552	430	427-9
1-octanamine[19]	0.134	-0.726	-2.167	8.207	452	448-50
1-decanamine[17]	-3.300	1.802	-9.270	14.128	494	489-91
1-dodecanamine[17]	3.301	-3.025	1.630	5.427	532	532

[a] nBT: normal boiling temperature.

2.2.7. Temperature Adjustments. Adjustments from the mean temperature of measurement, T_m , to a common temperature, T/K = 298.15, were achieved in the same way as described in Section 1.2.4. using only equations 1-3 and 1-4.

2.2.8. Uncertainties. Uncertainties in the temperature adjustment of vaporization enthalpy, eq 1-3, were calculated using an uncertainty of ±16 $J \cdot mol^{-1} \cdot K^{-1}$ for C_p(l). The uncertainty in the temperature adjustment of the fusion enthalpy, eq 1-4, has been estimated as 30% of the total adjustment.[20] Potential uncertainties in results from correlations were evaluated from both the uncertainty in the slope and intercept evaluated as $(u_1^2 + u_2^2 + ..)^{0.5}$. Uncertainties in derived results were evaluated similarly unless noted otherwise.

2.3. Results

2.3.1. Vaporization Enthalpies. As previously stated, due to the fact that the vapor pressures described by Ralston *et al.*[17] are older, the vaporization enthalpies for 1-tetradecanamine and 1-dodecanamine were treated as unknown and evaluated using their enthalpies of transfer as measured by gas chromatography and the experimental vaporization enthalpies of the C_7, C_8 and C_{10} 1-alkanamines previously reported.[9] The correlation acquired in runs 1/2 by correlating enthalpies of transfer with the experimental vaporization enthalpies listed in Table 2-5 is illustrated by equations 2-1 and 2-2 given underneath the table. Equation 2-6 describes the correlation acquired for run 1. Similar information for run 2 described by eq 2-2 is available in Appendix B. The vaporization enthalpies determined in run 1 are well within the experimental uncertainty of the literature values for 1-dodecanamine and 1-tetradecanamine. These details are listed in the last column of Table 2-5 and were not used in either correlation.

TABLE 2-5. Validation of the Vaporization Enthalpies of 1-Dodecanamine and 1-Tetradecanamine

Run 1	- slope T/K	intercept	ΔH_{trn}(439 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)
1-heptanamine	4354.0	11.024	36.20	50.0 ± 0.2	50.1 ± 1.4	
1-octanamine	4750.6	11.375	39.49	55.1 ± 0.5	54.9 ± 1.5	
1-decanamine	5577.9	12.247	46.37	65.0 ± 0.2	65.0 ± 1.6	
1-dodecanamine	6451.6	13.277	53.64		75.7 ± 1.8	75.2 ± 1.8
1-tetradecanamine	7331.0	14.344	60.95		86.5 ± 1.9	85.4 ± 2.0

Run 1:

$$\Delta_l^g H_m(298.15\text{ K})/(\text{kJ·mol}^{-1}) = (1.47 \pm 0.03)\ \Delta H_{trn}(439\text{K}) - (3.1 \pm 1.1) \qquad r^2 = 0.9997 \quad (2\text{-}1)$$

Run 2:

$$\Delta_l^g H_m(298.15\text{ K})/(\text{kJ·mol}^{-1}) = (1.54 \pm 0.04)\ \Delta H_{trn}(439\text{K}) - (5.7 \pm 1.7) \qquad r^2 = 0.9993 \quad (2\text{-}2)$$

Due to the overlap of retention times for some of the remaining primary amines in this work with some of the standards it was necessary to conduct duplicate evaluations using separate correlations. Correlation equations 2-3 through 2-8 for runs 3-8 are shown in Table 2-6. Table 2-6 shows details for only one set of correlations. A full listing of the details is available in Appendix B. The amines listed in these tables are given in order of their elusion off the column. The vaporization enthalpies calculated using eqs 2-1 through 2-8 for both the target compounds and standards are listed in Table 2-7. The data acquired for the standards is compared to their literature values in the last two columns of the table.

TABLE 2-6. Correlation of Vaporization Enthalpies with Enthalpies of Transfer of Some Primary Amines

Run 3	- slope T/K	intercept	ΔH_{trn}(449 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)
1-heptanamine	4187.9	10.619	34.82	50.0 ± 0.2	51.7 ± 3.2
1-octanamine	4565.9	10.934	37.96	55.1 ± 0.5	56.0 ± 3.4
(*dl*) α-methylbenzylamine	4356.7	10.314	36.22	55.2 ± 0.4	53.6 ± 3.3
2-phenethylamine	4540.9	10.462	37.75	57.2 ± 0.3	55.8 ± 3.3
α,α-dimethylphenethylamine	4801.1	10.730	39.91		58.8 ± 3.4
1-decanamine	5382.3	11.783	44.75	65.0 ± 0.2	65.4 ± 3.6
1-adamantylamine	4852.5	10.369	40.34		59.3 ± 3.4
1-dodecanamine	6242.9	12.784	51.90	75.5 ± 1.8	75.3 ± 3.9
(*dl*) 1-(1-adamantyl)ethylamine	5661.9	11.225	47.07		68.6 ± 3.7
1-tetradecanamine	7129.9	13.870	59.28	85.4 ± 2.0	85.5 ± 4.3

Run 3:

$\Delta_l^g H_m$(298.15 K)/(kJ·mol^{-1}) = (1.38 ± 0.06) ΔH_{trn}(449K) – (3.51 ± 2.5) $r^2 = 0.9913$ (2-3)

Run 4:

$\Delta_l^g H_m$(298.15 K)/(kJ·mol^{-1}) = (1.38 ± 0.06) ΔH_{trn}(449K) – (3.25 ± 2.5) $r^2 = 0.9917$ (2-4)

Run 5	- slope T/K	intercept	ΔH_{trn}(403 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)
benzylamine	4422.9	10.659	36.77	54.4 ± 0.6	54.2 ± 1.6
(*dl*) α-methylbenzylamine	4569.2	10.832	37.99	55.2 ± 0.4	55.4 ± 1.7
2-phenethylamine	4774.7	11.030	39.70	57.2 ± 0.3	57.2 ± 1.7
α,α-dimethylphenethylamine	5267.8	11.853	43.79		61.5 ± 1.8
1-decanamine	5662.7	12.456	47.08	65.0 ± 0.2	65.0 ± 1.9
trans 2-phenylcyclopropylamine	5256.3	11.527	43.70		61.4 ± 1.8
1-adamantylamine	5098.1	10.965	42.38		60.0 ± 1.8

Run 5:

$\Delta_l^g H_m$(298.15 K)/(kJ·mol^{-1}) = (1.05 ± 0.03) ΔH_{trn}(403K) – (15.6 ± 1.2) $r^2 = 0.9983$ (2-5)

Run 6:

$\Delta_l^g H_m$(298.15 K)/(kJ·mol^{-1}) = (1.05 ± 0.03) ΔH_{trn}(403K) – (15.7 ± 1.2) $r^2 = 0.9984$ (2-6)

Run 7	- slope T/K	intercept	ΔH_{trn}(469 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)
(*dl*) α-methylbenzylamine	4274.8	10.151	35.54	55.2 ± 0.4	55.0 ± 2.3
2-phenethylamine	4430.4	10.238	36.83	57.2 ± 0.3	56.7 ± 2.3
α,α-dimethylphenethylamine	4687.5	10.498	38.97		59.7 ± 2.4
trans 2-phenylcyclopropylamine	4637.9	10.169	38.56		59.1 ± 2.4
1-decanamine	5246.8	11.502	43.62	65.0 ± 0.2	66.1 ± 2.5
1-adamantylamine	4741.6	10.143	39.42		60.3 ± 2.4
1-dodecanamine	6058.0	12.396	50.36	75.5 ± 1.8	75.4 ± 2.7
1-tetradecanamine	6902.0	13.389	57.38	85.4 ± 2.0	85.1 ± 2.9

Run 7:

$$\Delta_l^g H_m(298.15\ \text{K})/(\text{kJ·mol}^{-1}) = (1.38 \pm 0.04)\ \Delta H_{trn}(469\text{K}) - (5.95 \pm 1.8)\quad r^2 = 0.9975 \quad (2\text{-}7)$$

Run 8:

$$\Delta_l^g H_m(298.15\ \text{K})/(\text{kJ·mol}^{-1}) = (1.37 \pm 0.04)\ \Delta H_{trn}(469\text{K}) - (6.28 \pm 1.8)\quad r^2 = 0.9975 \quad (2\text{-}8)$$

TABLE 2-7. A Summary and Comparison of the Vaporization Enthalpies (kJ·mol^{-1}) With Literature Values at T/K = 298.15.

	run 1	run 2	run 3	run 4	run 5	run 6	run 7	run 8	Avg[a]	Lit
benzylamine					54.2±1.6	54.2±1.6			54.2±1.6	54.6±0.6
1-heptanamine	50.1±0.7	50.5±1.4	51.7±3.2	51.6±3.2					51.0±2.1	50.0±0.2
(*dl*) α-methyl-benzylamine			53.6±3.3	53.7±3.2	55.4±1.7	55.4±1.7	55.0±2.3	55.0±2.3	54.7±2.4	55.2±0.4
2-phenethylamine			55.8±3.3	55.8±3.3	57.2±1.7	57.2±1.7	56.7±2.3	56.7±2.3	56.6±2.4	57.2±0.3
1-octanamine	54.9±0.7	54.9±1.5	56.0±3.4	56.0±3.3					55.5±2.2	55.1±0.5
trans 2-phenyl-cyclopropylamine					61.4±1.8	61.4±1.8	59.1±2.4	59.2±2.4	60.3±2.1	
α,α-dimethyl-phenethylamine			58.8±3.4	58.8±3.4	61.5±1.8	61.7±1.8			60.2±2.6	
1-adamantylamine			59.3±3.4	59.4±3.4	60.0±1.8	60.1±1.7	60.3±2.4	60.3±2.4	59.9±2.5	
1-decanamine	65.0±0.7	64.6±1.6	65.4±3.6	65.5±3.6	65.0±1.9	65.0±1.8	66.1±2.5	66.1±2.5	65.3±2.3	65.0±0.2
1-dodecanamine	75.5±0.8	75.1±1.7	75.3±3.9	75.3±3.9			75.4±2.7	75.4±2.7	75.3±2.6	75.2±1.8
(*dl*) 1-(1-adamantyl)-ethylamine			68.6±3.7	68.7±3.7					68.7±3.7	
1-tetradecanamine	86.2±0.9	85.8±1.8	85.5±4.3	85.5±4.2			85.1±2.9	85.1±2.9	85.5±2.8	85.4 ± 2.0

[a] The uncertanties are also averages

2.3.2. Liquid Vapor Pressures. Retention times in the form ln(t_o/t_a) have also been found to correlate well with vapor pressures given in the form ln(p/p_o). Summarized in Table 2-8 is the data from the correlation at T/K = 298.15 for the compounds in runs 3/4 of Table 2-6 using vapor pressures of the primary alkyl amines of Table 2-4 as standards. Values of (t_o/t_a) evaluated from each pair of runs in Table 2-6 were averaged and plotted as ln(t_o/t_a)$_{avg}$. With the aid of eq 1-10, the constants of Table 2-4 and available experimental data were used to calculate vapor pressures, which were then plotted as ln(p/p_o).[17,19] The quality of the correlation acquired at T/K = 298.15 is illustrated by equation 2-9.

TABLE 2-8. Correlation Between $\ln(t_o/t_a)_{\text{avg}}$ and Literature $\ln(p/p_o)$ Values For Runs 3 and 4 at T/K = 298.15

	$\ln(t_o/t_a)_{\text{run 3}}$	$\ln(t_o/t_a)_{\text{run 4}}$	$\ln(t_o/t_a)$ avg	$\ln(p/p_o)$ lit	$\ln(p/p_o)$ calc
1-heptanamine	-3.427	-3.443	-3.435	-5.868	-5.867
(*dl*) α-methylbenzylamine	-4.300	-4.323	-4.311		-6.785
1-octanamine	-4.380	-4.400	-4.39	-6.723	-6.868
2-phenethylamine	-4.768	-4.790	-4.779		-7.277
1-decanamine	-6.269	-6.291	-6.28	-9.139	-8.852
α,α-dimethylphenethylamine	-5.373	-5.395	-5.384		-7.912
1-adamantylamine	-5.907	-5.930	-5.918		-8.472
(*dl*) 1-(1-adamantyl)ethylamine	-7.765	-7.785	-7.775		-10.420
1-dodecanamine	-8.155	-8.174	-8.165	-10.686	-10.829
1-tetradecanamine	10.044	10.056	-10.05		-12.807

$\ln(p/p_o) = (1.049 \pm 0.69) \ln(t_o/t_a)_{\text{avg}} - (2.26 \pm 0.40)$ $r^2 = 0.9915$ (2-9)

Correlations were repeated at T/K = 10 increments from T/K = 298.15 to 500. The resultant correlation coefficients, r^2, were greater than 0.99 at all temperatures and neared 1.0 at higher temperatures. The resulting vapor pressures from each correlation were then fit to a third order polynomial, eq 1-10, as a function of temperature. Summarized in Table 2-9 are the estimated vapor pressures at T/K = 298.15 for both the target compounds and standards used in runs 3/4, along with the A-D constants of eq 1-10. Also incorporated in the last column of the table are the normal boiling temperatures predicted using eq 1-10. The coefficients of eq 1-10 for all target compounds investigated in subsequent correlations, runs 5-8, are included in this table, as well. Normal boiling temperatures, predicted vapor pressures at T/K = 298.15 and coefficients for eq 1-10 determined in runs 5-8 for both the target compounds and standards are listed in Appendix B.

TABLE 2-9. A-D Constants of Equation 3, Liquid Vapor pressures at *T*/K = 298.15 and Normal Boiling Temperatures (T_b/K) Evaluated from Runs 3/4, 5/6, and 7/8.

	$A\cdot10^{-8}$ /K^3	$B\cdot10^{-6}$ /K^2	$C\cdot10^{-3}$/K	D	$p_{(l)}$/Pa 298.15 K Calc	T_b/K calc
Runs 3/4						
1-heptanamine	-7.22	5.039	-16.688	20.657	287	429
(*dl*) α-methylbenzylamine	-4.76	3.083	-11.701	15.743	115	461
2-phenethylamine	-3.693	2.249	-9.737	14.025	70	473
1-octanamine	-5.062	3.353	-12.734	17.217	105	453
α,α-dimethylphenethylamine	-2.379	1.226	-7.383	12.04	37	488
1-adamantylamine	-0.732	-0.093	-3.926	8.506	21	515
1-decanamine	-0.969	0.17	-5.417	11.065	15	495
1-dodecanamine	2.99	-2.901	1.534	5.375	2	532
1-(1-adamantyl)ethylamine	3.275	-3.209	3.224	2.512	3	566
1-tetradecanamine	6.886	-5.917	8.307	-0.081	0.3	570
Runs 5 and 6						
Benzylamine	-5.306	3.503	-12.619	16.486	160	453
α,α-dimethylphenethylamine	-2.298	1.192	-7.623	12.7	30	483
trans 2-phenylcyclopropylamine	-1.114	0.219	-4.927	9.86	23	500
1-adamantylamine	-0.372	-0.416	-2.947	7.534	22	517
Runs 7 and 8						
α,α-dimethylphenethylamine	-2.400	1.248	-7.457	12.12	37	487
trans 2-phenylcyclopropylamine	-1.756	0.730	-6.019	10.521	31	500
1-adamantylamine	-0.805	-0.018	-4.190	8.802	21	514

A comparison of the coefficients of eq 1-10 acquired for the standards in Table 2-9 show little similarity to those listed in Table 2-4. When the predicted boiling temperatures for the standards in both tables are compared though, a difference of only a degree is seen. The subsequent vapor pressure predictions at *T*/K = 298.15 were acquired using the two sets of constants listed in Table 2-4 and 2-9, respectively (*p*/Pa): 1-heptylamine (288, 286), 1-octanamine (122, 105), 1-decanamine (10.8, 8.8), and 1-dodecanamine (2.3, 2.0). This shows that the constants listed in Tables 2-3 and 2-9 would perhaps be fairly accurate for supplying vapor pressures over the temperature range *T*/K = 298.15 to T_b, from room temperature to the respective boiling temperature of each compound.

Comparable correlations to those listed in Table 2-8 were replicated for runs 5/6 and for runs 7/8 over the temperature range *T*/K = 298.15 to 500. These correlations were also conducted at *T*/K = 10 increments. Information comparable to Table 2-8 for these runs is listed in Appendix B. 1-decanamine and the results from runs 3/4 for (*dl*) α-methylbenzylamine and 2-phenethylamine were used as standards for runs 5/6. The results for α-methylbenzylamine, 2-phenethylamine and 1-tetradecanamine also acquired from runs 3/4, along with 1-decanamine and 1-dodecanamine were used as standards in runs 7/8. Correlation coefficients, r^2, were greater than 0.999 at all temperatures. Included for runs 5/6 and 7/8 in Table 2-9 are liquid vapor pressures at *T*/K = 298.15, the A-D constants for eq 1-10 and predicted boiling temperatures for only the compounds treated as unknowns. Complete information for all compounds is listed in Appendix B. All correlation results are discussed below.

2.4. Discussion

2.4.1. Vaporization Enthalpies. The major structural feature common to all compounds is that they are all primary alkyl amines. This is shown in Table 2-7. Primary aromatic amines, such as the anilines, have previously been shown to not correlate as well with their aliphatic counterparts. Provided the amino functionality is not directly attached to the aromatic ring though, vaporization enthalpies for phenyl substituted alkyl amines appear to be replicated quite well by primary aliphatic amines as has been shown by this work. The correlation coefficients, r^2, were greater than 0.99 for all runs. The uncertainty listed in the second to last column of Table 2-7 is an average of the uncertainty associated with each run and is significantly less than 4 $kJ\cdot mol^{-1}$. The standard deviation related to the reproducibility of each value produced in runs 1-8 ranged from 0.44 $kJ\cdot mol^{-1}$for 1-

adamantylamine to 1.6 kJ·mol^{-1} for 2-phenethylamine. The vaporization enthalpies of the standards are well within the experiment error of the reported literature values. As stated in the introduction, the vaporization enthalpy of 1-adamantylamine of (59.9±2.5) kJ·mol^{-1} agrees favorably with the 60 kJ·mol^{-1} estimated using eq 1-6.

2.4.2. Liquid Vapor Pressures and Boiling Temperatures. The boiling temperature data of the correlations listed in Table 2-9 and predicted vapor pressures at T/K = 298.15 are compared to literature values or in a few cases to estimated values in Table 2-10.

TABLE 2-10. A Summary of Liquid/Subcooled Liquid Vapor Pressures and Normal Boiling Temperatures (T_b/K) in Table 9 and Comparison with Experimental or Estimated Values

	$p_{(l)}$/Pa 298.15 K calc	$p_{(l)}$/Pa 298.15 K exp[a]	T_b/K calc	T_b/K lit[b]
Benzylamine	160	87-110	453	457-8
1-heptanamine	287	288	429	427-9
(*dl*) α-methylbenzylamine	115/116/114	1.2-82	461/461/461	458
2-phenethylamine	70/70/71	43-44	473/473/473	470-3
1-octanamine	105	122	453	448-50
trans 2-phenylcyclopropylamine	31/23/31	15.6[c]	500/500	494[c]
α,α-dimethylphenethylamine	37/30/37	32[c]	488/483/487	478[d]
1-adamantylamine	21/22/21	21.8[c]	515/517/514	501[c]
1-decanamine	15/15/15	11	495/494/494	489-91
1-dodecanamine	2/2	2	532/532	532[f]
1-(1-adamantyl)ethylamine	3	6[c]	566	513[c]
1-tetradecanamine	0.3/0.3	0.03[g]/0.5[h]	570/569	565[e]

[a] Data and references available in Table 3 unless noted otherwise. [b] Normal boiling temperatures from the 2012-14 Handbook of Fine Chemicals, Sigma-Aldrich, unless noted otherwise. [c] Estimate from reference 22. [d] From reference 23. [e] From reference 24. [f] Lide, D. R. CRC Handbook of Chemistry and Physcis 76th ed. Boca Raton FL: CRC Press Inc. 1995, p 3-147. [g] Extrapolated from T/K = 382; the vapor pressures for this material did not correlate well with the other 1-alkanamines; reference 17. [h] From an experimental database; literature reference not provided, reference 22.

The values in columns 2 and 4 refer to predicted vapor pressures and boiling temperatures evaluated for up to three sets of independent correlations acquired from runs 3-8. The first of up to three entries is the value estimated using the compound as a target and the following values are those acquired using the same compound as a standard. Even though the three sets of correlations made use of some different standard compounds, vapor pressures and boiling temperatures are rather reproducible. At T/K = 298.15 vapor pressures seem to give the best reproducibility for aliphatic amines while the vapor pressures for primary amines with a phenyl group usually seem to be slightly overestimated. Normal boiling temperatures seem to be somewhat over predicted but they are otherwise well reproduced regardless of structure. The biggest discrepancies are seen with values that are estimated.

2.4.3. Fusion Enthalpies. The fusion enthalpies of both 1-dodecanamine and 1-tetradecanamine are available in literature. In general, equation 1-4 listed above has been successful in supplying suitable temperature adjustments of fusion enthalpies. This equation is dependent upon the estimation of heat capacities of both the solid and liquid phases at T/K = 298.15 through group additivity. For 1-adamantylamine, the heat capacity has been experimentally determined to be 266 $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$. In comparison, a value of 210 $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ has been estimated by group additivity for the crystalline phase and 294.6 $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ has been estimated for the liquid at T/K = 298.15. As previously stated, the powder pattern of 1-adamantylamine implies 50% crystallinity. The estimated value in this case is considerably different from the experimental value, a value almost in the middle of the value predicted for the solid and liquid phases of 1-adamantylamine.

The estimated and experimental heat capacities of some other polycyclic compounds of similar structure are provided in Table 2-11 for comparison.

TABLE 2-11. A Comparison of C_p(cr) Estimations With Experimental Values at T/K = 298.15 For Some Polycyclic Compounds With and Without Multiple Solid-Solid Phase Changes.

	T_{trs1}/K/T_{trs2}/K	$\Delta_{trs}H(T_{trs})$ kJ·mol^{-1}	T_{fus}/K	$\Delta_{cr}^{l}H(T_{fus})$ kJ·mol^{-1}	$C_p(cr)_{est}^{a}/C_p(cr)_{exp}$ J·mol^{-1}·K^{-1}	Ref.
1-adamantylamine	241/285	1.72/5.31	477.4	7.3	210/266	10
Adamantine	209	3.38	543	14.0	194/190	25/26
endo-tricyclo[5.2.1.0^{2,6}]decane	204	2.57	345	3.07	194/205	27
Hexamethylenetetramine				NA^{b}	152/154	23
1-adamantanol	357	11.3	553	12.4	212/197	28
2-adamantanol	238/322/389	0.16/2.3/8.0	569	11.9	205/207	28

^{a}Calculated using the following group values for crystalline materials[21]: -NH_2 (21.6); -OH (23.5); cyclic N(C_3) (1.2); cyclic C(C_2)(H_2); (24.6); cyclic C(C_3)(H) (11.7); cyclic C(C_3)(N), C(C_3)(O) (6.1) J·mol^{-1}·K^{-1}. ^{b}Not Available.

Below ambient temperature Adamantane displays a substantial phase transition, but is adequately crystalline for X-ray analysis. Single crystal data implies a disordered structure.[30] *endo*-Tricyclo[5.2.1.0^{2,6}]decane, whose crystal structure is not known, also displays a significant phase transition below room temperature. The phase transitions displayed by the two adamantanols, however, occur above T/K = 298.15 and hexamethylenetetramine does not seem to display any solid–solid phase transitions. The heat capacities of all these materials are well reproduced by estimation. The inconsistency in C_p(cr)(298.15 K) detected for 1-adamantylamine implies either greater motion and/or disorder in the solid state as compared to *endo*-tricyclo[5.2.1.0^{2,6}]decane or the group value used for solid aliphatic primary amines needs to re-evaluated. The current group value was determined on the basis of 38 entries consisting of either amino acids or aromatic amines. These were all effectively modeled with the current value for a primary amine.[21] To our knowledge, 6-aminohexanol seems to be the only other solid primary aliphatic amine whose C_p(cr)(298.15 K) has been measured,[31] in addition to 1-adamantylamine. The reported heat capacity of 230 J·mol^{-1}·K^{-1} compares with an estimated value of 207 J·mol^{-1}·K^{-1}. Even though the estimated value is about 23 J·mol^{-1}·K^{-1} lower that the reported value, it is within 10% of the experimental value and not enough to justify adjustment of the current value at this time. As a consequence, fusion enthalpy temperature adjustments to T/K = 298.15 of 1-adamantylamine used the experimental heat capacity for the solid while similar adjustments for 1-dodecanamine and 1-tetradecanamine made use of estimated values. All C_p(l) values were estimated. The results are listed in Table 2-12. Uncertainties for the fusion enthalpies of 1-dodecanamine and 1-tetradecanamine are not available.[31] Even though a somewhat negative fusion enthalpy is evaluated for 1-adamantylamine at T/K = 298.15, when the uncertainty in the temperature adjustment is taken into account a possible fusion enthalpy of up to 1.5 kJ·mol^{-1} is still consistent with the temperature adjustments.[32]

TABLE 2-12. Fusion, Vaporization and Sublimation Enthalpies at T/K = 298.15

	T_{fus}/K	$\Delta_{\mathrm{cr}}{}^{\mathrm{l}}H(T_{\mathrm{fus}})$ kJ·mol^{-1}	$C_p(\mathrm{l})_{\mathrm{est}}/C_p(\mathrm{cr})_{\mathrm{est}}$ J·mol^{-1}·K^{-1}	$\Delta C_{\mathrm{p}}\Delta T$ kJ·mol^{-1}	$\Delta_{\mathrm{cr}}{}^{\mathrm{l}}H$(298 K) kJ·mol^{-1}	$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H$(298 K) kJ·mol^{-1}	$\Delta_{\mathrm{cr}}{}^{\mathrm{g}}H$(298 K) kJ·mol^{-1}
1-adamantyl amine	477	7.3±0.2[a]	266[b]/295	-8.3±2.5	-1.0±2.5	59.9±2.5	~59.9±3.5[d]
1-dodecan amine	301.5	43.5[c]	445.2/354.1	-0.42±0.1	43.1±0.1	75.2±1.8	118.3±1.8
1-tetradecan amine	311.3	51.0[c]	509/407.9	-1.88±0.6	49.1±0.6	85.4±2.0	134.5±2.1

[a] Enthalpy for solid-liquid conversion of a partially crystalline phase, reference 10.
[b] Experimental value. [c] Reference 31. [d] See discussion in text.

2.4.4. Sublimation Enthalpies. If both the vaporization and sublimation enthalpies are adjusted to the same temperature, then they are related by equation 2-10:

$$\Delta_{\mathrm{cr}}{}^{\mathrm{g}}H(T) = \Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}(T) + \Delta_{\mathrm{cr}}{}^{\mathrm{l}}H(T) \tag{2-10}$$

The sublimation enthalpies for the three solid amines are calculated from the combination of the fusion enthalpies adjusted to T/K = 298.15 with the vaporization enthalpies from Table 2-7. These values are listed in the last column of Table 2-12. The sublimation enthalpy of 1-adamantylamine is the only value that has been measured of the three primary amines. Combination with a possible fusion enthalpy of up to 1.5 kJ·mol^{-1} gives a sublimation enthalpy of ~61.4±3.5 kJ·mol^{-1}. This agrees favorably with the experimental sublimation enthalpy of (61.7 ± 0.6) kJ·mol^{-1}.[10] At T/K = 298.15, sublimation enthalpies of 118.3±1.8 and 134.5±2.1 kJ·mol^{-1} are evaluated for 1-dodecanamine and 1-tetradecanamine, respectively. This is done by combining the vaporization enthalpies determined in this work with fusion enthalpies available in the literature which have been subsequently adjusted for temperature.

2.4.5. Sublimation Vapor Pressures. In order to independently verify the validity of both the vapor pressures calculated for 1-adamantylamine and its fusion enthalpy, it is also possible to determine the vapor pressure of the solid material and compare it to data from the literature. The vapor pressures of 1-adamantylamine over a T/K = 30 range centered at T_{fus}/K = 477.4 were independently evaluated using the constants for eq 1-10 reported in Table 2-9 for all three sets of runs. The Clausius-Clapeyron equation was then used to evaluate the vaporization enthalpy for each set of runs. A mean value for $\Delta_{\mathrm{l}}{}^{\mathrm{g}}H(T_{fus})$ of (43.8±0.6) kJ·mol^{-1} was determined. The vaporization enthalpy from each set of runs was then used in combination with the fusion enthalpy of (7.3±0.2) kJ·mol^{-1} to give a mean value for $\Delta_{\mathrm{cr}}{}^{\mathrm{g}}H(T_{\mathrm{fus}})$ of (51.1±0.7) kJ·mol^{-1}. Using the vapor pressure determined by eq 1-10 at T_{fus}/K = 477.4, used to approximate the triple point, a second application of the Clausius-Clapeyron equation modified to include a heat capacity adjustment term for the sublimation enthalpy, given by eqs 2-11 and 2-12, resulted in a mean vapor pressure for the solid phase of 11±1 Pa. at T/K = 298.15.[29,12] The individual vapor pressures resulting from each set of runs are summarized in Table 2-13.

TABLE 2-13. Solid Vapor Pressures

T/K	1-adamantylamine $p_{(cr)}$/Pa [a]	1-adamantylamine $p_{(cr)}$/Pa (lit) [b]	1-dodecanamine $p_{(cr)}$/Pa[c]	1-tetradecanamine $p_{(cr)}$/Pa[c]
298.15	11.5±2.1		1.6 ± 0.1	0.12 ± 0.04
293.6	8.0±1.6	7.8 (KE)		
297.1	10.6±2.0	10.7 (T)		

[a]Vapor pressures calculated from runs 3/4, 5/6, and 7/8, respectively; the uncertainty represents two standard deviations of the results. [b]KE, Knudsen effusion; T, transpiration, ref 10. [c]Vapor pressures calculated from runs 3/4 and 7/8, respectively; the same value resulted from both runs.

As listed in this table, the literature value measured by Knudsen effusion at T/K = 293.6 is 7.5 Pa. This compares with a value of (8.1±0.7) Pa acquired using eq 2-11. The vapor pressure determined by transpiration at T/K = 297.1 is reported as 10.7 Pa. The value obtained in this work is (10.8±0.8) Pa. In spite of our initial concern in regards to the use of 1-adamantylamine as a standard, the results from work previously reported by Bazyleva et al.[10] are completely consistent with our work and the agreement observed acts as a form of validation of our own results.

$$\ln(p_{(298}/\mathrm{Pa}_{)}) = [\Delta_{cr}{}^{g}H\,(T_{fus}) + \Delta_{cr}{}^{g}C_p\Delta T]\,[\,1/T_{fus,}\,\mathrm{K} - 1/298.15]/R + \ln(p_{(477}/\mathrm{Pa}_{)}) \quad (2\text{-}11)$$

$$\text{where: } \Delta_{cr}{}^{g}C_p\Delta T = [0.75 + 0.15\,C_p(\mathrm{cr})][(T_{fus/tp,}\,/\mathrm{K}\ -298.15)/2] \quad (2\text{-}12)$$

Using the same procedure, solid vapor pressures of 1.6 and 0.12 Pa for 1-dodecanamine and 1-tetradecanamine were calculated, respectively. Even though vapor pressures for the solid phase of these compounds are not known, the above observed agreement for 1-adamantylamine implies that these results are also likely to be dependable. Applying this procedure to a variety of other organic compounds, vapor pressures measured by other means have been reproduced well within a factor of three.[12,29] As implied by this work and others,[12,33,34] the accuracy of this protocol is most likely associated to the quality of available data and the suitability of the materials chosen as standards.

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Part 3: Tertiary Amines

Chapter 3: Evaluation of the Vaporization Enthalpies and Liquid Vapor Pressures of (R)-Deprenyl, (S)-Benzphetamine, Alverine and a Series of Aliphatic Tertiary Amines by Correlation Gas Chromatography at *T*/K = 298.15

3.1. Introduction

Used in combination with L DOPA (L 3,4-dihydroxyphenylalanine), (R)-Deprenyl ((α*R*)-*N*,α-dimethyl-*N*-2-propyn-1-yl-benzeneethanamine) is used in the early stages of Parkinson's disease.[1] It has a greater affinity for type B, which is generally found in the brain and is an irreversible inhibitor of monoamine oxidase (MAO). In the body it is partly metabolized to R-methamphetamine, which is found in over the counter nasal decongestants.[2,3] (S)-Benzphetamine ((2*S*)-*N*-benzyl-*N*-methyl-1-phenylpropan-2-amine, Didrex ^{TM}) is an anorectic and is used to control obesity in the short term. It is a member of the amphetamine class of compounds which include methamphetamine and amphetamine, among others.[4,5] Upon ingestion it is slowly transformed to amphetamine and S-methamphetamine. (S)-Benzphetamine is a schedule III controlled substance. The vapor pressures and vaporization enthalpies of both (S)-methamphetamine and amphetamine as determined by correlation gas chromatography have recently been reported.[6,7] Alverine is a smooth muscle relaxant and is used to manage GI tract disorders and other organs related to involuntary muscle spasms.[8] The structures of L deprenyl, (S)-benzphetamine and alverine are shown in Figure 3-1.

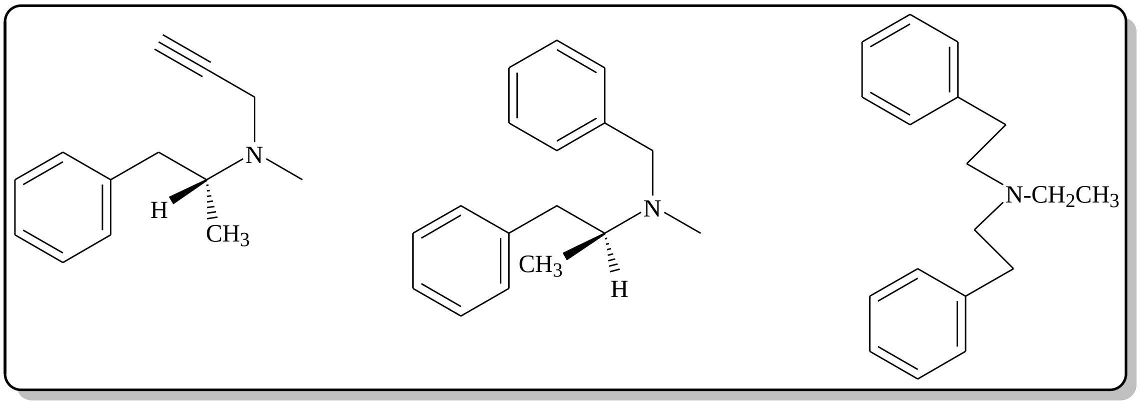

Figure 3-1. From left to right: L-deprenyl (*R*)-*N*-methyl-*N*-(1-phenylpropan-2-yl)prop-1-yn-3-amine) and benzphetamine (Didrex ^{TM}) (2*S*)-*N*-benzyl-*N*-methyl-1-phenylpropan-2-amine), alverine (*N*-ethyl-3-phenyl-*N*-(3-phenylpropyl)propan-1-amine).

Generally, these compounds are prescribed in their ammonium salt form. If the unused portions of these drugs are improperly disposed into the environment, it can lead to the production of the neutral parent species. This has led to concern over the environmental impact of discarded medications. The major pathways of dispersal are the aqueous and gas phases. Not much experimental data, such as vaporization enthalpies and vapor pressures, is available in literature. These are two important thermochemical properties which control the rate of a compound's dispersal through the atmosphere.

The ACD Labs software accessible through SciFinder Scholar[9] predicts vaporization enthalpies of [(51.1 ± 3.0), (57.7 ± 3.0) and (60.4 ± 3.0)] kJ·mol^{-1} for R-deprenyl, (S)-benzphetamine and alverine, respectively. These values were most probably determined at the compound's respective boiling temperatures. At T/K = 298.15, EPIWEB software[10] predicts sub-cooled liquid vapor pressures, p/Pa, of (2.1, 4.6·10^{-2}, and 4.5·10^{-3}) for R-deprenyl, (S)-benzphetamine, and alverine, respectively. Due to the normal boiling temperatures being larger than T/K = 500, adjustments to T/K = 298.15 are challenging. Described below is a simple two parameter equation that predicts vaporization enthalpies of [(68.6 ± 3.4), (87.3 ± 4.4), and (94.0 ± 4.7)][11] kJ·mol^{-1}. The liquid vapor pressures and vaporization enthalpies of these compounds at *T*/K = 298.15 have been determined by correlation gas chromatography and compared to their estimated values.

The availability of reliable data for functionally similar compounds which can be used as standards is a key component to the investigation of vapor pressures and vaporization enthalpies by correlation gas chromatography. The amount of moderately sized aliphatic tertiary amines that could serve as thermodynamic standards for these three drugs is extremely small. The available compounds are triethylamine,[12,13] tripropylamine,[12] *N*,*N*-dimethyloctylamine,[15] *N*,*N*-dimethyldodecylamine[16] and tri-*n*-octylamine.[17] One of the aims of this study was to determine the vapor pressures and vaporization enthalpies at and near *T*/K = 298.15 for a variety of additional aliphatic tertiary amines which could serve as standard compounds in this and in future work. The compounds investigated include tri-*n*-butylamine, triisobutylamine, *N*,*N*-dimethyltetradecylamine, *N*,*N*-dimethylhexadecylamine, and tri-*n*-octylamine. The structures of both the aliphatic amines investigated and the standards used are shown in Figure 3-2. Tri-*n*-butylamine,[18-20] triisobutylamine[20] and tri-*n*-octylamine[17] have previously been evaluated. A variety of concerns arose in regards to the available data for these three compounds which are discussed below. This study investigates the evaluation of vapor pressures and vaporization enthalpies of these tertiary aliphatic amines. In combination with the standards previously mentioned, this data was used to determine similar properties for the three drugs discussed above.

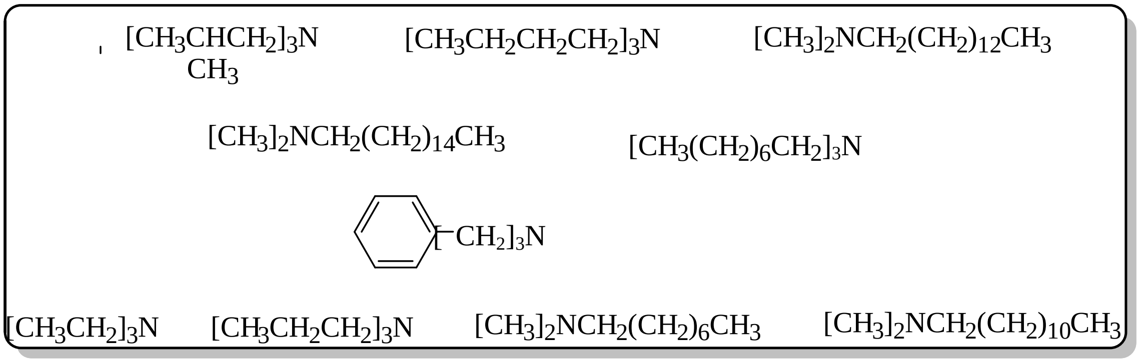

Figure 3-2. Vaporization enthalpies evaluated: tri-isobutylamine, tri-*n*-butylamine, *N*,*N*-dimethyltetradecylamine, *N*,*N*-dimethylhexadecylamine, tri-*n*-octylamine and tribenzylamine. Standards: triethylamine, tripropylamine, *N*,*N*-dimethyloctylamine, *N*,*N*-dimethyldodecylamine.

3.2. Experimental

3.2.1. Materials. The source and purity of the amines used in this study are included in Table 3-1.

TABLE 3-1. Origin of the Standards and Targets and Their Analysis

Compound		CAS RN	Supplier	Mass fraction	GC Anal
$C_6H_{15}N$	Triethylamine	[121-44-8]	Sigma Aldrich	0.98	
$C_9H_{13}N$	*N*,*N*-dimethylbenzylamine	[103-83-3]]	Sigma Aldrich	>0.99	
$C_9H_{21}N$	tri-*n*-propylamine	[102-69-2]	Sigma Aldrich	0.99	
$C_{10}H_{23}N$	*N*,*N*-dimethyloctylamine	[7378-99-6]	Sigma Aldrich	0.95	
$C_{12}H_{27}N$	Triisobutylamine	[1116-40-1]	Sigma Aldrich	0.98	
$C_{12}H_{27}N$	tri-*n*-butylamine	[102-82-9]	Sigma Aldrich	0.97	
$C_{13}H_{17}N$	(R)-deprenyl[a]	[14611-51-9]	Sigma Aldrich	>0.98	
$C_{14}H_{31}N$	*N*,*N*-dimethyldodecylamine	[112-18-5]	TCI	>0.95	
$C_{16}H_{35}N$	*N*,*N*-dimethyltetradecylamine	[112-75-4]	Sigma Aldrich	>0.95	
$C_{17}H_{21}N$	(S)-benzphetamine[a]	[156-08-1]	Mallinckrodt[c]		0.99+
$C_{18}H_{39}N$	*N*,*N*-dimethylhexadecylamine	[112-69-6]	Sigma Aldrich	>0.95	
$C_{20}H_{27}N$	alverine[b]	[150-59-4]	Sigma Aldrich		0.99+
$C_{21}H_{21}N$	Tribenzylamine	[620-40-6]	Eastman[d]		0.98+
$C_{24}H_{51}N$	tri-*n*-octylamine	[1116-76-3]	Sigma Aldrich	0.98	

[a]Available as the hydrochloride. [b]Available as the citrate salt. [c]Mallinckrodt Pharmaceutical. [d]Eastman Organic Chemicals.

Since the measurements are conducted by gas chromatography, the purity of the sample is considerably less important than with other methods. All amines in this study were used as commercially available. (R)-Deprenyl and (S)-benzphetamine are marketed as their hydrochloride salts. Alverine is available as the corresponding citrate. These materials were neutralized with 1 M NaOH prior to use and extracted with the solvent used in the experiments, hexanes, methylene chloride or diethyl ether or a mixture of two. The remaining standards were added to these amines until comparable concentrations of all were achieved. Since the drugs were available to us in small quantities as their salts and needed initial treatment with base, each was evaluated in a separate set of correlations. The purity of the drugs as well as their retention times were measured independently by gas chromatography.

3.2.2. Methods. Correlation-gas chromatography experiments were conducted in the same manner as previously described in Section 1.2.2.2. Each plot was characterized by a correlation coefficient of $r^2 > 0.99$. The only differences were that this time the columns used were a 15 m SPB-5 for some experiments and a 30 m DB-5 column for others, the temperature was maintained to T/K = 0.1 as monitored independently either using a Fluke digital thermometer or a Vernier stainless steel temperature probe equipped with a Go!Link USB interface running Logger Lite software, depending on the instrument used and hexanes, methylene chloride or diethyl ether or a mixture of two served as the non-retained reference. Both columns gave good separations and the shorter column reduced retention times. On the 15 m column, t/t_o <1 and was >2.0 on the 30 meter column. The relative retention times of tri-*n*-octylamine and tribenzylamine depended on temperature. On the 30 m column, at approximately T/K > 480, tri-*n*-octylamine eluted before tribenzylamine, whereas below this temperature the order of elution was reversed. All retention times are provided in Appendix C.

3.2.3. Fusion Enthalpy. The fusion enthalpy of tribenzylamine was measured on a Perkin Elmer DSC 7 instrument running the Pyris Thermal Analysis software. The instrument was standardized with indium metal, mass fraction 0.99999, supplied by Perkin Elmer. The standardization was checked with calorimetric grade benzoic acid supplied by Fisher and Gold Label scintillation grade naphthalene, w = > 0.99 supplied by Aldrich. The samples were run in 50 μL hermetically sealed aluminum pans under a flow of nitrogen. The commercial sample of tribenzylamine analyzed by gas chromatography, mass fraction 0.98+, was used as supplied. The compound exhibited a broad transition at T/K = (342.5 ± 0.4) and transition enthalpy, $\Delta H_t(343)/\text{kJ·mol}^{-1} = (1.1 \pm 0.1)$, fusion temperature T/K = (365.6± 0.1, onset temperature) and fusion enthalpy, $\Delta_{cr}{}^{l}H_m(366)/\ \text{kJ·mol}^{-1} = (23.0 \pm 0.1)$. Details are available in Appendix C.

3.2.4. Vaporization Enthalpy Estimations. Vaporization enthalpy estimations were conducted in the same manner as previously described in Section 1.2.6., again calculated using equation 1-6. Here though, the contribution of the functional group (b) is that of a tertiary amine (6.6 kJ·mol^{-1}).[11] The carbon bearing the nitrogen was treated as a quaternary carbon (n_Q). For amantadine, $C_{10}H_{17}N$, a vaporization enthalpy of 61.3 kJ·mol^{-1} is estimated. For compounds with carbon branching at acyclic sp^3 hybridized centers, a correction, C, of -2 kJ·mol^{-1}/branch is also included in the estimation.[11]

3.2.5. Temperature Adjustments. The vaporization enthalpies of the compounds used as standards are available over a range of different temperatures. Adjustments from the mean temperature of measurement, T_m , to a common temperature, T/K = 298.15, were achieved in the same way as described in Section 1.2.4. using only equations 1-3 and 3-1. Since the solid-solid phase transition in tribenzylamine occurred above T/K = 298.15, the enthalpy associated with the transition is also included in eq 3-1. Equations 1-3 and 3-1 have been shown to provide reasonable temperature adjustments up to approximately T/K = 500.[21-24]

$$\Delta_{cr}{}^{l}H_m(298.15\ \mathrm{K})/\mathrm{kJ{\cdot}mol^{-1}} = \Delta H_t(T_t) + \Delta_{cr}{}^{l}H_m(T_{fus}) +$$

$$[(0.15C_p(\mathrm{cr}) - 0.26C_p(\mathrm{l}))/\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}} - 9.93][T_{fus}/\mathrm{K} - 298.15]/1000 \qquad (3\text{-}1)$$

3.2.6. Uncertainties. A standard deviation of 16 $\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$ has generally been associated with the temperature independent portion of the second term in eq 1-3. The uncertainty associated with eq 3-1 has been estimated as 30% of the temperature adjustment. The correlations between experimental properties and those evaluated by gas chromatography were analyzed by linear regression. The uncertainty in the slope represents one standard deviation. Uncertainties in combined properties such as temperature adjustments were generally evaluated as $(u_1^2 + u_2^2 + \ldots)^{0.5}$ where u_i represents the standard deviation associated with measurement i.

3.2.7. Standards.

3.2.7.1. Vaporization Enthalpy. Vaporization enthalpies of the compounds that could serve as potential standards for the three drugs of interest are summarized in Table 3-2.

TABLE 3-2. Vaporization Enthalpies of Some Tertiary Amines As Potential Standards.

Compounds	$\Delta_l^g H_m(T_m)(T_m/K)$ kJ·mol^{-1}	$C_p(l)$ J·mol^{-1}·K^{-1}	$\Delta_l^g C_p \Delta T$ kJ·mol^{-1}	$\Delta_l^g H_m(298\ K)$ kJ·mol^{-1} exp	est^a	Ref.
triethylamine				34.9±0.1	37.7±2.0	12
triethylamine	34.4±0.2 (313)	222.4	1.0±0.2	35.4±0.3	37.7±2.0	13
tripropylamine				46.2±0.1	51.8±2.6	12
triisobutylamine	54.3 (320)	394.3	2.5±0.4	56.8	59.9±3.0	20
tri-*n*-butylamine	49.8 (450)	413.8	17.9±2.4	67.7±2.4	65.9±3.3	18
tri-*n*-butylamine	48.1 (378)	413.8	9.4±1.3	57.6±1.3	65.9±3.3	20
tri-*n*-butylamine	53.9 (378)	413.8	9.4±1.3	63.4±1.3	65.9±3.3	20
tri-*n*-butylamine				62.7±1.3	65.9±3.3	19
N,*N*-dimethyl benzylamine	48.9±0.4 (308)	248	0.8±0.2	49.7±0.4	51.8±2.6	14
N,*N*-dimethyl octylamine	54.0±0.5 (303)	360	0.53	54.5±0.5	56.5±2.8	15
N,*N*-dimethyl dodecylamine	69.3±0.3 (298)			69.3±0.3	75.3±3.8	16
tri-*n*-octylamine				110.0±15	122.2±6.1	20

^{a}Estimated using eq 1-6.

For triethylamine, two values both in good agreement with each other are available.[12,13] An average value of (35.2±0.2) kJ·mol^{-1} was used for the vaporization enthalpy. A calorimetric value of (46.2 ± 0.1) kJ·mol^{-1} is available for tripropylamine.[12] A single value is available for triisobutylamine from the compendium by Stephenson and Malanowski.[17] Since this source does not include original references, it is difficult to judge the quality of the value or its age. A similar situation exists for tri-*n*-butylamine for which there is a 10 kJ·mol^{-1} discrepancy in Table 3-2.[17-19] The most recent measurement for tributylamine requires an extremely large temperature adjustment, making this value also questionable.[18] The vaporization enthalpy of tri-*n*-butylamine has also been evaluated previously using correlation gas chromatography. In this instance the evaluation was based solely on using aromatic heterocyclic amines as standards.[19] More recent work with amines has demonstrated that best results for aliphatic primary amines are obtained using aliphatic primary amine standards as opposed to primary aromatic amines.[23] Therefore the existing vaporization enthalpy of tri-*n*-butylamine was re-evaluated by correlation gas chromatography in this case using tertiary aliphatic amines as standards. Values for *N*,*N*-dimethylbenzylamine (49.7 ± 0.4),[14] *N*,*N*-dimethyloctylamine (54.5 ± 0.5),[15] and *N*,*N*-dimethyldodecylamine (69.3±0.3)[16] kJ·mol^{-1} are relatively recent and from reputable sources. Finally it should be noted that a ±15 kJ·mol^{-1} uncertainty at T/K = 298.15 is associated with the largest tertiary aliphatic amine examined, tri-*n*-octylamine,[17] and it use as a standard was of some concern. Consequently, along with triisobutylamine and tri-*n*-butylamine, the following amines, *N*,*N*-dimethyltetradecylamine, *N*,*N*-dimethylhexadecylamine, and tri-*n*-octylamine were treated as unknowns and evaluated by correlation gas chromatography experiments. In view of the large difference in retention times between the smallest and largest tertiary amines, it was necessary to evaluate their vaporization enthalpies and vapor pressures in a series of independent correlations. All correlations were performed in duplicate. Details of the second correlation are available in Appendix C. The resulting vaporization enthalpies from all the runs are summarized below.

3.2.7.2. Vapor Pressure. Vapor pressures of potential standards are also limited and available only over a narrow temperature range, most near ambient temperatures. The vapor pressures of the standards are reported in the form of the Antoine equation, eq 3-2 where p_{ref} /Pa = 1. The constants for this equation and the temperature range to which they are applicable are provided in Table 3-3.

TABLE 3-3. Constants of the Antoine Equation

	A	B	C	T/K range	Ref
Triethylamine	21.1239	3071.65	-42.35	273-352	13
N,*N*-dimethylbenzylamine	24.94825	5892.03	0	288-328	14
N,*N*-dimethyloctylamine	25.94036	6491.58	0	283-323	15
N,*N*-dimethyldodecylamine	40.49339	17623.5	135.268	283-314	16
tri-*n*-octylamine	23.05555	6300.22	-101.205	415-537	17

The vapor pressures used in the correlations described below, however, were conducted in the form p/p_o where p_o/Pa = 101325. For tri-*n*-octylamine, the Antoine equation reported in the form $\log_{10}(p/\text{kPa})$ has been transformed to the form of eq 3-2.[17]

$$\ln(p/p_{\text{ref}}) = \text{A} - \text{B}/(\text{C} + T/\text{K}) \qquad (3\text{-}2)$$

3.3. Results

3.3.1. Vaporization Enthalpies. The vaporization enthalpy of tri-*n*-butylamine used in a number of the following correlations was investigated in a set of two different correlations. These two different correlations also performed separate investigations of triisobutylamine and *N*,*N*-dimethyltetradecylamine. The data from one of the two sets of correlations are listed in Tables 3-4 and 3-5.

TABLE 3-4. Evaluation of the Vaporization Enthalpy of Tributylamine and Triisobutylamine

Run 1	- slope T/K	intercept	ΔH_{trn}(388 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)
Triethylamine	3262.0	10.009	27.12	35.2±0.2	35.4±1.8
Tripropylamine	4263.8	10.833	35.45	46.2±0.1	46.0±2.0
N,*N*-dimethylbenzylamine	4577.9	10.842	38.06	49.7±0.4	49.3±2.0
Triisobutylamine	4858.8	11.475	40.39		52.3±2.1
N,*N*-dimethyloctylamine	5104.6	11.885	42.44	54.5±0.5	54.9±2.2
tri-*n*-butylamine	5464.5	12.285	45.43		58.7±2.3

$$\Delta_l^g H_m(298.15\text{ K})/\text{kJ·mol}^{-1} = (1.27 \pm 0.04)\Delta H_{\text{trn}}(388\text{ K}) + (0.91 \pm 1.4) \qquad r^2 = 0.9981 \qquad (3\text{-}3)$$

TABLE 3-5. Evaluation of the Vaporization Enthalpy of Tributylamine and *N*,*N*-Dimethyltetradecylamime

Run 3	$-\frac{\text{slope}}{T/\text{K}}$	intercept	$\Delta H_{\text{trn}}(439\text{ K})$ kJ·mol^{-1}	$\Delta_l^g H_m(298\text{ K})$ kJ·mol^{-1} (lit)	$\Delta_l^g H_m(298\text{ K})$ kJ·mol^{-1}(calc)
N,*N*-dimethylbenzylamine	4436.7	10.561	36.89	49.7±0.4	49.9±1.5
N,*N*-dimethyloctylamine	4923.4	11.498	40.93	54.5±0.5	54.2±1.5
tri-*n*-butylamine	5268.0	11.850	43.80		57.3±1.6
N,*N*-dimethyldodecylamine	6621.9	13.435	55.05	69.3±0.3	69.4±1.8
N,*N*-dimethyltetradecylamine	7509.0	14.530	62.43		77.3±1.9

$\Delta_l^g H_m(298.15\text{ K})/\text{kJ·mol}^{-1} = (1.07 \pm 0.03)\Delta H_{\text{trn}}(439\text{ K}) + (10.4 \pm 1.1)$ $r^2 = 0.9995$ (3-4)

Equations 3-3 and 3-4 given below each correlation describe the linearity of the fit. Data for all duplicate runs is listed in Appendix C. The data from runs 1 through 4 for tri-*n*-butylamine and runs 3/4 for *N*,*N*-dimethyltetradecylamine was then used in combination with numerous other tertiary amine standards to evaluate *N*,*N*-dimethylhexadecylamine, Table 3-6. The vaporization enthalpy of *N*,*N*-dimethylhexadecylamine determined in runs 5/6 then served as one of the standards to investigate tri-*n*-octyl and tribenzylamine in runs 7/8. Equation 3-5 listed below Table 3-6 and eq 3-6 listed below Table 3-7 illustrate the linearity of each respective correlation.

TABLE 3-6. Evaluation of the Vaporization Enthalpies of *N*,*N*-Dimethylhexadecylamine

Run 5	$-\frac{\text{slope}}{T/\text{K}}$	intercept	$\Delta H_{\text{trn}}(469\text{ K})$ kJ·mol^{-1}	$\Delta_l^g H_m(298\text{ K})$ kJ·mol^{-1} (lit)	$\Delta_l^g H_m(298\text{ K})$ kJ·mol^{-1}(calc)
N,*N*-dimethyloctylamine	4588.7	11.254	38.15	54.5±0.5	54.6±0.8
tri-*n*-butylamine	4949.2	11.633	41.15	58.0±1.9^{a}	57.8±0.9
N,*N*-dimethyldodecylamine	6240.3	13.157	51.88	69.3±0.3	69.5±1.0
N,*N*-dimethyltetradecylamine	7084.6	14.185	58.90	77.3±1.9^{b}	77.2±1.0
N,*N*-dimethylhexadecylamine	7930.6	15.228	65.93		84.8±1.1

$\Delta_l^g H_m(298.15\text{ K})/\text{kJ·mol}^{-1} = (1.09\pm0.013)\Delta H_{\text{trn}}(439\text{ K}) - (13.0\pm0.6)$ $r^2 = 0.9997$ (3-5)

^{a}Average value evaluated from runs 1-4. ^{b}Average value evaluated in runs 3 and 4.

TABLE 3-7. Evaluation of the Vaporization Enthalpy of Tribenzylamine and Tri-*n*-octylamine

Run 7	- slope T/K	intercept	ΔH_{trn}(500 K) kJ·mol^{-1}	$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298 K) kJ·mol^{-1} (lit)	$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298 K) kJ·mol^{-1}(calc)
tri-*n*-butylamine	4655.4	10.504	38.70	58.0±1.9	58±0.9
N,*N*-dimethyldodecylamine	5808.2	11.679	48.29	69.3±0.3	69.5±1.0
N,*N*-dimethyltetradecylamine	6566.2	12.508	54.59	77.3±1.9	77.1±1.0
N,*N*-dimethylhexadecylamine	7350.8	13.405	61.11	84.8±1.0[a]	84.9±1.1
tri-*n*-octylamine	8871.4	15.189	73.75		100.1±1.2
tribenzylamine	8091.0	13.559	67.27		92.3±1.2
$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K)/kJ·mol^{-1} = (1.20±0.013)ΔH_{trn}(500 K) + (11.5±0.7)				$r^2 = 0.9997$	(3-6)

[a] Average evaluated in runs 5/6.

The vaporization enthalpies determined in all 8 correlations are summarized in Table 3-8. The average values of the vaporization enthalpies are also listed in Table 3-8.

TABLE 3-8. A Summary of Vaporization Enthalpies (kJ·mol^{-1}) at T/K = 298.15 of Runs 1-8

	run 1	run 2	run 3	run 4	run 5	run 6	run 7	run 8	Avg[a]	Lit
triethylamine	35.6±1.6	35.4±1.6							35.6±1.6	35.2±0.2
tripropylamine	46.0±1.8	46.0±1.8							46.0±1.6	46.2±0.1
N,*N*-dimethyl-benzylamine	49.3±2.0	49.3±2.1	49.9±1.5	49.9±1.4					49.6±1.8	49.7±0.4
triisobutylamine	52.3±2.1	52.3±2.2							52.3±2.2	59.9±3.0
N,*N*-dimethyl-octylamine	54.9±2.2	54.9±2.2	54.2±1.5	54.3±1.4	4.6±0.8	54.6±0.8			54.9±1.9	54.5±0.5
tri-*n*-butylamine	58.7±2.3	58.7±2.3	57.3±1.6	57.3±1.5	57.8±0.9	57.8±0.8	58.0±0.9	58.1±1.1	58.0±1.9[b,c]	57.6±1.3
N,*N*-dimethyl-dodecylamine			69.4±1.8	69.4±1.7	69.5±1.0	69.5±0.9	69.5±1.0	69.3±1.2	69.4±1.3	69.3±0.3
N,*N*-dimethyl-tetradecylamine			77.3±1.9	77.2±1.8	77.2±1.0	77.2±0.8	77.1±1.0	77.0±1.3	77.3±1.9[b,d]	
N,*N*-dimethyl-hexadecylamine					84.8±1.0	84.8±0.9	84.9±1.1	85.0±1.4	84.8±1.0[b,e]	
tribenzylamine							92.3±1.2	92.4±1.5	92.4±1.4[b,f]	
tri-*n*-octylamine							100.1±1.2	100.0±1.6	100.1±1.4[b,f]	110±15

[a] Uncertainties are also average values. [b] Value based from runs evaluated as an unknown, value used as a known in subsequent correlations. [c] Evaluated in runs 1 through 4. [d] Evaluated in runs 3/4. [e] Evaluated in runs 5/6. [f] Evaluated in runs 7/8.

This data was then used in subsequent runs in combination with other literature values to determine the vaporization enthalpies of (R)-deprenyl, (S)-benzphetamine and alverine, also in duplicate. The correlation of one of each respective run is listed in Tables 3-9 through 3-11. Equations 3-7 through 3-9 listed below each respective table illustrate the linearity of the correlations.

TABLE 3-9. Evaluation of the Vaporization Enthalpy of L-Deprenyl

Run 9	- slope T/K	intercept	ΔH_{trn}(419 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)
N,*N*-dimethylbenzylamine	4429.0	10.477	36.82	49.7±0.4	49.9±1.4
N,*N*-dimethyloctylamine	4977.6	11.572	41.38	54.5±0.5	54.5±1.5
tri-*n*-butylamine	5344.6	13.720	56.19	58.0±1.9[a]	57.6±1.5
L- deprenyl	6141.9	11.986	44.43		64.3±1.6
N,*N*-dimethyldodecylamine	6758.5	12.594	51.06	69.3±0.3	69.5±1.7
$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.01±0.02)ΔH_{trn}(419 K) + (12.8±1.1)				$r^2 = 0.9989$	(3-7)

[a] Average value evaluated from runs 1-4.

TABLE 3-10. Evaluation of the Vaporization Enthalpy of (S)-Benzphetamine

Run 11	- slope T/K	intercept	ΔH_{trn}(491 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)
N,*N*-dimethylbenzylamine	4694.1	11.003	39.02	49.7±0.4	49.7±0.5
N,*N*-dimethyldodecylamine	6689.0	13.508	55.61	69.3±0.3	69.3±0.6
N,*N*-dimethyltetradecylamine	7498.9	14.436	62.34	77.3±1.9[a]	77.2±0.6
(S)-benzphetamine	7493.5	13.766	62.30		77.1±0.6
N,*N*-dimethylhexadecylamine	8302.2	15.364	69.02	84.8±1.0[a]	85.1±0.6
tribenzylamine	9034.0	15.491	75.11	92.4±1.4[a]	92.3±0.7
$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.18±0.01)ΔH_{trn}(491 K) + (3.69±0.4)				$r^2 = 0.9999$	(3-8)

[a] This work.

TABLE 3-11. Evaluation of the Vaporization Enthalpy of Alverine

Run 13	- slope T/K	intercept	ΔH_{trn}(494 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)
tri-*n*-butylamine	4871.8	10.997	40.50	58.0±1.9[a]	58.0±0.1
N,*N*-dimethyldodecylamine	6033.6	12.171	50.16	69.3±0.3	69.3±0.1
N,*N*-dimethylhexadecylamine	7627.9	13.993	63.41	84.8±1.0[a]	84.9±0.2
Alverine	8080.2	13.926	67.18		89.3±0.2
tri-*n*-octylamine	9186.8	15.850	76.38	100.1±1.4[a]	100.1±0.2
$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.17±0.01)ΔH_{trn}(494 K) + (10.5±0.1)				$r^2 = 0.9999$	(3-9)

[a] This work.

Data for each duplicate run is available in Appendix C. The vaporization enthalpies calculated for (R)-deprenyl, (S)-benzphetamine and alverine are listed in Table 3-12 as are the vaporization enthalpies acquired for the standards.

TABLE 3-12. A Summary of Vaporization Enthalpies (kJ·mol^{-1}) at T/K = 298.15 of Runs 9-14

Targets	run 9	run 10	run 11	run 12	run 13	run 14	Avg[a]	Lit
(R)-deprenyl	64.3±1.6	64.3±2.7					64.3±2.2	
(S)-benzphetamine			77.1±0.6	77.2±0.7			77.2±0.7	
Alverine					89.3±0.2	89.3±0.1	89.3±0.2	
Standards								
N,*N*-dimethyl benzylamine	49.9±1.4	50.1±2.3	49.7±0.5	49.6±0.6			49.8±1.4	49.7±0.4
N,*N*-dimethyl octylamine	54.5±1.5	54.2±2.4					54.2±2.0	54.5±0.5
tri-*n*-butylamine	57.6±1.5	57.4±2.5			58.0±0.1	58.0±0.1	57.8±1.0	58.0±1.9[b]
N,*N*-dimethyl dodecylamine	69.5±1.7	69.5±2.8	69.3±0.6	69.4±0.7	69.3±0.1	69.3±0.1	69.4±1.0	69.3±0.3
N,*N*-dimethyl tetradecylamine			77.2±0.6	77.3±0.7			77.3±0.7	77.3±3.0[b]
N,*N*-dimethyl hexadecylamine			85.1±0.6	85.1±0.7	84.9±0.2	84.9±0.1	85.0±0.4	84.8±1.0[b]
Tribenzylamine			92.3±0.7	92.1±0.8			92.2±0.8	92.4±1.4[b]
tri-*n*-octylamine					100.1±0.2	100.1±0.1	100.1±0.2	100.1±1.4[b]

[a] Uncertainties are also average values. [b] This work.

3.3.2. Vapor Pressures. Retention times in the form of ln(t_o/t_a) have also been found to correlate linearly with their respective vapor pressures, p, in the form of ln(p/p_o). Dependable vapor pressure data can be acquired for the target compounds by using the linear relationship observed between plots of ln(t_o/t_a) and ln(p/p_o) of the standards and the ln(t_o/t_a) values of the targets. From this ln(p/p_o) of the target compounds can be obtained. A vapor pressure-temperature profile of the target compounds can then be acquired when the correlation is repeated as a function of temperature.[6,7,19,23,25,26]

Vapor pressures near T/K = 298.15 are known for four of the five standard compounds used in this work. With the exception of *N*,*N*-dimethylbenzylamine, vapor pressures for all other standards are available over the temperature range, T/K = (283.15 to 313.15). The vapor pressure for *N*,*N*-dimethylbenzylamine needed a T/K = 5 extrapolation of the Antoine eq to T/K = 283.15. All compound vapor pressures were evaluated using eq 3-2 and the constants listed in Table 3-3.

An example of the correlation between $\ln(p/p_o)$ and $\ln(t_o/t_a)$ at T/K = 298.15 is described in Table 3-13 for runs 1/2 and runs 3/4. Values of (t_o/t_a) were evaluated from the intercepts and slopes of the standards given in Table 3-4 for run 1 and from Appendix C for run 2.

TABLE 3-13. Correlations Between $\ln(t_o/t_a)_{avg}$ and liquid $\ln(p/p_o)_{exp}$ at T/K = 298.15 for Runs 1/2 and 3/4

run 1/run 2	-slope/K	intercept	$\ln(t_o/t_a)_{avg}$	$\ln(p/p_o)_{exp}$	$\ln(p/p_o)_{calc}$	p/Pa calc
Triethylamine	3282.7	10.052				
	3262.0	10.009	-0.94	-2.41	-2.39	9270
Tripropylamine	4263.8	10.833				
	4290.7	10.895	-3.48		-5.26	524
N,*N*-dimethylbenzylamine	4577.9	10.842				
	4609.0	10.916	-4.53	-6.34	-6.45	161
Triisobutylamine	4858.8	11.475				
	4892.4	11.553	-4.84		-6.80	113
N,*N*-dimethyloctylamine	5104.6	11.885				
	5140.7	11.971	-5.25	-7.36	-7.27	71
tri-*n*-butylamine	5464.5	12.285				
	5500.2	12.368	-6.06		-8.18	28
run 3/run 4						
N,*N*-dimethylbenzylamine	4436.7	10.561				
	4544.8	10.804	-4.38	-6.34	-6.42	165
N,*N*-dimethyloctylamine	4923.4	11.498				
	5035.8	11.750	-5.08	-7.36	-7.25	72
tri-*n*-butylamine	5268.0	11.850				
	5379.9	12.101	-5.88	-8.18	-8.2	28
N,*N*-dimethyldodecylamine	6621.9	13.435				
	6732.9	13.685	-8.83	-11.69	-11.71	0.84
N,*N*-dimethyltetradecylamine	7509.0	14.530				
	7613.6	14.766	-10.71		-13.93	0.090

Run 1/2: $\ln(p/p_o) = (1.13\pm0.04)\ln(t_o/t_a) - (1.32\pm0.17)$ $r^2 = 0.9985$ (3-10)

Run 3/4: $\ln(p/p_o) = (1.19\pm0.03))\ln(t_o/t_a) - (1.23\pm0.18)$ $r^2 = 0.9988$ (3-11)

These values were then averaged and correlated as $\ln(t_o/t_a)_{avg}$ with corresponding standard $\ln(p/p_o)$ values. Likewise for runs 3/4, suitable values were acquired from Table 3-5 and Appendix C, averaged and then correlated with corresponding $\ln(p/p_o)$ values at T/K = 298.15. This resulted in eqs 3-10 and 3-11 listed at the bottom of Table 3-13. Vapor pressure – temperature profiles for tri-*n*-propylamine, triisobutylamine and tri-*n*-butylamine were obtained by repeating this process over the temperature range T/K = (283.15 to 313.15) at T/K = 5 intervals for runs 1/2. This data was then fit to eq 3-12. Vapor pressures for these compounds were then determined as needed within the specified temperature range above from the resulting slopes and intercepts for these compounds listed in columns 2 and 3 of Table 3-14. The vapor pressure of *N*,*N*-dimethyltetradecylamine at T/K = 298.15 in runs 3/4 is listed in Table 3-13. This data was obtained also using the vapor pressures of tri-*n*-butylamine, evaluated in runs 1/2 as a standard. Equation 3-11 given below the table describes the linearity of this correlation. Once the temperature dependence of a target compound was determined, it was available for use as a standard as needed. All correlation coefficients, r^2, were greater than 0.99 over the specified temperature range. The vapor pressures evaluated at T/K = 298.15 by direct correlation of $\ln(t_o/t_a)$ with $\ln(p/p_o)$ are listed in the last column of Table 3-13. Comparable correlations at T/K = 298.15 for runs 5-8 are listed in Appendix C along with their vapor pressures at T/K = 298.15. The remaining amines were either determined by interpolation or extrapolation. The vapor pressures of *N*,*N*-dimethylhexadecylamine were determined in runs 5/6 and tribenzylamine and tri-*n*-octylamine were evaluated in runs 7/8. The slopes and intercepts illustrating the vapor pressure - temperature dependence for all these compounds are given in Table 3-14.

$$\ln(p/p_o) = A' + B'/T \qquad (3\text{-}12)$$

TABLE 3-14. Slopes and Intercepts from ln(p/p_o) vs ln(t_o/t_a) Correlations and A Comparison of Vaporization Enthalpies From Vapor Pressure Studies and From Correlations of $\Delta_l^g H_m$(298.15) and $\Delta H_{trn}(T_m)$

	-slope/K[a] B'	intercept A'	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}	
Targets			from vp[b]	from ΔH_{trn}[c]
Tripropylamine	5455.7	13.034	45.4±0.1	46.2±1.6
Triisobutylamine	6209.8	14.028	51.6±0.1	52.3±2.2
tri-*n*-butylamine	6965.9	15.181	57.9±0.1	58.0±1.9
R-deprenyl	7697.8	15.211	64.0±0.2	64.3±2.2
N,*N*-dimethyltetradecylamine	9337.0	17.399	77.6±0.4	77.3±1.9
(S)-benzphetamine	9299.1	16.450	77.3±0.5	77.2±0.7
N,*N*-dimethylhexadecylamine	10270.3	18.368	85.4±0.2	84.8±1.0
Alverine	10792.7	18.087	89.7±0.7	89.3±0.3
Tribenzylamine	11175.4	18.361	92.9±0.7	92.4±1.4
tri-*n*-octylamine	12148.0	20.362	101.0±0.1	100.1±1.4
Standards				
Triethylamine	4174.3	11.606	34.7±0.1	35.6±1.6
N,*N*-dimethylbenzylamine	5909.7	13.386	49.1±0.1	49.6±1.8
N,*N*-dimethyloctylamine	6508.6	14.567	54.1±0.1	54.5±1.9
N,*N*-dimethyldodecylamine	8362.0	16.365	69.5±0.3	69.4±1.3

[a]Slopes and intercepts of eq 3-12, the Clausius-Clapyron eq, from a plot of ln(p/p_o) versus 1/T over the temperature range T/K = 283.15 to 313.15; p_o/Pa = 101325; all fits characterized by correlation coefficients, $r^2 > 0.99$; [b]The product of (-1/1000), the value of column 2, and the gas constant, 8.314 J·mol^{-1}·K^{-1}. [c]Vaporization enthalpies from direct correlations of enthalpies of transfer with literature vaporization enthalpies (Table 3-8).

The vapor pressure-temperature profiles for (R)-deprenyl, (S)-benzphetamine and alverine were determined using the vapor pressures of the standards from literature summarized in Table 3-3 and those determined in this study. Tri-*n*-octylamine, however, was not used for the reason previously discussed. All vapor pressures were determined from T/K = 283.15 to 313.15 at T/K = 5 intervals and then fit to eq 3-12. The slopes and intercepts for these compounds are listed in Table 3-14, as well. All correlation coefficients, r^2, were greater than 0.99. Characteristic results of correlations between ln(p/p_o) and ln(t_o/t_a) for (R)-deprenyl, (S)-benzphetamine and alverine at T/K = 298.15 are described in Table 3-15. Equations 3-13 through 3-15 listed at the bottom of the table describe the linearity of these correlations, respectively. Vapor pressures evaluated from these results are listed in the last column of the table.

TABLE 3-15. Correlations Between ln(t_o/t_a)$_{avg}$ and liquid ln(p/p_o)$_{exp}$ at T/K = 298.15 for Runs 9-14

run 9/run 10	-slope/K	intercept	ln(t_o/t_a)$_{avg}$	ln(p/p_o)$_{exp}$	ln(p/p_o)$_{calc}$	p/Pa calc
N,*N*-dimethylbenzylamine	4429.0	10.477				
	4382.6	10.378	-4.35	-6.34	-6.42	165
N,*N*-dimethyloctyl amine	4977.6	11.572				
	4858.8	11.298	-5.06	-7.36	-7.25	72
tri-*n*-butylamine	5344.6	13.720				
	5220.4	11.702	-5.87	-8.18[a]	-8.20	27.8
(R)-deprenyl	6141.9	11.986				
	6005.8	12.284	-7.93		-10.61	2.5
N,*N*-dimethyldodecylamine	6758.5	12.594				
	6607.9	13.382	-8.86	-11.69	-11.70	0.84
run 11/run 12						
N,*N*-dimethylbenzylamine	4694.1	11.003				
	4712.5	11.046	-4.75	-6.34	-6.34	179
N,*N*-dimethyldodecylamine	6689.0	13.508				
	6752.2	13.645	-8.96	-11.69	-11.67	0.87
N,*N*-dimethyltetradecylamine	7498.9	14.436				
	7569.9	14.59	-10.76	-13.93[a]	-13.93	0.090
(S)-benzphetamine	7493.5	13.766				
	7563.5	13.918	-11.41		-14.76	0.04
N,*N*-dimethylhexadecylamine	8302.2	15.364				
	8373.4	15.518	-12.52	-16.10[a]	-16.17	0.0097
Tribenzylamine	9034.0	15.491				
	9103.8	15.642	-14.85	-19.15[a]	-19.12	0.00051
run 13/run 14						
tri-*n*-butylamine	4908.9	11.083				
	4871.8	10.997	-5.36	-8.18[a]	-8.20	27.7
N,*N*-dimethyldodecylamine	6062.7	12.241				
	6033.6	12.171	-8.08	-11.69	-11.65	0.88
N,*N*-dimethylhexadecylamine	7653.0	14.055				
	7627.9	13.993	-11.60	-16.08[a]	-16.13	0.010
Alverine	8105.5	13.988				
	8080.2	13.926	-13.19		-18.14	0.0013/
tri-*n*-octylamine	9212.8	15.914				
	9186.8	15.85	-14.97	-20.41[a]	-20.41	$1.4\cdot10^{-4}$

Run 9/10: $\ln(p/p_o) = (1.17\pm0.028)\ \ln(t_o/t_a) - (1.32\pm0.17)$ $r^2 = 0.9989$ (3-13)

Run 11/12: $\ln(p/p_o) = (1.26\pm0.006))\ \ln(t_o/t_a) - (0.34\pm0.07)$ $r^2 = 0.9999$ (3-14)

Run 13/14: $\ln(p/p_o) = (1.27\pm0.005))\ \ln(t_o/t_a) - (1.40\pm0.06)$ $r^2 = 0.9999$ (3-15)

[a] Value based only on runs evaluated as an unknown.

3.4. Discussion

3.4.1. Vaporization Enthalpies. The results of this work are summarized in column 2 of Table 3-16. The vaporization enthalpy of (52.3 ± 2.2) kJ·mol^{-1} determined in this study for triisobutylamine is 4.5 kJ·mol^{-1} smaller than the literature value of 56.8 kJ·mol^{-1}. The vaporization enthalpy of (58.0 ± 1.9) kJ·mol^{-1} for tri-*n*-butylamine is in the lower range of previous measurements. The difference of (5.7 ± 2.9) kJ·mol^{-1} in the vaporization enthalpies between the two isomeric tributyl amines evaluated in this work is consistent with the value of approximately 2 kJ·mol^{-1}/branch observed in other similar systems.[11]

The vaporization enthalpy for tri-*n*-butylamine is (4.7 ± 2.3) kJ·mol^{-1} smaller than the previous value acquired by correlation gas chromatography with the use of aromatic heterocycles as standards.[9] This result is in line with similar findings on primary amines and shows the importance of choosing suitable standards.[23] The vaporization enthalpy acquired for tri-*n*-octylamine is 10 kJ·mol^{-1} smaller than the literature value, but still well within the cited uncertainty. It should be stated, however, that vaporization enthalpies for compounds larger than *N*,*N*-dimethyldodecylamine are extrapolated values. The standards do not compensate for heat capacity adjustments from the mean temperature of the gas chromatographic measurements to T/K = 298.15 as well as for those values determined by extrapolation (eq 1-2), unlike vaporization enthalpies acquired by interpolation. Thus the uncertainty related to the larger amines is possibly larger than the standard deviation associated with their reproducibility as shown in the second column of Table 3-16. Even though it is not possible to determine the probable uncertainty, the uncertainty is likely to increase as the extrapolation increases. An uncertainty of up to 10% of the value is definitely plausible for the largest tertiary amine, tri-*n*-octylamine.

Uncertainties of (±4.0, ±4.0, ±6.0, ±7.0, ±8.0 and ±10.0) kJ·mol^{-1} for *N,N*-dimethyltetradecylamine, (S)-benzphetamine, *N,N*-dimethylhexadecyl-amine, alverine, tribenzylamine and tri-*n*-octylamine, respectively, are most likely reasonable estimates.

TABLE 3-16. A Summary of the Vaporization Enthalpies (kJ·mol^{-1}) and Vapor Pressures at *T*/K = 298.15

		$\Delta_l^gH_m$(298 K)		*p*/Pa(298.15 K)	
	This work	Literature	Estimate (eq 1-6)[a]	This work[b]	Literature
Triethylamine		35.2±0.2	34.4±1.7	9241	9100[c]
Tripropylamine		46.2±0.1	48.5±2.4	524	201,[d] 355[e]
N,N-dimethylbenzylamine		49.7±0.4	48.5±2.4	163	179[c]
Triisobutylamine	52.3±2.2		56.6±2.8	113	73,[d] 70[e]
N,N-dimethyloctylamine		54.5±0.5	53.2±2.7	71	65[c]
tri-*n*-butylamine	58.0±1.9		62.6±3.1	28	21,[d] 20[e] (21, 54)[f,g]
R-deprenyl	64.3±2.2		65.3±3.4	2.5	2.1,[d] 0.8[e]
N,N-dimethyldodecylamine		69.3±0.3	72.0±3.6	0.86	0.85[c]
N,N-dimethyltetradecylamine	77.3±1.9		81.3±4.1	0.091	0.27,[d] 0.2[e]
(S)-benzphetamine	77.2±0.7		84.0±4.3	0.04	0.04,[d] 0.02[e]
N,N-dimethylhexadecylamine	84.8±6.0		90.7±4.5	0.011	0.038,[d] 0.035[e]
Alverine	89.3±1.0		90.7±4.5	$1.4\cdot10^{-3}$	(4.5,[d] 3.3)$\cdot10^{-3}$[e]
Tribenzylamine	92.4±1.4		104.8±2.2	$5.1\cdot10^{-4}$	(5.8,[d] 3.9)$\cdot10^{-4}$[e]
tri-*n*-octylamine	100.1±1.4	110±15	118.8±6.0	$1.4\cdot10^{-4}$	$1.32\cdot10^{-4}$[c,g]

[a] Using a group value of 3.3 kJ·mol^{-1} for nitrogen; uncertainties are based on 5% of the predicted value.[11] [b] Calculated using eq 3-12 and the slopes and intercepts listed in Table 3-14 at *T*/K = 298.15. [c] Calculated using eq 3-2 and the constants in Table 3-3 at *T*/K = 298.15. [d] Estimated ref 10. [e] Estimated, ref 25. [f] Reference 20. [g] Extrapolated value.

As previously stated, very few vaporization enthalpies of tertiary amines have been reported. The group value of 6.6 kJ·mol^{-1} for a tertiary nitrogen used in eq 1-6 for the estimation of vaporization enthalpies in Table 3-2 was based on only a few values. This work has shown some of these values to be too large. A new value for nitrogen in a tertiary aliphatic amine of 3.3 kJ·mol^{-1} has been determined using the literature vaporization enthalpies of the following compounds proposed as standards, triethylamine, tripropylamine, *N*,*N*-dimethylbenzylamine, *N*,*N*-dimethyloctylamine and *N*,*N*-dimethyldodecylamine. The group value for a tertiary amine was determined by minimizing the function: $\Sigma[(\Delta_l{}^gH(298.15\ \text{K}) - (4.69\text{n} + 3.0 + \text{N}))/\Delta_l{}^gH(298.15\ \text{K})]^2$ for N where n refers to the number of carbon atoms and N is the group value for a tertiary aliphatic nitrogen atom.

New estimated values that are in much better agreement with the results of this study are listed in column 4 of Table 3-16. These values were obtained using this new group value of 3.3 $\text{kJ}\cdot\text{mol}^{-1}$ for a tertiary aliphatic nitrogen. The uncertainties listed in this column represent 5% of the predicted value. This is the standard uncertainty related to this equation for compounds containing only one functional group.[11]

3.4.2. Vapor Pressures. The last two columns in Table 3-14 compare vaporization enthalpies evaluated by two different methods as a means to determine the quality of the vapor pressures acquired by correlating $\ln(t_o/t_a)_{avg}$ with $\ln(p/p_o)$ as a function of temperature. The data listed in column 4 of Table 3-14 was evaluated from the temperature dependence of vapor pressure using equation 3-12 measured over the temperature range T/K = (283.15 to 313.15). The values listed in the last column of Table 3-14 were acquired directly by correlating the enthalpies of transfer with the vaporization enthalpies of the standards at T/K = 298.15. The data agrees within the uncertainty related to their reproducibility.

The vapor pressures calculated at T/K = 298.15 in this study are compared with either literature or estimated values in the last two columns of Table 3-16. The vapor pressures listed in this table were evaluated using eq 3-12 and the slopes and intercepts are listed in columns 2 and 3 of Table 3-14. The reproducibility as determined by comparisons of the values acquired through direct correlation at T/K = 298.15, Tables 3-13 and 3-15, and those acquired from the temperature dependance of these correlations, Table 3-16, clearly show that the $\ln(p/p_o)$ and $\ln(t_o/t_a)$ of the standards correlate very well with temperature. The absolute uncertainties related to these results are difficult to judge since they rely highly on the accuracy of the vapor pressures of the standards. The uncertainty related to the tertiary amines acquired by extrapolation is highly likely to be greater than for those acquired by interpolation. The estimated values reported in Table 3-16, which are identified by footnotes d and e, compare with those of this study within a factor of four or less.

Since it is known that the Antoine equation does not extrapolate well with temperature, the vapor pressures and vaporization enthalpy for tri-*n*-octylamine were not used in these correlations. For example, a vaporization enthalpy of 120.4 $\text{kJ}\cdot\text{mol}^{-1}$ is evaluated for this material using extrapolated vapor pressures given by the constants listed in Table 3-3 at T/K = 298.15. This value differs significantly from the literature value reported[17] and the value calculated in this study. In spite of this, the vapor pressures evaluated at T/K = 298.15 from the Antoine constants are extremely close to those acquired through correlation. Figure 3-3 shows how the vapor pressures extrapolated from the Antoine constants vary with temperature.

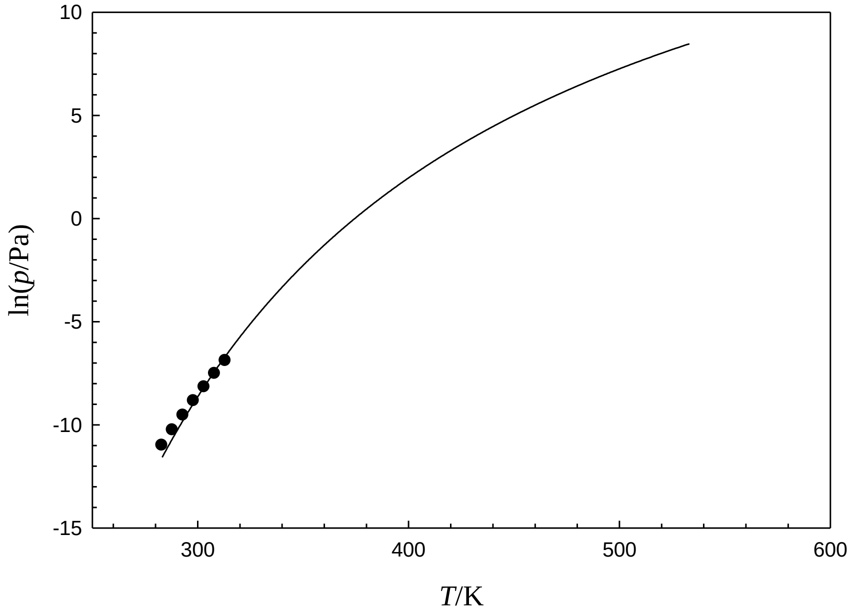

Figure 3-3. The vapor pressure temperature dependence of tri-*n*-octylamine. Line: vapor pressure of tri-*n*-octylamine calculated using eq 3-2 and the Antoine constants of Table 3-3[17] over the temperature range *T*/K = (283 – 533); circles: vapor pressures calculated from the slope and intercept of tri-*n*-octylamine from Table 3-14 plotted as ln(*p*/Pa).

The line represents the values evaluated as ln(*p*/Pa) using eq 3-2 and the Antoine constants of Table 3-3 extrapolated to *T*/K = 298.15. The solid circles represent the vapor pressures calculated using eq 3-12 and the slope and intercept from Table 3-14 for tri-*n*-octylamine also plotted as ln(*p*/Pa). The vapor pressure of tri-*n*-octylamine evaluatated by extrapolation of the Antoine constants, *p*/Pa = $1.32 \cdot 10^{-4}$ at *T*/K = 298.15, compares to a value of *p*/Pa = $1.4 \cdot 10^{-4}$ calulated in this study. This result implies that while extrapolations of the Antoine equation may not give dependable vaporization enthalpies, the resulting vapor pressures may be rather reasonable. Comparable results have been seen in other studies.[26]

3.4.3. Sublimation Enthalpy. Tribenzylamine is the only crystalline material at *T*/K = 298.15 of all the aliphatic amines investigated. Adjustment of the fusion enthalpy to ambient temperature using eq 3-1 gives a value of (18.9 ± 1.6) kJ·mol^{-1}. When combined with the vaporization enthalpy of the sub-cooled liquid of (92.4±8.0) kJ·mol^{-1} also at this temperature, a value of (111.3±8.2) kJ·mol^{-1}for the sublimation enthalpy is obtained for tribenzylamine. These results are summarized in Table 3-17. The fusion temperature of tribenzylamine and the vapor pressure of the solid were not calculated due to the fact that the vapor pressures of the standards do not extend to T/K = 365.6.

TABLE 3-17. The Fusion, Vaporization and Sublimation Enthalpy of Tribenzylamine at T/K = 298.15

	$\Delta_{cr}{}^{cr}H_t + \Delta_{cr}{}^{l}H(T_{fus})^a$ kJ·mol^{-1}	T_t/T_{fus}/K	$\Delta C_p \Delta T^b$ kJ·mol^{-1}	$\Delta_{cr}{}^{l}H$(298 K) kJ·mol^{-1}	$\Delta_l{}^{g}H_m$(298 K) kJ·mol^{-1}	$\Delta_l{}^{g}H_m$(298 K) kJ·mol^{-1}
tribenzylamine	24.1±0.14	342.5/365.6	-5.2±1.6	18.9±1.6	92.4±1.4	111.3±2.1

$^a\Delta_{cr}{}^{cr}H_m$(342.5 K)/kJ·mol^{-1} = (1.1 ± 0.1). ^bC_p(l)), C_p(cr))/ J·mol^{-1}·K^{-1} = 490.6, 400.2, respectively, ref 21.

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(10) Calculated using the EPI Suite. The EPI Suite is available as a free download

from http://www.epa.gov/oppt/exposure/pubs/episuitedl.htm.

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Chapter 4: The Vaporization Enthalpy and Vapor Pressure of Fenpropidin and Phencyclidine (PCP) at *T*/K = 298.15 by Correlation Gas Chromatography

4.1. Introduction

Fenpropidin (1-[3-[4-(1,1-dimethylethyl)phenyl]-2-methylpropyl]piperidine) is a fungicide used to combat rusts, powdery mildew, and leaf spots in cereals. Its mode of action is thought to block plant biosynthesis of ergosterol and it is commercially used as the racemic mixture.[1-3] Phencyclidine, (1-(1-phenyl- cyclohexyl)piperidine) also known as PCP or "Angel dust", was originally promoted as an anesthetic, but was found to produce hallucinogenic side effects.[4] Since users of this drug seem to be disconnected from the environment around them, it has been called a dissociative anesthetic. Due to its high tendency for abuse it has been classified as a Schedule II substance similar to methamphetamine and cocaine.[4] Phencyclidine has also found use as an anesthetic or tranquillizer in veterinary applications.[4]

At room temperature, Fenpropidin is a liquid, T_{fus}/K = 208[5], and phencyclidine is a solid, T_{fus}/K = 319.7.[6] This study reports the liquid vapor pressures and vaporization enthalpies of both from *T*/K = (283.2 to 313.2) as determined by correlation gas chromatography and compares the vapor pressure of the liquid forms to those given in the Pesticide Properties Database,[5] EPI Suite[6] and on Toxnet.[7] The vaporization enthalpy and vapor pressures of phencyclidine are that of the sub-cooled liquid. The limited quantity of available phencyclidine prohibited fusion enthalpy measurements. Indirect estimation of its fusion enthalpy was used in combination with its vaporization enthalpy to estimate a sublimation and vapor pressure of crystalline phencyclidine. The structures of the two compounds under investigation are shown in Figure 4-1.

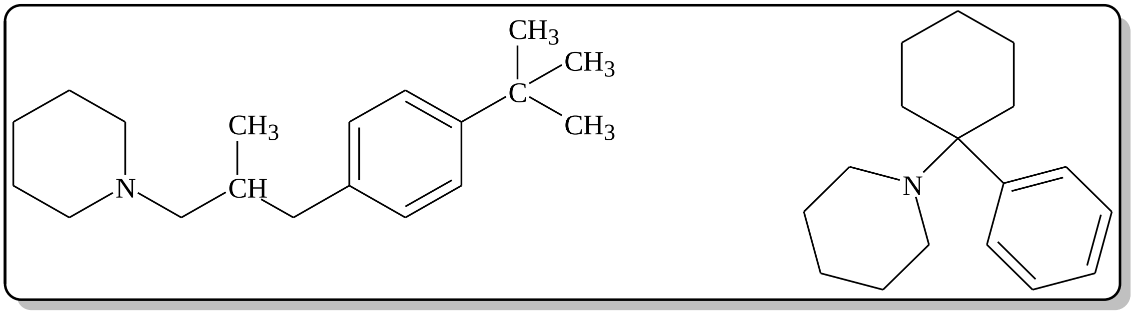

Figure 4-1. Structures of Fenpropidin and Phencyclidine (PCP).

The effectiveness of using the correlation gas chromatography method for determining thermodynamic properties of substances commercially available in only very small quantities is shown by the evaluation of phencyclidine. It is useful to investigate the vapor pressure of phencyclidine at room temperature due to the compound commonly being smoked or administered intra-nasally.[4] The volatility of fenpropidin affects levels of trace fungicide residues on consumable products and exposure levels to users.[8,9] Fenpropidin has been classified as moderately hazardous by the World Health Organization.[5]

4.2. Experimental

4.2.1. Materials. Table 4-1 lists the source and purity of the materials used in this study.

TABLE 4-1. Origin of the Standards and Targets and Their Analysis

	Compound	CAS RN	Supplier	Mass fraction	GC Anal
$C_9H_{13}N$	*N*,*N*-Dimethylbenzylamine	[103-83-3]]	Sigma Aldrich	>0.99	
$C_{12}H_{27}N$	Tri-*n*-butylamine	[102-82-9]	Sigma Aldrich	0.97	
$C_{10}H_{23}N$	*N*,*N*-Dimethyloctylamine	[7378-99-6]	Sigma Aldrich	0.95	
$C_{14}H_{31}N$	*N*,*N*-Dimethyldodecylamine	[112-18-5]	TCI	>0.95	
$C_{16}H_{35}N$	*N*,*N*-Dimethyltetradecylamine	[112-75-4]	Sigma Aldrich	>0.95	
$C_{17}H_{25}N$	Phencyclidine	[77-10-1]	Restek	RS[a]	0.98
$C_{18}H_{39}N$	*N*,*N*-Dimethylhexadecylamine	[112-69-6]	Sigma Aldrich	>0.95	
$C_{19}H_{31}N$	Fenpropidin	[067306-00-7]	Fluka	AS[b]	0.97
$C_{21}H_{21}N$	Tribenzylamine	[620-40-6]	Eastman[c]		0.98+
$C_{24}H_{51}N$	Tri-*n*-octylamine	[1116-76-3]	Sigma Aldrich	0.98	

[a]Reference standard. [b]Analytical standard. [c]Eastman Organic Chemicals.

Since phencyclidine is a Schedule II substance, it is only available in solution in limited quantities. It was purchased from Restek in single milligram quantities dissolved in methanol. The sample purity evaluated by gas chromatography was >0.98 mass fraction. Fenpropidin was purchased from Fluka. The analysis of fenpropidin by gas chromatography was 0.97 mass fraction. With the exception of tribenzylamine which was also analyzed by gas chromatography, the analysis of the compounds used as standards in Table 4-1 are those reported by the suppliers. Since the chromatography separates the impurities, purity is not the issue as with other methods. In a separate study,[10] we have found that there was no noticeable effect on the vaporization enthalpy and vapor pressure of two different materials that co-eluted over the entire temperature range.

4.2.2. Methods. Correlation-gas chromatography experiments were conducted in the same manner as previously described in Section 1.2.2.2. Each plot was characterized by a correlation coefficient of $r^2 > 0.99$. The only differences were that this time the columns used were a Supelco 15 m, 0.32 mm, 1.0 μm film thickness SPB-5 capillary column and a 0.25 mm, 30 m DB-5 column, the temperature was maintained to T/K = 0.1 as monitored independently using a Fluke digital thermometer and hexanes or hexanes/methylene chloride served as the non-retained reference. Column identity can be identified by the retention times, reported in Appendix D. On the 30 m column, the retention time of the solvent, $t_s/60 > 1$ and on the 15 m column, $t_s/60 < 1$.

4.2.3. Vaporization Enthalpy Standards. Table 4-2 summarizes the vaporization enthalpies of the standards used in this work. Vaporization enthalpies for *N,N*-dimethylbenzylamine,[11] *N,N*-dimethyloctyl[12] and *N,N*-dimethyldodecylamine[13] are literature values evaluated by various experimental techniques. The remaining standards in Table 4-2 were evaluated by correlation gas chromatography using these and other tertiary amines as standards.[14]

TABLE 4-2. Literature Vaporization Enthalpies of Some Tertiary Amines; p_o/Pa = 101325

Compounds	$\Delta_l^g H_m(T_m)$ kJ·mol^{-1}	T_m/K	C_p(l) J·mol^{-1}·K^{-1}	$\Delta_l^g C_p \Delta T$ kJ·mol^{-1}	$\Delta_l^g H_m$(298.15 K) kJ·mol^{-1} exp	Ref.
N,*N*-Dimethylbenzylamine	48.9±0.4	308	248	0.8±0.2	49.7±0.4	11
N,*N*-Dimethyloctylamine	54.0±0.5	303	360	0.5±0.1	54.5±0.5	12
Tri-*n*-butylamine	58.0±1.9	298			58.0±1.9	14
N,*N*-Dimethyldodecylamine	69.3±0.3	298			69.3±0.3	13
N,*N*-Dimethyltetradecylamine	77.3±1.9	298			77.3±1.9	14
N,*N*-Dimethylhexadecylamine	84.8±1.0	298			84.8±1.0	14
Tribenzylamine	92.4±1.4	298			92.4±1.4	14
Tri-*n*-octylamine	100.1±1.4	298			100.1±1.4	14

4.2.4. Vapor Pressure Standards. The compounds chosen as vaporization enthalpy standards also served as vapor pressure standards. The vapor pressures were all calculated using eq 3-2. The reference pressure for *N*,*N*-dimethyldodecylamine, p_{ref} = p_o/Pa = 1, while for the remaining compounds in Table 4-3, p_{ref} = p_o/Pa = 101325. The constants for most compounds reported in Table 4-3 are valid over the temperature range, *T*/K = (283-313). The vapor pressure values for *N*,*N*-dimethylbenzylamine required an extrapolation of *T*/K = 5 to lower temperature.

TABLE 4-3. Parameters of Eq 4-2 Used as Vapor Pressure Standards; p_o/Pa = 101325[a]; *T*/K = 298.15

	A	B	C	ln(p_o/Pa) 298.15 K	*T*/K range	ln(p/p_o)	Ref
N,*N*-Dimethylbenzylamine	13.422[a]	5892.0[a]	0		288-328	-6.34	11
N,*N*-Dimethyloctylamine	14.439[a]	6498.8[a]	0		284-323	-7.36	12
Tri-*n*-butylamine	15.181	6965.9	0		283-313	-8.18	14
N,*N*-Dimethyldodecylamine	40.49339	17623.5	135.268	-0.168[c]	283-314	-11.69	13
N,N-Dimethyltetradecylamine	17.399	9337.0	0		283-313	-13.92	14
N,*N*-Dimethylhexadecylamine	18.368	10270.3	0		283-313	-16.08	14
Tri-*n*-octylamine	20.362	12148	0		283-313	-20.38	14
Tribenzylamine	18.361	11175.4	0		283-313	-19.12	14

[a]Unless noted otherwise. [b]Calculated from the vapor pressure data reported. [c]p_o = 1 Pa.

4.2.5. Temperature Adjustments. Adjustments from the mean temperature of measurement, T_m , to a common temperature, *T*/K = 298.15, were achieved in the same way as described in Section 1.2.4. The vaporization enthalpies of all but two of the standards are all available at *T*/K = 298.15. In estimation of the sublimation enthalpy of phencyclidine at *T*/K = 298.15 as described below, it was also necessary to adjust both the vaporization and sublimation enthalpies for temperature. The two equations, eq 1-3 and 1-5, were used for these purposes. Equation 1-3 was used to adjust the vaporization enthalpy and eq 1-5 was used to adjust the sublimation enthalpy.

4.2.5. Uncertainties. All slopes and intercepts reported below were calculated by linear regression. Uncertainties associated with results derived by combination of two or more experimental values were derived as $(u_1^2 + u_2^2 + \ldots)^{0.5}$. All uncertainties refer to one standard deviation unless noted otherwise. Uncertainties evaluated from logarithmic terms are reported as the average of the two uncertainties calculated. The uncertainty associated with the C_p(l) term in eq 1-3 is 16 J·mol^{-1}·K^{-1}, while the uncertainty associated with eq 1-5 is 30% of the temperature adjustment. The heat capacity values used for each adjustment are provided in the tables below. Uncertainties associated with the slopes and intercepts of plots of ln(t_o/t_a) vs 1/T/K are provided in Appendix D. The standard deviations reported in the tables of experimental data are equivalent to the standard uncertainties, as defined by the Guide to the Expression of Uncertainty in Measurement.

4.3. Results

4.3.1. Vaporization Enthalpies. Summarized in Table 4-4 are a set of data for fenpropidin and two sets of data for phencyclidine with the use of somewhat different standards.

TABLE 4-4. Vaporization Enthalpy Results for Phencyclidine and Fenpropidin; Uncertainties are One Standard Deviation, p_o = 101325 Pa

Run 1	- slope T/K	intercept	ΔH_{trn}(464 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298.15 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298.15 K) kJ·mol^{-1}(calc)
N,N-Dimethylbenzylamine	4134.4	9.811	34.37	49.7±0.4	49.2±2.8
N,N-Dimethyloctylamine	4919.2	11.409	40.90	54.5±0.5	56.3±3.0
Tri-*n*-butylamine	4999.5	11.208	41.56	58.0±1.9	57.0±3.0
N,N-Dimethyldodecylamine	6335.0	12.791	52.67	69.3±0.3	69.0±3.4
N,N-Dimethylhexadecylamine	8084.2	14.952	67.21	84.8±1.0	84.8±3.9
Phencyclidine	7236.9	13.037	60.16		77.2±3.7

Run 3	- slope T/K	intercept	ΔH_{trn}(489 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298.15 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298.15 K) kJ·mol^{-1}(calc)
Tri-*n*-butylamine	4778.1	10.733	39.72	58.0±1.9	57.8±0.7
N,N-Dimethyldodecylamine	6033.4	12.148	50.16	69.3±0.3	69.5±0.8
N,N-Dimethylhexadecylamine	7696.7	14.130	63.99	84.8±1.0	85.0±0.9
Phencyclidine	6941.6	12.409	57.71		78.0±0.8
Tri-*n*-octylamine	9293.5	16.071	77.26	100.1±1.4	99.9±1.0

Run 5	- slope T/K	intercept	ΔH_{trn}(498 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298.15 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298.15 K) kJ·mol^{-1}(calc)
N,N-Dimethyldodecylamine	-5883.9	12.429	48.92	69.3±0.3	69.4±1.1
N,N-Dimethyltetradecylamine	-6629.8	13.251	55.12	77.3±3.0	76.9±1.2
N,N-Dimethylhexadecylamine	-7431.1	14.175	61.78	84.8±1.0	85.0±1.2
Fenpropidin	-7025.6	13.170	58.41		81.0±1.2
Tri-*n*-octylamine	-8904.9	15.915	74.03	100.1±1.4	99.9±1.4
Tribenzylamine	-8172.3	14.336	67.94	92.4±1.4	92.5±1.3

Run 1: $\Delta_l^g H_m(298.15\ \mathrm{K})/\mathrm{kJ{\cdot}mol^{-1}} = (1.085 \pm 0.047)\Delta H_{\mathrm{trn}}(489\ \mathrm{K}) + (11.90 \pm 2.30)$ $r^2 = 0.9943$ (4-1)

Run 3: $\Delta_l^g H_m(298.15\ \mathrm{K})/\mathrm{kJ{\cdot}mol^{-1}} = (1.122 \pm 0.01)\Delta H_{\mathrm{trn}}(489\ \mathrm{K}) + (13.21 \pm 0.60)$ $r^2 = 0.9998$ (4-2)

Run 5: $\Delta_l^g H_m(298.15\ \mathrm{K})/\mathrm{kJ{\cdot}mol^{-1}} = (1.216 \pm 0.014)\Delta H_{\mathrm{trn}}(498\ \mathrm{K}) + (9.903 \pm 0.88)$ $r^2 = 0.9996$ (4-3)

The data for duplicate runs of these experiments are listed in Appendix D. Since the retention times of the standards used in the first set of data did not bracket phencyclidine, a second series of correlations were performed. Shown at the bottom of the table are the equations of the lines, eqs 4-1 through 4-3. Similar tables and equations for duplicate runs are given in Appendix D. A summary of the results for all experiments are shown in Table 4-5. They are all within experimental error of one another. The average vaporization enthalpy determined for each compound is reported in the last column of Table 4-5. The uncertainty is an average of each standard deviation, as well. Vaporization enthalpies at *T*/K =298.15 of 77.6±2.1 and 80.9±1.6 kJ· mol^{-1} have been calculated for phencyclidine and fenpropidin, respectively.

TABLE 4-5. A Summary of the Vaporization Enthalpy of the Targets and Standards in kJ·mol^{-1} at *T*/K = 298.15; p_o =101325 Pa.

	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Average^a
Targets							
Phencyclidine	77.2±3.7	77.2±3.4	78.0±0.8	77.8±0.6			77.6±2.1
Fenpropidin					81.0±1.2	80.8±2.0	80.9±1.6
Standards							
N,*N*-Dimethylbenzylamine	49.2±2.8	49.3±2.6					49.3±2.7
N,*N*-Dimethyloctylamine	56.3±3.0	56.1±2.7					56.2±2.9
Tri-*n*-butylamine	57.0±3.0	57.0±2.8	57.8±0.7	57.9±0.5			57.4±1.8
N,*N*-Dimethyldodecylamine	69.0±3.4	69.1±3.1	69.5±0.8	69.4±0.5	69.4±1.1	69.3±1.8	69.3±1.8
N,*N*-Dimethyltetradecylamine					76.9±1.2	76.9±1.9	76.9±1.6
N,*N*-Dimethylhexadecylamine	84.8±3.9	84.8±3.6	85.0±0.9	85.0±0.6	85.0±1.2	85.3±2.0	85.0±2.0
Tri-*n*-octylamine			99.9±1.0	100.0±0.7	99.9±1.4	99.7±2.2	99.9±1.3
Tribenzylamine					92.5±1.3	92.6±2.1	92.6±1.7

^{a}The uncertainty is an average of the standard deviations reported in columns 2-7.

4.3.2. Vapor Pressures. Reported in Table 4-6 are the correlations between ln(p/p_o) with ln(t_o/t_a) of the standards at *T*/K = 298.15.

TABLE 4-6. Correlation of ln(p/p_o) with ln(t_o/t_a) for Runs 1-6 at T/K = 298.15; p_o = 101325.[a]

Run 1/2	-slope/K	Intercept	ln(t_o/t_a)$_{avg}$	ln(p/p_o)$_{lit}$	ln(p/p_o)$_{calc}$[a]
N,N-Dimethylbenzylamine	4134.4	9.811			
	4102.4	9.746	-4.034	-6.34	-6.29±0.16
N,N-Dimethyloctylamine	4919.2	11.409			
	4861.2	11.287	-5.053	-7.36	-7.52±0.16
Tri-*n*-butylamine	4999.5	11.208			
	4962.2	11.132	-5.535	-8.18	-8.11±0.17
N,N-Dimethyldodecylamine	6335.0	12.791			
	6296.6	12.713	-8.431	-11.69	-11.62±0.21
N,N-Dimethylhexadecylamine	8084.2	14.952			
	8062.8	14.911	-12.147	-16.08	-16.11±0.26
Phencyclidine	7236.9	13.037			
	7197.8	12.958	-11.209		-14.99±0.24
Run 3/4					
Tri-n-butylamine	4778.1	10.733			
	4811.4	10.812	-5.309	-8.18	-8.2±0.07
N,N-dimethyldodecylamine	6033.4	12.148			
	6020.2	12.131	-8.074	-11.65	-11.65±0.08
N,N-dimethylhexadecylamine	7696.7	14.13			
	7653.1	14.05	-11.651	-16.08	-16.12±0.10
Phencyclidine	6941.6	12.409			
	6899.4	12.331	-10.841		-15.11±0.09
Tri-*n*-octylamine	9293.5	16.071			
	9224.1	15.938	-15.049	-20.38	-20.37±0.11
Run 5/6					
N,N-Dimethyldodecylamine	5883.9	12.429			
	5915.1	12.49	-7.327	-11.69	-11.68±0.22
N,N-Dimethyltetradecylamine	6629.8	13.251			
	6672.2	13.334	-9.015	-13.92	-13.86±0.23
N,N-Dimethylhexadecylamine	7431.1	14.175			
	7510.5	14.332	-10.802	-16.08	-16.18±0.25
Tribenzylamine	8172.3	14.336			
	8234.3	14.458	-13.116	-19.12	-19.18±0.28
Tri-*n*-octylamine	8904.9	15.915			
	8940.9	15.986	-13.977	-20.38	-20.29±0.29
Fenpropidin	7025.6	13.17			
	7058.5	13.235	-10.417		-15.68±0.25

Run 1/2 $\ln(p/p_o) = (1.213\pm0.018)\ln(t_o/t_a) - (1.397\pm0.138)$; $r^2 = 0.9993$ (4-4)

Run 3/4 $\ln(p/p_o) = (1.249\pm0.006)\ln(t_o/t_a) - (1.565\pm0.065)$; $r^2 = 0.9999$ (4-5)

Run 5/6	$\ln(p/p_o) = (1.296 \pm 0.016)\ln(t_o/t_a) - (2.185 \pm 0.182)$; $r^2 = 0.9995$	(4-6)

[a]The uncertainty is one standard deviation.

Using both duplicate runs, values for (t_o/t_a) were calculated for each compound, averaged and then the $\ln(t_o/t_a)_{avg}$ value of the standards were correlated with the corresponding values of $\ln(p/p_o)$. The linearity of each set of correlations at T/K = 298.15 is shown by the correlation coefficients associated with equations 4-4 through 4-6. Combined with the $\ln(t_o/t_a)_{avg}$ of the target compounds these equations were then used to calculate their corresponding $\ln(p/p_o)$ values. Each correlation was then repeated at T/K = 5 intervals over the appropriate range of the constants given in Table 4-3, T/K = (283.2 to 313.2). Correlation coefficients, r^2, acquired at all temperatures in this range were greater than 0.99.

The slopes and intercepts from the plots of $\ln(p/p_o)$ versus $1/T$ for both phencyclidine and fenpropidin are given in Table 4-7. Vaporization enthalpies evaluated from the vapor pressures over the temperature range T/K = (283.2 to 313.2) are listed in the fourth column. The values are in agreement with those reported in Table 4-5. Vapor pressures and their associated uncertainties for the target compounds listed in column 5 of Table 4-7 are calculated from the slopes and intercepts of columns 2 and 3. The values in the last column of Table 4-7 are evaluated from the last column of Table 4-6. The vapor pressures evaluated from the slopes and intercepts listed in Table 4-7 are very similar to those reported in Table 4-6, except that their uncertainties are slightly smaller.

TABLE 4-7. Vaporization Enthalpies (p_o = 101325 Pa) and Vapor Pressures Evaluated From Correlation of ln(t_o/t_a)$_{avg}$ with ln(p/p_o)$_{lit}$, Uncertainties One Standard Deviation

	-Slope/K	Intercept	$\Delta_l^gH_m$(298.15 K)^c kJ·mol^{-1}	$10^2\cdot p_{298.15\,K}$/Pa^b	$10^2\cdot p_{298.15\,K}$/Pa^c
Run 1/2					
Phencyclidine	9288.8±10.7	16.169±0.036	77.2±0.1	3.1±0.2	3.1±0.7
Run 3/4					
Phencyclidine	9373.2±6.8	16.330±0.022	77.9±0.1	2.8±0.1	2.8±0.5
Run 5/6					
Fenpropidin	9759.6±8.2	17.055±0.028	81.1±0.1	1.6±0.001	1.6±0.4

[a] Calculated the product of the slope (column 2) and the gas constant. [b] Calculated the product of the slope and intercept; uncertainty is an average of one standard deviation. [c] Calculated from the last column of Table 4-6; uncertainty is an one standard deviation (average value).

Vapor pressures and vaporization enthalpies calculated from correlations of the standard compounds for each set of runs are included in Appendix D.

Summarized in Table 4-8 are the vapor pressures and vaporization enthalpies at T/K = 298.15 determined in this study. The vaporization enthalpies for both the standard and target compounds are the mean values listed in Table 4-5 while the vapor pressures are the average values given in the last column of Table 4-7. Experimental vaporization enthalpies for the two target compounds are not currently available. The vapor pressure of phencyclidine at T/K = 298.15 calculated in this work, p/Pa = (0.03±0.006), compares favorably to an estimated value of p/Pa = 0.04.[6] Vapor pressures for phencyclidine are for that of the sub-cooled liquid. The vapor pressure for fenpropidin at T/K = 298.15 evaluated in this study, p/Pa = (0.016±0.004), is within experimental error of the reported value of p/Pa = 0.017.[5] A reference to the original literature for fenpropidin is not available.

TABLE 4-8. A Summary of the Vaporization Enthalpies (p_o = 101325 pa) and Liquid Vapor Pressures at T/K = 298.15 Evaluated in This Work; Uncertainties are One Standard Deviation

Targets	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} this work	(lit)	$10^2\cdot p_{298.15\ \mathrm{K}}$/Pa avg	$10^2\cdot p_{298.15\ \mathrm{K}}$/Pa lit	Ref
Phencyclidine	77.6±2.1		3.0±0.6	4.0[a]	6
Fenpropidin	80.9±1.6		1.6±0.4	1.71[b]	5
Standards					
N,*N*-Dimethylbenzylamine	49.3±2.7	49.7±0.4	18800±2900	17900[b]	11
N,*N*-Dimethyloctylamine	56.2±2.9	54.5±0.5	5470±900	6300[b]	12
Tri-*n*-butylamine	57.4±1.8	58.0±1.9	2920±360	2830[c]	14
N,*N*-Dimethyldodecylamine	69.3±1.8	69.3±0.3	89±16	85[b]	13
N,*N*- Dimethyl tetradecylamine	76.9±1.6	77.3±3.0	9.6±2.3	9.2[c]	14
N,*N*-Dimethylhexadecylamine	85.0±2.0	84.8±1.0	1.0±0.2	1.1[c]	14
Tri-*n*-octylamine	99.9±1.3	100.1±1.4	0.015±0.0016	0.14[c], 0.13[d]	14,15
Tribenzylamine	92.6±1.7	92.4±1.4	0.05±0.01	0.05[c], 0.26[a]	14, 6

[a] Estimated vapor pressure of the sub-cooled liquid. [b] Experimental vapor pressure. [c] Evaluated previously by correlation. [d] Extrapolated value, ref 15.

4.3.3. Sublimation Enthalpy. As previously stated, phencyclidine is a solid at room temperature which melts at T_{fus}/K = 319.65. Given that it is a Schedule II drug, currently available commercial sample sizes prohibited the experimental measurement of its fusion enthalpy. A reasonably accurate method, however, has been developed to estimate the total phase change entropy from T/K = (0 to T_{fus}), ΔS_{tpce}.[16] Employing the assumption that no considerable solid-solid phase transitions occur in phencyclidine below T/K = 298.15, ΔS_{tpce} can be used in combination with the fusion temperature, $T_{\mathrm{fus}}\cdot\Delta S_{\mathrm{tpce}}$, to give a reasonable value for $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}(T_{\mathrm{fus}})$. A value for ΔS_{tpce} of (62.5±13) J·mol^{-1}·K^{-1} is determined through application of the developed protocol.[16] Details explaining the estimation are given in Appendix D. The product, $T_{\mathrm{fus}}\cdot\Delta S_{\mathrm{tpce}}$, gives a fusion enthalpy of (20±6) kJ·mol^{-1}.

Summarized in Table 4-9 is the vaporization enthalpy of phencyclidine adjusted to the fusion temperature using eq 1-3. A sublimation enthalpy of (95.0±6.3) kJ·mol^{-1} is calculated at T_{fus} when combined with the estimated fusion enthalpy of (20±5.9) kJ·mol^{-1}. Using eq 1-5, adjustment to T/K = 298.15 results in a sublimation enthalpy of (96.1±6.3) kJ·mol^{-1}. The temperature adjustment is listed in Table 4-9, as well.

TABLE 4-9. Vaporization and Estimated Sublimation Enthalpies for Phencyclidine and Their Temperature Adjustments, (p_{o} = 101325 Pa); Estimated Vapor Pressure of Solid Phencyclidine; Uncertainties are One Standard Deviation

$\Delta_{\text{l}}{}^{\text{g}}H_{\text{m}}$(298.15 K) kJ·mol^{-1}	T_{fus}/K	$\Delta_{\text{l}}{}^{\text{g}}C_p$ J·mol^{-1}·K^{-1}	$10^{-3}\cdot\Delta_{\text{l}}{}^{\text{g}}C_p\cdot\Delta T$ kJ·mol^{-1}	$\Delta_{\text{l}}{}^{\text{g}}H_{\text{m}}(T_{\text{fus}})$ kJ·mol^{-1}	ΔS_{tpce} J·mol^{-1}·K^{-1}	$\Delta_{\text{cr}}{}^{\text{l}}H_{\text{m}}(T_{\text{fus}})$ kJ·mol^{-1}
77.6±2.1	319.65	429.9	-2.63±0.3	75.0±2.2	62.5±13	20±5.9

$\Delta_{\text{cr}}{}^{\text{l}}H_{\text{m}}(T_{\text{fus}})^{a}$ kJ·mol^{-1}	$\Delta_{\text{l}}{}^{\text{g}}H_{\text{m}}(T_{\text{fus}})$ kJ·mol^{-1}	$\Delta_{\text{cr}}{}^{\text{g}}H_{\text{m}}(T_{\text{fus}})$ kJ·mol^{-1}	$\Delta_{\text{cr}}{}^{\text{g}}C_p$ J·mol^{-1}·K^{-1}	$10^{-3}\cdot\Delta_{\text{cr}}{}^{\text{g}}C_p\cdot\Delta T$ kJ·mol^{-1}	$\Delta_{\text{cr}}{}^{\text{g}}H_{\text{m}}$(298.15 K)^{a} kJ·mol^{-1}	$10^{2}\cdot p_{298}$/Pa^{a} tw^{b}/lit^{c}
20±5.9	75.0±2.2	95.0±6.3	349.3	1.1±0.3	96.1±6.3	1.9±0.07/2.6

^{a}Estimated. ^{b}This work. ^{c}Reference 6.

4.3.4. Sublimation Vapor Pressure. Equation 4-7 has been shown to reproduce experimental vapor pressures of numerous different organic solids within a factor of three by using experimental fusion and vaporization enthalpies and vapor pressures at T_{fus}.[17] In order to determine the vapor pressure of solid phencyclidine, as well as the sublimation enthalpy at the triple point temperature, the vapor pressure of the solid at this temperature is also needed. The vapor pressure of liquid phencyclidine is essentially within the available temperature range of the fusion temperature. Approximation of the triple point as T_{fus} = 319.7 and evaluation of the vapor pressure of phencyclidine from the slopes and intercepts of runs 1/2 and 3/4 from Table 4-7, which are then averaged, gives a vapor pressure of p/Pa = (0.25±0.05) at this temperature. Substituting the appropriate data into eq 4-7 gives a vapor pressure of the solid at T/K =298.15 of p/Pa = (0.019±0.007). In comparison, the EPI Suite predicts a vapor pressure of p/Pa = 0.026 at this temperature. This is the last entry in Table 4-9.[6]

$$\ln(p_{(298.15)}/p^{o}) = [\{\Delta H_{\mathrm{sub}}(T_{\mathrm{fus}}) + (\Delta_{\mathrm{cr}}{}^{\mathrm{g}}C_{p}\Delta T)/2\}/\mathrm{J{\cdot}mol^{-1}}][\mathrm{K}/T_{\mathrm{fus}} - 1/298.15)]/[\ (\mathrm{J{\cdot}K^{-1}mol^{-1}})/\mathrm{R}] + \ln(p_{(T\mathrm{fus})}/p^{o}) \qquad (4\text{-}7)$$

4.4. Summary

Liquid vapor pressures of p/Pa = (0.03±0.006) and (0.016±0.004) and vaporization enthalpies of (77.6±2.1) and (80.9±1.6) kJ·mol^{-1} at T/K = 298.15 have been determined by correlation gas chromatography for phencyclidine and fenpropidin, respectively. Experimental vaporization enthalpies are not available. An experimental vapor pressure of p/Pa = 0.0171 has been previously reported for fenpropidin.[12] Combining the vaporization enthalpy at T_{fus} with an estimated fusion enthalpy and adjustment of the sum back to T/K = 298.15, a sublimation enthalpy of (96.1±6.3) kJ·mol^{-1} at T/K = 298.15 has been estimated for phencyclidine. Adjusting the results to T/K = 298.15, the vapor pressure of liquid phencyclidine at the approximate temperature at which the solid is in equilibrium with the liquid, T_{fus}, in combination with the sublimation enthalpy calculated an estimated vapor pressure for solid phencyclidine at T/K = 298.15. The estimated vapor pressure of p/Pa = (0.019±0.07) from this study compares with a literature estimation of p/Pa = 0.026.[5]

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Chapter 5: The Vaporization Enthalpies and Vapor Pressures of a Series of Pharmaceutically Important Aliphatic Tertiary Amines and Evaluation of Correlation Viability of Aromatic and Aliphatic Tertiary Amines by Correlation Gas Chromatography

5.1 Introduction

Amitriptyline (3-(10,11-Dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene-5-ylidene)-*N*,*N*-dimethylpropan-1-amine) has been used to treat a variety of different mental illnesses including clinical depression, anxiety disorder, attention deficit hyperactivity disorder and bipolar disorder. It is the most widely used tricyclic antidepressant. It has also been used to prevent migraine headaches and to treat eating disorders and post-herpetic neuralgia; the burning, stabbing pains or aches that may last for months or years after a shingles infection. It works by increasing the amount of certain natural substances in the brain needed to maintain mental balance.[1] Terbinafine ([(2*E*)-6,6-dimethylhept-2-en-4-yn-1-yl](methyl)(naphthalen-1-ylmethyl)amine) is an antifungal drug used to treat fungal infections of the toenail and fingernail. It works by stopping fungal growth.[2] Cyproheptadine (4-(5*H*-dibenzo [a,d]cyclohepten-5-ylidene)-1-methylpiperidine) is an antihistamine used to treat red, irritated, itchy, watery eyes, sneezing and runny nose caused by allergies, irritants in the air, and hay fever. It can also be used to relieve the itching sensation of allergic skin conditions and to treat hives, as well as for the treatment of Cushing's Syndrome, an abnormal condition caused by excess hormones. It works by blocking the activity of histamine, a substance that causes allergic reactions in the body.[1] Naftifine ((2*E*)-*N*-methyl-*N*-(1-naphthylmethyl)-3-phenylprop-2-en-1-amine) is an antifungal drug used for the topical treatment of tinea pedis (athlete's foot), tinea cruris (jock itch) and tinea corporis (ringworm), fungal infections caused by the organisms Trichophyton rubrum, Trichophyton mentagrophytes, and Epidermophyton floccosum. While its exact mechanism of action is unknown, it is thought it may work by selectively blocking sterol biosynthesis via inhibition of the squalene 2,3-epoxidase enzyme.[1] The structures of amitriptyline, terbinafine, cyproheptadine, naftifine and tri-*n*-hexylamine are listed in Figure 5-1.

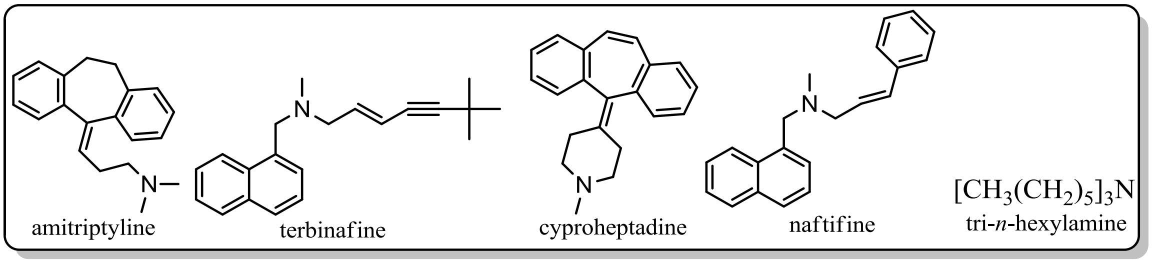

Figure 5-1. Tertiary Amines Investigated in This Study.

Usually, these pharmaceutical compounds are prescribed in their ammonium salt form. This can lead to the production of the neutral parent species when the unused portions are improperly disposed into the environment. Factors such as this have raised concerns over the environmental impact of discarded medications. With the aqueous and gas phases being the major routes of dispersal, an understanding of these drugs thermodynamic properties is essential.

5.2. Experimental

5.2.1. Materials. The source and composition for the materials used in this study are listed in Table 5-1. All amines in this work were used as commercially available. Amitriptyline, naftifine and terbinafine are sold as their hydrochloride salts. Cyproheptadine is marketed as its hydrochloride sesquihydrate salt. Alverine is available as the corresponding citrate. These compounds were neutralized with 1M NaOH prior to use and extracted with methylene chloride. The purities of some of these compounds were analyzed independently by gas chromatography.

TABLE 5-1. Origin of the Standards and Targets and Their Analysis

	Compound	CAS RN	Supplier	Mass fraction	GC Anal
$C_{12}H_{27}N$	Tri-*n*-butylamine	[102-82-9]	Sigma-Aldrich	0.97	
$C_{14}H_{31}N$	*N*,*N*-Dimethyl dodecylamine	[112-18-5]	TCI	>0.95	
$C_{16}H_{35}N$	*N*,*N*-Dimethyl tetradecylamine	[112-75-4]	Sigma-Aldrich	>0.95	
$C_{18}H_{39}N$	*N*,*N*-Dimethyl hexadecylamine	[112-69-6]	Sigma-Aldrich	>0.95	
$C_{18}H_{39}N$	Tri-*n*-hexylamine	[102-86-3]	Sigma-Aldrich	0.96	
$C_{20}H_{23}N$	Amitriptyline[a]	[549-18-8]	Sigma-Aldrich	≥0.98	
$C_{20}H_{27}N$	Alverine[b]	[150-59-4]	Sigma-Aldrich		0.99+
$C_{21}H_{21}N$	Naftifine[a]	[65473-14-5]	Sigma-Aldrich		0.99+
$C_{21}H_{21}N$	Cyproheptadine[c]	[41354-29-4]	Sigma-Aldrich	>0.98	
$C_{21}H_{21}N$	Tribenzylamine	[620-40-6]	Eastman[d]		0.98+
$C_{21}H_{25}N$	Terbinafine[a]	[78628-80-5]	Sigma-Aldrich		0.84+
$C_{24}H_{51}N$	Tri-*n*-octylamine	[1116-76-3]	Sigma-Aldrich	0.98	

[a]Available as the hydrochloride. [b]Available as the citrate salt. [c]Available as the hydrochloride sesquihydrate. [d]Eastman Organic Chemicals.

5.2.2 Methods. Correlation-gas chromatography experiments were conducted in the same manner as previously described in Section 1.2.2.2. Each plot was characterized by a correlation coefficient of $r^2 > 0.99$. The only differences were that this time for compounds amitriptyline, terbinafine, naftifine and tri-*n*-hexylamine, a 0.32 mm, 15 m SPB-5 column was used. For cyproheptadine, a 0.32 mm, 30 m DB-5 column was used. Also, the temperature was maintained to T/K = 0.1 as monitored independently using a Fluke digital thermometer and methylene chloride served as the non-retained reference. All retention times are provided in Appendix E.

5.2.3. Vaporization Enthalpy Estimations. Vaporization enthalpy estimations were conducted in the same manner as previously described in Section 1.2.6., again calculated using equation 1-6. Here though, the contribution of the functional group (b) is that of a tertiary amine (6.6 kJ·mol^{-1}).[2] For compounds with carbon branching at acyclic sp^3 hybridized centers, a correction, C, of -2 kJ·mol^{-1}/branch is also included in the estimation.[2]

5.2.4. Temperature adjustments. Adjustments from the mean temperature of measurement, T_m , to a common temperature, T/K = 298.15, were achieved in the same way as described in Section 1.2.4. using only equation 1-3.

5.2.5. Uncertainties. A standard deviation of ±16 J·mol^{-1}·K^{-1} for C_p(l) has been used to evaluate uncertainties in temperature adjustments. Linear regression was used to analyze the correlations between experimental properties and those determined by gas chromatography. The uncertainty in the slope represents one standard deviation. Potential uncertainties resulting from correlations are reported as standard deviations (u_i). Uncertainties in combined properties such as temperature adjustments were commonly evaluated as $(u_1^2 + u_2^2 + \ldots)^{0.5}$.

5.3. Standards

5.3.1. Vaporization Enthalpy Standards. Table 5-2 summarizes the vaporization enthalpies of the compounds used as standards in this study. The vaporization enthalpies for tri-*n*-butylamine, *N*,*N*-dimethyltetradecylamine, *N*,*N*-dimethylhexadecylamine, alverine, tribenzylamine and tri-*n*-octylamine are those values previously evaluated by our laboratory.[3] The vaporization enthalpy of (69.3 ± 0.3) kJ·mol^{-1} used for *N*,*N*-dimethyldodecylamine is relatively recent and was from a reputable source.[4] This value was confirmed to be accurate in comparison to the vaporization enthalpy of (69.4 ± 1.0) kJ·mol^{-1} obtained by our previous work.[3]

TABLE 5-2. Literature Vaporization Enthalpies of Some Tertiary Amines; p_o/Pa = 101325

Compounds	$\Delta_l^g H_m$(298.15 K) kJ·mol^{-1} exp	Ref.
Tri-*n*-butylamine	58.0±1.9	3
N,*N*-Dimethyldodecylamine	69.3±0.3	4
N,*N*-Dimethyltetradecylamine	77.3±1.9	3
N,*N*-Dimethylhexadecylamine	84.8±1.0	3
Alverine	89.3±0.2	3
Tri-*n*-octylamine	100.1±1.4	3
Tribenzylamine	92.4±1.4	3

5.3.2. Vapor Pressure Standards. The compounds used as vaporization enthalpy standards were also used as standards for vapor pressure measurements. All vapor pressures were calculated using eq 3-2. A reference pressure of $p_{ref} = p_o$/Pa = 101325 was used for all compounds in Table 5-3 except *N,N*-dimethyldodecylamine. For *N,N*-dimethyldodecylamine, a reference pressure of $p_{ref} = p_o$/Pa = 1 was used. The constants for all compounds reported in Table 5-3 are valid over the temperature range, *T*/K = (283-313).

TABLE 5-3. Parameters of Eq 3-2 Used as Vapor Pressure Standards; p_o/Pa = 101325^a; *T*/K = 298.15

	A	B	C	ln(p_o/Pa) 298.15 K	*T*/K range	ln(p/p_o)	Ref
Tri-*n*-butylamine	15.181	6965.9	0		283-313	-8.18	3
N,*N*-Dimethyl dodecylamine	40.49339	17623.5	135.268	-0.168^b	283-314	-11.69	4
N,N-Dimethyl tetradecylamine	17.399	9337.0	0		283-313	-13.92	3
N,*N*-Dimethyl hexadecylamine	18.368	10270.3	0		283-313	-16.08	3
Alverine	18.087	10792.7	0		283-313	-18.14	3
Tri-*n*-octylamine	20.362	12148	0		283-313	-20.38	3
Tribenzylamine	18.361	11175.4	0		283-313	-19.12	3

^{a}Unless noted otherwise. ^{b}p_o = 1 Pa.

5.4. Results and Discussion

5.4.1. Vaporization Enthalpies. The standard compounds common to all runs 1 to 8 are *N*,*N*-dimethyldodecylamine, *N*,*N*-dimethylhexadecylamine and tribenzylamine. The other previously listed standards are used variously throughout the experiments. Table 5-4 summarizes the results for terbinafine in run 1. Equations 5-1 and 5-2 listed below the table summarize the linearity of both correlations. Similar details for all duplicate runs are available in Appendix E. The vaporization enthalpy for terbinafine examined by correlation in runs 1/2 of (94.7±1.1) kJ·mol^{-1} compares with the estimated value of (100.7±5.0) kJ·mol^{-1}.

TABLE 5-4. Evaluation of $\Delta_l^g H_m$(298 K) for Terbinafine

Run 1	- slope T/K	Intercept	ΔH_{trn}(468 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298.15 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298.15 K) kJ·mol^{-1}(calc)
N,*N*-Dimethyl dodecylamine	6197.7±23	13.291±0.05	51.5±0.19	69.3±0.3	69.4±0.9
N,*N*-Dimethyl tetradecylamine	7016.9±24	14.267±0.05	58.3±0.20	77.3±1.9	77.1±0.9
N,*N*-Dimethyl hexadecylamine	7846.4±28	15.277±0.06	65.2±0.23	84.8±1.0	85.0±1.0
Alverine	8286.7±26	15.199±0.06	68.9±0.22	89.3±0.2	89.1±1.0
Terbinafine	8874.8±32	16.100±0.07	73.8±0.27		94.7±1.1
Tribenzylamine	8639.0±29	15.544±0.06	71.8±0.24	92.4±1.4	92.5±1.0

Run 1

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.14±0.01)ΔH_{trn}(493 K) - (10.7±0.70) $r^2 = 0.9997$ (5-1)

Run 2

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.13±0.01)ΔH_{trn}(493 K) - (10.8±0.73) $r^2 = 0.9997$ (5-2)

The results for naftifine in run 3 are summarized in Table 5-5. The linearity of both correlations is described by equations 5-3 and 5-4 given below the table. The vaporization enthalpy for naftifine determined by correlation in runs 3/4 of (98.8±1.2) kJ·mol^{-1} compares with the estimated value of (108.1±5.4) kJ·mol^{-1}.

TABLE 5-5. Evaluation of $\Delta_l^g H_m$(298 K) for Naftifine

Run 3	- slope T/K	Intercept	ΔH_{trn}(493 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298.15 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298.15 K) kJ·mol^{-1}(calc)
N,*N*-Dimethyl dodecylamine	5862.0±53	12.583±0.10	48.7±0.44	69.3±0.3	69.4±1.4
N,*N*-Dimethyl tetradecylamine	6663.8±41	13.520±0.08	55.4±0.34	77.3±1.9	77.1±1.4
N,*N*-Dimethyl hexadecylamine	7474.5±38	14.490±0.08	62.1±0.31	84.8±1.0	84.8±1.5
Alverine	7936.5±39	14.458±0.08	66.0±0.33	89.3±0.2	89.2±1.6
Tri-*n*-octylamine	9034.9±39	16.379±0.08	75.1±0.33	100.1±1.4	99.8±1.7
Tribenzylamine	8327.2±48	14.870±0.10	69.2±0.40	92.4±1.4	93.0±1.6
Naftifine	8923.9±35	15.378±0.07	74.2±0.29		98.7±1.7

Run 3

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.15±0.02)ΔH_{trn}(493 K) - (13.3±1.07) $r^2 = 0.9991$ (5-3)

Run 4

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.20±0.01)ΔH_{trn}(493 K) - (11.1±0.44) $r^2 = 0.9999$ (5-4)

Table 5-6 summarizes the results for tri-*n*-hexylamine and amitriptyline in run 5. Equations 5-6 and 5-7 listed below the table summarize the linearity of both correlations. A vaporization enthalpy of (78.4±0.84) kJ·mol^{-1} was calculated for tri-*n*-hexylamine in runs 5/6 and compares with the estimated value of (94.0±4.7) kJ·mol^{-1}. For amitriptyline in runs 5/6, a vaporization enthalpy of (90.3±0.92) kJ·mol^{-1} was evaluated which compares with the estimated value of (103.4±5.2) kJ·mol^{-1}.

TABLE 5-6. Evaluation of $\Delta_l^g H_m$(298 K) for Tri-*n*-hexylamine and Amitriptyline

Run 5	- slope T/K	Intercept	ΔH_{trn}(468 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298.15 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298.15 K) kJ·mol^{-1}(calc)
N,*N*-Dimethyl dodecylamine	6202.9±100	13.175±0.21	51.6±0.83	69.3±0.3	69.4±0.9
N,*N*-Dimethyl tetradecylamine	7022.4±102	14.154±0.22	58.4±0.85	77.3±1.9	77.1±0.9
Tri-*n*-hexylamine	7154.9±102	14.324±0.22	59.5±0.85		78.4±0.9
N,*N*-Dimethyl hexadecylamine	7850.8±106	15.164±0.23	65.3±0.88	84.8±1.0	85.0±1.0
Alverine	8292.0±99	15.086±0.21	68.9±0.83	89.3±0.2	89.2±1.0
Amitriptyline	8407.0±100	15.146±0.21	69.9±0.83		90.2±1.0
Tribenzylamine	8640.2±101	15.413±0.21	71.8±0.84	92.4±1.4	92.5±1.0

Run 5

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.14±0.01)ΔH_{trn}(493 K) - (10.6±0.67) $r^2 = 0.9997$ (5-6)

Run 6

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.13±0.01)ΔH_{trn}(493 K) - (12.0±0.57) $r^2 = 0.9998$ (5-7)

The results for cyproheptadine in run 7 are summarized in Table 5-7. The linearity of both correlations is described by equations 5-8 and 5-9 listed below the table. The vaporization enthalpy for cyproheptadine evaluated by correlation in runs 7/8 of (93.8±0.25) kJ·mol^{-1} compares with the estimated value of (108.1±5.4) kJ·mol^{-1}. In each case, the experimental vaporization enthalpy of the target compound was lower than that of the estimated value. The vaporization enthalpies of terbinafine, naftifine, amitriptyline and cyproheptadine are those of the sub-cooled liquid since these compounds are solid at room temperature.

TABLE 5-7. Evaluation of $\Delta_l^g H_m$(298 K) for Cyproheptadine

Run 7	- slope T/K	Intercept	ΔH_{trn}(509 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298.15 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298.15 K) kJ·mol^{-1}(calc)
Tri-*n*-butylamine	4768.6±41	10.744±0.08	39.6±0.34	58.0±1.9	58.0±0.2
N,*N*-Dimethyl dodecylamine	5896.4±44	11.849±0.09	49.0±0.37	69.3±0.3	69.4±0.2
N,*N*-Dimethyl hexadecylamine	7429.1±51	13.548±0.10	61.8±0.42	84.8±1.0	84.8±0.2
Tri-*n*-octylamine	8945.9±55	15.321±0.11	74.4±0.46	100.1±1.4	100.1±0.3
Tribenzylamine	8168.5±51	13.695±0.10	67.9±0.42	92.4±1.4	92.3±0.2
Cyproheptadine	8320.1±53	13.683±0.11	69.2±0.44		93.8±0.2

Run 7

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.21±0.003)ΔH_{trn}(493 K) - (9.8±0.16) $r^2 = 1.0000$ (5-8)

Run 8

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.22±0.003)ΔH_{trn}(493 K) - (9.0±0.17) $r^2 = 1.0000$ (5-9)

As we have discussed previously,[5] primary aromatic amines do not correlate well with primary aliphatic amines if the amino group is directly attached to the aromatic ring. To investigate this phenomenon in tertiary amine systems, we conducted a set of experiments using compounds with known thermodynamic data of both aliphatic and aromatic tertiary amines. Our results confirm this also is the case in tertiary amine systems with our inability to reproduce literature vaporization enthalpies when using one set of the tertiary amines as standards to verify the vaporization enthalpies of the others.

An example of these results is listed in Table 5-8. Tables similar to Table 5-8 which explain the results of the remaining experiments are listed in Appendix E.

TABLE 5-8. Enthalpies of Transfer and Vaporization Enthalpies Used to Compare Aliphatic and Aromatic Tertiary Amines with Aliphatic Amines Used as Standards[a]

Run 9	- slope T/K	Intercept	ΔH_{trn}(454 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)
N,*N*-dimethyl dodecylamine	6417.5±32	13.588±0.07	53.4±0.27	69.3±0.3	69.4±1.6
N,*N*-dimethyl-1-naphthylamine	5901.5±30	12.296±0.07	49.1±0.25	66.9±0.2	64.8±1.6
N,*N*-dimethyl tetradecylamine	7280.8±34	14.662±0.08	60.5±0.28	77.3±1.9	77.1±1.7
Tri-*n*-hexylamine[b]	7406.7±34	14.819±0.07	61.6±0.28	78.5±1.0	78.3±1.8
9-Methylcarbazole	6840.3±33	13.117±0.07	56.9±0.28	79.5±3.2	73.2±1.7
9-Ethylcarbazole	7024.3±37	13.410±0.08	58.4±0.31	83.9±0.5	74.8±1.7
N,*N*-dimethyl hexadecylamine	8143.8±38	15.746±0.08	67.7±0.32	84.8±1.0	84.9±1.7
Triphenylamine[c]	7898.6±40	14.691±0.09	65.7±0.33	90.2±1.2	82.3±1.8
$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.08±0.02)ΔH_{trn}(454 K) - (11.8±1.2)				r^2 = 0.9997	(5-10)

[a] Literature values for *N*,*N*-dimethyldodecylamine, *N*,*N*-dimethyltetradecylamine and *N*,*N*-dimethylhexadecylamine only were used as standards. [b] Tri-*n*-hexylamine was left as an unknown to verify validity of aliphatic correlations. [c] Literature value of triphenylamine is unreliable as it was determined through correlation using standard compounds with dissimilar functional groups.

5.4.2. Vapor Pressures. Vapor pressures were calculated using eq 3-2. As previously stated, the compounds used as standards in vapor pressure measurements are the same compounds used as standards for the analysis of vaporization enthalpies. The constants for these standards are listed in Table 5-3. Constants for tri-*n*-butylamine, *N*,*N*-dimethyltetradecylamine, *N*,*N*-dimethylhexadecylamine, alverine, tribenzylamine and tri-*n*-octylamine are those evaluated in our previous work.[3] The constants for *N*,*N*-dimethyldodecylamine are those determined by Fulem et al.[4] Values of ln(t_o/t_a) for duplicate runs were first measured as a function of temperature over a T/K = 30 range at T/K = 5 intervals at a mean temperature of T/K = 468 for runs 1/2 and 5/6, T/K = 493 for runs 3/4 and T/K = 509 for runs 7/8 and plotted against 1/T for both the standard and target compounds. The resulting slopes and intercepts from runs 1/2, 3/4, 5/6 and 7/8 were used to evaluate an average value of ln(t_o/t_a), ln(t_o/t_a)$_{avg}$. This term was then correlated against the corresponding ln(p/p_o) of the standards. An example of the results of the correlation between ln(t_o/t_a)$_{avg,}$ and ln(p/p_o) at T/K = 298.15 for runs 1/2 is provided in Table 5-9.

TABLE 5-9. Correlations Between ln(t_o/t_a)$_{avg}$ and ln(p/p_o)$_{exp}$ at T/K = 298.15 for Runs 1/2[a]

Run 1/Run 2	-slope/K	intercept	ln(t_o/t_a)$_{avg}$	ln(p/p_o)$_{exp}$	ln(p/p_o)$_{calc}$	$p\cdot10^3$/Pa calc/lit
N,*N*-Dimethyl Dodecylamine	6197.70	13.291				
	6204.32	13.305	-7.500	-11.694	-11.684	854/850[b]
N,*N*-Dimethyl tetradecylamine	7016.90	14.267				
	7029.58	14.293	-9.276	-13.917	-13.908	92/92[c]
N,*N*-Dimethyl hexadecylamine	7846.44	15.277				
	7866.04	15.318	-11.052	-16.079	-16.133	10.0/11.0[c]
Alverine	8286.74	15.199				
	8302.22	15.231	-12.604	-18.112	-18.077	1.4/1.4[c], 4.5[d], 3.3[e]
Terbinafine	8874.80	16.100				
	8892.61	16.137	-13.677		-19.420	0.37/NA[f]
Tribenzylamine	8639.03	15.544				
	8651.30	15.569	-13.440	-19.121	-19.122	0.50/0.50[c], 2.6[g]

Run 1/2: ln(p/p_o) = (1.252±0.008) ln(p/p_o) – (2.290±0.086) r^2 = 0.9999 (5-11)

[a]Run 1and 2: slope and intercept measured at a mean temperature of T_m/K = 468. [b]Ref 4. [c]Ref 3. [d]Estimated, Ref 6. [e]Estimated, Ref 7. [f]Not Available. [g]Estimated vapor pressure of the sub-cooled liquid, Ref 8.

Values of ln(p/p_o) of the standards were determined using eq 3-2 with the appropriate constants from Table 5-3. The linearity of these correlations at T/K = 298.15 is illustrated by eq 5-11 listed below Table 5-9. The vapor pressures calculated from experimental values are compared to those obtained by correlation at T/K = 298.15 in the last column of Table 5-9. The temperature range used for all vapor pressure calculations in this study included T/K = (283 to 313) with vapor pressures evaluated at T/K = 5 intervals. The correlation coefficients, r^2, were greater than 0.99 at all temperatures. The vapor pressures as a function of temperature were then fit to eq 3-2. The constants of eq 3-2 for compounds used as standards in this work are listed in Table 5-3. Tables similar to Table 5-9 that include all the compounds in the mixtures for runs 3/4, 5/6 and 7/8 are available in Appendix E. The sub-cooled liquid vapor pressures at T/K = 298.15 of new compounds investigated in this work are summarized in Table 5-11. The vapor pressure listed for tri-*n*-hexylamine is its liquid vapor pressure since it is a liquid at room temperature. It should be noted that several attempts were made to crystallize terbinafine and amitriptyline from their ammonium salt form, yet only a gel was produced from each successive attempt. The limited amount of available compound and the high price of both naftifine and cyproheptadine led to the investigation of their fusion enthalpies not being conducted. Tri-*n*-hexylamine is a liquid at room temperature and thus its fusion enthalpy did not need to be measured.

TABLE 5-10. A Summary of the Vaporization Enthalpies (kJ·mol^{-1}) From Runs 1 to 8.

	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Avg[a]	Lit
Tri-*n*-butylamine							58.0±0.2	58.0±0.2	58.0±0.2	58.0±1.9
N,*N*-Dimethyl dodecyl amine	69.4±0.9	69.4±0.9	69.4±1.4	69.5±0.6	69.4±0.9	69.3±0.7	69.4±0.2	69.3±0.2	69.4±0.7	69.3±0.3
N,*N*-Dimethyl tetradecyl amine	77.1±0.9	77.1±1.0	77.1±1.4	77.1±0.6	77.1±0.9	77.2±0.8			77.1±0.9	77.3±1.9
N,*N*-Dimethyl hexadecyl amine	85.0±1.0	85.0±1.0	84.8±1.5	84.8±0.6	85.0±1.0	85.0±0.8	84.8±0.2	84.8±0.2	84.9±0.8	84.8±1.0
Tri-*n*-hexylamine					78.4±0.9	78.5±0.8			78.5±0.9	
Amitriptyline					90.2±1.0	90.3±0.8			90.3±0.9	
Alverine	89.1±1.0	89.1±1.1	89.2±1.6	89.3±0.6	89.2±1.0	89.2±0.8			89.2±1.0	89.3±0.2
Naftifine			98.7±1.7	99.0±0.7					98.9±1.2	
Cypro-heptadine							93.8±0.2	93.8±0.3	93.8±0.3	
Tribenzyl amine	92.5±1.0	92.4±1.1	93.0±1.6	92.5±0.7	92.5±1.0	92.4±0.9	92.3±0.2	92.3±0.3	92.5±0.9	92.4±1.4
Terbinafine	94.7±1.1	94.7±1.1							94.7±1.1	
Tri-*n*-octylamine			99.8±1.7	100.1±0.7			100.1±0.3	100.2±0.3	100.1±0.8	100.1±1.4

[a]The uncertainties are also averages

5.5. Summary

The vaporization enthalpies and liquid vapor pressures of a series of tertiary amines were analyzed by correlation gas-chromatography. A summary of the vaporization enthalpies for the standard and target compounds of all runs are included in Table 5-10. The vaporization enthalpies and sub-cooled liquid vapor pressures at T/K = 298.15 of new compounds evaluated in this work are listed in Table 5-11.

TABLE 5-11. A Summary of New Vaporization Enthalpies and Liquid Vapor Pressures at T/K = 298.15 From This Work

	$\Delta_l^g H_m$(298.15 K) kJ·mol^{-1} (calc)	$p \cdot 10^3$/Pa calc
Tri-*n*-hexylamine	78.5±0.9	65.1
Amitriptyline[a]	90.3±0.9	0.95
Cyproheptadine[a]	93.8±0.3	0.26
Terbinafine[a]	94.7±1.1	0.37
Naftifine[a]	98.9±1.2	0.067

[a] Vapor pressures are that of the sub-cooled liquid

There is a slight source of concern with the data for naftifine and cyproheptadine as due to the large size of these compounds they were unable to be bracketed with standards of known thermodynamic data during evaluation. The compounds used as standards in these calculations did however correspond to their literature values even though none of these standards exhibited long enough retention times to bracket the target compounds. This was not observed for terbinafine, tri-*n*-hexylamine or amitriptyline as a standard compound with known thermodynamic data which did bracket the target compounds was available for use. This could lead to more reliability in the data for these three compounds as compared to the data for naftifine and cyproheptadine.

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(6) Calculated using the EPI Suite. The EPI Suite is available as a free download from http://www.epa.gov/oppt/exposure/pubs/episuitedl.htm. Accessed (12/1/12).

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(8) Estimation Program Interface EPI Suite Version 4.11 (Nov. 2012); available at http://www.epa.gov/opptintr/exposure/pubs/episuite.htm. Accessed (7/23/13).

Part 4: A Comparison of Gas Chromatographic Methods

Chapter 6: A Comparison of Results by Correlation Gas Chromatography with Another Gas Chromatographic Retention Time Technique. The Effects of Retention Time Coincidence on Vaporization Enthalpy and Vapor Pressure

6.1. Introduction

Gas chromatography has been used for the analysis of thermodynamic data of a wide range of organic compounds. To achieve these investigations, several related but slightly different methods have been developed which make use of retention time properties.[1-3] Several variations of this procedure, the gas chromatographic-retention time method (GC-RT method), have been compared experimentally by Koutek et al.[3] and the theory has been discussed by Letcher and Naicker.[4] Even though this method has supplied dependable results in many cases, this has not always been true. [3,5] Letcher and Naicker came to the conclusion that one of the biggest causes of error in the technique was the assumption that the activity of the targets and standards on the column are similar and cancel. Generally, the columns employed by the GC-RT technique have been non-polar.

An alternative method was originally investigated by Peacock and Fuchs.[6] They measured retention time data as a function of temperature using packed columns and then used that data to evaluate the enthalpy of transfer of the analyte from the column to the vapor phase, $\Delta_{\mathrm{trn}}H_{\mathrm{m}}(T_{\mathrm{m}})$. Their work was able to, according to eq 6-1, acquire a good reproduction of the vaporization enthalpy ($\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}(T\ )$) measured by other techniques through the use of an independent measurement of the enthalpy of solution ($\Delta_{\mathrm{sln}}H_{\mathrm{m}}(T)$) of the analyte in the liquid used as the column coating and combination of the two measurements. Our lab has previously discussed some possible reasons for the small differences observed.[7]

$$\Delta_{\mathrm{trn}}H_{\mathrm{m}}(T_{\mathrm{m}}) = \Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}(T) + \Delta_{\mathrm{sln}}H_{\mathrm{m}}(T) \tag{6-1}$$

We have observed that when using capillary columns if standard compounds are carefully chosen, particularly in regards to their functional groups, as well as demonstrating experimentally that the vaporization enthalpies of the standard compounds display a linear correlation with their corresponding enthalpies of transfer, the concern related to the differences in activity seems to be sufficiently addressed and therefore accurate vapor pressures and vaporization enthalpies of the target compounds within the mixture can be determined.[7-9] Given that the values of the standard compounds used are available at the same temperature, these correlations have shown to be successful with providing vapor pressures and vaporization enthalpies at temperatures other than at the mean temperature of measurement, T_{m}. The most desirable results were acquired when the retention times of the standard compounds bracket those of the target compounds. This technique has been called correlation gas chromatography (C-GC) so as to differentiate it from other GC-RT techniques. Standard compound selection is of great importance for this method. If the target compound is a hydrocarbon, the structure of the hydrocarbon does not seem to be an important factor in the selection of standards as long as they are all hydrocarbons. The quality of both the vapor pressures and vaporization enthalpies investigated are, however, significantly affected by substitution with heteroatom containing functional groups. As a result, standards have been selected to mimic both the nature and the amount of functional groups present in the compounds of interest. An inspection of the literature has shown that these principles have not always been thoroughly applied in the various other GC-RT methods.[4,10]

Recently we reported the vapor pressure and vaporization enthalpy of empenthrin, (*E*)-(*RS*)-1-ethynyl-2-methylpent-2-enyl (1*RS*)-*cis*-*trans*-2,2-dimethyl-3-(2-methylprop-1-enyl)-cyclopropane-carboxylate (CAS [54406-48-3]), a synthetic pyrethrin.[8]

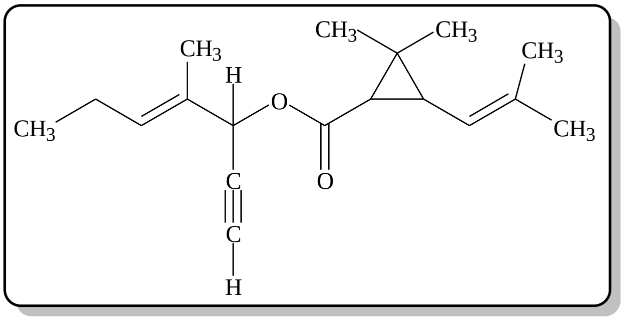

Figure 6-1. Empenthrin [54406-48-3]. 1-Ethynyl-2-methyl-2-penten-1-yl 2,2-dimethyl-3-(2-methyl-1-propen-1-yl)-cyclopropanecarboxylate.

The commercially available compound shown in Figure 6-1 is a possible mixture of four diastereomers. Three of the isomers could be discerned by chromatography, two in equal amounts and a minor third. The vapor pressure of the mixture was reported previously by Tsuzuki using a variation of the GC-RT technique described below.[10] Using two phthalate esters as standards, the vapor pressure reported for the mixture at T/K = 298.15 was p/Pa = 0.023. This vapor pressure was within experimental error of the values acquired by correlation gas chromatography, p/Pa = (0.059±0.038) and 0.060±0.038), for the two major diastereomers with the use of mono-esters as standards. Work previously unreported by our laboratory suggested that monoesters and diesters did not correlate well with each other. This study investigates how the vapor pressures and vaporization enthalpies of monoesters, diesters and *n*-alkanes, another class of compounds with significant use as standards in the GC-RT method, compare when investigated concurrently by correlation gas chromatography and by the GC-RT method reported by Hamilton.[1] In this work, the monoesters were used as the standard compounds. The column employed was a poly(dimethyl siloxane) column, the column of choice for the GC-RT method.

Throughout the course of this study, these compounds were investigated on a poly(5% diphenyl 95% dimethyl siloxane) column, as well. On this column, two of the compounds within the mixture under investigation, ethyl octadecanoate and docosane, were seen to display identical retention times over the entire temperature range, T/K = (495-525). This retention time coincidence gave us the ability to address an area of some concern. Specifically, what effect does this coincidence have on the thermodynamic properties investigated?

6.2. Experimental

6.2.1. Materials. Table 6-1 reports the origin and analysis of the materials used in this study.

TABLE 6-1. Origin of the standards and Targets

Compound	CAS registry no	Supplier	Mass fraction
Alkanes			
n-Eicosane	112-95-8	Sigma Aldrich	0.99
n-Docosane	629-97-0	Sigma Aldrich	0.99
n-Tetracosane	646-31-1	Sigma Aldrich	0.99
n-Pentacosane	629-99-2	Aldrich	0.99
n-Hexacosane	630-01-3	Sigma	0.99
n-Octacosane	630-02-4	Sigma	0.99
Esters			
Methyl hexadecanoate			
Methyl octadecanoate	112-61-8	Eastman	0.99
Ethyl octadecanoate	111-61-5	Sigma Aldrich	0.99
Methyl eicosanoate	1120-28-1	Sigma	0.99
Methyl heneicosanoate	6064-90-0	Sigma	0.99
Diesters			
Dimethyl phthalate	131-11-3	Supelco/Aldrich	0.99+
Diethyl phthalate	84-66-2	Supelco/Aldrich	0.99+
Di-*n*-butyl phthalate	84-74-2	Supelco	0.99
Benzyl butyl phthalate	85-68-7	Supelco	AS[a]
bis (2-Ethylhexyl) phthalate	117-81-7	Supelco/Aldrich	0.99+
Di-*n*-octyl phthalate	117-84-0	Supelco	AS[a]

[a] Analytical Sample, see Section 6.2.1.

bis (2-Ethylhexyl) phthalate was purchased presumably as a mixture of two diastereomers, a *meso* and *dl* pair. This material was used as purchased. The chromatography did not separate the two diastereomers at the temperatures and columns used. Although individual samples of most of the materials have been purchased separately, a phthalate mixture, EPA 606-M Phthalate Esters Mix was also purchased from Supelco. This mixture contained methanol as the solvent and the following phthalates: benzyl butyl, dioctyl, dibutyl, *bis*(2-ethylhexyl), diethyl and dimethyl esters which were used in one set of runs. These materials were available as analytical standards. The analysis of this mixture has previously been discussed.[11]

6.2.2. Methods. Retention times were measured on a 5890 Gas Chromatograph running Chemstation using a Supelco 15 m x 0.32 mm ID SPB-5 capillary column (1.0 μm film thickness, bonded poly(5% diphenyl/95% dimethyl siloxane)), and 5890 Gas Chromatograph Series II also running Chemstation on a 30 m x 0.32 mm ID Restek RTX-1 crossbonded 100% poly(dimethyl siloxane) capillary column (0.5 μm film thickness), both using helium as the carrier gas. Split ratios of approximately 100/1 were used. The temperature was maintained at ±0.1 K by both instruments and monitored independently using a Fluke 50S K/J digital thermometer. The solvent was not retained by the column at the temperature of the experiments. The adjusted retention time, t_a, was calculated from an analyte's retention time and the retention time of the solvent by difference. Experimental retention times are provided in Appendix F. Compounds reported in the tables below are segregated by functional groups in the order of their elution off the column.

6.2.3. Correlation Gas Chromatography. Plots of $\ln(t_o/t_a)$ versus $1/T$ of each analyte resulted in straight lines with correlation coefficients, $r^2 > 0.99$. The term t_o refers to the reference time, 60 s. The enthalpy of transfer of each analyte from the column to the gas phase, $\Delta H_{trn}(T_m)$, was calculated as the product of the slope of the line and the gas constant, –slope·R, where T_m refers to the mean temperature of measurement. The term $\Delta H_{trn}(T_m)$ is related to the vaporization enthalpy, $\Delta_l^g H_m(T_m)$, by eq 6-1.[6] In this context, the term $\Delta_{sln}H_m(T_m)$ refers to the enthalpy of interaction of the analyte with the stationary phase of the column.

Provided the standards are properly chosen, a second plot of $\Delta_l^g H_m(T)$ versus $\Delta_{trn}H_m(T_m)$ where T_m and T may differ, is also linear and the resulting correlation equation in conjunction with the appropriate enthalpy of transfer can then be used to evaluate the vaporization enthalpy of the targets. Similarly, if the vapor pressures of the standards (p) are also well known, plots of $\ln(p/p_o)$, where p_o is a reference pressure versus $\ln(t_o/t_a)$ results in a linear relationship that can be used to evaluate the corresponding $\ln(p/p_o)$ of the target(s). Repeating this process as a function of temperature has been successful in providing a temperature profile of the vapor pressure of the targets, as well.

6.2.4. GC-RT Method. The vapor pressure-retention time method as reported by Hamilton,[1] consists in plotting $\ln[(t_r)_{tar}/(t_r)_{std}]_T$ against $\ln(p_{std,T})$ at different temperatures T, where $(t_r)_{tar}$ and $(\Delta_l^g H)_{tar}$ are the relative retention time and vaporization enthalpy of the target and $(t_r)_{std}$ and $(\Delta_l^g H)_{std}$ refer to the corresponding properties of the standard. This results in the following linear relationship:

$$\ln[(t_r)_{tar}/(t_r)_{std}]_T = [1- (\Delta_l^g H_m)_{tar}/(\Delta_l^g H_m)_{std}]\ \ln(p_{std,\,T}) - C \qquad (6\text{-}2)$$

The slope and intercept of the line obtained is given by $[1- (\Delta_l^g H)_{tar}/(\Delta_l^g H)_{std}]$ and -C, respectively. The vapor pressure of the target at T = 298.15 K is obtained from:

$$\ln(p_{tar,\,298.15\ K}/\mathrm{Pa}) = [(\Delta_l^g H_m)_{tar}/(\Delta_l^g H_m)_{std}]\ \ln(p_{std,\,298.15\ K}/\mathrm{Pa}) + C \qquad (6\text{-}3)$$

Although not always reported, the vaporization enthalpy can be calculated from the slope of the line and the vaporization enthalpy of the standard. Two standards bracketing the retention times of the targets frequently have been used. Vaporization enthalpies at T/K = 298.15 were evaluated in this work for the GC-RT method by evaluating vapor pressure as a function of temperature from T/K = (283.15 to 313.15) at T/K = 5 intervals. The standards used in this work included methyl hexadecanoate, methyl octadecanoate and methyl eicosanoate for the GC-RT method. The latter two compounds were used as standards for the C-GC method.

6.2.5. Vaporization Enthalpies and Vapor Pressures of the Standards. Table 6-2 summarizes the vaporization enthalpies and vapor pressures from the literature at *T*/K = 298.15 of the compounds used in this study.

TABLE 6-2. Vaporization Enthalpies and Vapor Pressures of the Compounds Investigated

Compounds	$\Delta_l^g H_m$(298.15 K) kJ·mol^{-1}	$10^6 \cdot p$/Pa (298.15 K)	Reference
Alkanes			
n-Eicosane	101.81±0.5	2091	18
n-Docosane	111.9±2.7	215	12
n-Tetracosane	121.9±2.8	23.7	12
n-Pentacosane	126.8±2.9	8.1	12
n-Hexacosane	131.7±3.2	2.8	12
n-Octacosane	141.9±4.9	0.31	12
Esters			
Methyl hexadecanoate	96.84±0.63	7142	
Methyl octadecanoate	105.87±1.4	798	13
Ethyl octadecanoate	109.6±4.4	427	8
Methyl eicosanoate	116.43±1.54	104	13
Methyl heneicosanoate	120.9±2.5	32	14
Diesters			
Dimethyl phthalate	77.0±1.2	304243	15
Diethyl phthalate	82.1±0.5	98826	16
Di-*n*-butyl phthalate	95.0±1.1	3873	11
Benzyl butyl phthalate	106.2±2.4	199	11
bis (2-Ethylhexyl) phthalate	116.7±0.5	5.4	11,17
Di-*n*-octyl phthalate	122.6±1.4	0.11	11

Table 6-3 provides the constants and reference pressures for equations 6-4 through 6-6 used to evaluate the vapor pressures of these compounds at and around *T*/K = 298.15. Note that the reference pressure, $p_{o,}$ in Table 6-3 may be defined differently for each compound. The term T_o refers to a reference temperature.

Cox Equation:

$$\ln(p/p_o) = (1 - T_o/T)\cdot\exp(A_o + A_1\cdot T + A_2\cdot T^{2}) \qquad (6\text{-}4)$$

Third Order Polynomial:

$$\ln(p/p_o) = A\cdot T^{3} + B\cdot T^{2} + C\cdot T + D \qquad (6\text{-}5)$$

Clark and Glew Equation:

$$R\cdot\ln(p/p_o) = -\Delta_l^g G_m(\theta)/\theta + \Delta_l^g H_m(\theta)\cdot(1/\theta - 1/T) + \Delta_l^g C_p(\theta)\cdot\{\theta/T - 1 + \ln(T/\theta)\} \qquad (6\text{-}6)$$

TABLE 6-3. Vapor Pressure Equations of the Compounds Investigated

A. Parameters of the Cox Equation, Eq 6-4.

	A_o	$-10^3\cdot A_1/K$	$10^6\cdot A_2/K^2$	p_o/kPa / T_o/K	T_{range}/K
Eicosane[a]	3.31181	2.102218	1.34878	101.325 / 617.415	
Dimethyl phthalate[b]	3.076854	1.650657	1.171631	101.325 / 555.799	324-522
Diethyl phthalate[c]	3.844479	0.9201487	0.5406641	$2.9\cdot10^{-6}$ / 269.922	270-520

B. Parameters of the Third Order Polynomial, Equation, Eq 6-5; p_o/Pa = 101325

	$10^{-8}\cdot A/T^{3}$	$10^{-6}\cdot B/T^{2}$	C/T	D
n-Heneicosane[d]	1.9989	-2.9075	-98.135	6.6591
n-Docosane[d]	2.1713	-3.1176	110.72	6.5353
n-Tetracosane[d]	2.5072	-3.5286	530.15	6.2817
n-Pentacosane[d]	2.6738	-3.7307	741.19	6.1496
n-Hexacosane[d]	2.8244	-3.9193	910.53	6.0704
n-Octacosane[d]	3.1389	-4.3120	1279.4	5.8835
Ethyl octadecanoate[e]	3.2679	-3.9880	2696.76	4.2020
Methyl heneicosanoate[f]	4.2013	-5.2388	5943.62	1.2615
Dibutyl phthalate[g]	3.4691	-3.6241	1436.92	5.780
bis 2-Ethylhexyl phthalate[g]	6.2867	-6.0032	5619.8	2.7650
Benzyl butyl phthalate[g]	5.4237	-5.2700	4726.8	2.9210
bis Di-*n*-octyl phthalate[g]	7.2473	-6.8015	7148.4	1.5480

C. Parameters of Clark and Glew Equation, Eq 6-6; p_o/Pa = 1

	$\Delta_l^g H_m$(298 K) ($J\cdot mol^{-1}$)	$\Delta_l^g G_o$(298 K) ($J\cdot mol^{-1}$)	$\Delta_l^g C_p$(298 K) ($J\cdot mol^{-1}\cdot K^{-1}$)	θ K
Methyl hexadecanoate[h]	83320±405	-13771±101	-137	397
Methyl octadecanoate[h]	89968±280	-10273±79	-155	401
Methyl eicosanoate[h]	97836±204	-8131±66	-172	406

[a]Ref 18. [b]Ref 15. [c]Ref 16. [d]Ref 12. [e]Ref 8. [f]Ref 14. [g]Ref 11. [h]Ref 13.

6.2.6. Uncertainties. Unless noted otherwise, all uncertainties refer to one standard deviation. All slopes and intercepts reported below were calculated by linear regression.

Uncertainties (u) for combined results and those associated with the correlations between $\Delta H_{\mathrm{trn}}(T_{\mathrm{m}})$ and $\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}(T_{\mathrm{m}})$ were calculated as $(\sigma_1{}^2 + \sigma_2{}^2{}_{\ldots})^{0.5}$. Vapor pressures fit as a function of temperature were fit by non-linear least squares. Uncertainties in boiling temperatures were evaluated by setting $\ln(p/p_{\mathrm{o}}) = 0$ and solved by standard methods. Details are provided in the supporting information. Uncertainties derived from logarithmic terms are reported as an average value of the two uncertainties evaluated.

6.3. Results and Discussion

6.3.1. Vaporization Enthalpies by C-GC. All chosen compounds had known vapor pressures and vaporization enthalpies at T/K = 298.15 so as to compare the data acquired by the C-GC and GC-RT methods. Two different mixtures with somewhat different compositions were investigated, both in duplicate. The data was analyzed by C-GC using two distinctly different procedures since both mixtures contained compounds with different functionalities. The results of runs 1 and 3, where the components of the mixture are separated according to functionality and values of $\Delta_{\mathrm{trn}}H_{\mathrm{m}}(T_{\mathrm{m}})$ correlated with their respective vaporization enthalpies, are listed in Tables 6-4 and 6-5. The result was good linear relationships shown by eqs 6-7 through 6-9 and 6-10 through 6-12 given below each respective correlation.

TABLE 6-4. Correlation of Vaporization Enthalpies With Enthalpies of Transfer on a Poly(dimethyl siloxane) Column Using All Compounds as Standards; Uncertainties are One Standard Deviation, p_o = 101325 Pa

Run 1	- slope T/K	intercept	ΔH_{trn}(532 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (Lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(Calc)
Eicosane	7147.1	12.803	59.42	101.81±0.5	101.8±0.7
Docosane	7856.6	13.595	65.32	111.9±2.7	111.8±0.7
Tetracosane	8567.8	14.398	71.23	121.9±2.8	121.9±0.8
Pentacosane	8924.0	14.804	74.19	126.8±2.9	126.9±0.8
Hexacosane	9270.9	15.194	77.07	131.7±3.2	131.8±0.8
Octacosane	9968.2	15.985	82.87	141.9±4.9	141.7±0.8
$\Delta_l^g H_m(298.15\ \text{K})/\text{kJ}\cdot\text{mol}^{-1} = (1.703\pm0.007)\cdot\Delta H_{trn}(532\ \text{K}) + (0.590\pm0.541);\ r^2 = 0.9999$ (6-7)					
Methyl octadecanoate	7509.0	13.175	62.43	105.9±1.4	106.0±4.1
Ethyl octadecanoate	7769.2	13.485	64.59	109.6±4.4	109.6±4.1
Methyl eicosanoate	8223.0	13.997	68.36	116.43±1.5	116.1±4.2
Methyl heneicosanoate	8579.2	14.380	71.32	120.9±2.5	121.1±4.3
$\Delta_l^g H_m(298.15\ \text{K})/\text{kJ}\cdot\text{mol}^{-1} = (1.705\pm0.044)\cdot\Delta H_{trn}(532\ \text{K}) - (0.490\pm2.97);\ r^2 = 0.9986$ (6-8)					
Dimethyl phthalate	4830.3	9.952	40.16	77.0±1.2	76.9±0.4
Diethyl phthalate	5343.5	10.537	44.42	82.1±0.5	82.2±0.4
Di-*n*-butyl phthalate	6598.1	11.896	54.85	95.0±1.1	95.2±0.5
Butyl benzyl phthalate	7638.6	12.828	63.50	106.2±2.4	106.0±0.5
bis (2-Ethylhexyl) phthalate	8659.4	14.245	71.99	116.7±0.5	116.6±0.5
Di-*n*-octyl phthalate	9251.7	15.194	76.92	122.6±1.4	122.7±0.5
$\Delta_l^g H_m(298.15\ \text{K})/\text{kJ}\cdot\text{mol}^{-1} = (1.247\pm0.006)\cdot\Delta H_{trn}(532\ \text{K}) + (26.78\pm0.34);\ r^2 = 0.9999$ (6-9)					

TABLE 6-5. Correlation of Vaporization Enthalpies With Enthalpies of Transfer on a Poly(dimethyl siloxane) Column) Using All Compounds as Standards; Uncertainties in Calculated Values are One Standard Deviation, p_o = 101325 Pa

Run 3	- slope T/K	intercept	ΔH_{trn}(516 K) kJ·mol^{-1}	$\Delta_l{}^gH_m$(298 K) kJ·mol^{-1} (Lit)	$\Delta_l{}^gH_m$(298 K) kJ·mol^{-1}(Calc)
Eicosane	7390.7	13.258	61.44	101.8±0.5	101.9±0.3
Docosane	8137.5	14.124	67.65	111.9±2.7	111.9±0.4
Tetracosane	8880.6	14.99	73.83	121.9±2.8	121.8±0.4
Pentacosane	9250.8	15.423	76.91	126.8±2.9	126.8±0.4
Hexacosane	9619.4	15.855	79.97	131.7±3.2	131.7±0.4
$\Delta_l{}^gH_m$(298.15 K)/kJ·mol^{-1} = (1.61±0.004)·ΔH_{trn}(516 K) + (2.70±0.26); r^2 = 0.9999 (6-10)					
Methyl hexadecanoate	7032.5	12.822	58.47	96.8±0.63	96.5±3.0
Methyl octadecanoate	7783.1	13.688	64.71	105.9±1.4	106.3±3.2
Ethyl octadecanoate	8057.4	14.027	66.99	109.6±4.4	109.9±3.2
Methyl eicosanoate	8532.3	14.56	70.93	116.4±1.5	116.4±3.3
Methyl heneicosanoate	8904.9	14.995	74.03	120.9±2.5	120.9±3.4
$\Delta_l{}^gH_m$(298.15 K)/kJ·mol^{-1} = (1.56±0.034)·ΔH_{trn}(516 K) + (5.07±2.29); r^2 = 0.9986 (6-11)					
Dimethyl phthalate	4976.4	10.195	41.37	77.0±1.2	76.8±0.6
Diethyl phthalate	5513.3	10.835	45.84	82.1±0.5	82.2±0.6
Di-*n*-butyl phthalate	6831.1	12.327	56.79	95.0±1.1	95.2±0.7
bis (2-Ethylhexyl) phthalate	8983.8	14.858	74.69	116.7±0.5	116.6±0.8
$\Delta_l{}^gH_m$(298.15 K)/kJ·mol^{-1} = (1.19±0.009)·ΔH_{trn}(516 K) + (27.46±0.48); r^2 = 0.9999 (6-12)					

Data for the duplicate runs (runs 2 and 4) is available in Appendix F. Figure 6-2 describes the individual correlations determined according to functional group for each group in run 1 reported in Table 6-4. As illustrated by Figure 6-2, the functional group has a significant impact on the relationship between $\Delta_{trn}H_m(T_m)$ and $\Delta_l{}^gH_m(T_m)$ in C-GC. In this example, the figure implies that monoesters and hydrocarbons should correlate fairly well with each other regardless of whether a monoester or alkane is chosen as a standard. With the use of monoesters as standard compounds for analysis of diesters, distinct differences in the correlative behavior are expected.

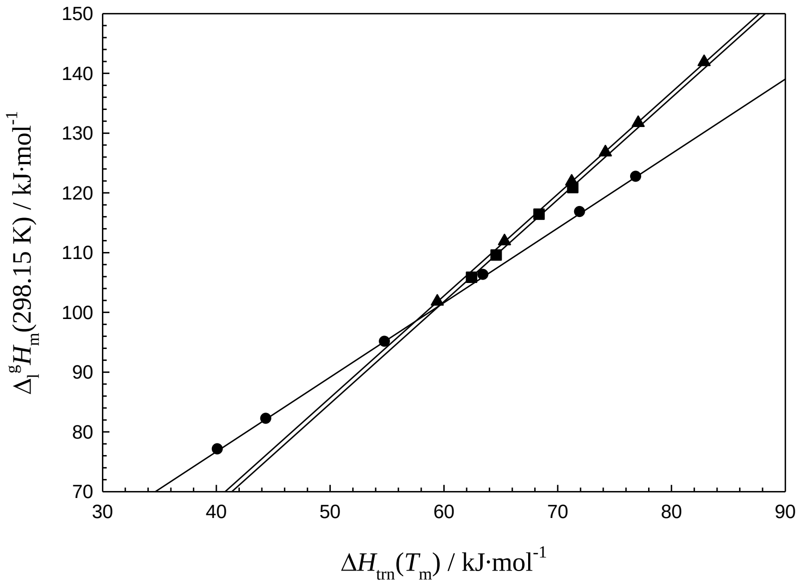

Figure 6-2. Correlation between vaporization enthalpies and enthalpies of transfer for run 1 on a dimethyl silicone column as reported in Table 4. Circles (●): dimethyl phthalate, diethyl phthalate, di-*n*-butyl phthalate, benzyl butyl phthalate, bis-(2-ethylhexyl) phthalate, di-*n*-octyl phthalate; triangles (▲): eicosane, docosane, tetracosane, pentacosane, hexacosane, octacosane; squares (■): methyl octanoate, ethyl octanoate, methyl eicosanoate, methyl henicosanoate.

This is observed more quantitatively in Tables 6-6 and 6-7 where all vaporization enthalpies are determined by C-GC using the two esters, methyl octadecanoate and methyl eicosanoate, as standard compounds. Equations 6-13 and 6-14 given below each correlation illustrate the relationship between $\Delta_l^g H_m(T_m)$ and $\Delta_{trn}H_m(T_m)$ for these two materials.

TABLE 6-6. Correlation of Vaporization Enthalpies With Enthalpies of Transfer Using Methyl Octadecanoate and Methyl Eicosanoate as the Only Standards for Run 1 Poly(dimethyl siloxane) Column, p_o = 101325 Pa)

Run 1	- slope T/K	intercept	ΔH_{trn}(532 K) kJ·mol^{-1}	$\Delta_l^gH_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^gH_m$(298 K) kJ·mol^{-1} (Calc)^a	 (Lit)
Eicosane	7147.1	12.803	59.42		100.5±2.9	101.81±0.5
Docosane	7856.6	13.595	65.32		111±0.01	111.9±2.7
Tetracosane	8567.8	14.398	71.23		121.5±2.9	121.9±2.8
Pentacosane	8924.0	14.804	74.19		126.8±4.4	126.8±2.9
Hexacosane	9270.9	15.194	77.07		131.9±5.8	131.7±3.2
Octacosane	9968.2	15.985	82.87		142.3±8.6	141.9±4.9
Methyl octadecanoate	7509.0	13.175	62.43	105.9±1.4	105.9±1.4	
Ethyl octadecanoate	7769.2	13.485	64.59		109.7±0.3	109.6±4.4
Methyl eicosanoate	8223.0	13.997	68.36	116.4±1.5	116.4±1.5	
Methyl heneicosanoate	8579.2	14.380	71.32		121.7±2.9	120.9±2.5
Dimethyl phthalate	4830.3	9.952	40.16		66.2±12.2	77.0±1.2
Diethyl phthalate	5343.5	10.537	44.42		73.8±10.2	82.1±0.5
Di-*n*-butyl phthalate	6598.1	11.896	54.85		92.4±5.1	95.0±1.1
Butyl benzyl phthalate	7638.6	12.828	63.50		107.8±0.9	106.2±2.4
bis (2-Ethylhexyl) phthalate	8659.4	14.245	71.99		122.9±3.3	116.7±0.5
Di-*n*-octyl phthalate	9251.7	15.194	76.92		131.7±5.7	122.6±1.4

$\Delta_l^gH_m$(298.15 K)/kJ·mol^{-1} = (1.781)·ΔH_{trn}(532 K) - (5.304) (6-13)

^{a}Uncertainties estimated by using values of (105.9+1.4) and (116.4-1.5) kJ·mol^{-1} for the two standards.

TABLE 6-7. Correlation of Vaporization Enthalpies With Enthalpies of Transfer (C-GC) Using Methyl Octadecanoate and Methyl Eicosanoate as the Only Standards for Run 3 Poly(dimethyl siloxane) Column, p_o = 101325 Pa)

Run 3	-slope T/K	intercept	ΔH_{trn}(516 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}	
					(Calc)^a	(Lit)
Eicosane	7390.7	13.258	61.44		100.3±2.9	101.8±0.5
Docosane	8137.5	14.124	67.65		110.9±0.01	111.9±2.7
Tetracosane	8880.6	14.990	73.83		121.4±2.9	121.9±2.8
Pentacosane	9250.8	15.423	76.91		126.6±4.3	126.8±2.9
Hexacosane	9619.4	15.855	79.97		131.8±5.7	131.7±3.2
Methyl hexadecanoate	7032.5	12.822	58.47		95.3±4.3	96.8±0.63
Methyl octadecanoate	7783.1	13.688	64.71	105.9±1.4	105.9±1.4	
Ethyl octadecanoate	8057.4	14.027	66.99		109.7±0.4	109.6±4.4
Methyl eicosanoate	8532.3	14.56	70.93	116.4±1.5	116.4±1.5	
Methyl heneicosanoate	8904.9	14.995	74.03		121.7±3.0	120.9±2.5
Dimethyl phthalate	4976.4	10.195	41.37		66.2±12.3	77.0±1.2
Diethyl phthalate	5513.3	10.835	45.84		73.8±10.2	82.1±0.5
Di-*n*-butyl phthalate	6831.1	12.327	56.79		92.4±5.1	95.0±1.1
bis(2-Ethylhexyl) phthalate	8983.8	14.858	74.69		122.8±3.2	116.7±0.5

$$\Delta_l^g H_m(298.15\ \mathrm{K})/\mathrm{kJ\cdot mol^{-1}} = (1.6984)\cdot\Delta H_{trn}(516\ \mathrm{K}) - (3.99) \qquad (6\text{-}14)$$

^{a}Uncertainties estimated by using values of (105.9+1.4) and (116.4-1.5) kJ·mol^{-1} for the two standards.[13]

6.3.2. Vaporization Enthalpies by GC-RT. Using the retention times given in Appendix F and discussed in section 6.3.1, three esters, methyl hexanoate, methyl octanoate and methyl eicosanoate, were chosen as standard compounds and the vaporization enthalpies of the remaining compounds were determined using the procedure described in section 6.2.4. Vapor pressures were calculated from T/K = (283.15 to 313.15) at 5 K intervals and the vaporization enthalpy was evaluated at the mean temperature, T/K = 298.15, from a plot of ln(p/p_o) versus 1/T. The results are listed in columns 2-6 of Table 6-8. The vaporization enthalpies of the standard compounds in each run are listed in bold italics. They were not used in calculating the average. Column 7 lists the average values acquired by the GC-RT method and columns 8 and 9 compare the results to literature values and the average values calculated by C-GC, respectively. The average C-GC values are those calculated using the two monoesters described above as standards for runs 1-4.

TABLE 6-8. A Comparison of Vaporization Enthalpies in kJ·mol^{-1} at T/K = 298.15 (p_o =101325 Pa) Evaluated by GC-RT and by C-GC Using Mono-Esters as Standards[a]

	GC-RT Run 1	GC-RT Run 2	GC-RT Run 1	GC-RT Run 2	GC-RT Run 2	GC-RT Avg	lit	C-GC[b]
Eicosane	102.9±1.5	102.6±2.2	107.5±5.7	106.9±5.1	99.8±2.0	103.9±3.2	101.8±0.5	100.4±2.9
Docosane	108.8±3.1	108.8±4.2	113.4±1.5	113.1±1.5	106.0±5.9	110.0±3.2	111.9±2.7	111.0±0.1
Tetracosane	114.7±7.2	115.0±6.2	119.3±2.6	119.3±2.6	112.2±9.8	116.1±3.1	121.9±2.8	121.5±2.9
Pentacosane	117.6±9.2	118.1±7.1	122.3±4.6	122.4±4.4	115.3±12	119.1±3.1	126.8±2.9	126.7±4.4
Hexacosane	120.5±11	121.1±8.1	125.1±6.6	125.5±6.3	118.3±11	122.0±3.1	131.7±3.2	131.8±5.7
Octacosane	126.3±16		130.9±11			128.6±3.3	141.9±4.9	142.3±8.6
Methyl hexadecanoate		99.6±2.7		104.0±7.1	***96.8±0.6***	101.8±3.1	96.8±0.6	95.3±4.3
Methyl octadecanoate	***105.9±1.4***	***105.9±1.4***	110.5±14	110.2±4.3	103.1±2.9	107.9±4.2	105.9±1.4	
Ethyl octadecanoate	108.0±1.6	108.1±3.4	112.7±3.0	112.5±2.9	105.4±4.3	109.3±3.2	109.6±4.4	109.7±0.3
Methyl Eicosanoate	111.8±4.6	112.1±4.9	***116.4±1.5***	***116.4±1.5***	109.3±7.1	111.1±1.5	116.4±1.5	
Methyl heneicosanoate	114.8±6.1	115.2±5.6	119.4±1.5	119.5±1.5	112.4±8.6	116.3±3.1	120.9±2.5	121.7±2.9
Dimethyl Phthalate	83.6±6.6	82.6±4.2	88.2±11.2	86.9±9.9	79.8±2.7	84.2±3.4	77.0±1.2	66.4±12
Diethyl Phthalate	87.9±5.8	87.0±3.9	92.5±10	91.3±9.2	84.2±2.1	88.6±3.4	82.1±0.5	73.9±10
Di-*n*-butyl Phthalate	98.3±3.3	98.0±2.8	102.9±0.1	102.3±7.3	95.2±0.6	99.3±3.2	95.0±1.1	92.4±5.1
Benzyl butyl Phthalate	107.9±1.5		111.6±6.8			109.8±2.6	106.2±2.4	107.9±0.9
bis(2-Ethylhexyl) phthalate	115.4±1.6	115.8±3.2	120.1±4.9	120.2±3.5	113.0±3.7	116.9±3.8	116.7±0.5	122.8±3.3
Di-*n*-octyl Phthalate	120.3±2.3		125.0±4.0			122.7±3.2	122.6±1.4	131.6±5.7

[a] Vaporization enthalpies in bold italics in columns 2-6 used as standards in the GC-RT protocol. Not included in the average value. Uncertainties in columns 2-6 are an average of the uncertainty calculated using the uncertainty associated with the vaporization enthalpy of the standard. Uncertainties in column 7 are the standard deviation associated with the mean. [b] Average values from runs 1-4 using only methyl octadecanoate and methyl eicosanoate as standards for all runs; uncertainties were generated using the standard deviations associated with the values of the two standards.[13]

6.3.3. Comparison of Vaporization Enthalpy Results. As implied by Figure 6-2, the coincidence viewed in the slopes and intercepts between $\Delta_{trn}H_m(T_m)$ and $\Delta_l{}^gH_m(298.15)$ of the *n*-alkanes and monoesters by C-GC generated good reproducibility of the resulting vaporization enthalpies of the *n*-alkanes. Using the two esters as standard compounds, similar data is acquired for the remaining monoesters. Good agreement for eicosane, methyl and ethyl octadecanoate is acquired by the GC-RT method, as well. The results, however, seem to diverge as the size of the alkane or monoester increases. The incremental increase per CH_2 group does not seem to be modeled as well for these compounds by this technique. As anticipated, the C-GC technique is significantly less successful in modeling the vaporization enthalpies of the dialkyl phthalate esters, except close to where the two lines in Figure 6-2 intersect. In this case, the data from the GC-RT method is significantly closer to the literature values for the larger dialkyl phthalates. They also, however, diverge as the size decreases. The average absolute errors relative to the literature values in $kJ\cdot mol^{-1}$ are as follows: *n*-alkanes: C-GC: 0.57; GC-RT: 6.73; monoesters: C-GC, 0.48; GC-RT, 2.5; dialkyl phthalates: C-GC, 6.36; GC-RT: 3.6. When using esters as standards, the C-GC method does best with both monoesters and the *n*-alkanes. The results for the dialkyl phthalates as determined by the GC-RT method, however, are significantly better.

6.3.4. Comparison of Vapor Pressures by C-GC and GC-RT. In Table 6-9 the relative vapor pressures determined by the GC-RT and C-GC methods are compared. The literature values are reported in column 2. In columns 3-7 data for the GC-RT method is reported as a ratio relative to the literature values. The average of 5 evaluations by the GC-RT method is reported in column 8. The standard compounds are designated by the number 1, listed in bold italics, and were not used in producing the statistics. Column 9 lists the average value determined by C-GC using the values for methyl octadecanoate and methyl eicosanoate as standard compounds (Appendix F contains a summary of the ratio of the individual values from runs 1-4).

TABLE 6-9. A Comparison of the Ratio of Literature Vapor Pressures (p_{lit}) to Those Evaluated by C-GC and GC-RT (p_{calc}) Using Mono-Esters as Standards at T/K = 298.15 K, p_o = 101325 Pa

	$10^4 \cdot p_{\text{lit}}$/ Pa	$p_{\text{lit}}/p_{\text{calc}}$ GC-RT[a]					$p_{\text{lit}}/p_{\text{calc}}$ GC-RT[b] Avg	$p_{\text{lit}}/p_{\text{calc}}$ C-GC[c] Avg
		Run 1	Run 2	Run 1	Run 2	Run 2		
Eicosane	20.9	0.89	0.93	0.23	0.24	1.59	0.78±0.57	0.80±0.17
Docosane	2.15	1.76	1.75	0.84	0.85	3.01	1.64±0.89	0.62±0.14
Tetracosane	0.24	3.28	3.12	2.79	2.79	5.36	3.47±1.08	0.51±0.13
Pentacosane	0.081	4.35	4.05	4.95	4.91	6.95	5.04±1.13	0.48±0.12
Hexacosane	0.028	5.82	5.25	8.82	8.64	9.02	7.51±1.82	0.44±0.12
Octacosane	0.0032	11.0		29.5			20.2±13.1	0.31±0.16
Methyl hexadecanoate	71.4		0.58		0.11	***1***	0.35±0.33	1.15±0.002
Methyl octadecanoate	8.0	***1***	***1***	0.36	0.36	1.72	0.81±0.79	***1***
Ethyl octadecanoate	4.3	1.07	1.05	0.47	0.48	1.8	0.97±0.55	1.1±0.002
Methyl eicosanoate	1.04	1.56		***1***	***1***	2.56	2.06±0.71	***1***
Methyl heneicosanoate	0.32	2.32	2.16	1.99	1.97	3.71	2.43±0.73	0.84±0.001
Dimethyl phthalate	3042	0.83	0.98	0.03	0.04	1.67	0.71±0.69	0.23±0.04
Diethyl phthalate	988	0.82	0.94	0.05	0.05	1.62	0.7±0.66	0.31±0.05
Di-*n*-butyl phthalate	38.7	1.22	1.29	0.2	0.21	2.21	1.03±.085	0.45±0.09
Benzyl butyl phthalate	2.0	1.83		0.73			1.28±0.78	0.54±0.021
bis (2-Ethylhexyl) phthalate	0.23	2.12	1.98	1.94	1.93	3.4	2.27±0.63	0.90±0.23
Di-*n*-octyl phthalate	0.055	3.19		4.77			3.98±1.1	0.89±0.59

[a]Values of ***1***in bold italics in columns 3-7 and column 9 used as standards in the GC-RT and C-GC protocols, respectively. [b]Uncertainties in column 8 represent one standard deviation associated with the average of columns 3-7; standards not included. [c]Average values from runs 1-4 using methyl octadecanoate and methyl eicosanoate as standards for all runs; uncertainties represent one standard deviation associated with the average value (see Appendix F for more information).

Vapor pressures of the *n*-alkanes as determined by the GC-RT technique seem to diverge considerably as the size of the molecule increases. The ratio of $p_{\text{lit}}/p_{\text{calc}}$ evaluated by the GC-RT technique varies from 0.78 to 20.2 and increases as the vapor pressure decreases. The exact opposite effect is seen for the same compounds by the C-GC method, which decreases from 0.8 to 0.31. The GC-RT technique displays a similar but slightly diminished increasing trend for the monoesters, increasing from 0.35 to 2.06 as the size of the molecule increases. For the C-GC method, excluding the standard compounds, the ratio decreases from 1.15 to 0.84. The GC-RT method reproduces the dialkyl phthalates quite well. It does also, however, display a similar divergence as the size of the molecule increases. In regards to the dialkyl phthalates, both techniques generally show an increase in the ratio with increasing size, from 0.7 to 3.98 for the GC-RT method and 0.23 to 0.90 for the C-GC method.

Unlike vaporization enthalpies, the vapor pressures of the *n*-alkanes determined by C-GC using the two esters as standard compounds are also not as well reproduced. In addition, the reproduction quality decreases as the size of the alkane increases. This implies that the near coincidence in both slope and intercept seen in Figure 6-2 does not automatically guarantee the same quality in vapor pressures as what is seen for vaporization enthalpies. Using only two standard compounds, the vapor pressures of the monoesters are reproduced rather well. As shown by the magnitude of the uncertainty, significantly less scatter in the average value is seen between runs. In regards to the dialkyl phthalates, the best results are observed with compounds close to where the lines intersect in Figure 6-2. Since the intersection point is unpredictable, the quality of the results acquired for the dialkyl phthalates by either technique is highly dependent on the compounds chosen for investigation.

6.3.5. Effects of Retention Time Coincidence.

6.3.5.1. Vaporization Enthalpies. One of the advantages of gas chromatography is that it has the ability to provide pure component properties on compounds that can be complex mixtures. Some properties investigated previously have been for mixtures. These mixtures have commonly been composed of diastereomers that are either not resolved by the chromatography, as is the circumstance here for the two diastereomers of *bis* (2-ethylhexyl) phthalate, or only partly resolved.[8,11] An ongoing concern in the use of C-GC is associated with the effects of retention time coincidence on the thermodynamic results determined in situations where the chromatography is not capable of resolving all of the components. As previously stated, the compounds used in this work were also analyzed on a poly(5% diphenyl/95% dimethyl siloxane) column. This column failed to resolve two of the compounds, docosane and ethyl octadecanoate, over the entire 30K temperature range investigated. Since the thermodynamic properties of these two compounds are available, it was of interest to investigate the effect of this coincidence on the evaluated vaporization enthalpy and vapor pressure.

The correlation of $\Delta_l{}^gH_m(298.15)$ with $\Delta_{trn}H_m(T_m)$, which is again separated according to functional group for run 5, is summarized in Table 6-10. The complete correlation table and retention times, along with a summary of the two runs that also include data for the dialkyl phthalates in the mixture are given in Appendix F. Both docosane and methyl octadecanoate had identical retention times and thus their slopes and intercepts are also identical. Even though the resulting vaporization enthalpies are similar, they are different since the two use different standards in their correlations. In the last two columns of Table 6-10 a comparison of the values acquired by correlation with literature values shows that any effect of this coincidence on the vaporization enthalpy is quite small. In short, both results are reproduced well within the cited experimental uncertainties. It seems that retention time coincidence is not a significant concern, at least not in regards to the compounds evaluated in this work. Appendix F also compares vaporization enthalpy data acquired on the two columns with literature values. All data is well within experimental error.

TABLE 6-10. Results on the Effects of Retention Time Coincidence on Vaporization Enthalpy Poly(5% diphenyl/95% dimethyl siloxane) Column, p_o = 101325 Pa[a]

Run 5	- slope T/K	intercept	ΔH_{trn}(510 K) kJ·mol^{-1}	$\Delta_l^gH_m$(298 K) kJ·mol^{-1} (Lit)	$\Delta_l^gH_m$(298 K) kJ·mol^{-1}(Calc)	$\Delta_l^gH_m$(298 K) kJ·mol^{-1}(Lit)
Docosane	**8191.5**	**14.921**	**68.10**		**111.4±1.5**	**111.9±2.7**
Tetracosane	8968.8	15.827	74.56	121.9±2.8	121.8±1.5	
Pentacosane	9338.2	16.253	77.63	126.8±2.9	126.8±1.6	
Hexacosane	9713.0	16.691	80.75	131.7±3.2	131.8±1.6	
Octacosane	10453.8	17.555	86.91	141.9±4.9	141.8±1.7	
$\Delta_l^gH_m$(298.15 K)/kJ·mol^{-1} = (1.62±0.015)·ΔH_{trn}(510 K) + (1.033±1.13); r^2 = 0.9998						(5-15)
Methyl hexadecanoate	7153.1	13.701	59.47	96.84±0.63	96.6±3.4	
Methyl octadecanoate	7914.5	14.579	65.80	105.87±1.4	106.4±3.5	
Ethyl octadecanoate	**8191.5**	**14.921**	**68.10**		**109.9±3.6**	**109.6±4.4**
Methyl eicosanoate	8674.8	15.462	72.12	116.43±1.5	116.1±3.7	
Methyl heneicosanoate	9053.7	15.904	75.27	120.9±2.5	121.0±3.8	
$\Delta_l^gH_m$(298.15 K)/kJ·mol^{-1} = (1.54±0.037)·ΔH_{trn}(510 K) + (4.96±2.5); r^2 = 0.9988						(5-16)

[a] Values in bold correspond to the compounds with identical retention times. Uncertainties represent one standard deviation.

6.3.5.2. Vapor Pressures. The effect of retention time coincidence on the resulting vapor pressures from run 5 determined from correlation of $\ln(p/p_o)$ with $\ln(t_o/t_a)$ of the standards at T/K = 298.15 is examined in Table 6-11.

TABLE 6-11. Correlation of $\ln(p/p_o)$ with $\ln(t_o/t_a)$ and Evaluated Vapor Pressures at T/K = 298.15 For Docosane and Ethyl Octadecanoate For Run 5; Poly(5% diphenyl/95% dimethyl siloxane) Column, p_o/Pa = 101325[a]

Run 5	-slope	intercept	$-\ln(t_o/t_a)$	$-\ln(p/p_o)_{lit}$	$-\ln(p/p_o)_{calc}$	$\ln(p/p_o)_{lit}$	$10^4 \cdot (p_{calc}/p_{lit})$
Docosane	**8191.5**	**14.921**	12.553		19.91±0.15	-19.97	**$(2.29 \pm 0.34)^b$/ 2.15**
Tetracosane	8968.8	15.827	14.255	22.175	22.17±0.16		
Pentacosane	9338.2	16.253	15.067	23.244	23.24±0.16		
Hexacosane	9713.0	16.691	15.886	24.309	24.33±0.17		
Octacosane	10453.8	17.555	17.507	26.490	26.48±0.18		
$\ln(p/p_o) = (1.326 \pm 0.007) \ln(t_o/t_a) - (3.259 \pm 0.117)$;					$r^2 = 0.9999$		(6-17)
Methyl hexadecanoate	7153.1	13.701	10.290	16.468	16.47±0.43		
Methyl octadecanoate	7914.5	14.579	11.966	18.659	18.63±0.47		
Ethyl octadecanoate	**8191.5**	**14.921**	12.553		19.38±0.26	-19.29	**$(3.88 \pm 1.0)^c$/4.25**
Methyl eicosanoate	8674.8	15.462	13.663	20.697	20.77±0.5		
Methyl heneicosanoate	9053.7	15.904	14.462	21.885	21.84±0.52		
$\ln(p/p_o) = (1.286 \pm 0.0207) - (3.235 \pm 0.263)$;					$r^2 = 0.9995$		(6-18)

[a] Uncertainties represent one standard deviation. [b] A vapor pressure of p/Pa = $(2.24 \pm 0.21) \cdot 10^{-4}$ is calculated at T/K = 298.15 on a poly(dimethyl siloxane) column (Run 1). [c] A vapor pressure of p/Pa = $(3.82 \pm 0.5) \cdot 10^{-4}$ is calculated at T/K = 298.15 on a poly(dimethyl siloxane) column (Run 1).

The comparison given in the last column of Table 6-11 shows that the evaluated vapor pressures for both docosane and ethyl octadecanoate at T/K = 298.15 agree favorably with the literature values. The vapor pressures evaluated from run 1 for the two esters on a poly(dimethyl siloxane) column are also included in the table as footnotes a and b. Both sets of values are within experimental error of the literature values and with each other. This shows that the vapor pressure results are also independent of which of the two columns are used.

The correlation between $\ln(p/p_o)$ and $\ln(t_o/t_a)$ of the standards from run 5 was then repeated from T/K = (298.15 to 500) at 10 K intervals and the data was fit to the third order polynomial, eq 6-5. The r^2 values for all correlations exceeded 0.99. Table 6-12 lists the coefficients of eq 6-5 for both docosane and ethyl octadecanoate.

TABLE 6-12. Parameters of Eq 6-5 and A Comparison of Boiling Temperatures (BT) at p/Pa = 101325 Evaluated For Docosane and Ethyl Octadecanoate for Run 5 from T/K = (298.15 to 500)

	$10^{-8}\cdot A/T^3$	$10^{-6}\cdot B/T^2$	$10^{-2}\cdot C/T$	D	T_{boil}/K Calc/Lit
Docosane	2.1812±0.00001	-3.1217±0.0001	1.5076±0.00113	6.4725±0.0001	644.1±0.1/642.2[a]
Ethyl octadecanoate	3.523±0.0598	-4.2925±0.048	36.0768±1.276	3.5143±0.112	447.4±1.8/443.2[b]

[a] Reference 19. [b] Boiling temperature at p/Pa = 267, ref 20.

The temperature dependence of both compounds is illustrated in Figure 6-3. The line represents the literature values evaluated using eqs 6-4 and 6-6 with suitable constants from Table 6-3 and the symbols represent the value evaluated by correlation. Boiling temperatures were then predicted by extrapolating the temperature until $\ln(p/p_o) = 0$. The boiling temperature for docosane at p/Pa = 101325 was predicted within T/K = 2. The normal boiling temperature of ethyl octadecanoate is not available. The boiling temperature at a reference pressure p_o/Pa = 267 of T_b/K = 443.2, however, was reproduced within 4.2 K.

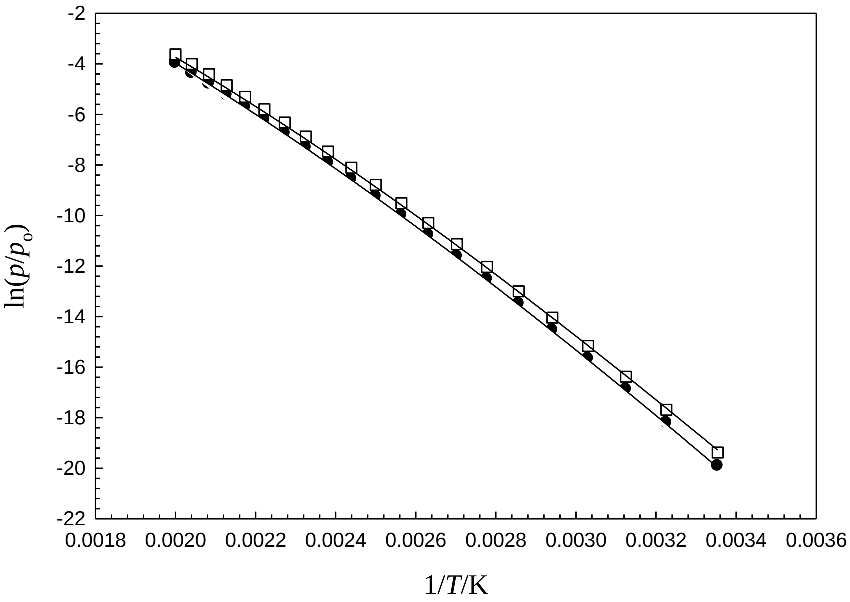

Figure 6-3. A comparison of calculated (symbols) and literature vapor pressures (lines). Docosane, circles (●), and ethyl octadecanoate, squares (□) plotted as ln(p/p_o) versus 1/T (K) evaluated from coincidental retention times (p_o/Pa = 101325).

6.4. Summary

The significance of selecting appropriate standards regardless of the chosen GC method is supported by the results of this work. When the functional group of the standards matches the target compound's functional group much better data is acquired. No matter which GC method was used, vaporization enthalpies were generally within 10% of the literature values. Significantly more scattering, however, is seen when the GC-RT method is used. This is most likely due to one standard being used for each calculation in comparison to the averaging out that occurs when more than one is used. The CH_2 increment commonly seen in homologous series seems to be reduced in this study by the GC-RT method. Regardless of the standards chosen for use both techniques were able to reproduce the vapor pressures of the compounds in this work within an order of magnitude. A value within this range may be adequate depending on the application.

When the functional groups of the standard compounds correspond to those of the target compounds the vapor pressures and vaporization enthalpies improve considerably.

An explanation for the success in determining the vaporization enthalpy and vapor pressure of empenthrin, discussed in the introduction, is also shown by the data acquired from the GC-RT method for the dialkyl phthalates using esters as standards, even though in this instance the functional groups of the standards and targets were reversed. The standards chosen for use by Tsuzuki included dibutyl phthalate and *bis* (2-ethylhexyl) phthalate. The vaporization enthalpies of these two compounds are close to where the two lines representing esters and diesters in Figure 6-2 intersect. This data does indeed validate the need to be careful in choosing standards with the same functional groups as the target compounds to be investigated.

Lastly, within experimental error, there does not appear to be a noticeable effect of retention time coincidence on either the vapor pressure or vaporization enthalpy.

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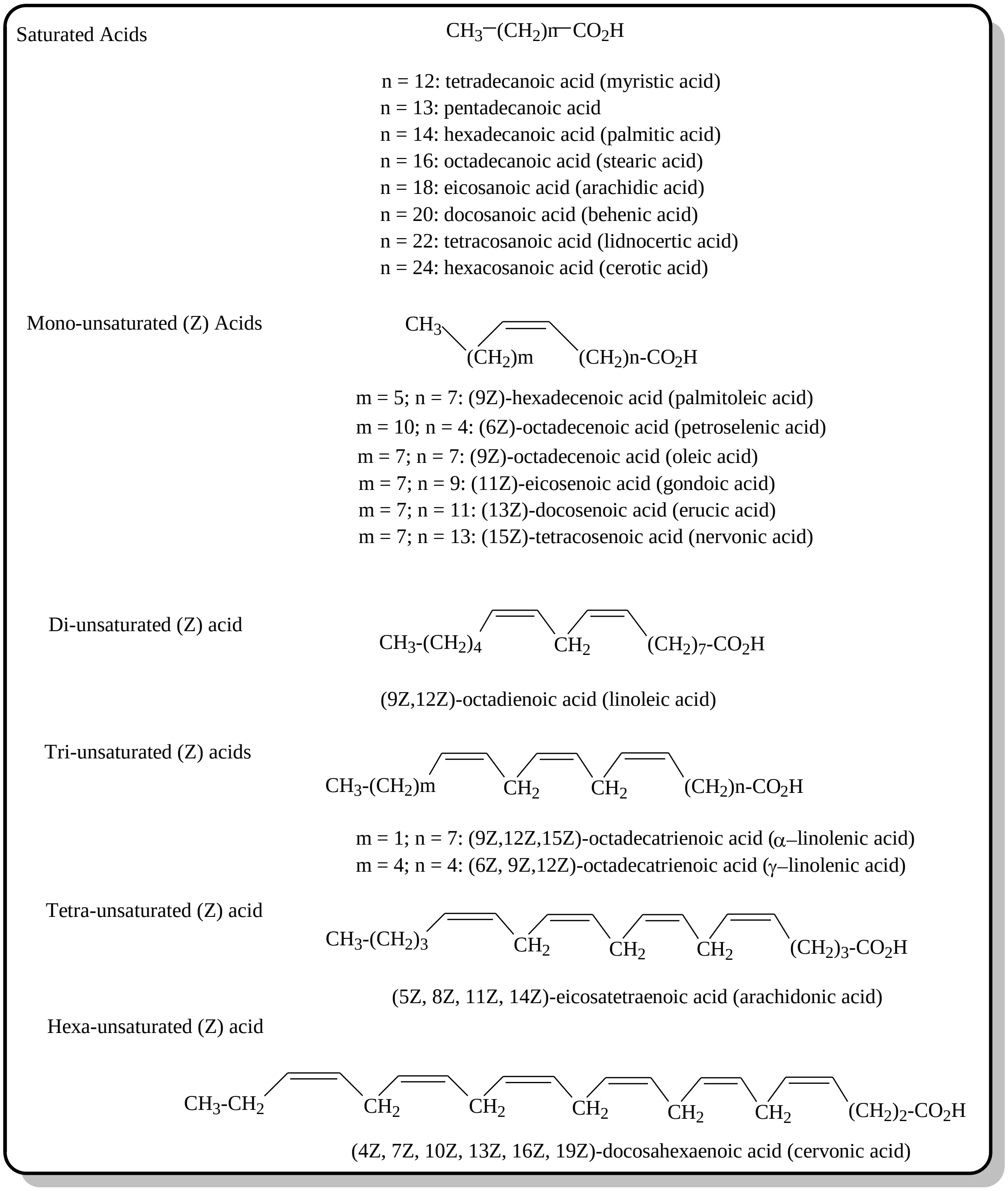
Part 5: Miscellaneous Measurements

Chapter 7: Vaporization Enthalpies and Vapor Pressures of Other Chemical Systems Investigated by Correlation Gas Chromatography

7.1. Introduction

As has already been shown correlation gas chromatography is a useful method for the analysis of thermodynamic data of various organic compounds. This chapter highlights other chemical systems in which this technique has proven useful. One such area is that of the saturated and unsaturated fatty acids. Our lab had previously reported the liquid vapor pressures as a function of temperature and vaporization enthalpies at T/K = 298.15 of several saturated and unsaturated fatty acids by correlation gas chromatography.[1] Additional analysis of two saturated and several unsaturated fatty acids was conducted[2] due to their immense biological and industrial importance and subsequent environmental concerns that arose in regards to their presence in aerosols resulting from the large scale production of these materials from biogenic and combustion sources. The compounds investigated include (9Z)-hexadecenoic acid (palmitoleic acid), (6Z)-octadecenoic acid (petroselinic acid), (9Z)-octadecenoic acid (oleic acid), (5Z,8Z,11Z,14Z)-eicosatetraenoic acid (arachidonic acid), (11Z)-eicosenoic acid (gondoic acid), (4Z,7Z,10Z,13Z,16Z,19Z)-docosahexenoic acid (cervonic acid), (15Z)-tetracosenoic acid (nervonic acid), n-tetracosanoic acid (lignoceric acid), and n-hexacosanoic acid (cerotic acid). The structures of the target compounds and other compounds used either as standards or discussed in the text are shown in Figure 7-1.



Saturated Acids

$CH_3-(CH_2)n-CO_2H$

n = 12: tetradecanoic acid (myristic acid)
n = 13: pentadecanoic acid
n = 14: hexadecanoic acid (palmitic acid)
n = 16: octadecanoic acid (stearic acid)
n = 18: eicosanoic acid (arachidic acid)
n = 20: docosanoic acid (behenic acid)
n = 22: tetracosanoic acid (lidnocertic acid)
n = 24: hexacosanoic acid (cerotic acid)

Mono-unsaturated (Z) Acids

m = 5; n = 7: (9Z)-hexadecenoic acid (palmitoleic acid)
m = 10; n = 4: (6Z)-octadecenoic acid (petroselenic acid)
m = 7; n = 7: (9Z)-octadecenoic acid (oleic acid)
m = 7; n = 9: (11Z)-eicosenoic acid (gondoic acid)
m = 7; n = 11: (13Z)-docosenoic acid (erucic acid)
m = 7; n = 13: (15Z)-tetracosenoic acid (nervonic acid)

Di-unsaturated (Z) acid

(9Z,12Z)-octadienoic acid (linoleic acid)

Tri-unsaturated (Z) acids

m = 1; n = 7: (9Z,12Z,15Z)-octadecatrienoic acid (α–linolenic acid)
m = 4; n = 4: (6Z, 9Z,12Z)-octadecatrienoic acid (γ–linolenic acid)

Tetra-unsaturated (Z) acid

(5Z, 8Z, 11Z, 14Z)-eicosatetraenoic acid (arachidonic acid)

Hexa-unsaturated (Z) acid

(4Z, 7Z, 10Z, 13Z, 16Z, 19Z)-docosahexaenoic acid (cervonic acid)

Figure 7-1. Structures of the fatty acids discussed and/or measured in this work.

Another example of the viability of this method is in the analysis of γ and δ-lactones.[3] A number of these compounds are important components in flavors. γ-dodecanolactone, for example, is said to have a waxy, fatty sweet aroma with green rind-like notes. δ-dodecanolactone, on the other hand, is described as having fruity, peach-like and buttery notes.[4] Almost all the γ and δ-lactones from C_6 to C_{14} are GRAS chemicals

(Generally Recognized As Safe) as recognized by the US Federal Food, Drug and Cosmetic Act[5] and are used as components in flavors. The vapor pressures over the temperature range T/K = (298.15 to 350) and vaporization enthalpies at T/K = 298.15 of γ-octanolactone, γ- and δ-undecanolactone and γ and δ-dodecanolactone were determined in our laboratory by correlation gas chromatography. The structures of both the γ and δ-lactones as well as the corresponding ω-lactones to which they are compared to are shown in Figure 7-2.

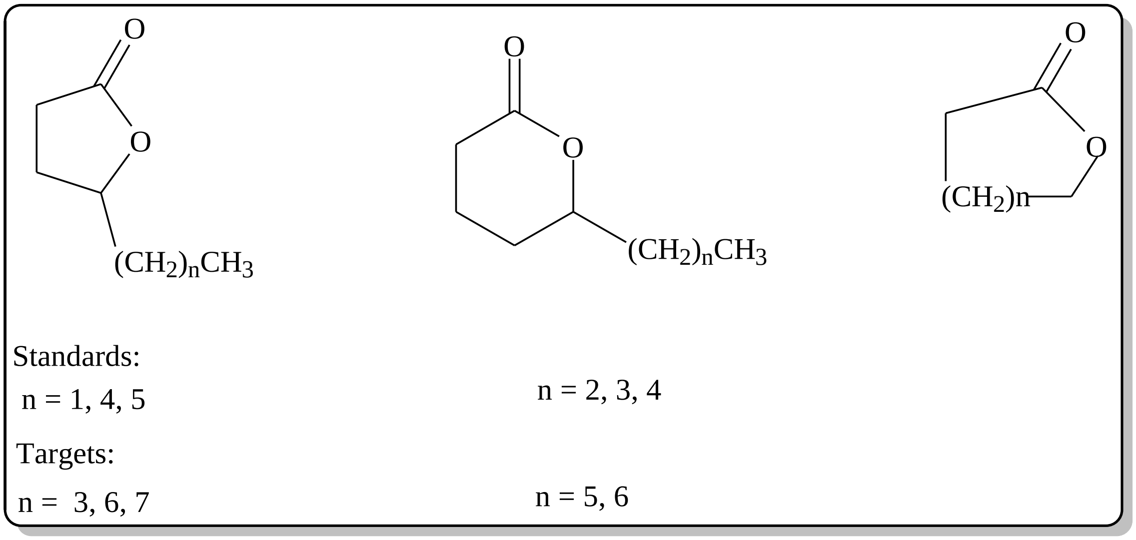


Figure 7-2. The structures of the γ and δ-lactone standards and targets and the ω-lactones.

Lastly, the correlation gas chromatography technique was recently employed by our laboratory to investigate the vaporization enthalpies and vapor pressures of a series of insect pheromones at T/K = 298.15.[6] Probably one of the soundest ecological methods of pest control in the environment is the appropriate use of insect pheromones. While the pheromones themselves may not be lethal, they commonly target a specific insect or insects. In combination with appropriate strategies, their use can offer an effective means to control insect populations. The compounds studied include: *Z* 8-dodecenyl acetate, *Z*

4-tridecenyl acetate, *E* 11-tetradecenyl acetate, *E,E* 9,11-tetradecadienyl acetate, ethyl *S* (2*E*,4*E*)-3,7,11-trimethyl-2,4-dodecadienoate (*S*-hydroprene), *R*,*S* 2-propynyl (2*E*,4*E*)-3,7,11-trimethyl-2,4-dodecadienoate (*R*,*S* kinoprene) and *Z* 13-octadecenyl acetate. The structures of all the target molecules are given in Figure 7-3.

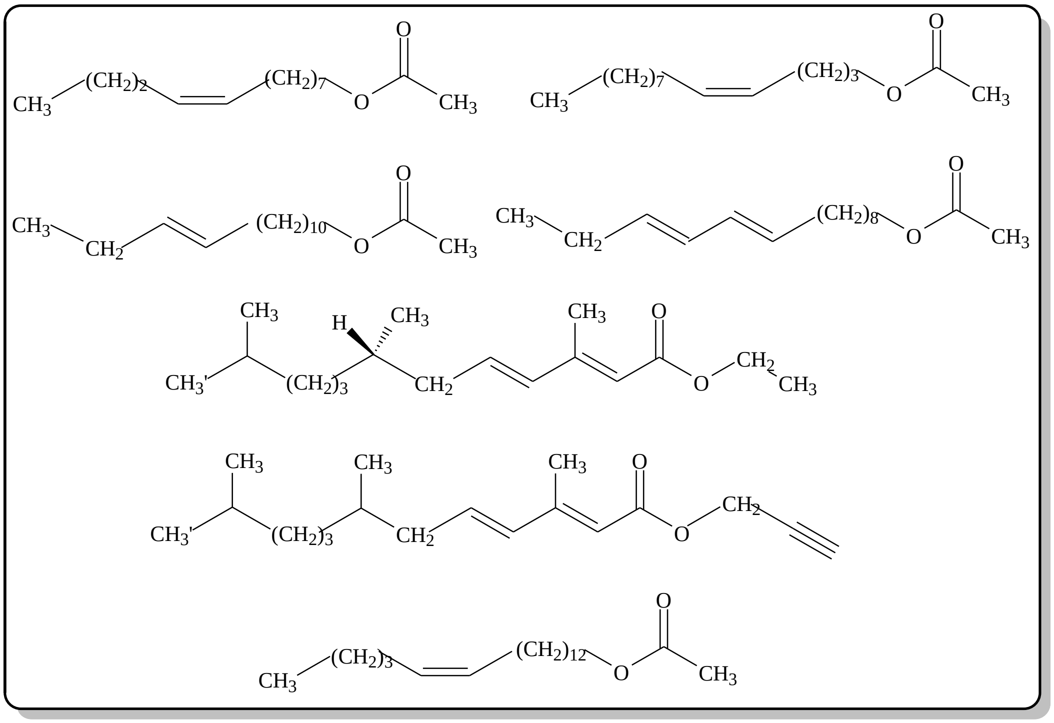


Figure 7-3. Structures of the insect pheromones. From left to right, top to bottom: *Z* 8-dodecenyl acetate, *Z* 4-tridecenyl acetate, *E* 11-tetradecenyl acetate, *E*, *E* 9,11-tetradecadienyl acetate, (*S*)-ethyl (2*E*,4*E*)-3,7,11-trimethyl-2,4-dodecadienoate, 2-propynyl (2*E*,4*E*)-3,7,11-trimethyl-2,4-dodecadienoate and *Z* 13-octadecenyl acetate.

Z 8-Dodecenyl acetate is a component of the sex pheromone of several insects that include the macadamia nut borer (*Cryptophlebia ombrodelta*), the plum fruit moth (*Cydia funebrana*), the oriental fruit moth (*Grapholita molesta*), and the koa seedworm (*Cryptophlebia illepida*) (Ref 1 from insect pheromone paper). *Z* 4-Tridecenyl acetate is used for the disruption of the sex pheromone of the Tomato Pin Worm (*Keiferia lycopersicella*) (Ref 2 from insect pheromone paper). A mixture of *E* 11-tetradecenyl acetate and *E*, *E* 9,11-tetradecadienyl acetate (LBAM) has been used to combat the light brown apple moth (*Epiphyas postvittana*). LBAM is used to disturb the mating behavior of the moth (Ref 3 from insect pheromone paper). S Ethyl (2*E*,4*E*)-3,7,11-trimethyl-2,4-dodecadienoate (hydroprene) is classified as an insect growth regulator and is considered a biopesticide by the US Environmental Protection Agency. It is used to disrupt the normal development and growth of cockroaches, beetles and moths.[7] Structurally similar *S* 2-propynyl (2*E*,4*E*)-3,7,11-trimethyl-2,4-dodecadienoate (S-kinoprene) is also an insect growth regulator used to control other insect species.[8]

7.2. Experimental

7.2.1. Materials.

7.2.1.1. Saturated and Unsaturated Fatty Acids. All fatty acids were acquired from Supelco. Their CAS number, molecular formula, both systematic and common name and their purities as provided by the supplier are listed in Table 7-1.

TABLE 7-1. Names and Chemical Composition of the Acids[a]

CAS #	Molecular Formula	Chemical Name (Common name)[a]	mass fraction
544-63-8	$C_{14}H_{28}O_2$	tetradecanoic acid (myristic acid (cr))	0.99
373-49-9	$C_{16}H_{30}O_2$	(9Z)-hexadecenoic acid (palmitoleic acid (l))	0.98
57-10-3	$C_{16}H_{32}O_2$	hexadecanoic acid (palmitic acid, (cr))	0.98
60-33-3	$C_{18}H_{32}O_2$	(9Z,12Z)-octadecadienoic acid (linoleic acid, (l))	0.99
593-39-5	$C_{18}H_{34}O_2$	(6Z)-octadecenoic acid (petroselinic acid, (cr))	0.98
112-80-1	$C_{18}H_{34}O_2$	(9Z)-octadecenoic acid (oleic acid (l))	0.994
506-32-1	$C_{20}H_{32}O_2$	(5Z,8Z,11Z,14Z)-eicosatetraenoic acid (arachidonic acid (l))	0.98
5561-99-9	$C_{20}H_{38}O_2$	(11Z)-eicosenoic acid (gondoic acid, (cr))	0.97
506-30-9	$C_{20}H_{40}O_2$	eicosanoic acid (arachidic acid, (cr))	0.98
6217-54-5	$C_{22}H_{36}O_2$	(4Z,7Z,10Z,13Z,16Z,19Z)-docosahexenoic acid (cervonic acid, (l))	0.98
112-86-7	$C_{22}H_{42}O_2$	(13Z)-docosenoic acid (erucic acid, (cr))	0.99
112-85-6	$C_{22}H_{44}O_2$	docosanoic acid (behenic acid, (cr))	0.99
506-37-6	$C_{24}H_{46}O_2$	(15Z)-tetracosenoic acid (nervonic acid, (cr))	0.99
557-59-5	$C_{24}H_{48}O_2$	tetracosanoic acid (lignoceric acid, (cr))	0.99
506-46-7	$C_{26}H_{52}O_2$	hexacosanoic acid (cerotic acid, (cr))	0.99

[a] Supplier: Supelco.

7.2.1.2. γ and δ-Lactones. The origin and purity of both the standard and target compounds are listed in Table 7-2. The commercial samples are all assumed to be racemic. Several of the compounds used in this work are also reported as a mixture of isomers. All materials were analyzed by gas chromatography to evaluate their chemical composition. While our analyses differ slightly from the values reported by the suppliers in a few instances, some of our samples were acquired some time ago. The isomers which were present in some of the samples were not identified. All were present in minor amounts. As previously stated, the ability to acquire reliable thermodynamic data with impure samples is one of the advantages of the correlation gas chromatography method.

TABLE 7-2. Origin of the standards and targets and their analysis

Compound	FEMA	CAS registry no	Supplier	Supplier	GC
γ-hexanolactone FCC	2556	695-06-7	Bedoukian	>0.98	0.993
γ-octanolactone FCC	2796	104-50-7	Bedoukian	>0.97	0.996
δ-octanolactone FCC	3214	698-76-0	Bedoukian	0.98[a]	0.989[a,b]
γ-nonanolactone FCC	2781	104-61-0	Bedoukian	0.98	0.982
δ-nonanolactone FCC	3356	3301-94-8	Citrus and Allied Essences	0.98	0.86
γ-decanolactone FCC	2360	706-14-9	Bedoukian	0.97	0.984
δ-decanolactone FCC	2361	705-86-2	Bedoukian	0.98[a]	0.975[a,c]
γ-undecanolactone FCC	3091	104-67-6	SAFC	>0.98	0.984
δ-undecanolactone FCC	3294	710-04-3	Bedoukian	0.98[a]	0.948[a,d]
γ-dodecanolactone FCC	2400	2305-05-7	Bedoukian	0.97	0.930
δ-dodecanolactone FCC	2401	713-95-1	Bedoukian	0.98[a]	0.983[a,e]

[a] Sum of isomers, reference 9. [b] Two isomers: 0.977:0.23; the minor isomer separated but was not identified. [c] Two isomers: 0.788, 0.212 ; the minor isomer separated but was not identified. [d] Two isomers: 0.928, 0.072; the minor isomer separated but was not identified. [e] Two isomers: 0.985; 0.015; the minor isomer separated but was not identified.

7.2.1.3. Insect Pheromones. The supplier and purity of the materials used in this work are given in Table 7-3. The purities of the standards are values provided by the supplier. Analyses for some of the target substances were not provided by the suppliers. These were analyzed by gas chromatography.

TABLE 7-3. Origin and Analysis of the Standards and Targets

Targets	CAS registry no	Supplier	Mass fraction Analysis
Z 8-Dodecenyl acetate	28079-04-1	Bedoukian	>0.96
Z 4-Tridecenyl acetate	65954-19-0	Bedoukian	0.96
E 11-Tetradecenyl acetate	33189-72-9	Bedoukian	E11: 0.79; 2E,4E: 0.04[a]
E,*E* 9,11-Tetradecadienyl acetate	54664-98-1	Bedoukian	2E,4E: 0.04; E11: 0.79[a]
S (+)-Ethyl (2*E*,4*E*)-3,7,11-trimethyl-2,4-dodecadienoate	65733-18-8	Fluka	0.95[b]
R,*S* 2-Propynyl (2*E*,4*E*)-3,7,11-trimethyl-2,4-dodecadienoate	42588-37-4	Chem Service	0.987[b]
Z 13-Octadecenyl acetate	60037-58-3	Bedoukian	0.946[b]
Standards			
Methyl decanoate	110-42-9	Sigma Aldrich	0.99
Methyl dodecanoate	111-82-0	Sigma Aldrich	>0.97
Methyl tetradecanoate	124-10-7	Sigma Aldrich	0.99
Methyl pentadecanoate	7132-64-1	Sigma Aldrich	0.99
Methyl octadecanoate	112-61-8	Sigma Aldrich	0.97
Methyl eicosanoate	1120-28-1	Sigma Aldrich	0.99
Methyl heneicosanoate	6064-90-0	Sigma Aldrich	0.99

[a] See section 2.1 from ref 6 for more details. [b] Analysis by GC.

7.2.2. Methods.

7.2.2.1. Saturated and Unsaturated Fatty Acids. A Hewlett Packard 5890 Series II gas chromatograph equipped with a flame ionization detector on a 15 m 0.32 mm ID J&W FFAP column (nitroterephthalic acid modified polyethylene glycol) was used for the measurements. Helium was used as the carrier gas. The injector and detector were maintained at 300°C. Methylene chloride was used as solvent and also served as the non-retained reference material. Chromatographs were stored on a computer using HP Chemstation software. Temperature was controlled by the instrument to T/K = ±0.1 and monitored independently using a Fluke 5OS digital thermometer. Experiments were conducted over a T/K = 30 at 5 K intervals. All measurements were calculated in the same manner as Section 1.2.2.2. Retention times are provided in Appendix G.

7.2.2.2. γ and δ-Lactones. The measurements were performed on an HP 5890 gas chromatograph running HP Chemstation. Isothermal chromatograms were obtained over a T = 30 K temperature range at intervals of T = 5 K on a Supelco 15 m, 0.32 mm, 1.0 μm film thickness SPB-5 capillary column at a split ratio of approximately 100/1 using helium as the carrier. The column temperature was monitored continuously using a Vernier stainless steel temperature probe with a Go!Link USB interface running Logger Lite software. The column temperature was maintained by the instrument at ±0.1 K. The solvent used was methanol which also served as the non-retained reference at the temperatures of the experiments. All measurements were calculated in the same manner as explained in Section 1.2.2.2. Retention times are provided in Appendix G.

7.2.2.3. Insect Pheromones. Experiments were conducted on an HP 5890 Gas Chromatograph running HP Chemstation on a 15 m Supelco SPBE capillary column, (0.32 mm I. D., 1 μm film thickness) at a split ratio of approximately 100/1. The carrier gas used was helium and the temperature, controlled by the instrument to T/K = ± 0.1 K, was independently monitored by a Fluke digital thermometer. All analyses were performed over a T/K = 30 temperature range at T/K = 5 intervals in a sequential manner. The standards and targets were injected simultaneously. Retention times are provided in Appendix G. All measurements were calculated in the same manner as explained in Section 1.2.2.2.

7.2.2.3.1. Insect Pheromones GC/MS Experiments. GC/MS analyses were carried out using a Hewlett Packard GC/MS System Model 5698A system operating in the EI mode at 70 eV, equipped with a Supelco SLB^{TM}-5 MS capillary column (30 m x 0.25 mm; 0.5 μm film thickness) using He as the carrier at an oven temperature, T/K = 483. The mass spectra were compared with those available in the NIST/EPA/NIH MS library. Comparison spectra are provided in Appendix G.

7.2.3. Fusion Enthalpy. Fusion enthalpy measurements for the saturated and unsaturated fatty acids were conducted in the same as previously described in Section 1.2.3. Fusion enthalpy measurements were not conducted for either the γ and δ-lactones or insect pheromones.

7.2.4. Vaporization Enthalpy Estimations. Vaporization enthalpy estimations are calculated in the same manner as previously discussed in Section 1.2.6. The b value contribution for a carboxylic acid functional group is 38.8 kJ·mol^{-1} and for an ester it is 10.5 kJ·mol^{-1}.

7.2.5. Temperature Adjustments. Temperature adjustments for all experiments can be calculated in the same manner as described in Section 1.2.4.

7.2.6. Uncertainties. Uncertainties for all calculations can be determined in the same manner as described in Section 1.2.5.

7.2.7. Vaporization Enthalpy and Vapor Pressure Standards.

7.2.7.1. Saturated and Unsaturated Fatty Acids. Vaporization enthalpies for tetradecanoic through to eicosanoic acids are values evaluated previously by De Kruif et al.[10] These compounds were used as standards in a previous study to evaluate the vaporization enthalpies of (9Z,12Z)-octadecadienoic (linoleic) acid, (13Z)-docosenoic (erucic) acid, and docosanoic acids.[1] These acids along with tetradecanoic, hexadecanoic, and eicosanoic acid have been used as standards in this study. Since the vaporization enthalpies of many of the saturated acids are available at different temperatures, they have been adjusted to T/K = 298.15 in Table 7-4 using eq 1-3. Temperature adjustments of several other aliphatic acids discussed below are provided in Appendix G.

TABLE 7-4. Vaporization Enthalpies of the Standards and Their Adjustments to T/K = 298.15

	$\Delta_l^g H_m(T_m)$ kJ·mol^{-1} (lit)	T_m/K	C_p(l) J·mol^{-1}·K^{-1}	$\Delta C_p \Delta T$ kJ·mol^{-1}	$\Delta_l^g H_m$ (298 K) kJ·mol^{-1}
tetradecanoic acid	104.1±2.0[a]	348.6	505.1	7.2±0.8	111.3±2.2
hexadecanoic acid	110.2±2.0[a]	364.1	568.9	10.5±1.1	120.7±2.3
(9Z,12Z)-octadecadienoic acid	134.1±10.3[b]	298.15			134.1±10.3
eicosanoic acid	125.5±2.0[a]	392.5	696.5	18.1±1.5	143.6±2.5
(13Z)-docosenoic acid	154.5±7.3[b]	298.15			154.5±7.3
docosanoic acid	154.7±7.3[b]	298.15			154.7±7.3

[a]Reference 12. [b]Reference 1.

The compounds in Table 7-4 were also used as vapor pressure standards. Equation 1-10 describes their liquid vapor pressure-temperature dependence and the constants for this equation are reported in Table 7-5. The constants of eq 1-10 reported for the acids in Table 7-5 were all derived previously by correlation[1] from work reported by De Kruif et al.[10] who used the equation of Clarke and Glew[11], eq 7-1, to describe their vapor pressure - temperature profile. Tetradecanoic through to octadecanoic acid were the compounds used previously as vapor pressure standards.[1] Both equations 1-10 and 7-1 have been shown to extrapolate well with temperature as illustrated in the predictions of boiling temperatures listed in last two columns of Table 7-5 for the first three entries.[12-14] All vapor pressures evaluated in this work are reported in terms of eq 1-10. Vapor pressures for the last three entries in the table also used as standards in the tables below were derived by correlation using the constants for the C_{14} to C_{18} acids reported by De Kruif et al. The boiling temperatures listed in the last column of Table 7-5 for these compounds are estimated.[15,16] The vapor pressures of other saturated acids used in the discussion below were derived from eq 1-10 or the Clarke and Glew[11] equation. These constants are provided in Appendix G. Please note that the reference pressure in eq 1-10 is p_o/Pa =101325 Pa, whereas in eq 7-1, the reference pressure p_o/Pa = 1 and θ refers to a reference temperature.

$$\ln(p/p_o) = AT^{-3} + BT^{-2} + CT^{-1} + D \qquad (1\text{-}10)$$

$$R\cdot\ln(p/p^o) = -\Delta_l^gG°(\theta)/\theta + \Delta_l^gH°(\theta)(1/\theta - 1/T) + \Delta_l^gCp(\theta)\{\theta/T - 1 + \ln(T/\theta\} \qquad (7\text{-}1)$$

TABLE 7-5. Coefficients of Polynomial Equation 1-10 of the Standards

Standards	$10^{-8}\cdot$A/K^3	$10^{-6}\cdot$B/K^2	$10^{-3}\cdot$C/K	D	T_b/K$_\mathrm{calc}$	T_b/K$_\mathrm{lit}$
tetradecanoic acid	4.348	-4.830	4.645	3.697	598.4	599.4[a]
hexadecanoic acid	4.707	-5.228	4.978	3.552	622.0	622.3[a]
(9Z,12Z)-octadecadienoic acid	5.440	-5.946	6.061	2.549	661.3[b]/450.8[c]	450.2[c,d]
eicosanoic acid	5.488	-6.097	5.926	2.954	667.8	650[e]
(13Z)-docosenoic acid	5.699	-6.424	6.224	2.630	695.9	705.2[f]
docosanoic acid	5.523	-6.276	5.809	3.115	688.2	701.7[f]

[a]Ref 12. [b]Ref 13. [c]Boiling temperature at p/Pa = 67. [d]Ref. 14. [e]Estimated value, Ref 15. [f]Estimated value, Ref 16.

7.2.7.2. γ and δ-Lactones. The compounds used as standards in this work are γ-hexanolactone, δ-octanolactone, γ-nonanolactone, δ-nonanolactone, γ-decanolactone and δ-decanolactone listed in Table 7-6. The vaporization enthalpies of all the standards are available at T/K = 298.15.[17,18] The temperature range of available vapor pressures varies some but generally data are available from T/K = (298.15 to 350). All literature vapor pressure data have been fit to equation 7-2.[17,18] Vaporization enthalpies and the A, B, and C constants of equation 7-2 are reported in Table 7-6.

$$\ln(p/\mathrm{Pa}) = [A - B/T(K) - C\cdot\ln(T/(K)/298.15)]/R \qquad (7\text{-}2)$$

TABLE 7-6. Thermochemical properties of the γ and δ lactones used as standards[a]

	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}	A	B	C	T/K(range)
γ-hexanolactone[17]	57.2±0.3	288.7	79641.4	62.7	283-353
δ-octanolactone[17]	67.0±0.2	310.7	90681.9	79.2	288-353
γ-nonanolactone[18]	70.3±0.3	325.1	96899.9	89.2	296-363
δ-nonanolactone[17]	70.7±0.4	323.6	96826.6	87.6	293-348
γ-decanolactone[18]	75.6±0.3	342.0	104666.1	97.5	298-365
δ-decanolactone[17]	74.2±0.3	332.6	102792.2	95.9	309-358

[a] A, B, and C are constants of equation 7-2.

7.2.7.3. Insect Pheromones. The standards used in these experiments and their vaporization enthalpies and constants for calculation of their vapor pressures, eq 7-1 and 1-10 are provided in Table 7-7. The constants used for the Clarke and Glew equation, eq 7-1, are those for θ /K = 298.15.[19] The constants for equation 1-10 for methyl heneicosanoate were derived previously from standards whose vapor pressures were calculated from equation 7-1 but evaluated by correlation gas chromatography.[20]

TABLE 7-7. Vaporization Enthalpies and Vapor Pressure Constants for Equations 7-1 and 1-10 (p_o = 101325)

Standards Eq 7-1: θ/K = 298.15[a]	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}	$\Delta_l^g G_m$(298 K) kJ·mol^{-1}	$\Delta_l^g Cp$(298 K) J·mol^{-1}·K^{-1}		
Methyl decanoate	66.10±0.17	-4.26±0.05	-83		
Methyl dodecanoate	76.59±0.41	1.33±0.10	-101		
Methyl tetradecanoate	85.94±0.76	6.73±0.15	-119		
Methyl pentadecanoate	89.29±0.79	9.07±0.4	-128		
Methyl octadecanoate	105.7±3.8	17.68±0.23	-155		
Methyl eicosanoate	116.43±1.5	22.74±0.27	-172		
Eq 1-10[b]		A·10^{-6}	B·10^{-4}	C	D
Methyl heneicosanoate	120.90±1.8	420.126	-523.876	5943.62	1.2615

[a] From Ref 19. [b] From Ref 20.

7.3. Results and Discussion

7.3.1. Saturated and Unsaturated Fatty Acids.

7.3.1.1. Vaporization Enthalpy Results. The correlation between enthalpies of transfer of the standards as determined by gas chromatography, $\Delta_{trn}H_m(T_m)$, and their literature vaporization enthalpies at T/K = 298.15 for two of the four runs conducted are summarized in Table 7-8.

TABLE 7-8. A Summary of the Correlation Between Enthalpies of Transfer and Vaporization Enthalpies

Run 1	-slope T/K	intercept	$\Delta_{trn}H_m$(490 K) kJ·mol^{-1}	$\Delta_l^gH_m$ (298 K) kJ·mol^{-1} (lit)	$\Delta_l^gH_m$ (298 K) kJ·mol^{-1} (calc)
tetradecanoic acid	8683.5	17.806	72.19	111.3±2.2	110.6±6.6
hexadecanoic acid	9442.1	18.728	78.5	120.7±2.3	121.9±6.8
(9Z)-hexadecenoic acid	9549.0	18.816	79.39		123.5±6.8
(9Z)-octadecenoic acid	10185.6	19.538	84.68		132.9±7.1
eicosanoic acid	10848.7	20.399	90.19	143.6±2.5	142.8±7.3
arachidonic acid[a]	10984.5	20.254	91.32		144.8±7.3
docosanoic acid	11668.7	21.372	97.01	154.7±7.3	155.0±7.6
Run 3	-slope T/K	intercept	$\Delta_{trn}H_m$(501 K) kJ·mol^{-1}	$\Delta_l^gH_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^gH_m$(298 K) kJ·mol^{-1} (calc)
hexadecanoic acid	9239.2	18.293	76.81	120.7±2.3	120.7±2.3
(6Z)-octadecenoic acid	9842.6	18.848	81.83		130.9±2.3
(9Z,12Z)-octadecadienoic acid	10043.8	19.086	83.59	134.1±10.3	134.3±2.4
eicosanoic acid	10578.9	19.829	87.95	143.6±2.5	143.3±2.4
(11Z)-eicosenoic acid	10589.8	19.760	88.04		143.5±2.4
(13Z)-docosenoic acid	11245.4	20.512	93.49	154.5±7.3	154.6±2.5
tetracosanoic acid	12266.8	22.042	101.98		171.9±2.6
(15Z)-tetracosenoic acid	12260.4	21.941	101.93		171.8±2.6
cervonic acid[b]	11745.5	20.857	97.65		163.1±2.6
hexacosanoic acid	12570.9	22.134	104.51		177.0±2.7

Run 1: $\Delta_l^gH_m(298.15\ \text{K})/\text{kJ·mol}^{-1} = (1.79 \pm 0.06)\ \Delta_{trn}H_m(490\ \text{K}) - (18.4\pm1.1);\ r^2 = 0.9978$ (7-3)

Run 2: $\Delta_l^gH_m(298.15\ \text{K})/\text{kJ·mol}^{-1} = (1.81 \pm 0.05)\ \Delta_{trn}H_m(490\ \text{K}) - (10.9\pm4.3);\ r^2 = 0.9982$ (7-4)

Run 3: $\Delta_l^gH_m(298.15\ \text{K})/\text{kJ·mol}^{-1} = (2.04 \pm 0.02)\ \Delta_{trn}H_m(501\ \text{K}) - (36.0\pm1.6);\ r^2 = 0.9998$ (7-5)

Run 4: $\Delta_l^gH_m(298.15\ \text{K})/\text{kJ·mol}^{-1} = (1.98 \pm 0.014)\ \Delta_{trn}H_m(499\ \text{K}) - (33.9\pm1.3);\ r^2 = 0.9999$ (7-6)

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[a] (5Z,8Z,11Z,14Z)-Eicosatetraenoic acid. [b] (4Z,7Z,10Z,13Z,16Z,19Z)-Docosahexenoic acid.

The details of the other two correlations are given in Appendix G. The linearity of the correlations for all four runs is described by equations 7-3 through 7-6 provided in Table 7-8. Table 7-9 summarizes the results of all four runs. The experimental values of the standards compounds reproduce their literature vaporization enthalpies within ±1.0 $kJ \cdot mol^{-1}$. The reproducibility of the remaining carboxylic acids is within ±2 $kJ \cdot mol^{-1}$. An estimated vaporization enthalpy of each acid is also included in the last column of Table 7-9. It is obvious the gap between the experimental and estimated value increases as the size of the carboxylic acid increases. In spite of this fact, the deviation from pentanoic to hexacosanoic acid varies from 3.2 to 8.2% for an average of 5.5%. Only two of the acids, however, are over-predicted. This implies that the contribution of each methylene group in saturated fatty acids is slightly greater than 4.69 $kJ \cdot mol^{-1}$. The average absolute deviation was 5.3 $kJ \cdot mol^{-1}$. Provided in Appendix G is a comparison of experimental and estimated vaporization enthalpies for most of the C_5 to C_{26} saturated fatty acids adjusted to $T/K = 298.15$.

TABLE 7-9. A Summary of the Results of Runs 1-4

Targets	Run 1	Run 2	Run 3	Run 4	$\Delta_l^g H_m$(298.15 K) kJ·mol^{-1}		
					avg	standards	est
(9Z)-hexadecenoic acid	122.4±5.9	123.5±6.8			123.0±6.4		116.8±5.8
(9Z)-octadecenoic acid	132.2±6.1	132.9±7.1			132.6±6.6		126.2±6.3
(6Z)-octadecenoic acid			130.9±2.3	131.4±1.8	131.2±2.1		126.2±6.3
(11Z)-eicosenoic acid			143.5±2.4	143.4±1.9	143.5±2.2		135.6±6.8
arachidonic acid[a]	145.7±6.3	144.8±7.3			145.3±6.8		135.6±6.8
cervonic acid[b]			163.1±2.6	162.6±2.0	162.9±2.3		145±7.2
tetracosanoic acid			171.9±2.6	169.5±2.0	170.7±2.3		154.4±7.7
(15Z)-tetracosenoic acid			171.8±2.6	169.4±2.0	170.6±2.3		154.4±7.7
hexacosanoic acid			177.0±2.7	177.3±2.0	177.2±2.4		163.7±8.2
Standards							
tetradecanoic acid[c]	110.8±5.6	110.6±6.6			110.7±6.1	111.3±2.2	107.5±5.4
hexadecanoic acid[c]	121.7±5.8	121.9±6.8	120.7±2.3	120.8±1.7	121.3±4.2	120.7±2.3	116.8±5.8
(9Z,12Z)-octadecadienoic acid[d]			134.3±2.4	134.0±1.8	134.2±2.1	134.1±10.3	126.2±6.3
eicosanoic acid[c]	142.7±6.3	142.8±7.3	143.6±2.4	143.5±1.9	143.2±4.5	143.6±2.5	135.6±6.8
(13Z)-docosenoic acid[d]			154.6±2.5	154.6±1.9	154.6±2.2	154.5±7.3	145±7.2
docosanoic acid[d]	155.1±6.5	155.0±7.6			155.1±7.1	154.7±7.3	145±7.2

[a] (5Z,8Z,11Z,14Z)-Eicosatetraenoic acid. [b] (4Z,7Z,10Z,13Z,16Z,19Z)-Docosahexenoic acid. [c] From Ref 10. [d] From Ref 1.

7.3.1.2. Liquid Vapor Pressure Results. Vapor pressure measurements were conducted in the same manner as previously described in Section 1.2.2.2. In this case, since the same standards were used in runs 1 and 2, and likewise in runs 3 and 4, values of t_o/t_a from runs 1 and 2 for each material were evaluated from the corresponding $\ln(t_o/t_a)$ values, averaged and then plotted as $\ln(t_o/t_a)_{avg}$ against $\ln(p/p_o)_{std}$ of the standards; similarly for runs 3 and 4. The linearity of the plots at T/K = 298.15 is illustrated by equations 7-7 and 7-8 listed below Table 7-10.

TABLE 7-10. The Correlation Between $\ln((t_o/t_a)_{std}$ and $\ln(p/p_o)_{std}$ for Runs 1 and 2 and Runs 3 and 4 at T/K = 298.15

Runs 1 and 2	$\ln(t_o/t_a)_{run\ 1}$	$\ln(t_o/t_a)_{run\ 2}$	$\ln(t_o/t_a)_{avg}$	$\ln(p/p_o)_{std}$	$\ln(p/p_o)_{calc}$	p_l/Pa·10^8 This work/Lit
tetradecanoic acid	-11.319	-10.83	-11.04	-18.65	-18.7±0.5	(78100±49100)/83800[10]
hexadecanoic acid	-12.941	-12.398	-12.63	-20.80	-20.8±0.5	(9200±5600)/10200[10]
(9Z)-hexadecenoic acid	-13.211	-12.579	-12.85		-21.1±0.5	(6900±4200)/NA[c]
(9Z)-octadecenoic acid	-14.625	-14.011	-14.27		-23.0±0.5	(1010±600)/NA[c]
eicosanoic acid	-15.988	-15.425	-15.67	-25.05	-24.9±0.5	(155±90)/130[1]
arachidonic acid[a]	-16.588	-16.108	-16.32		-25.8±0.6	(65±37)/NA[c]
docosanoic acid	-17.765	-17.163	-17.42	-27.16	-27.3±0.6	(15±8)/NA[c]

Runs 3 and 4	$\ln(t_o/t_a)_{run\ 3}$	$\ln(t_o/t_a)_{run\ 4}$	$\ln(t_o/t_a)_{avg}$	$\ln(p/p_o)_{std}$	$\ln(p/p_o)_{calc}$	p_l/Pa·10^8
hexadecanoic acid	-12.70	-12.82	-12.76	-20.8	-20.8±0.1	(9410±8500)/10230[10]
(6Z)-octadecenoic acid	-14.60	-14.71	-14.24		-22.9±0.1	(1130±1000)/NA[c]
(9Z,12Z)-octadecadienoic acid	-15.65	-15.81	-14.66	-23.49	-23.5±0.1	(627±560)/640[1]
eicosanoic acid	-17.21	-17.38	-15.73	-25.05	-25.0±0.1	(135±120)/130[1]
(11Z)-eicosenoic acid	-14.16	-14.33	-15.83		-25.2±0.1	(118±105)/NA[c]
(13Z)-docosenoic acid	-15.76	-15.90	-17.29	-27.26	-27.3±0.1	(14.7±13)/10.0[1]
tetracosanoic acid	-19.10	-19.12	-19.11		-29.9±0.1	(1.1±1.0)/NA[c]
(15Z)-tetracosenoic acid	-19.18	-19.19	-19.19		-30.0±0.1	(1.0±0.9)/NA[c]
cervonic acid[b]	-18.54	-18.69	-18.61		-29.1±0.1	(2.2±2.0/NA[c]
hexacosanoic acid	-20.03	-20.26	-20.14		-31.3±0.1	(0.25±0.22)/NA[c]

$\ln((p/p_o)_{runs\ 1\&2} = (1.347 \pm 0.026) \ln(t_o/t_a)_{avg} - (3.807 \pm 0.38)$ $r^2 = 0.9993$ (7-7)

$\ln(p/p_o)_{runs\ 3\&4} = (1.426 \pm 0.005) \ln(t_o/t_a)_{avg} - (2.606 \pm 0.079)$ $r^2 = 0.9999$ (7-8)

[a](5Z,8Z,11Z,14Z)-Eicosatetraenoic acid. [b](4Z,7Z,10Z,13Z,16Z,19Z)-Docosahexenoic acid. [c]Not Available.

The vapor pressure measurements were repeated from T/K = (298.15 to 500) at 10K intervals. The correlations at all temperatures were characterized with r^2 greater than 0.99. The resulting values of $\ln(p/p_o)$ as a function of $1/T$ of both the targets and standards were then fit to eq 1-10. The constants of eq 1-10 for both the standard and target compounds are listed in Table 7-11. Comparisons of boiling temperature predictions of eq 1-10 with either experimental or estimated values are also losted in the last two columns of this table.

TABLE 7-11. The Constants for Equation 1-10 and Predicted Boiling Temperatures

Targets: Runs 1 & 2	$\cdot 10^{-8}\cdot A/K^3$	$10^{-6}\cdot B/K^2$	$10^{-3}\cdot C/K$	D	$T_\mathrm{b}/\mathrm{K}_\mathrm{calc}$	$T_\mathrm{b\ lit}$
(9Z)-hexadecenoic acid	4.805	-5.317	5.139	3.345	628.7	636.8[a]
(9Z)-octadecenoic acid	5.110	-5.680	5.528	3.051	651.4	633[b,c], 658.8[d,e]
arachidonic acid[f]	5.664	-6.313	6.515	2.010	694.8	680.4[a], 692.8[b,c]
Standards: Runs 1 & 2						
tetradecanoic acid	4.396	-4.863	4.705	3.659	598.7	599
hexadecanoic acid	4.707	-5.234	4.999	3.529	622.2	622.3
eicosanoic acid	5.313	-5.961	5.652	3.155	666.1	670.9
docosanoic acid	5.650	-6.373	6.003	2.975	689.5	688.2
Targets: Runs 3 & 4						
(6Z)-octadecenoic acid	5.213	-5.749	5.748	2.805	653.1/518.8[g]	658.8[d,e]/510.7[b,e,g]
(11Z)-eicosenoic acid	5.506	-6.126	6.043	2.703	675	699±14[a]
tetracosanoic acid	5.942	-6.772	6.159	3.251	702	679±8.0[a], 725[e]
(15Z)-tetracosenoic acid	6.031	-6.851	6.391	2.912	709.5	752±14[a]
cervonic acid[h]	6.256	-6.978	7.231	1.494	735.5	NA[i]
hexacosanoic acid	6.303	-7.147	6.797	2.494	729.1	692±8.0[a], 748[e]
Standards Runs 3 & 4						
hexadecanoic acid	4.809	-5.293	5.115	3.450	622.4	622.3[j]
(9Z,12Z)-octadecadienoic acid	5.305	-5.682	5.884	2.688	660.4	661.2[k]
eicosanoic acid	5.418	-6.046	5.816	3.029	667.8	670.9[k]
(13Z)-docosenoic acid	5.802	-6.493	6.373	2.518	696.4	695.9[k]

[a]Estimate, ACD Labs from SciFinder Scholar, Ref 15. [b]Experimental properties. [c]Scifinder Scholar, Ref 15. [d]Estimate. [e]EPIWEB, Ref 16. [f](5Z,8Z,11Z,14Z)-Eicosatetraenoic acid. [g]Boiling temperature at $p/\mathrm{Pa} = 2400$. [h](4Z,7Z,10Z,13Z,16Z,19Z)-Docosahexenoic acid. [i]Not available. [j]Ref 10. [k]Ref 1.

7.3.1.3. Fusion Enthalpy Results. The fusion enthalpies measured in this study are listed in Table 7-12.

TABLE 7-12. Temperature Adjustments of Fusion or Total Phase Change Enthalpy

	T_{fus}/K	$\Delta H_{\mathrm{tpce}}(T_{\mathrm{fus}})^{a}$ kJ·mol^{-1}	C_p(l)/C_p(cr) J·mol^{-1}·K^{-1}	$\Delta C_p\ \Delta T$ kJ·mol^{-1}	$\Delta H_{\mathrm{tpce}}(298\ \mathrm{K})^{a}$ kJ·mol^{-1}
(9Z)-hexadecenoic acid	275.2	$32.1^{b,c}$	560.7/455.3	0	32.1 (275.2 K)
(6Z)-octadecenoic acid	303.7/302.7	$47.5^{b,c}/59.9^{b,d}$	624.5/509.1	(-0.5/-0.4)±0.1	(47/59.5)±0.1
(9Z)-octadecenoic acid	289.4	$57.9^{b,c}$	624.5/509.1	0	57.9 (289 K)
(11Z)-eicosenoic acid	296.5	$49.7^{b,c}$	688.5/562.5	0	49.7 (297 K)
(13Z)-docosenoic acid	307.2	$54.0^{b,c}$	752.1/616.7	-1.0±0.3	53.0±0.3
(15Z)-tetracosenoic acid	315±0.3	$60.3\pm0.5^{b,e}$	816.1/670.5	-2.0±0.6	58.3±0.8
tetracosanoic acid	356.5±0.2	$89.4\pm0.5^{e,f}$	824.1/681.5	-7.1±2.1	82.3±2.2
hexacosanoic acid	358.8±0.3	$88.5\pm1.0^{e,g}$	887.9/735.3	-7.9±2.4	80.6±2.6

[a] Total phase change enthalpy of solid-liquid and any solid-solid transitions occurring between T/K = (298.15 and T_{fus}). [b] Fusion enthalpy. [c] Reference 21, 22. [d] Ref 23. [e] This work. [f] Sum of the fusion peak ($\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}(T_{\mathrm{fus}})$/kJ·mol^{-1} = (84.5 ± 0.5) and two broad overlapping peaks centered at approximately T_{t}/K = (347 and 351), ($\Delta_{\mathrm{cr}}^{\mathrm{cr}}H_{\mathrm{m}}(T_{\mathrm{t}})$/kJ·mol^{-1} = (4.94±0.1). [g] Sum of an overlapping transition at T_{t}/K = (354.3±0.1) and the fusion peak.

Previous literature results reported for several of the acids studied as summarized by Sato et al.[16] are also listed in this table. Additional solid-solid phase transitions and/or polymorphism are exhibited by many of the saturated and unsaturated fatty acids including those in this table. The compounds, (9Z)-hexadecenoic acid (palmitoleic acid) and (9Z)-octadecenoic acid (oleic acid) are liquids at T/K = 298.15 but since they melt very close to this temperature their fusion enthalpies are also included. Two recent fusion enthalpy values are available for (6Z)-octadecenoic acid (petroselinic acid, $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}(T_{\mathrm{fus}})$/ kJ·mol^{-1}, T_{fus}/K: 47.5, 303.7;[22] 59.9, 302.7[23]). This compound is known to exhibit polymorphism where the low melting form can switch to the higher one upon melting.[22] Both values are listed in the table since it is unclear if the two values reported represent fusion properties of the two polymorphs. Also included in Table 7-12 are temperature adjustments to T/K = 298.15 for acids which melt above room temperature. (13Z)-Docosenoic (erucic acid) and (15Z)-tetracosenoic acids (nervonic acid) did not exhibit any solid-solid phase transitions between T/K = (298.15 and T_{fus}). Transitions are known to occur at lower temperatures, however, for erucic acid.[21] The total phase change enthalpy reported for the four compounds just discussed, $\Delta_{\mathrm{tpce}}H_{\mathrm{m}}$, refers to the fusion enthalpy. Additional transitions were shown by both tetracosanoic and hexacosanoic acids. With the base line resolved from the fusion transition, two overlapping solid-solid phase transitions for tetracosanoic acid (lignoceric acid) appeared at around T/K = (346 and 350). The solid-solid phase transition overlapped with the fusion peak for hexacosanoic acid (cerotic acid). The total enthalpy change is listed for these two compounds in column 2 of Table 7-12. See Appendix G for additional details.

7.3.1.4. Vaporization Enthalpy Discussion. De Kruif and Oonk[24] and De Kruif et al.[10] have previously studied the vaporization enthalpies of linear saturated fatty acid from C_5 to C_{20}. All vaporization enthalpies have been measured at different temperatures. The vaporization enthalpies from C_5 to C_{13} determined by torsion-mass effusion have been adjusted to T/K = 298.15 and compared to the larger values acquired by correlation in order to compare the results acquired in this and previous work[1] by correlation as a function of carbon number. Temperature adjustments are listed in Appendix G. Figure 7-4 shows how these values correlate as a function of the number of carbon atoms.

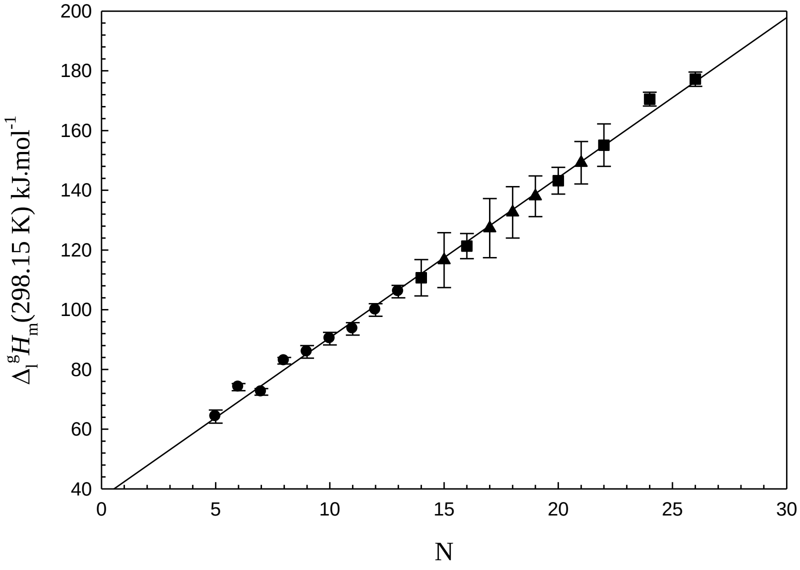

Figure 7-4. The vaporization enthalpies of the saturated fatty acids and their uncertainties as a function of the number of carbon atoms, N. Circles(●): from Ref 10; squares (■): this work; triangles (▲): from Ref 1. The equation of the line is given by $\Delta_l^gH_m$(298.15 K/kJ·mol^{-1} = (5.36±0.076)·N + (37.07±1.22); r^2 = 0.9963.

The circles represent those values measured by torsion and mass effusion. The squares and triangles distinguish values determined by correlation in this and in previous work, respectively.[1] Using values of the saturated C_{14} to C_{20} fatty acids derived from the torsion-mass effusion studies reported by De Kruif et al. as standards[10,24], all the vaporization enthalpies determined by correlation have been indirectly derived. A numerical comparison of the two sets of vaporization enthalpy results is listed in Appendix G. Since they are highly dimerized, carboxylic acids smaller than pentanoic acid are not listed.[10] The vaporization enthalpies seem to differ linearly as a function of the number of carbon atoms.

Various unsaturated fatty acids have been investigated by correlation gas chromatography, as well. Their relationship between carbon number and vaporization enthalpy is shown in Figure 7-5.

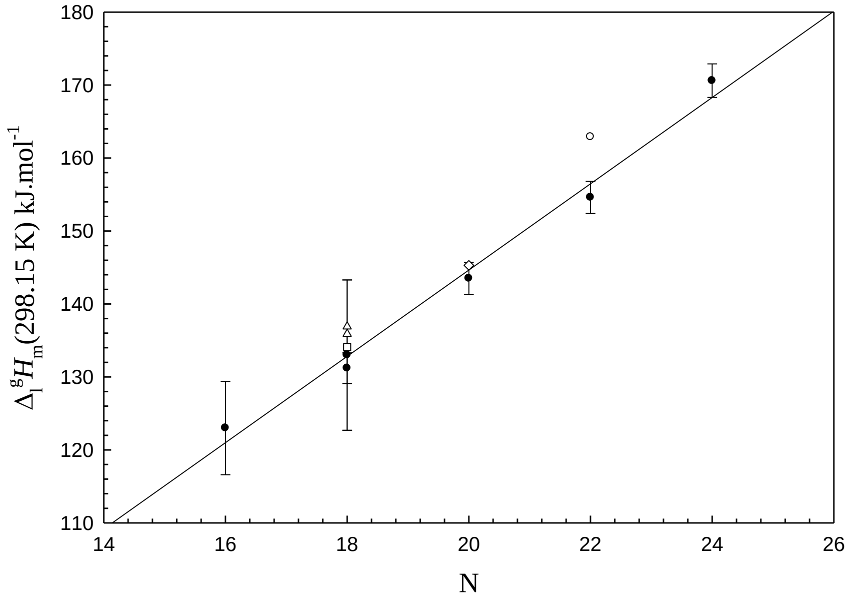

Figure 7-5. Vaporization enthalpies of the unsaturated fatty acids as a function of the number of carbon atoms, N. Circles (●): mono-unsaturated fatty acids and their uncertainties; square (□): linoleic acid (diene); triangles: α and γ linolenic acids (trienes); diamond (◊): arachidonic acid (tetraene); circle (○): cervonic acid (hexaene). The line represents the mono-unsaturated fatty acids and is given by: $\Delta_l{}^g H_m$(298.15 K/kJ·mol^{-1} = (5.91±0.27)·N + (26.4±5.3); (r^2 = 0.9896).

The vaporization enthalpies of six mono-unsaturated fatty acids are represented by the solid circles. These also seem to differ linearly with carbon number. Small differences, however, are seen between isomers which vary in regards to the location of the double bond. Listed in Table 7-9 is the identity of each mono-unsaturated carboxylic acid. The vaporization enthalpy also seems to be affected by the degree of unsaturation. A single double bond does not seem to impart much effect, but it increases as the degree of unsaturation increases. With its six double bonds, (4Z,7Z,10Z,13Z,16Z,19Z)-Docosahexenoic acid (cervonic acid) is represented by the circle in Figure 7-5 and has a vaporization enthalpy noticeably larger than (13Z)-docosenoic acid, and docosanoic acid, $\Delta_l{}^g H_m$(298.15 K)/ kJ·mol^{-1} = (162.9 ± 2.3) compared to (154.5 ± 7.3) and (154.7 ± 7.3), respectively. An increase in the available surface area is probably the result of the rigidity and planarity associated with the two or more sp^2 hybridized carbon atoms. The efficacy of dipole-dipole and/or other dispersive interactions may also be increased by the polarizability of the π cloud. More effective intermolecular interactions are the result of both effects. Longer gas chromatographic retention times than their saturated parents are also the result.

7.3.1.5. Liquid Vapor Pressure Discussion. The vapor pressures of both the standard and target compounds at T/K = 298.15 are given in the last column of Table 7-10 along with the original values used as standards. In the case of tetra- and hexadecanoic acids, the comparisons are to the vapor pressures evaluated directly from the equation of Clarke and Glew. For the other standard compounds, the vapor pressures are compared to those previously determined by correlation using results evaluated from eq 1-10 as standards.[1] These values of the standard compounds in the form $\ln(p/p_o)$ are reproduced within the uncertainties reported. In Figure 7-6, vapor pressures in the form $\ln(p/p_o)$ have been plotted against the number of carbon atoms at T/K = 298.15 in order to evaluate how well the results for the saturated fatty acids acquired by correlation compare with other homologues.

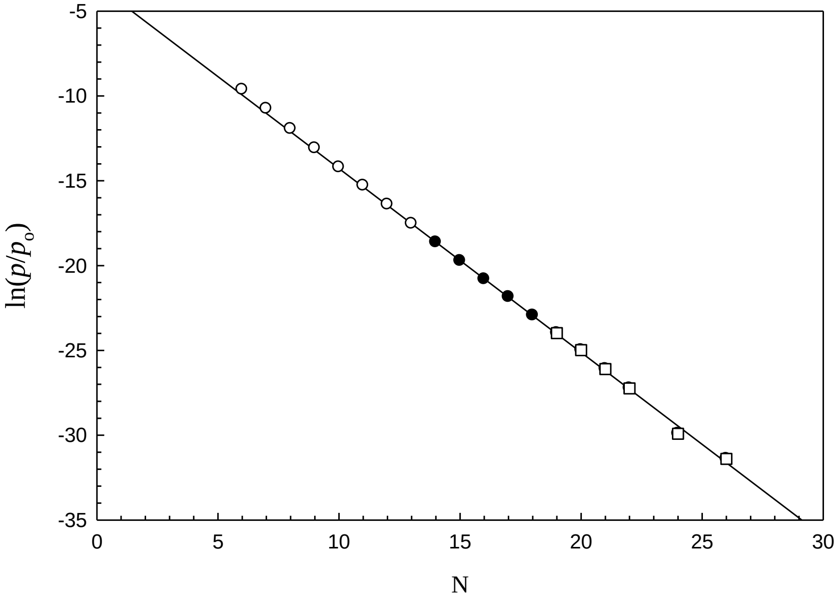

Figure 7-6. Liquid vapor pressures of the saturated carboxylic acids as a function of the number of carbon atoms, N. Circles (○), vapor pressures of the fatty acids calculated directly from the equation of Clark and Glew as reported by De Kruif et al.;[10] circles (●): vapor pressures calculated by correlation using the values of C_{14} to C_{18} as standards;[1] squares (□): extrapolated vapor pressures obtained by correlation (Ref 1 and this work). The eq of the line using all the data is given by: $\ln(p/p_o) = -(1.095 \pm 0.006) \cdot N - (3.2 \pm 0.09)$, ($r^2 = 0.9996$); p_o/Pa = 101325.

For the C_6 to C_{13} acids, vapor pressures were determined directly from the constants of the Clark and Glew[10] equation. Values illustrated by the solid circles for saturated C_{14} to C_{18} acids are vapor pressures acquired by correlation in this or in previous work.[1] All data was determined from values acquired by correlation using vapor pressures evaluated from the equation of Clarke and Glew as standard compounds. The squares are representative of extrapolated values acquired by correlation also using the saturated C_{14} to C_{18} acids as standard compounds and the results seem to be rather linear. The constants of the Clarke and Glew equation and those of eq 1-10 used to evaluate the $\ln(p/p_o)$ values in this figure are provided in Appendix G. In Figure 7-7, liquid vapor pressures of the unsaturated fatty acids in the form of $\ln(p/p_o)$ are plotted against carbon number. All values have been determined by correlation in this study or in previous work.[1] The mono-unsaturated acids are represented by solid circles. Dienoic acid (linoleic acid) is represented by a diamond. The hollow circles signify two trienoic acids (α and γ-linolenic acids). The square is representative of a tetraenoic acid (arachidonic acid). The triangle represents a hexaenoic acid (cervonic acid). An increase in intermolecular interactions and a decrease in volatility are commonly caused by an increase in unsaturation. This is also seen with the corresponding vaporization enthalpies. In addition, the volatility of the acid may be minimally affected by the location of an internal non-conjugated double bond in the mono-unsaturated acids.

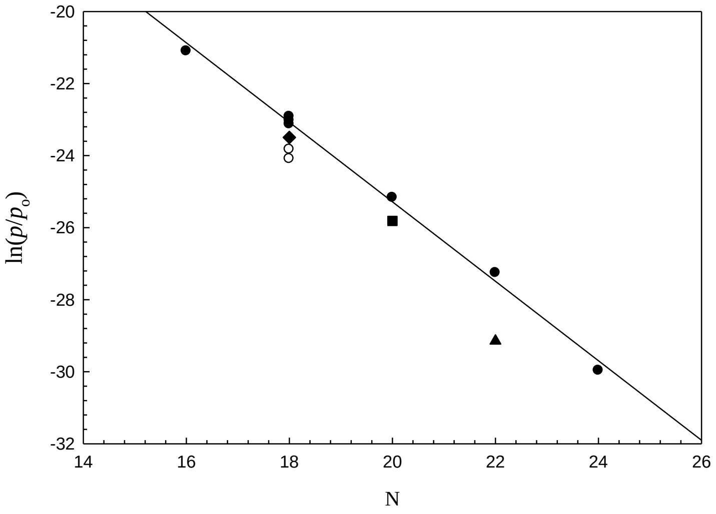

Figure 7-7. Liquid vapor pressures of the unsaturated carboxylic acids as a function of the number of carbon atoms, N. Circles (●), vapor pressures of the mono-unsaturated fatty acids; diamond (◊), linoleic acid (diene); circles (○), vapor pressures of α and γ linolenic acids (trienes); square (□): arachidonic acid (tetraene); triangle (▲): cervonic acid (hexaene). The equation of the line for the mono-unsaturated acids is given by: $\ln(p/p_o) = -(1.10 \pm 0.031)\cdot N - (3.20 \pm 0.61)$, ($r^2 = 0.9960$); p_o/Pa = 101325.

7.3.1.6. Sublimation Enthalpy Discussion. Some of the fatty acids in this work are solids near or above ambient temperature. Sublimation enthalpies of several of the compounds studied are reported in column 4 of Table 7-13 by using the vaporization enthalpies at T/K = 298.15 reported in Table 7-9 according to eq 7-9 in combination with the literature fusion or total phase change enthalpies adjusted to T/K = 298.15 reported in Table 7-12. These three thermodynamic phenomena are related by the following equation, provided they have been adjusted to the same temperature, T:

$$\Delta_{\mathrm{cr}}{}^{\mathrm{g}}H(T) = \Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}(T) + \Delta_{\mathrm{cr}}{}^{\mathrm{l}}H(T) \qquad (7\text{-}9)$$

Where $\Delta_{\mathrm{cr}}{}^{\mathrm{g}}H(T)$ is the sublimation enthalpy, $\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}(T)$ is the vaporization enthalpy and $\Delta_{\mathrm{cr}}{}^{\mathrm{l}}H(T)$ is the fusion enthalpy.

TABLE 7-13. A Comparison of Sublimation Enthalpies and Solid –Liquid Vapor Pressures

	ΔH_{tpce}(298 K) kJ·mol^{-1}	$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298 K) kJ·mol^{-1}	$\Delta_{\mathrm{cr}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298 K)^{a} kJ·mol^{-1}	$\Delta_{\mathrm{cr}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298 K)^{b} kJ·mol^{-1}	$(p_{\mathrm{cr}}{}^{298c}/p_{\mathrm{l}}{}^{298}/\mathrm{Pa})\cdot 10^{8}$
(9Z)-hexadecenoic acid	32.1^{cd}	120.0±6.4^{cd}	152.1±6.4 ^{cd}		123/(123±75)^{d}
(6Z)-octadecenoic acid	47/59.5	131.2±2.1	(178.2/190.7)± 2.1	173.9/186.3	845, 784/(1130±1000)
(9E)-octadecenoic acid^{e}			189.8±10.3	185.5	220/(930±500)
(9Z)-octadecenoic acid	57.9^{f}	131.1±6.6^{f}	189±6.6^{f}		213/(213±120)^{f}
(11Z)-eicosenoic acid	49.7^{g}	143.2±2.2^{g}	192.9±2.2^{g}		95/(118±105)^{g}
(13Z)-docosenoic acid	53.0±0.3	154.5±7.3	207.5±7.3	200	7.8/(14.7±13)
(15Z)-tetracosenoic acid	58.3±0.8	156.9±2.3	228.9±2.4	218.9	0.27/(1.0±0.9)
tetracosanoic acid	82.3±2.2	170.7±2.3	253±3.2	243.6	0.004/(1.1±1.0)/
hexacosanoic acid	80.6±2.6	177.2±2.4	257.8±3.5	248.1	0.0008/(0.25±0.22)

[a]Sublimation enthalpy calculated by combining ΔH_{tpce}(298 K) or ($\Delta_{\mathrm{cr}}{}^{\mathrm{l}}H_{\mathrm{m}}$(298 K), (Table 7-12) with $\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298 K) (Table 7-9). [b]Sublimation enthalpy calculated using vapor pressures calculated according to eq 7-10 at T/K = 298.15 or as indicated. [c]Sublimation vapor pressures are believed know accurate to within a factor of three ref. 20. [d]At T_{fus}/K = 275.2. [e]From Ref 1. [f]At T_{fus}/K = 289.4. [g]At T_{fus}/K = 296.5.

The vaporization enthalpies were corrected to the suitable temperature using eq 1-3 for those compounds which melt somewhat below T/K = 298.15. For (6Z)-octadecenoic acid, two sublimation enthalpies are evaluated and the two values vary significantly. The sublimation enthalpies are quite large with the value for hexacosanoic acid among the largest on record[25], which is expected for carboxylic acids of this size. Both correlation gas chromatography and differential scanning calorimetry have previously been used to determine the sublimation enthalpies for most of the saturated fatty acids discussed in this work. Davies and Malpass[26] have also previously investigated the even C_{14} to C_{22} fatty acids by mass effusion. A comparison of results from this work with those evaluated using values from Davies and Malpass adjusted to *T*/K = 298.15 is displayed in Figure 7-8. Appendix G provides a summary of the sublimation enthalpies used to build Figure 7-8. The sublimation enthalpy reported by this group is slightly smaller than the values calculated using eq 7-9, with the exception of eicosanoic acid. It should be noted, however, that the sublimation enthalpy values of Davies and Malpass previously adjusted to *T*/K = 298.15 by our laboratory in Table 14 of reference 1 were reported in error. The corrected temperature adjusted values are reported in Appendix G.

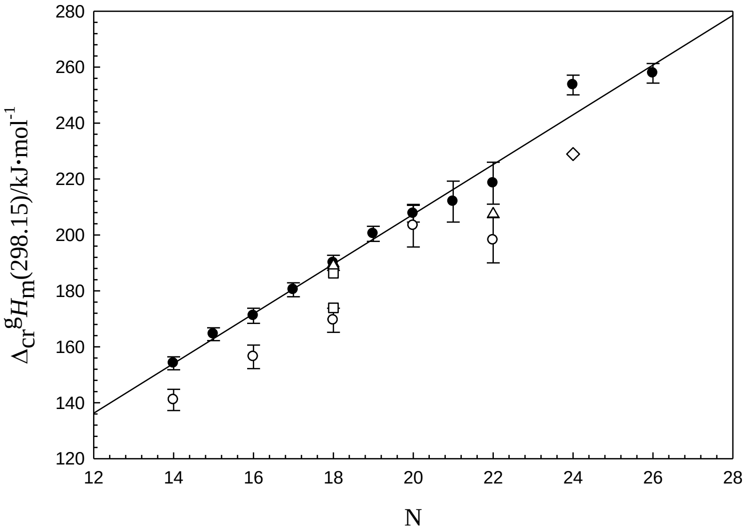

Figure 7-8. Sublimation enthalpies of the crystalline fatty acids at *T*/K = 298.15 calculated from vaporization enthalpies from Table 7-9 and fusion enthalpies from Table 7-12 as a function of the number of carbon atoms. Circles (●): sublimation enthalpies evaluated from a combination of correlation gas chromatography and DSC; circles (○): sublimation enthalpies adjusted to *T*/K = 298.15 using the mass effusion studies of Davies and Malpass.[26] Squares (□): two sublimation enthalpies for (6Z)-octadecenoic acid; triangles (Δ): (9E)-octadecenoic acid, (13Z)-docosenoic acid; diamond (◊): (15Z)-tetracosenoic acid, respectively. The equation of the line associated with the saturated

fatty acids (solid circles) is given by: $\Delta_l{}^g H_m$(298.15 K)/kJ·mol^{-1} = (8.87 ± 0.38)N + (29.9 ± 7.6), (r^2 = 0.9842).

Sublimation enthalpies at T/K = 298.15 for four mono-unsaturated fatty acids, (6Z)-octadecenoic, (9E)-octadecenoic, (13Z)-docosenoic, and (15Z)-tetracosenoic acids are also listed in Figure 7-8. Although unsaturated fatty acids seem to have somewhat larger vaporization enthalpies, all sublimation enthalpies tend to be similar or smaller than the corresponding saturated acid. At T/K = 298.15, differences of (11.8 ± 3.4 and/or -0.7 ± 3.4), (0.3 ± 10.6), (10.9 ± 10.5) and (24.1 ± 4.0) kJ·mol^{-1} are seen in the sublimation enthalpy between the saturated and unsaturated fatty acids for (6Z)-octadecenoic, (9E)-octadecenoic (13Z)-docosenoic, and (15Z)-tetracosenoic acids, respectively. The effect on the sublimation enthalpy is probably due to the effect of packing on the fusion enthalpy initiated by the kink in the chain by the double bond. It's unclear though, if the total solid to liquid phase change enthalpy from T/K = (0 to T_{fus}) would differ substantially since many of these acids have additional phase transitions occurring at lower temperatures.

7.3.1.7. Sublimation Vapor Pressure Discussion. The vapor pressures of the liquid and solid converge at the triple point, which is closely approximated by the fusion temperature. Sublimation enthalpies at the respective fusion temperatures for those fatty acids which are solid near or above room temperature are the result of combining the vaporization enthalpies evaluated at their mean fusion temperatures using the Clausius-Clapeyron equation with their respective vapor pressures evaluated from the constants of eq 1-10 and their fusion enthalpies. A second application of the Clausius-Clapeyron equation gives a means to evaluate their respective solid vapor pressures, p_{cr}, at room temperature, eqs 7-10 and 7-11. This is done by including their sublimation enthalpy, an adjustment for the heat capacity contribution to the sublimation enthalpy and the vapor pressure common to both phases.

$$\ln(p_{\mathrm{cr}}^{(298)}) \;=\; [\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}(T_{\mathrm{fus}}) + \Delta C_p(\mathrm{cr})\Delta T][\,1/T_{\mathrm{fus}}\,/\mathrm{K} - 1/298.15]/\mathrm{R} + \ln(p_{\mathrm{cr}}^{T_{\mathrm{fus}}})) \qquad (7\text{-}10)$$

$$\text{where}\;\; \Delta C_p(\mathrm{cr})\Delta T = (0.75 + 0.15\; C_p(\mathrm{cr}))((T_{\mathrm{fus}}/\mathrm{K}\; {-298.15}\;\mathrm{K})/2) \qquad (7\text{-}11)$$

When compared to vapor pressures which have been directly determined, this procedure has been shown to reproduce vapor pressures within a factor of three.[27] Columns 4 and 5 of Table 7-13 also compare sublimation enthalpies at T/K = 298.15 evaluated by two different methods in order to determine how well the vapor pressures of the crystalline phase are evaluated by this procedure. The values in column 4 of the table were determined by combining vaporization enthalpies acquired through correlation (Table 7-9) with fusion enthalpies at T/K = 298.15 (Table 7-12). The values in column 5, however, were determined using the solid vapor pressures evaluated according to eq 7-10 at a mean temperature of T/K = 298.15. In this instance, the largest discrepancy between the two methods is 10 kJ·mol^{-1} in a value of more than 200 kJ·mol^{-1}. Between the two methods, the former one is probably more accurate. This is because the vaporization enthalpies of the standards are commonly known with more accuracy than their vapor pressures. The latter method is usually determined by extrapolation. The second method does, however, provide a means to internally check the accuracy of the correlation between $\ln(p/p_{\mathrm{o}})$ and $\ln(t_{\mathrm{o}}/t_{\mathrm{a}})$ of the standards.

The vapor pressures of the liquid and crystalline phases at T/K = 298.15 of the saturated and unsaturated fatty acids investigated are compared in the last column of Table 7-13. The vapor pressure ratio of the liquid to solid differs from roughly 1.4/1 for (6Z)-octadecenoic acid to 300/1 for hexacosanoic acid. The vapor pressure of the solid and liquid are identical at their fusion temperature for (9Z)-hexadecenoic acid, (9Z)-octadecenoic acid, and (11Z)-eicosenoic acid, compounds which melt near but below room temperature. Unlike their liquid counterparts, sublimation vapor pressures of the unsaturated acids generally seem to be slightly more volatile than their saturated relatives. A summary of the vapor pressures of several saturated and corresponding unsaturated derivatives are listed in Appendix G.

7.3.2. γ and δ-Lactones.

7.3.2.1. Vaporization Enthalpies. A good linear relationship is acquired for the correlation between $\Delta H_{\mathrm{trn}}(T_{\mathrm{m}})$ and $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ (298.15 K) if suitable standards are chosen, despite the fact that the two enthalpies are referenced to different temperatures. This correlation is shown in Figure 7-9 for the lactones used as standards in run 1. The details of two correlations are summarized in Tables 7-14 and 7-15 and equations 7-12 and 7-13 listed below each respective table. The results of both runs are summarized and compared to the literature values in Table 7-16. The vaporization enthalpies of the standards are reproduced with an uncertainty of ±1.3 $\mathrm{kJ \cdot mol^{-1}}$ (2σ), in spite of the uncertainty of approximately 4 $\mathrm{kJ \cdot mol^{-1}}$ evaluated from the correlation equations.

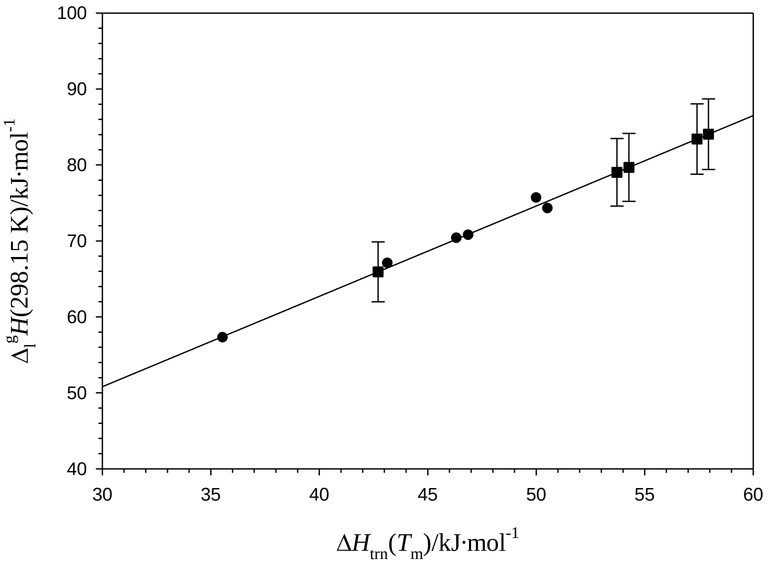

Figure 7-9. The correlation observed between the vaporization enthalpy, $\Delta_l{}^g H_m(T_m)$, and the enthalpy of transfer, $\Delta H_{trn}(T_m)$, for run 1. The line represents the results of a linear regression analysis of the standards (circles). The squares (and their associated uncertainties) are the vaporization enthalpies calculated for the targets.

TABLE 7-14. The correlation of enthalpies of transfer with vaporization enthalpies for Run 1

Run 1	- slope T/K	Intercept	ΔH_{trn}(434 K) kJ·mol^{-1}	$\Delta_l{}^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l{}^g H_m$(298 K) kJ·mol^{-1}(calc)
γ-hexanolactone	-4254.4	10.338	35.37	57.2±0.3	57.5±3.6
γ-octanolactone	-5115.1	11.381	42.52		65.9±3.9
δ-octanolactone	-5169.5	11.362	42.98	67.0±0.2	66.5±3.9
γ-nonanolactone	-5555.6	11.927	46.19	70.3±0.3	70.3±4.0
δ-nonanolactone	-5624.2	11.941	46.76	70.7±0.4	70.9±4.1
γ-decanolactone	-6003.5	12.49	49.91	75.6±0.3	74.7±4.2
δ-decanolactone	-6063.8	12.495	50.41	74.2±0.3	75.2±4.2
γ-undecanolactone	-6450.8	13.057	53.63		79.1±4.4
δ-undecanolactone	-6513.9	13.07	54.15		79.7±4.4
γ-dodecanolactone	-6896.6	13.622	57.34		83.4±4.6
δ-dodecanolactone	-6961.5	13.641	57.88		84.1±4.6

$\Delta_l{}^g H_m$(298.15 K)/kJ·mol^{-1} = (1.18±0.062)ΔH_{trn}(434 K) + (15.62±2.8) $r^2 = 0.9890$ (7-12)

TABLE 7-15. The correlation of enthalpies of transfer with vaporization enthalpies for Run 2

Run 2	- slope T/K	Intercept	ΔH_{trn}(434 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)
γ-hexanolactone	-4279.8	10.387	35.58	57.2±0.3	57.2±3.7
γ-octanolactone	-5137.4	11.424	42.71		66.1±3.9
δ-octanolactone	-5192.6	11.407	43.17	67.0±0.2	66.6±4.0
γ-nonanolactone	-5574.8	11.962	46.35	70.3±0.3	70.6±4.1
δ-nonanolactone	-5641.8	11.974	46.9	70.7±0.4	71.3±4.1
γ-decanolactone	-6018.1	12.513	50.03	75.6±0.3	75.2±4.3
δ-decanolactone	-6080.4	12.526	50.55	74.2±0.3	75.8±4.3
γ-undecanolactone	-6462.2	13.075	53.72		79.7±4.4
δ-undecanolactone	-6527.5	13.094	54.27		80.4±4.5
γ-dodecanolactone	-6905.9	13.64	57.41		84.3±4.6
δ-dodecanolactone	-6969.5	13.655	57.94		85.0±4.7

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.19±0.063)ΔH_{trn}(434 K) + (15.12±2.9) r^2 = 0.9889 (7-13)

TABLE 7-16. A Summary of the vaporization enthalpies in kJ·mol^{-1}of both standards and targets

	Run 1	Run 2	Avg	Lit
γ-hexanolactone	57.5±3.6	57.2±3.7	57.4±3.7	57.2±0.3
γ-octanolactone	65.9±3.9	66.1±3.9	66.0±3.9	
δ-octanolactone	66.5±3.9	66.6±4.0	66.6±4.0	67.0±0.2
γ-nonanolactone	70.3±4.0	70.6±4.1	70.5±4.1	70.3±0.3
δ-nonanolactone	70.9±4.1	71.3±4.1	71.1±4.1	70.7±0.4
γ-decanolactone	74.7±4.2	75.2±4.3	75.0±4.3	75.6±0.3
δ-decanolactone	75.2±4.2	75.8±4.3	75.5±4.3	74.2±0.3
γ-undecanolactone	79.1±4.4	79.7±4.4	79.4±4.4	
δ-undecanolactone	79.7±4.4	80.4±4.5	80.1±4.5	
γ-dodecanolactone	83.4±4.6	84.3±4.6	83.9±4.6	
δ-dodecanolactone	84.1±4.6	85.0±4.7	84.6±4.7	

7.3.2.2. Vapor Pressures. Vapor pressures derived from equation 7-2 at T/K = 298.15 were first converted to values of p/p_o where p_o = 101325 Pa. These values were then correlated as $\ln(p/p_o)$ with the corresponding values of $\ln(t_o/t_a)$ evaluated from the slopes and intercepts given in Tables 7-14 and 7-15 for both runs 1/2. Shown in Figure 7-10 and summarized by equation 7-14 in Table 7-17 are the results of plotting $\ln(p/p_o)$ against $\ln(t_o/t_a)$ at T/K = 298.15 for run 1. The values of $\ln(p/p_o)$ of the target compounds evaluated using equation 7-14 are represented by the square symbols and their associated uncertainties in the figure.

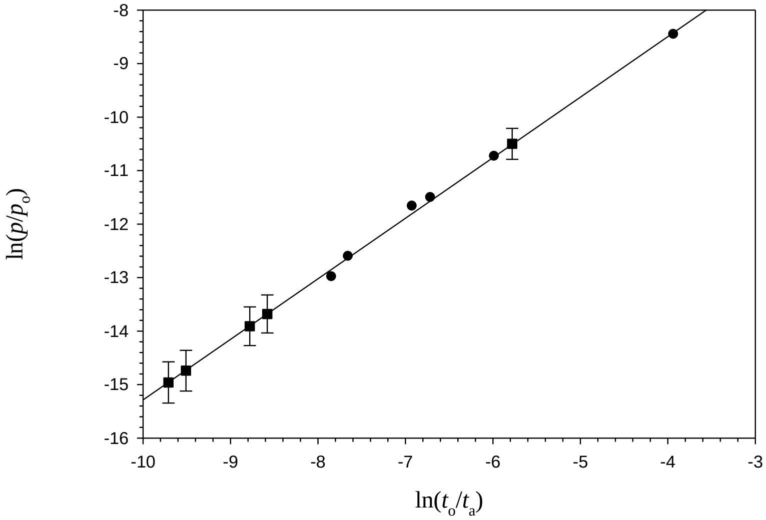

Figure 7-10. The correlation observed between ln(p/p_o) and ln(t_o/t_a) for run 1. The line represents the results of a linear regression analysis of the standards (circles). The squares (and their associated uncertainties) are the vapor pressures calculated for the targets.

TABLE 7-17. Correlation of ln(t_o/t_a) with ln(p/p_o)$_{exp}$ at T = 298.15 K for run 1

	ln(t_o/t_a)	ln(p/p_o)$_{exp}$	ln(p/p_o)$_{calc}$	p/Pa$_{lit}$	p/Pa$_{calc}$
γ-hexanolactone[a]	-3.93	-8.46	-8.41±0.25	21.6	22.5±6.4
γ-octanolactone	-5.78		-10.5±0.29		2.78±0.9
δ-octanolactone	-5.98	-10.74	-10.73±0.29	2.2	2.21±0.8
γ-nonanolactone	-6.71	-11.51	-11.56±0.31	1.01	0.97±0.4
δ-nonanolactone	-6.92	-11.67	-11.80±0.31	0.87	0.76±0.3
γ-decanolactone	-7.65	-12.61	-12.62±0.33	0.34	0.33±0.1
δ-decanolactone	-7.84	-12.99	-12.85±0.33	0.23	0.27±0.1
γ-undecanolactone	-8.58		-13.68±0.35		0.12±0.05
δ-undecanolactone	-8.78		-13.91±0.36		0.09±0.04
γ-dodecanolactone	-9.51		-14.74±0.38		0.04±0.02
δ-dodecanolactone	-9.71		-14.96±0.38		0.03±0.02

[a] A vapor pressure of p/Pa = 213 also reported for γ-hexanolactone was not used, reference 28.

Run 1

ln(p/p_o)$_{calc}$ = (1.134±0.033) ln(p/p_o)$_{exp}$ - (3.95±0.22) r^2 = 0.9967 (7-14)

Run 2

ln(p/p_o)$_{calc}$ = (1.137±0.033) ln(p/p_o)$_{exp}$ - (3.90±0.22) r^2 = 0.9967 (7-15)

Equation 7-15 summarizes the results for run 2. A table similar to Table 7-17 is given in Appendix G. These correlations were then repeated from T/K = (298.15 to 350) at 10K intervals (not shown). The correlation coefficients for each temperature evaluated, r^2, exceeded 0.99. The vapor pressures acquired over this 50K temperature range were then fit to equation 7-16. Table 7-18 provides the slopes and intercepts of the fits for run 1. In most cases, the vapor pressures evaluated over this temperature range for run 2 were practically identical to those of run 1 after rounding off. These are not reported here. Vapor pressure data for run 2 is given in Appendix G. All fits of $\ln(p/p_o)$ determined by correlation as a function of temperature as $1/T$ were characterized by correlation coefficients, r^2, greater than 0.99.

$$\ln(p/p_o) = A' + B'/(T/K) \qquad (7\text{-}16)$$

TABLE 7-18. The slopes and intercepts of equation 7-16 and the vaporization enthalpy at T = 298.15 K calculated from correlations of $\ln(t_o/t_a)$ with $\ln(p/p_o)_{exp}$ for run 1 from T = (298.15 to 350) K

	A'	B'	$\Delta_l^g H_m(T_m)^a$ kJ·mol^{-1}	$C_{p(298\ K)}$(l) J·mol^{-1}·K^{-1}	$\Delta_l^g H_m$(298.15 K) kJ·mol^{-1}	
					calc	lit
γ-hexanolactone	14.14	-6720.5	55.9±0.2	206.6	57.5±0.5	57.2±0.3[b]
γ-octanolactone	15.32	-7693.9	64.0±0.3	270.4	66.1±0.5	66.0±3.9[c]
δ-octanolactone	15.30	-7755.4	64.5±0.3	264.4	66.5±0.5	67.0±0.2[b]
γ-nonanolactone	15.94	-8192.2	68.1±0.3	302.3	70.4±0.5	70.3±0.3[b]
δ-nonanolactone	15.95	-8269.7	68.8±0.3	296.3	71.0±0.5	70.7±0.4[b]
γ-decanolactone	16.57	-8698.8	72.3±0.4	334.2	74.8±0.6	75.6±0.3[b]
δ-decanolactone	16.58	-8766.9	72.9±0.4	328.2	75.4±0.6	74.2±0.3[b]
γ-undecanolactone	17.21	-9204.7	76.5±0.4	366.1	79.3±0.6	79.4±4.4[c]
δ-undecanolactone	17.23	-9276.0	77.1±0.4	360.1	79.8±0.6	80.1±4.5[c]
γ-dodecanolactone	17.85	-9709.0	80.7±0.4	398	83.7±0.6	84.3±4.6[c]
δ-dodecanolactone	17.87	-9782.3	81.3±0.4	392	84.2±0.6	85.6±4.7[c]

[a] T_m = 324 K. [b] Ref 17,18. [c] This work.

Vaporization enthalpies were determined from the product of the slope of line of equation 7-16 and the gas constant (R) for each compound as a means to independently determine the overall quality of these correlations as a function of temperature. The third column of Table 7-18 summarizes these values. This data was then adjusted back to *T*/K = 298.15 using equation 7-2 and the heat capacities listed in column 5 of the table. Column 6 of Table 7-18 lists these vaporization enthalpies adjusted to *T*/K = 298.15 and compares them to the values used as standards or to the values reported in the last column of Table 7-16. The vaporization enthalpies of both the standard and target compounds are all reproduced with a standard deviation of ±1.5 $\text{kJ}\cdot\text{mol}^{-1}$ (2 σ).

In columns 2 and 5 of Table 7-19, the vapor pressures at *T*/K = 298.15 from the last column of Table 7-17, which were evaluated using equation 7-14 and reproduced in column 3 of Table 7-19, are compared with available experimental and estimated values, respectively.

TABLE 7-19. A Comparison of the Literature Vapor Pressures with This Work Using Equations 7-14 and 7-16 (Run 1)

	p/Pa 298.15 K lit^a	*p*/Pa (298.15 K) this work eq 7-14	eq 7-16	*p*/Pa 298.15 K EPI$_{est}$^{b}	*p*/Pa 293.15 K lit^c	*p*/Pa 293.15 K this work^d
γ-hexanolactone	21.6	22.5±6.4	22.8±3.3	22	80.0	15.5±2.3
γ-octanolactone		2.8±0.9	2.8±0.5	8.46	5.47	1.8±0.3
δ-octanolactone	2.2	2.2±0.8	2.3±0.4	3.63	2.29	1.5±0.3
γ-nonanolactone	1.01	1.0±0.4	1.0±0.2	1.57	0.97	0.62±0.1
δ-nonanolactone	0.87	0.8±0.4	0.8±0.2	1.45	0.89	0.48±0.1
γ-decanolactone	0.34	0.33±0.1	0.34±0.1	0.683	0.42	0.21±0.05
δ-decanolactone	0.23	0.27±0.1	0.27±0.1	0.633	0.39	0.17±0.04
γ-undecanolactone		0.12±0.05	0.12±0.03	0.545	0.34	0.070±0.02
δ-undecanolactone		0.09±0.04	.095±0.02	0.261	0.14	0.056±0.01
γ-dodecanolactone		0.04±0.02	0.41±0.01	0.141	0.08	0.024±0.006
δ-dodecanolactone		0.03±0.02	0.033±0.01	0.132	0.08	0.019±0.005

[a]From Ref 17,18 unless noted otherwise. [b]Calculated using the EPI Suite, reference 29. [c]MSDS sheets, Ref 9. [d]Using equation 7-16 and the constants of Table 7-18.

The uncertainties related to equation 7-14 were determined from the corresponding uncertainties in the slope and intercept of the equation as described above. Vapor pressures evaluated using equation 7-16 and the constants of Table 7-18, listed in column 4 of Table 7-19, vary somewhat but also reproduce both literature values. Those determined using equation 7-14 are well within the uncertainties cited. Using both equation 7-14 and by combining equation 7-16 with the constants of Table 7-18, the vapor pressures of the standard compounds are reproduced within 9 % of their value. Vapor pressures evaluated at T/K = 293.15 using equation 7-16 and the constants of Table 7-18 are compared in the last two columns of the table. The vapor pressures listed in column 6 are from MSDS sheets made available by the supplier.[9] It is unknown if they represent estimated or experimental values. The vapor pressures determined in this study are consistently smaller than the MSDS values by approximately a factor of 4. The constants of Table 7-18 in combination with equation 7-16 can be used to provide vapor pressures of the compounds investigated in this study from T/K = (298.15 to 350).

7.3.2.3. Vaporization Enthalpy Estimates. A group additivity protocol for predicting the vaporization enthalpies of γ and δ-lactones has been reported by Emel'yanenko *et al.*[18] The group values they reported are listed in Table 7-20.

TABLE 7-20. Group additivity values for vaporization enthalpy calculation of γ and δ-lactones[a]

Group Increment		GroupValue/ kJ·mol^{-1}
$C^{\gamma}_{lactone}$	five membered lactone ring	53.9
$C^{\delta}_{lactone}$	six membered lactone ring	58.7
$C\text{-}(H)_3(C_{lactone})$	methyl ring substitient	1.11
$C\text{-}(H)_2(C_{lactone})$	methylene ring substitient	-0.67
$C\text{-}(H)_3(C)$	methyl group	6.33
$C\text{-}(H)_2(C)_2$	methylene group	4.52
$(C\text{-}C)_{1\text{-}4}$	1,4-carbon-carbon interaction	0.26
$(C\text{-}O)_{1\text{-}4}$	1,4-carbon-oxygen interaction	-3.26

[a]From Ref 18.

The predicted values are compared with the experimental vaporization enthalpies previously reported and those evaluated in this study in Table 7-21. Agreement with the results determined here are well within the experimental uncertainties. All values in column 4 are somewhat over predicted, but are reproduced with a standard deviation of ±1.0 kJ·mol^{-1} (2σ).

TABLE 7-21. A comparison of estimated vaporization enthalpies with experimental values

	$\Delta_l^g H_m$(298.15 K) kJ·mol^{-1} Estimation	$\Delta_l^g H_m$(298.15 K) kJ·mol^{-1} Literature[17,18]	$\Delta_l^g H_m$(298.15 K) kJ·mol^{-1} This Work
γ-butanolactone	53.9	54.4	
γ-pentanolactone	55.1	53.9	
γ-hexanolactone	56.6	57.2	
γ-heptanolactone	61.4	62.3	
γ-octanolactone	66.1		66.0±3.9
γ-nonanolactone	70.9	70.3	
γ-decanolactone	75.7	75.6	
γ-undecanolactone	80.5		79.4±4.4
γ-dodecanolactone	85.2		83.9±4.6
δ-pentanolactone	58.7	58.2	
δ-hexanolactone	59.8	61.0	
δ-octanolactone	66.1	67.0	
δ-nonanolactone	70.9	70.7	
δ-decanolactone	75.7	74.2	
δ-undecanolactone	80.5		80.1±4.5
δ-dodecanolactone	85.3		84.6±4.7

7.3.2.4. Vaporization Enthalpy Comparisons. Besides the γ and δ-lactones investigated, Wiberg and Waldron[30] reported the vaporization enthalpies of a corresponding series of ω-lactones. Table 7-22 shows the comparison of these results. It is worth noting that ω and γ-butanolactone and ω and δ-pentanolactone refer to the same material and are included to demonstrate the reproducibility of literature values. The vaporization enthalpies seem to attenuate as the ring size increases and becomes more flexible. In line with this interpretation, an alternative estimation equation, eq 7-17, derived from the vaporization enthalpies of acyclic esters[31], vastly underestimates the vaporization enthalpies of both the smaller γ and δ-lactones. It does however seem to give an improved estimation of the larger ones as indicated in the last column of Table 7-22.

Also underestimated by eq 7-17 are the cyclic ethers oxetane, tetrahydrofuran, and pyran.[25] The n_C, n_Q and b terms in equation 7-17 refer to the total number of carbons, the number of quaternary sp^3 hybridized carbons (0), and the contribution of the functional group (10.5 kJ·mol^{-1}), respectively.

$$\Delta_l^g H_m(298\text{ K})/\text{ kJ}\cdot\text{mol}^{-1} = 4.69(n_C - n_Q)\ 1.3n_Q + 3.0 + b \qquad (7\text{-}17)$$

TABLE 7-22. A comparison of the vaporization enthalpies of a series of γ, δ, and ω-lactones

		$\Delta_l^g H_m$(298 K) kJ·mol^{-1}		$\Delta_l^g H_m$(298 K) kJ·mol^{-1}
	γ[a]	δ[b]	ω[c]	Est (Eq 7-17)
butanolactone	54.4±0.4		55.6±1.4[d]	32.3
pentanolactone	53.9±0.2	58.2±0.3[e]	60.2±1.3[f]	37.0
hexanolactone	57.2±0.3	61.0±0.1[e]	62.0±1.3	41.6
octanolactone	66.0±3.9[b]	67.0±0.2[e]	52.8±1.3	51.0
nonanolactone	70.3±0.2	71.1±4.1	59.0±1.3	55.7
decanolactone	75.6±0.3	75.5±4.3	63.0±1.5	60.4
undecanolactone	79.4±4.4[b]	80.1±4.5	66.2±1.3	65.1
dodecanolactone	83.9±4.6[b]	84.6±4.7	70.5±1.7	69.8

[a] From Ref 18 unless noted otherwise. [b] This work unless noted otherwise. [c] From reference 30. [d] Same as γ-butanolactone. [e] From Ref 17. [f] Same as δ-pentanolactone.

7.3.3. Insect Pheromones.

7.3.3.1. Vaporization Enthalpies. There were two sets of correlations conducted, each in duplicate runs. Table 7-23 displays the vaporization enthalpy data for runs 1 and 3. The relationship between $\Delta_{trn}H_m(T_m)$ and $\Delta_l^g H_m$(298.15 K) is described by equations 7-18 and 7-19 provided below each respective table for runs 1 and 3. The correlation coefficient gives a measure of the scatter of the data. The details of the remaining runs are given in Appendix G.

TABLE 7-23. Correlation of Vaporization Enthalpies (p_o/Pa =101325) with Enthalpies of Transfer[a]

Run 1	- slope T/K	intercept	ΔH_{trn}(450 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (Lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(Calc)
Methyl decanoate	5606.9±20	12.544±0.06	46.61±0.22	66.10±0.17	66.6±4.8
Methyl dodecanoate	6450.7±30	13.544±0.06	53.63±0.23	76.59±0.41	75.9±5.1
Z 8-Dodecenyl acetate	6756.1±30	13.885±0.07	56.17±0.26		79.3±5.3
Z 4-Tridecen-1-yl acetate	7058.6±30	14.210±0.07	58.68±0.27		82.6±5.4
Methyl tetradecanoate	7303.9±40	14.584±0.08	60.72±0.29	85.94±0.76	85.3±5.5
Methyl pentadecanoate	7727.7±40	15.104±0.08	64.24±0.31	89.29±0.79	90.0±5.6

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.328±0.065)·ΔH_{trn}(450 K) + (4.72±3.7); r^2 = 0.9951 (7-18)

Run 3	- slope T/K	intercept	ΔH_{trn}(449 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (Lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(Calc
Methyl tetradecanoate	6929.4±40	13.906±0.08	57.61±0.34	85.94±0.76	85.2±3.5
E 11-Tetradecenyl acetate	7265.2±40	14.327±0.09	60.40±0.35		89.6±3.5
Methyl pentadecanoate	7321.9±40	14.363±0.09	60.87±0.36	89.29±0.79	90.3±3.5
E,*E* 9,11-Tetradecadienyl acetate	7480.7±40	14.506±0.09	62.19±0.36		92.3±3.6
S-Hydroprene[b]	7487.1±40	15.783±0.09	70.80±0.36		92.4±3.6
R,*S* Kinoprene[c]	7927.4±50	15.049±0.1	65.90±0.39		98.1±3.7
Methyl octadecanoate	8516.0±50	15.783±0.1	62.24±0.41	105.87±1.37	105.7±3.8
Z 13-Octadecen-1-yl acetate	8757.9±50	16.029±0.1	72.81±0.41		108.8±3.9
Methyl eicosanoate	9317.2±50	16.754±0.11	77.46±0.45	116.43±1.5	116.0±4.0
Methyl henicosanoate	9717.2±60	17.241±0.12	80.78±0.47	120.90±1.8	121.2±4.1

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.552±0.038)·ΔH_{trn}(449 K) + (4.21±2.67); r^2 = 0.9982 (7-19)

[a] Uncertainties represent one standard deviation. [b] *S* (+)-Ethyl (2*E*,4*E*)-3,7,11-trimethyl-2,4-dodecadienoate. [c] *R*,*S* 2-Propynyl (2*E*,4*E*)-3,7,11-trimethyl-2,4-dodecadienoate.

The results for all four runs are summarized in Table 7-24. Also included in Table 7-24 are comparisons of the experimental results with estimated values. These are typically within experimental error. The only literature value that that could be found was for *Z* 13-octadecen-1-yl acetate, 108.7 kJ·mol^{-1}.[32] This vaporization enthalpy for *Z* 13-octadecen-1-yl acetate was also acquired by a similar gas chromatographic method with the use of a series of alkane standard compounds according to Hamilton's method [33] and compares to a value of (108.8±3.9) determined in this study. Agreement between the two techniques in this instance is very good.

TABLE 7-24. A Summary of the Vaporization Enthalpies in kJ·mol^{-1} (p_o/Pa = 101325) of Runs 1-4

Run	1	2	3	4	Average^a	Est^b
Targets						
Z 8-Dodecenyl acetate	79.3±5.3	79.3±5.5			79.3±5.4	79.2±4.0
Z 4-Tridecen-1-yl acetate	82.6±5.4	82.7±5.6			82.7±5.5	83.9±4.2
E 11-Tetradecenyl acetate			89.6±3.5	89.6±3.5	89.6±3.5	88.5±4.4
E, E 9,11-tetradecadienyl acetate			92.3±3.6	92.3±3.5	92.3±3.6	88.5±4.4
S-Hydroprene^c			92.4±3.6	92.5±3.6	92.4±3.6	89.2±4.5
R,*S*-Kinoprene^d			98.1±3.7	98.1±3.6	98.1±3.7	93.9±4.7
Z 13-Octadecen-1-yl acetate			108.8±3.9	109.0±3.8	108.8±3.9	108.7^e
Standards						Lit^f
Methyl decanoate	66.6±4.8	66.6±5.0			66.6±4.9	66.10±0.17
Methyl dodecanoate	75.9±5.1	75.9±5.4			75.9±5.3	76.59±0.41
Methyl tetradecanoate	85.3±5.5	85.3±5.7	85.2±3.5	85.2±3.4	85.3±4.5	85.94±0.76
Methyl pentadecanoate	90.0±5.6	90.0±5.9	90.3±3.5	90.3±3.5	90.2±4.6	89.29±0.79
Methyl octadecanoate			105.7±3.8	105.8±3.8	105.8±3.8	89.29±0.79
Methyl eicosanoate			116.0±4.0	116.1±4.0	116.0±4.0	116.43±1.54
Methyl henicosanoate			121.2±4.1	121.1±4.1	121.2±4.1	120.9±1.8^g

[a] The uncertainty reported is an average of the standard deviation of runs 1-4; all uncertainties are one standard deviation. [b] Estimated value, ref 34, unless noted otherwise. [c] *S* Ethyl (2*E*,4*E*)-3,7,11-trimethyl-2,4-dodecadienoate. [d] *R*,*S* 2-Propynyl (2*E*,4*E*)-3,7,11-trimethyl-2,4-dodecadienoate. [e] Ref 32. [f] Ref 19 unless noted otherwise. [g] Ref 20.

Quality enthalpy data that can be used as standards for compounds containing certain functional groups can often be difficult to find, especially for more complex substances containing multiple functionalities. A potential solution to this problem is the demonstration that other functional groups can function as substitutes. This was tested by using esters as standards to evaluate *Z* 13-Octadecen-1-yl acetate by correlation gas chromatography. The $\Delta_{\mathrm{trn}}H_{\mathrm{m}}(T_{\mathrm{m}})$ of alkanes have been shown recently to correlate quite well with $\Delta_l^gH_m$ (298.15 K) of mono-esters.[35] This is confirmed by the agreement between the two results using two different sets of standards.

7.3.3.2. Vapor Pressures. As previously mentioned, correlations of $\ln(t_o/t_a)$ with $\ln(p/p_o)$ are also linear. The effect of correlating $\ln(p/p_o)$ with $\ln(t_o/t_a)$ at T/K = 298.15 is shown in Table 7-25. Calculated values of t_o/t_a from runs 1/2 were averaged and correlated as $\ln(t_o/t_a)_{avg}$ since duplicate runs of both sets of correlations were conducted under similar conditions. Runs 3/4 were treated in a similar manner. The quality of the fit is described by equations 7-20 and 7-21 below each respective set of runs.

TABLE 7-25. Correlations Between $\ln(t_o/t_a)_{avg}$ and Liquid $\ln(p/p_o)_{exp}$ Values at T/K = 298.15 for All Runs, p_o = 101325; Uncertainties are One Standard Deviation.

Run 1(top)/Run 2(bottom)	-slope/K	intercept	$\ln(t_o/t_a)_{avg}$	$\ln(p/p_o)_{exp}$	$\ln(p/p_o)_{calc}$
Methyl decanoate	5606.9	12.544	-6.285	-9.807	-9.85±0.24
	5665.7	12.695			
Methyl dodecanoate	6450.7	13.544	-8.114	-12.063	-12.02±0.27
	6512.1	13.705			
Z 8-Dodecenyl acetate	6756.1	13.885	-8.801		-12.83±0.28
	6825.2	14.064			
Z 4-Tridecen-1-yl acetate	7058.6	14.210	-9.493		-13.65±0.29
	7134.4	14.406			
Methyl tetradecanoate	7303.9	14.584	-9.942	-14.241	-14.18±0.29
	7379.0	14.779			
Methyl pentadecanoate	7727.7	15.104	-10.845	-15.185	-15.25±0.31
	7810.7	15.320			

$\ln(p/p_o) = (1.185\pm0.022)\cdot\ln(t_o/t_a) - (2.40\pm0.197)$ $r^2 = 0.9993$ (7-20)

Run 3 (top)/Run 4 (bottom)	-slope/K	intercept	$\ln(t_o/t_a)_{avg}$	$\ln(p/p_o)_{exp}$	$\ln(p/p_o)_{calc}$
Methyl tetradecanoate	6929.4	13.906	-9.293	-14.241	-14.18±0.27
	6883.3	13.834			
E 11-Tetradecenyl acetate	7265.2	14.327	-9.999		-15.08±0.27
	7220.3	14.258			
Methyl pentadecanoate	7321.9	14.363	-10.152	-15.185	-15.28±0.28
	7275.7	14.292			
E,*E* 9,11-Tetradecadienyl acetate	7480.7	14.559	-10.486		-15.71±0.28
	7431.2	14.481			
S Hydroprene[a]	7487.1	14.506	-10.566		-15.81±0.28
	7445.0	14.443			
R,*S* Kinoprene[b]	7927.4	15.049	-11.494		-16.99±0.29
	7877.6	14.971			
Methyl octadecanoate	8516.0	15.783	-12.736		-18.58±0.31
	8468.9	15.711		-18.659	
Z 13-Octadecen-1-yl acetate	8757.9	16.029	-13.31		-19.32±0.31
	8721.4	15.977			
Methyl eicosanoate	9317.2	16.754	-14.447	-20.7	-20.77±0.33
	9262.2	16.665			
Methyl henicosanoate	9717.2	17.241	-15.297	-21.885	-21.86±34
	-9655.0	17.137			

$\ln(p/p_o) = (1.278\pm0.017)\cdot\ln(t_o/t_a) - (2.305\pm0.215)$ $r^2 = 0.9994$ (7-21)

[a] *S* Ethyl (2*E*,4*E*)-3,7,11-trimethyl-2,4-dodecadienoate. [b] *R*,*S* 2-Propynyl (2*E*,4*E*)-3,7,11-trimethyl-2,4-dodecadienoate.

This correlation was repeated at T/K = 10 intervals over the temperature range T/K = (298.15 – 500). The correlation coefficient, r^2, > 0.99 for both sets of runs over the entire temperature range. The resulting data was fit to a third order polynomial, eq 1-10, by non-linear least squares. Table 7-26 provides the constants of eq 1-10 for the target compounds.

TABLE 7-26. Constants for the Third Order Polynomial Eq 1-10 for Evaluated From Runs 1/2 and Runs 3/4[a]

Targets: Run1/2	A	B	$10^{-6}\cdot C/K^2$	$10^{-6}\cdot D/K^3$
Z 8-Dodecenyl acetate	4.8377±0.1147	1722.17±132.54	-2.906±0.050	245.180±6.315
Z 4-Tridecenyl acetate	4.3471±0.1292	2162.00±149.37	-3.137±0.057	266.067±7.116
Targets: Runs 3/4				
E 11-Tetradecenyl acetate	4.5304±0.1307	2111.77±151.09	-3.301±0.057	276.766±7.198
E,*E* 9,11-tetradecadienyl acetate	4.2442±0.1298	2434.36±149.96	-3.476±0.057	291.272±7.145
S Hydroprene[b]	4.0327±0.1359	2602.90±157.10	-3.540±0.06	298.134±7.485
R,*S* Kinoprene[c]	3.6966±0.1261	3069.85±145.71	-3.828±0.055	320.001±6.942
Z 13-Octadecen-1-yl acetate	2.9275±0.1111	4061.90±128.36	-4.415±0.049	365.763±6.116

[a]Uncertainties are one standard deviation, p_o/Pa = 101325. [b]*S* Ethyl (2*E*,4*E*)-3,7,11-trimethyl-2,4-dodecadienoate. [c]*R*,*S* 2-Propynyl (2*E*,4*E*)-3,7,11-trimethyl-2,4-dodecadienoate.

Values for both standard and target compounds and the vapor pressures and their uncertainties determined at each temperature are listed in Appendix G. Boiling temperatures at p/Pa = 101325 were estimated by solving for T when $\ln(p/p_o) = 0$. Reported in Table 7-27 are the resulting vapor pressures at T/K = 298.15 and normal boiling temperatures at p/Pa = 101325 acquired by extrapolation. Some comparisons are given at reduced pressures, as well. Whenever available, comparisons with experimental values or with estimated values are included. Estimated values are given in italics.

TABLE 7-27. A Summary of Liquid/Subcooled Liquid Vapor Pressures and Normal Boiling Temperatures (p = 101325 Pa) and Comparison with Experimental or Estimated Values (in italics); Uncertainties are One Standard Deviation

Run 1/2 Targets	$(10^2)\cdot p_{(l)}$ /Pa 298.15 K This work	$(10^2)\cdot p_{(l)}$/Pa 298.15 K Lit	T_b/K Calc	T_b/K lit
Z 8-Dodecenyl acetate	27±7.6	*55*[a]	557.8±1.2, 386[b]	376[b, c]
Z 4-Tridecenyl acetate	12±3.5	*21*[a]	573.9±1.5	*574.2*[a]
Standards				
Methyl decanoate	540±130	560	505.2±1.0	497.2[d]
Methyl dodecanoate	61±17	59	542.9±1.0	540.2[d]
Methyl tetradecanoate	7.0±0.21	6.6	578.7±1.3	568.2[d]
Methyl pentadecanoate	2.4±0.76	2.6	596.1±1.6, 419.7[e]	418.2[e, f]
Run 3/4 Targets	$(10^4)\cdot p_{(l)}$ /Pa 298.15 K calc	$(10^4)\cdot p_{(l)}$/Pa 298.15 K Lit		
E 11-Tetradecenyl acetate	280±80	*1200*[a]	591.3±1.5; 335[g]	353[g, h]
E,*E* 9,11-Tetradecadienyl acetate	150±43	*920*[a]	600.3±1.6; 353[i]	373[i, j]
S Ethyl (2*E*,4*E*)-3,7,11-trimethyl-2,4-dodecadienoate	140±39	250[d]	604.3±1.8, 398.8[k]	412[k,l]
R,*S* 2-Propynyl (2*E*,4*E*)-3,7,11-trimethyl-2,4-dodecadienoate	42±12 21±6.9[m]	9.6[m, n]	618.1±1.9	NA[o]
Z 13-Octadecenyl acetate	4.1±1.3	4.6[p]	646.4±2.3	*652.7±11*[q]
Standards				
Methyl tetradecanoate	700±190	660	581.1±0.1	568.2[d]
Methyl pentadecanoate	230±66	260	595±1.6, 420[e]	418.2[e, f]
Methyl octadecanoate	8.6±2.7	8.0	457±2.0	455.2[m]
Methyl eicosanoate	0.97±0.32	1.0	494.6±2.2[r]	488.2[r, s]
Methyl heneicosanoate	0.33±0.11	0.32	673±2.4	*656*[a]

[a]Estimated, ref 36. [b]At p/Pa = 267. [c]Ref 37. [d]Ref 38. [e]At p/Pa = 400. [f]Experimental, ref 36. [g]At p/Pa = 1.33 Pa. [h]Ref 39. [i]At p/Pa = 4. [j]Ref 40. [k]At p/Pa =93.3. [l]Ref 41. [m]Vapor pressure at T/K = 293.2. [n]Ref 42. [o]Not available. [p]Ref 32. [q]Predicted value; SciFinder Scholar. [r]At p/Pa = 1333. [s]Ref 43.

Vapor pressure comparisons in Table 7-27 for *Z* 8-dodecenyl acetate and *Z* 4-tridecenyl acetate are estimated values. This is the same for *E* 11-tetradecenyl acetate. Comparisons with estimated values do not agree very well. Comparisons with literature values for the remaining target compounds become increasingly better. Over the temperature range T/K = (298.15 to 500), the vapor pressures of the standards in runs 1/2 and 3/4 were reproduced within 1.0 to 5.5% and 5.0 to 7.0% of their literature value, respectively. It is also worth noting that the literature vapor pressure of *Z* 13-octadecenyl acetate also evaluated by gas chromatography using alkanes as standards[32] agrees quite favorably with the data from this study. Boiling point comparisons for four out of five experimental values reported for the target compounds are at reduced pressures. No data could be found for 2-propynyl (2*E*,4*E*)-3,7,11-trimethyl-2,4-dodecadienoate and the value for *Z* 13-octadecenyl acetate is an estimate.

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Part 6: Conclusion

As previously stated thermodynamic properties, such as vaporization enthalpy and vapor pressure, are crucial to numerous significant fields of study. Along with this, the influence of these properties can also be seen within the environment as thermodynamic properties determine the atmospheric concentration of a compound and the fate of its dispersal within the environment. As such, there is an increasing need to evaluate the impact of the many compounds in use and this requires thermochemical data.

There have been various methods developed throughout the years to analyze thermodynamic properties, including both direct and indirect methods. The direct methods are useful, but more sample is required than when using an indirect method and the compound must also be pure for analysis to be conducted.[1] In addition to this, the indirect methods are valuable due to the relative speed of the experiments, taking just a few hours.[2]

Correlation gas chromatography is a quick and dependable method for analyzing vapor pressures and vaporization enthalpies, as long as appropriate standards with reliable thermodynamic data are chosen. This means using three or more standard compounds of known thermodynamic data which contain the same functional group as the compound(s) of interest and which bracket those target compound(s). As has been shown over the previous chapters of this thesis, as long as those qualifications are met, then correlation gas chromatography is a useful method for the analysis of thermodynamic data of various organic compounds.

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Appendix A

TABLE A-1. Fusion Enthalpy of Dicyclohexyl Phthalate

Run 1	Mass/mg	$\Delta_{cr}^{g}H_{m}(T_{m})$ kJ·mol^{-1}	T_m/K onset	$\Delta_{cr}^{g}H_{m}(T_{m})_{avg}$ kJ·mol^{-1}	T_m/K$_{avg}$ onset
dicyclohexyl phthalate	17.14	31.46	336.4	32.3 ± 1.4	336.5 ± 0.3
	20.23	31.41	336.1		
	18.83	34.38	336.5		
	20.52	31.96	336.8		

2.2 **Vapour pressure measurements on di-*n*-butyl-phthalate.**

The vapour pressures and vaporization enthalpy of dibutylphthalate were determined using the transpiration method and applying the Clausius-Clapeyron equation. Approximately 0.4 g of the sample was mixed with glass beads and putted into a thermostated U-shaped tube with 20 cm length and 0.5 cm diameter. Glass beads with diameter of 1 mm were used to provide enough surface for vapor-liquid equilibration. A nitrogen stream was passed through the U-tube at constant temperature (± 0.1 K) transporting examined substance to the cooling trap. The nitrogen stream flow rate was measured using a soap bubble flow meter and optimized in order to reach the saturation equilibrium of the transporting gas at each temperature under study. The flow rate of the nitrogen stream in the saturation tube is restricted on the one hand by the requirements of the nitrogen stream saturation with the compound, on another hand to avoid the substance transport due to the diffusion. To restrict the boundaries of appropriate flow rates the apparatus was tested at different carrier gas flow rates of the carrier gas. It was shown that the contribution of the vapor condensed in the trap by diffusion becomes negligible at a flow rate up to 0.45 dm3·h-1. The upper limit is at a flow rate of 9.0 dm3·h-1. The amount of condensed substance was determined by GC analysis using an external standard (hydrocarbon n-$C_{12}H_{24}$). The amount of substance collected within definite period of time was used then to calculate the saturated vapor pressure pi at each temperature Ti. The residual vapor pressure at the temperature of condensation calculated from linear correlation between ln(pi) and T^{-1} obtained by iteration was added. Using Dalton`s law of partial pressures which were assumed as valid the values of pisat were calculated:

$$p_i^{sat} = \frac{m_i R T_a}{V M_i}; \qquad V = V_{N2} + V_i; \qquad (VN_2 \text{ » } V_i)$$

where m_i - the mass of transported compound, M_i - the molar mass of the compound, V_{N2} - the volume of transporting gas, V_i - volume contribution of studied compound to the gaseous phase,T_a - the temperature of the soap bubble meter, R = 8.314472 J·K^{-1}·mol^{-1}.

TABLE A-2A. Experimental Retention Times of Various Dialkyl Benzenedicarboxylates

Run 1	485	490	495.1	500.1	505.2	510.2	515.2
t_o = 60 s				t/t_o			
methylene chloride	0.376	0.383	0.381	0.385	0.388	0.392	0.395
dimethyl phthalate	0.874	0.828	0.780	0.743	0.710	0.683	0.659
dimethyl terephthalate	0.965	0.908	0.849	0.804	0.763	0.730	0.701
diethyl phthalate	1.171	1.085	1.002	0.936	0.878	0.830	0.788
di-n-butyl phthalate	3.130	2.740	2.405	2.129	1.897	1.706	1.542
dicyclohexyl phthalate	17.13	14.258	11.917	10.009	8.473	7.212	6.188
bis(2-ethylhexyl) phthalate	19.348	15.864	13.058	10.816	9.022	7.589	6.421
bis(2-ethylhexyl) terephthalate	36.360	29.305	23.690	19.288	15.816	13.071	10.865

TABLE A-2B. Enthalpies of Transfer and Vaporization Enthalpies Used to Evaluate Vaporization Enthalpies of Dicyclohexyl Phthalate and *bis*(2-Ethylhexyl) Terephthalate[a]

Run 1	- slope T/K	intercept	ΔH_{trn}(500 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)
dimethyl phthalate	**5262.4**	**11.549**	43.75	77.0±1.2	76.7±0.8
dimethyl terephthalate	**5438.2**	**11.744**	45.21	78.4±2.4	78.4±0.8
diethyl phthalate	**5839.5**	**12.272**	48.55	82.1±0.5	82.2±0.8
di-n-butyl phthalate	7248.4	13.936	60.26	95.0±1.0	95.4±0.9
dicyclohexyl phthalate	8788.8	15.307	73.07		109.9±1.0
bis(2-ethylhexyl) phthalate	9487.3	16.624	78.87	116.7±0.5	116.5±1.0
bis(2-ethylhexyl) terephthalate	10212.0	17.478	84.9		123.3±1.1

$\Delta_l^g H_m(298.15\ K)/kJ{\cdot}mol^{-1} = (1.13{\pm}0.015)\Delta H_{trn}(500\ K) - (27.21{\pm}0.61)$ $r^2 = 0.9997$ (A-1)

[a]Values in bold used to evaluate vapor pressures of dimethyl terephthalate.

TABLE A-3A. Experimental Retention Times of Various Dialkyl Benzenedicarboxylates

Run 2	485.1	490	495.1	500.2	505.2	510.2	515.2
t_o = 60 s				t/t_o			
methylene chloride	0.377	0.376	0.38	0.379	0.383	0.384	0.382
dimethyl phthalate	0.87	0.815	0.773	0.732	0.701	0.671	0.642
dimethyl terephthalate	0.96	0.893	0.841	0.792	0.753	0.718	0.683
diethyl phthalate	1.164	1.068	0.992	0.922	0.866	0.817	0.77
di-n-butyl phthalate	3.102	2.702	2.377	2.1	1.872	1.681	1.514
dicyclohexyl phthalate	16.945	14.072	11.769	9.885	8.363	7.128	6.103
bis(2-ethylhexyl) phthalate	19.155	15.665	12.893	10.679	8.907	7.491	6.337
bis(2-ethylhexyl) terephthalate	35.981	28.933	23.382	19.045	15.618	12.902	10.723

TABLE A-3B. Enthalpies of Transfer and Vaporization Enthalpies Used to Evaluate Vaporization Enthalpies of Dicyclohexyl Phthalate and *bis*(2-Ethylhexyl) Terephthalate[a]

Run 2	- slope T/K	intercept	$\Delta H_{trn}(500\ K)$ $kJ{\cdot}mol^{-1}$	$\Delta_l^g H_m(298\ K)$ $kJ{\cdot}mol^{-1}$ (lit)	$\Delta_l^g H_m(298\ K)$ $kJ{\cdot}mol^{-1}$(calc)
dimethyl phthalate	**5295.4**	**11.628**	44.02	77.0±1.2	76.8±0.7
dimethyl terephthalate	**5463.6**	**11.808**	45.42	78.4±2.4	78.4±0.7
diethyl phthalate	**5862.5**	**12.331**	48.74	82.1±0.5	82.1±0.7
di-n-butyl phthalate	7273.6	13.998	60.47	95.0±1.0	95.4±0.8
dicyclohexyl phthalate	8810.0	15.361	73.24		109.9±0.9
bis(2-ethylhexyl) phthalate	9517.7	16.696	79.13	116.7±0.5	116.5±0.9
bis(2-ethylhexyl) terephthalate	10243.5	17.552	85.16		123.3±1.0

$\Delta_l^g H_m(298.15\ K)/kJ{\cdot}mol^{-1} = (1.13{\pm}0.01)\Delta H_{trn}(500\ K) - (26.98{\pm}0.05)$ $r^2 = 0.9998$ (A-2)

[a]Values in bold used to evaluate vapor pressures of dimethyl isophthalate.

TABLE A-4A. Experimental Retention Times of Various Dialkyl Benzenedicarboxylates

Run 3	419.3	424.5	429.6	434.8	439.9	444.9	450
t_o = 60 s				t/t_o			
methylene chloride	0.330	0.353	0.352	0.358	0.356	0.36	0.362
dimethyl phthalate	3.527	3.041	2.623	2.291	2.002	1.774	1.581
dimethyl isophthalate	4.552	3.88	3.312	2.861	2.474	2.168	1.912
diethyl phthalate	6.578	5.51	4.631	3.938	3.355	2.894	2.513
di-n-butyl phthalate	35.658	28.25	22.51	18.124	14.658	11.969	9.845

TABLE A-4B. Slopes and Intercepts from Plots of ln(t_o/t_a) Versus 1/T

Run 3	- slope	intercept
	T/K	
dimethyl phthalate	5925.84	12.973
dimethyl isophthalate	6165.75	13.267
diethyl phthalate	6558.37	13.812
di-n-butyl phthalate	8087.86	15.727

TABLE A-5A. Experimental Retention Times of Various Dialkyl Benzenedicarboxylates

Run 4	419.3	424.4	429.6	434.7	439.9	444.9	450
t_o = 60 s	t/t_o						
methylene chloride	0.352	0.351	0.354	0.354	0.354	0.358	0.291
dimethyl phthalate	3.55	3.033	2.616	2.276	1.998	1.77	1.509
dimethyl isophthalate	4.577	3.869	3.303	2.843	2.469	2.163	1.838
diethyl phthalate	6.6	5.495	4.618	3.914	3.348	2.888	2.439

TABLE A-5B. Slopes and Intercepts from Plots of ln(t_o/t_a) Versus 1/T

Run 4	- slope	intercept
	T/K	
dimethyl phthalate	5884.79	12.883
dimethyl isophthalate	6160.71	13.258
diethyl phthalate	6550.36	13.797
di-n-butyl phthalate	8070.92	15.692

TABLE A-6A. Experimental Retention Times of Various Dialkyl Phthalates

Run 5	485.1	491	495.3	500.4	505.5	510.6	515.4
t_o = 60 s	t/t_o						
Methanol	0.765	0.769	0.774	0.783	0.788	0.794	0.798
dimethyl phthalate	1.719	1.618	1.533	1.466	1.403	1.354	1.308
dimethyl isophthalate	1.928	1.797	1.688	1.601	1.521	1.456	1.398
diethyl phthalate	2.283	2.102	1.952	1.831	1.722	1.635	1.556
di-n-butyl phthalate	5.98	5.212	4.591	4.081	3.646	3.295	3.001
benzyl butyl phthalate	19.464	16.313	13.813	11.776	10.099	8.75	7.663
bis(2-ethylhexyl) phthalate	36.204	29.559	24.384	20.27	16.956	14.319	12.26

TABLE A-6B. Correlations Between Enthalpies of Transfer and Vaporization Enthalpies

Run 5	- slope T/K	intercept	ΔH_{trn}(500 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298.15 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298.15 K) kJ·mol^{-1}(calc)
dimethyl phthalate	5206.7	10.782	43.29	77.0±1.2	76.6±2.8
dimethyl isophthalate	5506.9	11.201	45.78	78.8±1.2	79.4±2.8
diethyl phthalate	5776.1	11.491	48.02	82.1±0.5	81.9±2.9
di-n-butyl phthalate	7173.5	13.136	59.64	95.0±1.0[a]	95.0±3.2
benzyl butyl phthalate	8346.5	14.276	69.39		105.9±3.6
bis(2-ethylhexyl) phthalate	9404.5	15.817	78.19		115.8±3.9

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.12±0.04)ΔH_{trn}(500 K) - (28.0±2.1) $r^2 = 0.9971$ (A-3)

[a] An average of (96.0±0.8), (95.0±1.1) and (94.1±1.0) kJ·mol^{-1}.

TABLE A-7A. Experimental Retention Times of Various Dialkyl Phthalates

Run 6	485.1	491.1	495.2	500.4	505.5	510.6	515.3
t_o = 60 s				t/t_o			
Methanol	0.775	0.779	0.784	0.791	0.784	0.782	0.807
dimethyl phthalate	1.74	1.638	1.552	1.478	1.408	1.347	1.325
dimethyl isophthalate	1.951	1.819	1.709	1.615	1.526	1.449	1.417
diethyl phthalate	2.311	2.127	1.975	1.847	1.729	1.629	1.578
di-n-butyl phthalate	6.055	5.264	4.636	4.115	3.671	3.297	3.052
benzyl butyl phthalate	19.703	16.454	13.936	11.875	10.178	8.781	7.806
bis(2-ethylhexyl) phthalate	36.613	29.831	24.597	20.441	17.089	14.376	12.486

TABLE A-7B. Correlations Between Enthalpies of Transfer and Vaporization Enthalpies

Run 6	- slope T/K	intercept	ΔH_{trn}(500 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298.15 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298.15 K) kJ·mol^{-1}
dimethyl phthalate	5203.3	10.763	43.26	77.0±1.2	76.6±2.7
dimethyl isophthalate	5502.3	11.181	45.74	78.8±1.2	79.4±2.8
diethyl phthalate	5771.8	11.471	47.98	82.1±0.5	81.9±2.9
di-n-butyl phthalate	7171.7	13.122	59.62	95.0±1.0[a]	95.0±3.2
benzyl butyl phthalate	8342.6	14.258	69.36		105.9±3.6
bis(2-ethylhexyl) phthalate	9404.3	15.807	78.18		115.8±3.9

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.12±0.04)ΔH_{trn}(500 K) - (28.1±2.1) $r^2 = 0.9972$ (A-4)

[a] An average of (96.0±0.8), (95.0±1.1) and (94.1±1.0) kJ·mol^{-1}.

TABLE A-8A. Experimental Retention Times of Various Dialkyl Phthalates

Run 7 t_o = 60 s	505.3	510.4	515.5	520.6 t/t_o	525.7	530.7	535.7
Methanol	0.799	0.802	0.81	0.819	0.816	0.826	0.832
dimethyl phthalate	1.426	1.368	1.322	1.288	1.241	1.216	1.189
diethyl phthalate	1.752	1.652	1.571	1.508	1.436	1.388	1.342
di-n-butyl phthalate	3.722	3.336	3.022	2.765	2.528	2.34	2.176
benzyl butyl phthalate	10.331	8.875	7.703	6.746	5.928	5.25	4.681
bis(2-ethylhexyl) phthalate	17.361	14.536	12.323	10.523	9.033	7.813	6.807
di-n-octyl phthalate	29.22	24.112	20.105	16.892	14.277	12.144	10.401

TABLE A-8B. Evaluation of $\Delta_l^g H_m$(298 K) for Di-n-octyl Phthalate

Run 7	- slope T/K	intercept	ΔH_{trn}(520 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)
dimethyl phthalate	4995.2	10.356	41.53	77.0±1.2	76.8±1.0
diethyl phthalate	5543.3	11.023	46.08	82.1±0.5	82.1±1.0
di-n-butyl phthalate	6898.5	12.585	57.35	95.0±1.0[a]	95.4±1.1
benzyl butyl phthalate	8051	13.685	66.93		106.7±1.2
bis(2-ethylhexyl) phthalate	9051.6	15.114	75.25	116.7±0.5	116.5±1.3
di-n-octyl phthalate	9668.7	15.794	80.38		122.6±1.4

$\Delta_l^g H_m(298.15\ \mathrm{K})/\mathrm{kJ\cdot mol^{-1}} = (1.18\pm0.014)\Delta H_{trn}(521\ \mathrm{K}) - (27.8\pm0.8)$ $r^2 = 0.9997$ (A-5)

[a] An average of (96.0±0.8), (95.0±1.1) and (94.1±1.0) kJ·mol^{-1}.

TABLE A-9A. Experimental Retention Times of Various Dialkyl Phthalates

Run 8 t_o = 60 s	505.2	510.3	515.5	520.6 t/t_o	525.7	530.8	535.7
Methanol	0.814	0.812	0.816	0.82	0.825	0.823	0.825
dimethyl phthalate	1.456	1.384	1.333	1.29	1.251	1.212	1.181
diethyl phthalate	1.79	1.671	1.584	1.512	1.446	1.385	1.334
di-n-butyl phthalate	3.815	3.379	3.05	2.777	2.544	2.341	2.169
benzyl butyl phthalate	10.6	8.996	7.775	6.784	5.96	5.265	4.681
bis(2-ethylhexyl) phthalate	17.813	14.748	12.43	10.589	9.083	7.841	6.813
di-n-octyl phthalate	29.98	24.44	20.278	17.001	14.345	12.184	10.418

TABLE A-9B. Evaluation of $\Delta_{l}^{g}H_{m}$(298 K) for Di-n-octyl Phthalate

Run 8	- slope T/K	intercept	ΔH_{trn}(520 K) kJ·mol^{-1}	$\Delta_{l}^{g}H_{m}$(298 K) kJ·mol^{-1} (lit)	$\Delta_{l}^{g}H_{m}$(298 K) kJ·mol^{-1}(calc)
dimethyl phthalate	5184.4	10.713	43.1	77.0±1.2	76.7±1.0
diethyl phthalate	5725.9	11.367	47.6	82.1±0.5	82.1±1.1
di-n-butyl phthalate	7064.8	12.897	58.73	95.0±1.0[a]	95.4±1.2
benzyl butyl phthalate	8196.7	13.956	68.14		106.7±1.3
bis(2-ethylhexyl) phthalate	9189.1	15.369	76.39	116.7±0.5	116.5±1.4
di-n-octyl phthalate	9798.8	16.036	81.46		122.6±1.4

$\Delta_{l}^{g}H_{m}$(298.15 K)/kJ·mol^{-1} = (1.19±0.014)ΔH_{trn}(520 K) - (25.3±0.84) $r^2 = 0.9997$ (A-6)

[a] An average of (96.0±0.8), (95.0±1.1) and (94.1±1.0) kJ·mol^{-1}.

TABLE A-10. Correlations Between $\ln(t_o/t_a)_{avg}$ and $\ln(p/p_o)_{exp}$ at T/K = 298.15 for Runs 1 and 2[a]

run 1/run2	-slope/K	intercept	$\ln(t_o/t_a)_{avg}$	$\ln(p/p_o)_{exp}$	$\ln(p/p_o)_{calc}$	$p\cdot 10^3$/Pa calc/lit
dimethyl phthalate	5262.39	11.549				
	5295.37	11.628	-6.117	-12.716	-12.667	319/304
dimethyl terephthalate	5434.18	11.7439				
	5463.56	11.808	-6.506		-13.068	214/NA[b]
diethyl phthalate	5839.50	12.2722				
	5862.46	12.331	-7.323	-13.840	-13.908	92.3/98.8
dibutyl phthalate	7248.39	13.936				
	7273.57	13.998	-10.386	-17.080	-17.061	3.9/3.87[c]
dicyclohexyl phthalate	8788.75	15.307				
	8810.00	15.361	-14.179		-20.964	0.08/
bis (2-ethylhexyl)	9487.27	16.624				
Phthalate	9517.67	16.696	-15.212		-22.027	0.028/0.013[c]
bis (2-ethylhexyl)	10212.0	17.478				
Terephthalate	10243.5	17.552	-16.788		-23.650	0.0054

[a] Run 1and 2: slope and intercept measured at a mean temperature of T_m/K = 500. [b] Not available. [c] EPA Guidelines.

TABLE A-11. Correlations Between ln(t_o/t_a)$_{avg}$ and ln(p/p_o)$_{exp}$ at T/K = 298.15 for Runs 5 and 6[a]

run 5/run 6	-slope/K	intercept	ln(t_o/t_a)$_{avg}$	ln(p/p_o)$_{exp}$	ln(p/p_o)$_{calc}$	$p\cdot10^3$/Pa calc/lit
dimethyl phthalate	5206.7	10.782				
	5203.3	10.763	-6.685	-12.716	-12.51	373/304
dimethyl isophthalate	5506.9	11.201				
	5502.3	11.181	-7.271	-13.840	-13.14	200/263[b]
diethyl phthalate	5776.1	11.491				
	5771.8	11.471	-7.885	-13.840	-13.79	104/98.8
dibutyl phthalate	7173.5	13.136				
	7171.7	13.122	-10.928	-17.080	-17.05	4.0/3.87[c]
benzyl butyl phthalate	8346.5	14.276				
	8342.6	14.258	-13.723		-20.05	0.2/1.1[c]
bis (2-ethylhexyl) Phthalate	9404.5	15.817				
	9404.3	15.807	-15.730		-22.20	0.023/0.013

[a] Run 5and 6: slope and intercept measured at a mean temperature of T_m/K = 500. [b] Extrapolation of the Wagner eq, ref 12. [c] EPA Guidelines.

TABLE A-12. Correlations Between ln(t_o/t_a)$_{avg}$ and ln(p/p_o)$_{exp}$ at T/K = 298.15 for Runs 7 and 8[a]

run 7/run 8	-slope/K	intercept	ln(t_o/t_a)$_{avg}$	ln(p/p_o)$_{exp}$	ln(p/p_o)$_{calc}$	$p\cdot10^3$/Pa calc/lit
dimethyl phthalate	4995.2	10.356				
	5184.4	10.713	-6.527	-12.716	-12.64	327/304
diethyl phthalate	5543.3	11.023				
	5725.9	11.367	-7.694	-13.840	-13.90	93/98.8
dibutyl phthalate	6898.5	12.585				
	7064.8	12.897	-10.668	-17.080	-17.08	3.9/3.87[b]
benzyl butyl phthalate	8051.0	13.685				
	8196.7	13.956	-13.421	-20.046	-20.08	0.19/1.1[b]
bis (2-ethylhexyl) phthalate	9051.6	15.114				
	9189.1	15.369	-15.730	-22.198	-22.15	0.024/0.013
di-n-octyl phthalate	9668.7	15.794				
	9798.8	16.036			-23.64	0.0055/0.013

[a] Run 7and 8: slope and intercept measured at a mean temperature of T_m/K = 521. [b] EPA Guidelines.

TABLE A-13. Evaluation of the Constants of Eq 1-10 for Runs 5 and 6

	A”’·10^{6}	B”·10^{4}	C” ·10^{2}	D”
dimethyl phthalate	82.924291	-141.7992	-24.6431	8.577
dimethyl isophthalate	110.909505	-165.482	-21.31432	8.441
diethyl phthalate	152.125869	-200.0137	-14.74585	7.910
dibutyl phthalate	339.477148	-357.3325	13.42286	5.833
benzyl butyl phthalate	542.367858	-527.0011	47.2675	2.921
bis(2-ethylhexyl) phthalate	628.671862	-600.3165	56.19802	2.765

TABLE A-14. Evaluation of the Constants of Eq 1-10 for Runs 7 and 8

	A”’·10^{6}	B”·10^{4}	C” ·10^{2}	D”
dimethyl phthalate	75.11647	-137.1280	-26.14768	8.719
diethyl phthalate	146.2789	-196.70237	-15.79776	8.005
dibutyl phthalate	346.9105	-362.40705	14.36958	5.780
benzyl butyl phthalate	539.3424	-524.54449	46.3684	3.029
bis(2-ethylhexyl) phthalate	632.5369	-603.20200	57.19202	2.656
di-n-octyl phthalate	724.7293	-680.152864	71.48372	1.548

TABLE A-15. Evaluation of the Constants for Eq 1-10 for Runs 1 and 2 and 5 Through 8

Runs 1 and 2	A”·10^{-6}	B”·10^{-4}	C” ·10^{-2}	D”	T_b/K calc/lit	$p·10^{6}$/Pa 298.15 K calc/lit
dimethyl phthalate	74.296	-136.828	-26.2625	8.729	555/557	
dimethyl terephthalate	100.864	-158.906	-22.02396	8.388	560/561	
diethyl phthalate	145.816	-196.376	-15.9193	8.019	571/568	
dibutyl phthalate	339.3640	-357.347	13.4093	5.837	613/613	
dicyclohexyl phthalate	635.470	-602.922	64.3113	1.319	490/497	80/116
bis (2-ethylhexyl) phthalate	638.697	-606.365	58.174	2.577	677/657	28/13
bis (2-ethylhexyl) terephthalate	738.488	-689.358	73.312	1.448	699/673	5.4/173
Runs 5 and 6						
dimethyl phthalate	82.924	-141.799	-24.643	8.577		
dimethyl terephthalate	110.91	-165.482	-21.314	8.441		
diethyl phthalate	152.126	-200.014	-14.746	7.91		
dibutyl phthalate	339.477	-357.332	13.423	5.833		
benzyl butyl phthalate	542.368	-527.001	47.268	2.921	667/643	200/1100
bis(2-ethylhexyl) phthalate	628.672	-600.317	56.198	2.765	677/657	23/13
Runs 7 and 8						
dimethyl phthalate	75.1165	-137.128	-26.1477	8.719		
dimethyl terephthalate	146.279	-196.702	-15.7978	8.005		
diethyl phthalate	346.911	-362.407	14.3696	5.78		
dibutyl phthalate	539.342	-524.545	46.3684	3.029		
benzyl butyl phthalate	632.537	-603.202	57.1920	2.656		
di-n-octyl phthalate	724.729	-680.153	71.484	1.548	700/663	5.5/13.3

$$\ln(p/p_o) = A”(T/K)^{-3} + B”(T/K)^{-2} + C”(T/K)^{-1} + D” \qquad \text{(A-7)}$$

TABLE A-16. A Comparison of Estimated and Experimental Heat Capacities, Evaluation of the Uncertainty

	C_p(l)/J·mol^{-1}·K^{-1}		C_p(l)$_{error}$/ J·mol^{-1}·K^{-1}	C_p(cr)/J·mol^{-1}·K^{-1}	
	Est	Exp	Value Used	Est	Exp^b
dimethyl phthalate	314	314^a, 310^b	±16		
dimethyl terephthalate	314		±16	240.8	211.4^b
dimethyl isophthalate	314	288.7^c	±16	240.8	246.2^b, 237^c
diethyl phthalate	377.8	369^a	±16		
di-n-butyl phthalate	505.4	476^a	±29		
benzyl butyl phthalate	531	499.3^a	±31		
bis(2-ethylhexyl) phthalate	747.6	706^a	±41		
di-n-octyl phthalate	760.6		±41		

[a] Heat Capacities of Some Phthalate Esters. Rohac, V.; Fulem, M.; Schmidt, H. –G.; Ruzicka, V.; Ruzicka, K.; Wolf, G. *J. Therm. Anal. Calorim.*, **2002**, *70*, 455–466. [b] Roux, M. V. ; Jimenez, P.; Davalos, J. Z.; Turrion, C.; Afeefy, H. Y.; Liebman, J. F. Enthalpies of formation of methyl benzenecarboxylates. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 887-90. [c] Steele, W.V.; Chirico, R.D.; Knipmeyer, S.E.; Nguyen, A. Vapor Pressure, Heat Capacity, and Density Along the Saturation Line, Measurements for Dimethyl Isophthalate, Dimethyl Carbonate, 1,3,5-Triethylbenzene, Pentafluorophenol, 4-*tert*-Butylcatechol, α-Methylstyrene, and *N*,*N*-*bis*(2-Hydroxyethyl)ethylenediamine. *J. Chem. Eng. Data*, **1997**, *42*, 1008-1020.

TABLE A-17. Antoine Constants Used to Evaluate Vapor Pressures[a]

	A	b	c	T/K range
dicyclohexyl phthalate	10.065	5069		391-475
benzyl butyl phthalate	9.1472	4647.5		416-516
bis(2-ethylhexyl) phthalate	11.8564	6416.2	36.74	373-660
di-n-octyl phthalate	9.897	5197.4		423-523

[a] log (p/kPa) = a - b/(c + T/K). Stephenson, R. M.; Malanowski, S. *Handbook of the Thermodynamics of Organic Compounds*. Elsevier: N. Y. 1987.

TABLE A-18A. Experimental Retention Times of Various Dialkyl Phthalates

Run 1	478.6	483.6	488.5	493.6	498.5	503.5	508.4
t_o = 60 s				t/t_o			
Hexanes/acetone	0.547	0.545	0.545	0.554	0.553	0.559	0.562
Dimethyl phthalate	1.302	1.213	1.141	1.086	1.030	0.988	0.949
Diethyl phthalate	1.779	1.622	1.492	1.391	1.294	1.219	1.151
Diisobutyl phthalate	3.757	3.291	2.905	2.597	2.323	2.103	1.914
Di-*n*-butyl phthalate	4.995	4.322	3.764	3.322	2.934	2.622	2.355
Di-*n*-pentyl phthalate	9.067	7.671	6.524	5.617	4.845	4.225	3.706
Di-*n*-hexyl phthalate	16.886	13.987	11.653	9.817	8.288	7.076	6.073
Benzyl *n*-butyl phthalate	17.088	14.237	11.933	10.105	8.576	7.355	6.336
Dicyclohexyl phthalate	28.612	23.627	19.577	16.399	13.771	11.679	9.947
bis(2-Ethylhexyl) phthalate	32.978	26.742	21.808	18.016	14.891	12.449	10.468

TABLE A-18B. Enthalpies of Transfer and Vaporization Enthalpies Used to Evaluate Vaporization Enthalpies of Diisobutyl Phthalate, Dipentyl Phthalate and Di-*n*-hexyl Phthalate (p_o/Pa =101325)[a]

Run 1	- slope T/K	intercept	ΔH_{trn}(493 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)
Dimethyl phthalate	5432.6±29	11.64±0.06	45.16±0.2	77.0±1.2	76.8±0.6
Diethyl phthalate	6004.1±29	12.34±0.06	49.92±0.2	82.1±0.5	82.1±0.6
Diisobutyl phthalate	7051.1±32	13.57±0.06	58.62±0.3		92.0±0.7
Di-*n*-butyl phthalate	7406.2±35	13.99±0.07	61.57±0.3	95.0±1.1	95.3±0.7
Di-*n*-pentyl phthalate	8132.2±35	14.86±0.07	67.61±0.3		102.1±0.7
Di-*n*-hexyl phthalate	8864.3±38	15.73±0.08	73.69±0.3		109.0±0.8
Benzyl *n*-butyl phthalate	8581.5±35	15.13±0.07	71.34±0.3	106.2±2.4	106.4±0.7
Dicyclohexyl phthalate	8936.0±37	15.34±0.07	74.29±0.3	109.9±1.0	109.7±0.8
bis (2-Ethylhexyl) phthalate	9671.5±45	16.74±0.09	80.40±0.4	116.7±0.5	116.6±0.8

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.13±0.01)ΔH_{trn}(493 K) - (25.8±0.5) r^2 = 0.9998   (A-8)

[a] Uncertainties represent 1 standard deviation.

TABLE A-19A. Experimental Retention Times of Various Dialkyl Phthalates

Run 2	478.6	483.6	488.5	493.6	498.5	503.5	508.4
t_o = 60 s				t/t_o			
Hexanes/acetone	0.547	0.555	0.555	0.561	0.563	0.562	0.565
Dimethyl phthalate	1.309	1.233	1.159	1.101	1.046	0.994	0.954
Diethyl phthalate	1.789	1.646	1.516	1.409	1.314	1.225	1.157
Diisobutyl phthalate	3.789	3.335	2.950	2.628	2.354	2.113	1.922
Di-*n*-butyl phthalate	5.040	4.377	3.821	3.360	2.971	2.634	2.365
Di-*n*-pentyl phthalate	9.155	7.761	6.624	5.682	4.902	4.244	3.720
Di-*n*-hexyl phthalate	17.055	14.142	11.813	9.924	8.382	7.105	6.093
Benzyl *n*-butyl phthalate	17.272	14.417	12.110	10.223	8.676	7.382	6.358
Dicyclohexyl phthalate	28.945	23.908	19.837	16.597	13.929	11.719	9.979
bis(2-Ethylhexyl) phthalate	33.251	27.000	22.123	18.190	15.056	12.502	10.503

TABLE A-19B. Enthalpies of Transfer and Vaporization Enthalpies Used to Evaluate Vaporization Enthalpies of Diisobutyl Phthalate, Dipentyl Phthalate and Di-*n*-hexyl Phthalate (p_o/Pa =101325)[a]

Run 2	- slope T/K	intercept	ΔH_{trn}(493 K) kJ·mol^{-1}	$\Delta_l^gH_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^gH_m$(298 K) kJ·mol^{-1} calc
Dimethyl phthalate	5483.9±29	11.73±0.06	45.59±0.2	77.0±1.2	76.7±0.7
Diethyl phthalate	6059.8±29	12.45±0.06	50.38±0.2	82.1±0.5	82.1±0.8
Diisobutyl phthalate	7115.1±32	13.69±0.06	59.15±0.3		92.0±0.8
Di-*n*-butyl phthalate	7470.6±34	14.11±0.07	62.11±0.3	95.0±1.1	95.3±0.8
Di-*n*-pentyl phthalate	8197.8±35	14.98±0.07	68.15±0.3		102.2±0.9
Di-*n*-hexyl phthalate	8929.8±38	15.86±0.08	74.24±0.3		109.0±0.9
Benzyl *n*-butyl phthalate	8658.5±35	15.28±0.07	71.98±0.3	106.2±2.4	106.5±0.9
Dicyclohexyl phthalate	9013.6±37	15.49±0.07	74.94±0.3	109.9±1.0	109.8±0.9
bis (2-Ethylhexyl) phthalate	9721.6±44	16.830±0.09	80.82±0.4	116.7±0.5	116.4±1.0
$\Delta_l^gH_m$(298.15 K)/kJ·mol^{-1} = (1.13±0.01)ΔH_{trn}(493 K) - (25.4±0.5)				r^2 = 0.9997	(A-9)

[a] Uncertainties represent 1 standard deviation.

TABLE A-20A. Experimental Retention Times of Various Dialkyl Phthalates

Run 3	444.0	448.9	454.1	459.1	464.1	469.2	473.6
t_o = 60 s				t/t_o			
Hexanes/acetone	0.552	0.554	0.561	0.558	0.558	0.569	0.575
Dimethyl phthalate	2.567	2.285	2.068	1.866	1.697	1.576	1.460
Diethyl phthalate	4.183	3.625	3.197	2.813	2.492	2.257	2.040
Diisobutyl phthalate	11.919	9.900	8.363	7.058	5.989	5.197	4.497
Di-*n*-butyl phthalate	17.301	14.197	11.840	9.873	8.273	7.088	6.057
bis(4-Methyl-2-pentyl) phthalate[a]	27.708	22.397	18.402	15.118	12.480	10.541	8.867
bis(4-Methyl-2-pentyl) phthalate[b]	28.197	22.789	18.703	15.354	12.663	10.683	8.978
Di-*n*-pentyl phthalate	36.975	29.657	24.158	19.684	16.120	13.492	11.267

TABLE A-20B. Enthalpies of Transfer and Vaporization Enthalpies Used to Evaluate Vaporization Enthalpies of *Bis*(4-methyl-2-pentyl) Phthalate Isomers (p_o/Pa =101325)[a]

Run 3	- slope T/K	intercept	ΔH_{trn}(459 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)
Dimethyl phthalate	5780.5±51	12.32±0.11	48.06±0.4	77.0±1.2	76.9±0.8
Diethyl phthalate	6382.6±53	13.09±0.12	53.06±0.4	82.1±0.5	82.2±0.8
Diisobutyl phthalate	7484.1±58	14.43±0.13	62.22±0.5	92.0±0.8[b]	91.9±0.9
Di-*n*-butyl phthalate	7857.2±59	14.88±0.13	65.32±0.5	95.0±1.0	95.2±0.9
bis(4-Methyl-2-pentyl) phthalate[c]	8343.7±63	15.50±0.14	69.37±0.5		99.5±0.9
bis(4-Methyl-2-pentyl) Phthalate[d]	8377.6±62	15.56±0.14	69.65±0.5		99.8±0.9
Di-*n*-pentyl phthalate	8626.0±61	15.84±0.13	71.71±0.5	102.2±0.8[b]	102.0±1.0

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.06±0.01)ΔH_{trn}(459 K) - (25.1±0.6) r^2 = 0.9997 (A-10)

[a] Uncertainties represent 1 standard deviation. [b] Average value from Runs 1/2 used as a standard. [c] 1st isomer through from column. [d] 2nd isomer through column.

TABLE A-21A. Experimental Retention Times of Various Dialkyl Phthalates

Run 4	444.0	448.9	454.1	459.1	464.1	469.2	473.6
t_o = 60 s				t/t_o			
Hexanes/acetone	0.571	0.573	0.573	0.574	0.577	0.579	0.583
Dimethyl phthalate	2.629	2.341	2.098	1.897	1.730	1.587	1.483
Diethyl phthalate	4.282	3.713	3.240	2.856	2.538	2.270	2.073
Diisobutyl phthalate	12.201	10.137	8.476	7.158	6.091	5.219	4.571
Di-*n*-butyl phthalate	17.709	14.535	12.004	10.013	8.414	7.118	6.158
bis(4-Methyl-2-pentyl) phthalate[a]	28.353	22.920	18.663	15.338	12.697	10.579	9.020
bis(4-Methyl-2-pentyl) phthalate[b]	28.888	23.324	18.966	15.578	12.882	10.725	9.131
D-*n*-pentyl phthalate	37.866	30.360	24.490	19.968	16.399	13.551	11.453

TABLE A-21B. Enthalpies of Transfer and Vaporization Enthalpies Used to Evaluate Vaporization Enthalpies of *Bis*(4-methyl-2-pentyl) Phthalate Isomers (p_o/Pa =101325)[a]

Run 4	- slope T/K	intercept	ΔH_{trn}(459 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)
Dimethyl phthalate	5865.0±27	12.49±0.06	48.76±0.2	77.0±1.2	76.9±0.8
Diethyl phthalate	6465.7±27	13.26±0.06	53.75±0.2	82.1±0.5	82.2±0.8
Diisobutyl phthalate	7573.0±29	14.61±0.06	62.96±0.2	92.0±0.8[b]	92.0±0.9
Di-*n*-butyl phthalate	7944.7±30	15.06±0.06	66.05±0.2	95.0±1.0	95.2±0.9
bis(4-Methyl-2-pentyl) phthalate[c]	8427.6±31	15.67±0.07	70.06±0.3		99.5±0.9
bis(4-Methyl-2-pentyl) phthalate[d]	8467.3±32	15.74±0.07	70.39±0.3		99.8±0.9
Di-*n*-pentyl phthalate	8714.9±33	16.02±0.07	72.45±0.3	102.2±0.8[b]	102.0±0.9

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.06±0.01)ΔH_{trn}(459 K) - (25.1±0.6) r^2 = 0.9997 (A-11)

[a] Uncertainties represent 1 standard deviation. [b] Average value from Runs 1/2 used as a standard. [c] 1st isomer through from column. [d] 2nd isomer through column.

TABLE A-22A. Experimental Retention Times of Various Dialkyl Phthalates

Run 5	508.2	513.2	518.2	523.2	528.2	533.2	538.2
t_o = 60 s				t/t_o			
Hexanes/acetone	0.608	0.606	0.609	0.608	0.609	0.608	0.612
Dimethyl phthalate	1.012	0.970	0.937	0.905	0.879	0.854	0.838
Diethyl phthalate	1.225	1.156	1.100	1.048	1.005	0.966	0.938
Diisobutyl phthalate	2.031	1.850	1.701	1.570	1.459	1.364	1.288
Di-*n*-butyl phthalate	2.499	2.249	2.041	1.863	1.711	1.582	1.478
bis(4-Methyl-2-pentyl) phthalate	3.301	2.924	2.614	2.350	2.127	1.939	1.787
Di-*n*-pentyl phthalate	3.929	3.453	3.060	2.729	2.450	2.216	2.025
Di-*n*-hexyl phthalate	6.437	5.541	4.801	4.189	3.681	3.258	2.915
Benzyl *n*-butyl phthalate	6.724	5.810	5.051	4.419	3.893	3.452	3.094
Di-*n*-octyl phthalate	18.489	15.350	12.806	10.766	9.117	7.772	6.695
Di-*n*-nonyl phthalate	31.869	26.035	21.377	17.680	14.742	12.369	10.478

TABLE A-22B. Enthalpies of Transfer and Vaporization Enthalpies Used to Evaluate Vaporization Enthalpies for Di-*n*-nonyl Phthalate with *Bis*(4-methyl-2-pentyl) Phthalate (p_o/Pa =101325)[a]

Run 5	- slope T/K	intercept	ΔH_{trn}(523 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298.15 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298.15 K) kJ·mol^{-1}(calc)
Dimethyl phthalate	5343.2±37	11.43±0.07	44.42±0.3	77.0±1.2	77.0±0.4
Diethyl phthalate	5853.9±38	12.01±0.07	48.67±0.3	82.1±0.5	82.2±0.4
Diisobutyl phthalate	6807.7±40	13.05±0.07	56.60±0.3	92.0±0.8[c]	91.9±0.4
Di-*n*-butyl phthalate	7135.3±42	13.41±0.08	59.32±0.3	95.0±1.0	95.2±0.5
bis(4-Methyl-2-pentyl) phthalate[b]	7577.3±45	13.93±0.09	62.99±0.4		99.7±0.5
Di-*n*-pentyl phthalate	7805.0±44	14.16±0.08	64.89±0.4	102.2±0.8[c]	102.0±0.5
Di-*n*-hexyl phthalate	8483.4±46	14.94±0.09	70.53±0.4	109.0±0.9[c]	108.9±0.5
Benzyl *n*-butyl phthalate	8240.6±44	14.41±0.08	68.51±0.4	106.2±2.4	106.4±0.5
Di-*n*-octyl phthalate	9846.2±52	16.50±0.10	81.86±0.5	122.6±1.4	122.7±0.5
Di-*n*-nonyl phthalate	10526.5±55	17.28±0.10	87.51±0.5		129.6±0.9

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.22±0.01)ΔH_{trn}(523 K) - (22.8±0.3) r^2 =0.9999   (A-12)

[a] Uncertainties represent 1 standard deviation. [b] Only one peak. [c] Average value from Runs 1/2.

TABLE A-23A. Experimental Retention Times of Various Dialkyl Phthalates

Run 6	508.2	513.2	518.2	523.2	528.2	533.2	538.2
t_o = 60 s				t/t_o			
Hexanes/acetone	0.604	0.609	0.608	0.611	0.609	0.615	0.618
Dimethyl phthalate	1.012	0.975	0.937	0.910	0.882	0.864	0.845
Diethyl phthalate	1.226	1.162	1.101	1.055	1.009	0.977	0.946
Diisobutyl phthalate	2.036	1.858	1.703	1.579	1.466	1.378	1.298
Di-*n*-butyl phthalate	2.506	2.257	2.043	1.872	1.719	1.597	1.489
bis(4-methyl-2-pentyl) phthalate	3.311	2.935	2.616	2.361	2.138	1.957	1.799
Di-*n*-pentyl phthalate	3.941	3.464	3.062	2.740	2.461	2.233	2.037
Di-*n*-hexyl phthalate	6.459	5.550	4.802	4.208	3.695	3.280	2.928
benzyl *n*-butyl phthalate	6.739	5.812	5.045	4.433	3.903	3.471	3.104
Di-*n*-octyl phthalate	18.521	15.338	12.795	10.790	9.141	7.805	6.708
Di-*n*-nonyl phthalate	31.878	25.993	21.338	17.699	14.765	12.406	10.489

TABLE A-23B. Enthalpies of Transfer and Vaporization Enthalpies Used to Evaluate Vaporization Enthalpies for Dinonyl Phthalate (p_o/Pa =101325)[a]

Run 6	- slope T/K	intercept	ΔH_{trn}(523 K) kJ·mol^{-1}	$\Delta_l^gH_m$(298.15 K) kJ·mol^{-1} (lit)	$\Delta_l^gH_m$(298.15 K) kJ·mol^{-1}(calc)
Dimethyl phthalate	5297.6±39	11.33±0.08	44.04±0.3	77.0±1.2	76.9±0.4
Diethyl phthalate	5819.6±43	11.93±0.08	48.38±0.4	82.1±0.5	82.2±0.4
Diisobutyl phthalate	6776.1±45	12.98±0.09	56.33±0.4	92.0±0.8[b]	91.9±0.5
Di-*n*-butyl phthalate	7105.9±48	13.35±0.9	59.08±0.4	95.0±1.0	95.2±0.5
bis(4-Methyl-2-pentyl) phthalate	7545.2±49	13.86±0.09	62.73±0.4		99.6±0.5
Di-*n*-pentyl phthalate	7780.4±49	14.11±0.09	64.68±0.4	102.2±0.8[b]	102.0±0.5
Di-*n*-hexyl phthalate	8463.6±51	14.90±0.1	70.36±0.4	109.0±0.9[b]	108.9±0.5
benzyl *n*-butyl phthalate	8222.0±48	14.37±0.09	68.35±0.4	106.2±2.4	106.4±0.5
Di-*n*-octyl phthalate	9825.1±53	16.46±0.10 .	81.68±0.4	122.6±1.4	122.6±0.6
Di-*n*-nonyl phthalate	10501.8±56	17.23±0.01	87.31±0.5		129.4±0.5

$\Delta_l^gH_m$(298.15 K)/kJ·mol^{-1} = (1.21±0.005)ΔH_{trn}(523 K) - (23.5±0.3) $r^2 = 0.9999$ (A-13)

[a] Uncertainties represent 1 standard deviation. [b] Average values from runs 1/2 in this work used as standard values.

TABLE A-24. Literature Vaporization Enthalpies Adjustments to From the Mean Temperature of Measurement to T/K = 298.15

	$\Delta_l^gH_m(T_m/K)$ kJ·mol^{-1}	T_m/K	Cpl[a] J·K^{-1}·mol^{-1}	$\Delta Cp\Delta T$[b] kJ·mol^{-1}	$\Delta_l^gH_m$(298.15 K) kJ·mol^{-1}	Ref
Di-*n*-pentyl phthalate	87.4	360	569.2±18	9.8±1.1	97.2±0.7	S1
	99.4	343	569.2±18	7.1±0.8	106.5±0.8	S3
Di-*n*-hexyl phthalate	102.9	360	633±18	11.7±1.1	114.7±1.1[c]	S3
	103.0	365	633±18	10.8±1.1	113.7±1.1[c]	S2
Di-*n*-octyl phthalate	107.5	408	760.6±18	36.4±3.1	135.9±3.1	S3
	99.5	473	760.6±18	22.8±2.0	122.4±2.0	S3
Di-*n*-nonyl phthalate	108.9	348	824.4±18	11.2±0.9	120.1±0.9	S3

[a] Chickos, J. S.; Hesse, D. G.; Liebman, J. F. A. Group Additivity Approach for the Estimation of Heat Capacities of Organic Liquids and Solids at 298 K. *Struct. Chem.* **1993**, *4*, 261-269. [b] Chickos, J. S.; Hosseini, S.; Hesse, D. G.; Liebman, J. F. Heat Capacity Corrections to a Standard State: A Comparison of New and Some Literature Methods for Organic Liquids and Solids. *Struct. Chem.* **1993**, *4*, 271-8. [c] Both these values are probably derived from the same article since the mean temperature of measurement was estimated from a graph.

S1.) Perry, E. S. ; Weber, W. H. Vapor Pressures of Phlegmatic Liquids. II High Molecular Weight Esters and Silicone Oils. *J. Am. Chem. Soc.* **1949**, *71*, 3726-3730.

S2.) Small, P. A.; Small, K. W.; Cowley, P. The Vapor Pressure of Some High Boiling Esters. *Trans. Faraday Soc.* **1948**, 44, 810-6.

S3.) Stephenson, R. M.; Malonowski, S. *Handbook of the Thermodynamics of Organic Compounds*; Elsevier: New York, 1987.

TABLE A-25. A Summary of the Vaporization Enthalpies (kJ·mol^{-1}) at T/K = 298.15 of Runs 1 to 6.

Targets	**Runs 1/2**	**Runs 3/4**	**Runs 5/6**	Average	Lit.
diisobutyl phthalate[a]	92.0±0.7/ 92.0±0.8			92.0±0.8	NA[f]
dipentyl phthalate[a]	102.1±0.7/ 102.2±0.9			102.2±0.8	93.6±0.7[g] 106.5±0.8[h]
di-*n*-hexyl phthalate[a]	109.0±0.8/ 109.0±0.9			109.9±0.9	121.8±3.1[i] 113.5±1.1[h]
bis(4-methyl-2-pentyl) phthalate[b]		99.5±0.9/99.5±0.9		99.5±0.9	NA[f]
bis(4-methyl-2-pentyl) phthalate[c]		99.8±0.9/99.8±0.9		99.8±0.9	NA[f]
bis(4-methyl-2-pentyl) phthalate[d]			99.7±0.5/99.6±0.5	99.6±0.5	NA[f]
di-*n*-nonyl phthalate			129.6±0.9/129.4±0.5	129.5±0.7	120.1±0.9[i]
Standards					Value Used[j]
dimethyl phthalate	76.8±0.6/ 76.7±0.7	76.9±0.8/76.9±0.8	77.0±0.4/76.9±0.4	76.9±0.6	77.0±1.2
diethyl phthalate	82.1±0.6/ 82.1±0.8	82.2±0.8/82.2±0.8	82.2±0.4/82.2±0.4	82.2±0.6	82.1±0.5
diisobutyl phthalate[a]		91.9±0.9/92.0±0.9	91.9±0.4/91.9±0.5	91.9±0.7	92.0±0.8[e]
di-*n*-butyl phthalate	95.3±0.7/ 95.3±0.8	95.2±0.9/95.2±0.9	95.2±0.5/95.2±0.5	95.2±0.7	95.0±1.1
di-*n*-pentyl phthalate[a]		102.2±1.0/ 102.0±0.9	102.0±0.5/102.0±0.5	102.0±0.7	102.2±0.9
di-*n*-hexyl phthalate[a]			108.9±0.5/108.9±0.5	108.9±0.5	109.0±0.9
benzyl butyl phthalate	106.4±0.7/ 106.5±0.9		106.4±0.5/106.4±0.3	106.4±0.6	106.2±2.4
dicyclohexyl phthalate	109.7±0.8/ 109.8±0.9			109.8±0.9	109.9±1.0
bis (2-ethylhexyl) phthalate	116.6±0.8/ 116.4±1.0			116.5±0.9	116.7±0.5
di-*n*-octyl phthalate			122.6±0.3/122.6±0.6	122.6±0.5	122.6±1.4

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[a]Evaluated in runs 1and 2 only; average value used as a standards in subsequent runs. [b]1st isomer through column. [c]2nd isomer through column. [d]Analyzed as a mixture of diasterioisomers. [e]Evaluated in runs 3 and 4 only; average value used as a standard in runs 5 and 6. [f] NA: not available. [g]Reference 24. [h]Reference 18. [i]Reference 2. [j]See Table 1-24 for references unless noted otherwise.

TABLE A-26A. Evaluation of the Constants of Eq 1-10 for Runs 1/2

	$A\cdot10^{-6}$	$B\cdot10^{-4}$	$C\cdot10^{-2}$	D
Dimethyl phthalate	83.05±0.78	-143.99±0.62	-24.36±0.16	8.568±0.014
Diethyl phthalate	157.518±1.1	-205.972±0.84	13.381±0.22	7.797±0.019
Diisobutyl phthalate	302.085±1.1	-326.273±0.87	8.569±0.23	6.153±0.020
Di-*n*-butyl phthalate	350.635±1.1	-366.679±0.89	-15.919±0.24	5.606±0.020
Benzyl *n*-butyl phthalate	541.920±0.61	-525.767±0.48	47.076±0.13	2.942±-.011
Di-*n*-pentyl phthalate	448.865±1.3	-448.432±1.0	30.71±0.26	4.518±0.023
Dicyclohexyl phthalate	616.222±2.2	-587.53±1.7	-60.237±0.45	1.664±0.039
Di-*n*-hexyl phthalate	547.152±1.5	-530.237±1.2	45.46±0.30	3.441±0.260
bis(2-Ethylhexyl) phthalate	651.351±1.9	-616.995±1.5	-60.869±0.39	2.353±0.034

TABLE A-26B. Evaluation of the Constants of Eq 1-10 for Runs 3/4

	$A\cdot10^{-6}$	$B\cdot10^{-4}$	$C\cdot10^{-2}$	D
Dimethyl phthalate	86.544±1.1	-146.441±0.89	23.849±0.23	8.547±0.020
Diethyl phthalate	159.528±1.1	-207.4330.91	12.97±0.24	7.762±0.021
Diisobutyl phthalate	300.132±0.88	-324.79±0.70	8.34±0.18	6.154±0.016
Di-*n*-butyl phthalate	348.143±0.81	-364.871±0.64	-15.59±0.17	5.612±0.015
Benzyl *n*-butyl phthalate	533.584±0.83	-519.185±0.66	45.06±0.17	3.13±0.015
Di-*n*-pentyl phthalate	444.413±0.78	-445.283±0.62	30.02±0.16	4.554±0.014
bis (4-Methyl-2-pentyl) phthalate (*meso* and *dl*)	409.542±0.89	-416.189±0.71	24.69±0.19	4.967±0.016
Di-*n*-hexyl phthalate	541.104±0.81	-526.063±0.65	44.46±0.17	3.507±0.015
Di-*n*-octyl phthalate	733.96±0.92	-687.192±0.73	-73.21±0.19	1.428±0.017
Di-*n*-nonyl phthalate	830.026±0.98	-767.452±0.78	87.54±0.21	0.392±0.018

TABLE A-26C. Evaluation of the Constants of Eq 1-10 for Runs 5/6

	$A\cdot10^{-6}$	$B\cdot10^{-4}$	$C\cdot10^{-2}$	D
Dimethyl phthalate	85.345±0.78	-145.826±0.71	23.844±0.19	8.517±0.016
Diethyl phthalate	157.63±1.10	-205.991±0.85	13.353±0.22	7.793±0.019
Diisobutyl phthalate	299.551±0.74	-324.163±0.59	8.038±0.15	6.199±0.013
Di-*n*-butyl phthalate	347.879±0.84	-364.414±0.67	-15.364±0.18	5.648±0.015
bis(4-Methyl-2-pentyl) phthalate (1)	406.879±0.86	-413.533±0.68	23.994±0.18	5.043±0.016
bis(4-Methyl-2-pentyl) phthalate (2)	408.918±1.03	-415.201±0.82	24.077±0.22	5.068±0.019
Di-*n*-pentyl phthalate	443.731±0.79	-444.204±0.63	29.564±0.17	4.625±0.014

TABLE A-27. Vapor Pressures Evaluated By Correlation as A Function of Temperature p/Pa, (p_o/Pa = 101325)^{a,b}

T/K	Runs 1/2 DIBP	Runs 1/2 DPP	Runs 1/2 DHP	Runs 5/6 DIBP	Runs 5/6 MPP(1, 2)	Runs 3/4 DNP	Runs 3/4 MPP(1)	Runs 3/4 MPP(2)
				$10^4\cdot p$/Pa				
298.15	86±10	7.7±1.0	1.5±0.21	88±6.2	14±1.1	0.011±0.001	14±9.5	13±9.1
310	340±41	35±4.6	7.6±1.1	350±28	61±4.9	0.072±0.008	63±42	60±40
320	1000±100	116±14	27±3.5	1000±72	190±16	0.32±0.04	200±130	190±130
330	2800±280	360±43	89±11	2800±200	580±46	1.3±0.13	600±400	570±380
340	7100±700	1000±100	270±33	7200±500	1600±110	5.0±0.5	1700±1100	1600±1000
				$10^2\cdot p$/Pa				
350	170±15	27±2.7	7.7±0.84	170±10	42±3.0	0.17±0.02	43±28	41±27
360	390±31	67±6	20±2.0	390±24	100±7.1	0.56±0.5	100±66	100±65
370	840±67	160±14	51±4.6	850±51	230±14	1.7±0.13	240±150	230±150
380	1700±120	350±28	120±11	1700±87	510±31	4.7±0.37	530±320	510±310
390	3400±200	740±52	270±21	3400±170	1100±53	12±0.90	1100±650	1100±640
400	6400±380	1500±110	570±40	6400±260	2100±110	30±2.1	2200±1300	2100±1300
				p/Pa				
410	110±6.0	29±1.7	12±0.7	120±4.6	40±1.2	0.71±0.04	41±24	40±24
420	200±10	54±3	23±1	201±8	74±3	1.6±0.1	76±43	74±43
430	340±14	97±5	42±2	340±10	130±5	3±0.2	130±75	130±74
440	560±22	170±7	76±4	560±17	220±7	6.8±0.3	230±130	230±130
450	890±27	280±11	130±5	890±27	370±11	13±0.5	380±210	380±210
460	1400±41	460±14	220±9	1400±28	600±18	25±1	620±330	610±330
470	2100±42	740±22	370±11	2100±42	940±19	44±1.8	970±510	950±510
480	3100±62	1100±23	590±18	3100±62	1400±29	78±2	1500±780	1500±770
490	4500±90	1700±34	900±18	4500±45	2200±42	130±4	2200±1100	2200±1100
500	6400±64	2500±51	1400±27	6400±64	3200±32	210±6	3200±1700	3200±1700

[a] Vapor pressures are values calculated directly from the correlation of ln(p/p^o) and ln(t_o/t_a) at each temperature, T/K = T. [b] Vapor pressures rounded to 2 significant figures; DIBP: diisobutyl phthalate; DPP: di-n-pentyl phthalate; DHP: di-n-hexyl phthalate; MPP(1,2): *bis* 4-methyl-2-pentyl phthalates; DNP: di-n-nonyl phthalate. MPP(1,2): co-eluting *bis* 4-methyl-2-pentyl phthalate MPP(1): *bis* 4-methyl-2-pentyl phthalate to elute first; MPP(2): to elute second.

Appendix B

Table B-1. Validation of the Vaporization Enthalpies of 1-Dodecanamine and 1-Tetradecanamine

Run 1	423.7	428.8	433.8	438.8	443.8	448.7	453.8
				t/t_o			
Hexanes	2.721	2.732	2.727	2.729	2.749	2.772	2.755
1-heptanamine	3.196	3.153	3.098	3.06	3.047	3.04	2.995
1-octanamine	3.574	3.479	3.379	3.305	3.261	3.228	3.161
1-decanamine	5.236	4.882	4.562	4.315	4.13	3.977	3.805
1-dodecanamine	9.789	8.621	7.635	6.877	6.279	5.788	5.328
1-tetradecanamine	22.084	18.503	15.556	13.318	11.559	10.135	8.904

Experimental Retention Times (t_o = 60 s)

Run 1	- slope T/K	intercept	ΔH_{trn}(439 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)
1-heptanamine	4354.0	11.024	36.20	50.0 ± 0.2	50.1 ± 1.4	
1-octanamine	4750.6	11.375	39.49	55.1 ± 0.5	54.9 ± 1.5	
1-decanamine	5577.9	12.247	46.37	65.0 ± 0.2	65.0 ± 1.6	
1-dodecanamine	6451.6	13.277	53.64		75.7 ± 1.8	75.2 ± 1.8
1-tetradecanamine	7331.0	14.344	60.95		86.5 ± 1.9	85.4 ± 2.0

$$\Delta_l^g H_m(298.15\ \text{K})/\text{kJ·mol}^{-1} = (1.47 \pm 0.03)\Delta H_{trn}(439\ \text{K}) - (3.1 \pm 1.1) \quad r^2 = 0.9997 \quad \text{(B-1)}$$

Run 2	423.7	428.8	433.8	438.8	443.8	448.7	453.8
				t/t_o			
Hexanes	2.736	2.731	2.755	2.763	2.787	2.721	2.815
1-heptanamine	3.217	3.154	3.132	3.099	3.089	2.989	3.059
1-octanamine	3.595	3.48	3.416	3.346	3.305	3.178	3.226
1-decanamine	5.259	4.884	4.613	4.372	4.183	3.929	3.88
1-dodecanamine	9.821	8.641	7.732	6.981	6.365	5.751	5.43
1-tetradecanamine	22.279	18.641	15.824	13.586	11.78	10.162	9.103

Experimental Retention Times (t_o = 60 s)

Run 2	- slope T/K	intercept	ΔH_{trn}(439 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)
1-heptanamine	4364.2	11.036	36.28	50.0 ± 0.2	50.2 ± 2.2	
1-octanamine	4732.4	11.325	39.34	55.1 ± 0.5	54.9 ± 2.3	
1-decanamine	5529.5	12.129	45.97	65.0 ± 0.2	65.1 ± 2.5	
1-dodecanamine	6391.8	13.131	53.14		76.1 ± 2.8	75.2 ± 1.8

1-tetradecanamine	7269	14.187	60.43		87.3 ± 3.0	85.4 ± 2.0

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.54±0.04)ΔH_{trn}(439 K) - (5.7±1.7) r^2 = 0.9993 (B-2)

TABLE B-2A. Retention Times of Some Simple Aliphatic Amines (t_o = 60 s)

Run 3	433.8	438.8	443.8	448.7	453.7	458.6	463.6
				t/t_o			
Hexanes	2.79	2.813	2.835	2.858	2.868	2.889	2.9
1-heptanamine	3.171	3.155	3.142	3.134	3.118	3.115	3.105
1-octanamine	3.455	3.403	3.36	3.327	3.288	3.265	3.239
(*dl*) α-methylbenzylamine	3.553	3.494	3.444	3.405	3.36	3.332	3.301
2-phenethylamine	3.796	3.707	3.631	3.569	3.504	3.46	3.414
α,α-dimethylphenethylamine	4.192	4.05	3.93	3.829	3.732	3.66	3.59
1-decanamine	4.659	4.436	4.25	4.095	3.952	3.843	3.743
1-adamantylamine	5.056	4.81	4.6	4.422	4.256	4.126	4.006
1-dodecanamine	7.787	7.055	6.451	5.952	5.522	5.181	4.885
(*dl*) 1-(1-adamantyl)ethylamine	9.01	8.178	7.479	6.889	6.375	5.959	5.592
1-tetradecanamine	15.839	13.627	11.847	10.395	9.197	8.243	7.445

TABLE B-2B. Correlation of Vaporization Enthalpies with Enthalpies of Transfer of Some Primary Amines

Run 3	- slope T/K	intercept	ΔH_{trn}(449 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)
1-heptanamine	4187.9	10.619	34.82	50.0 ± 0.2	51.7 ± 3.2
1-octanamine	4565.9	10.934	37.96	55.1 ± 0.5	56.0 ± 3.4
(*dl*) α-methylbenzylamine	4356.7	10.314	36.22	55.2 ± 0.4	53.6 ± 3.3
2-phenethylamine	4540.9	10.462	37.75	57.2 ± 0.3	55.8 ± 3.3
α,α-dimethylphenethylamine	4801.1	10.73	39.91		58.8 ± 3.4
1-decanamine	5382.3	11.783	44.75	65.0 ± 0.2	65.4 ± 3.6
1-adamantylamine	4852.5	10.369	40.34		59.3 ± 3.4
1-dodecanamine	6242.9	12.784	51.9	75.5 ± 1.8	75.3 ± 3.9
(*dl*) 1-(1-adamantyl)ethylamine	5661.9	11.225	47.07		68.6 ± 3.7
1-tetradecanamine	7129.9	13.87	59.28	85.4 ± 2.0	85.5 ± 4.3

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.38±0.06)ΔH_{trn}(449 K) + (3.51±2.5) r^2 = 0.9913 (B-3)

TABLE B-2C. Experimental Retention Times of Some Simple Aliphatic Amines (t_o = 60 s)

Run 4	433.8	438.8	443.8	448.8	453.8	458.6	463.6
				t/t_o			
Hexanes	2.797	2.804	2.818	2.832	2.855	2.87	2.889
1-heptanamine	3.179	3.145	3.124	3.107	3.103	3.094	3.094
1-octanamine	3.462	3.393	3.341	3.297	3.271	3.243	3.227
(*dl*) α-methylbenzylamine	3.561	3.484	3.424	3.375	3.343	3.31	3.289
2-phenethylamine	3.804	3.695	3.61	3.538	3.486	3.437	3.402
α,α-dimethylphenethylamine	4.2	4.038	3.907	3.796	3.712	3.635	3.577
1-decanamine	4.666	4.422	4.224	4.059	3.931	3.818	3.729
1-adamantylamine	5.064	4.794	4.572	4.383	4.233	4.099	3.991
1-dodecanamine	7.795	7.031	6.412	5.902	5.491	5.147	4.867
(*dl*) 1-(1-adamantyl)ethylamine	9.017	8.149	7.432	6.832	6.338	5.919	5.571
1-tetradecanamine	15.835	13.575	11.77	10.313	9.142	8.19	7.417

TABLE B-2D. Correlation of Vaporization Enthalpies with Enthalpies of Transfer of Some Primary Amines

Run 4	- slope T/K	intercept	ΔH_{trn}(449 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)
1-heptanamine	4205.1	10.66	34.96	50.0 ± 0.2	51.6 ± 3.2
1-octanamine	4586.7	10.984	38.13	55.1 ± 0.5	56.0 ± 3.3
(*dl*) α-methylbenzylamine	4381.6	10.373	36.43	55.2 ± 0.4	53.7 ± 3.2
2-phenethylamine	4563.9	10.517	37.94	57.2 ± 0.3	55.8 ± 3.3
α,α-dimethylphenethylamine	4824.2	10.785	40.11		58.8 ± 3.4
1-decanamine	5405.5	11.839	44.94	65.0 ± 0.2	65.5 ± 3.6
1-adamantylamine	4876.7	10.427	40.54		59.4 ± 3.4
1-dodecanamine	6264.1	12.835	52.08	75.5 ± 1.8	75.3 ± 3.9
(*dl*) 1-(1-adamantyl)ethylamine	5683.2	11.277	47.25		68.7 ± 3.7
1-tetradecanamine	7143.9	13.905	59.39	85.4 ± 2.0	85.5 ± 4.2

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.38±0.06)ΔH_{trn}(449 K) + (3.25±2.5 r^2 = 0.9917 (B-4)

TABLE B-3A. Experimental Retention Times of Some Simple Aliphatic Amines (t_o = 60 s)

Run 5	387.8	392.9	398.1	403.3	408.5	413.6	418.7
				t/t_o			
Hexanes	2.641	2.636	2.654	2.659	2.669	2.68	2.694
Benzylamine	4.759	4.454	4.222	4.018	3.853	3.717	3.605

(*dl*) α-methylbenzylamine	5.243	4.856	4.559	4.303	4.095	3.923	3.782
2-phenethylamine	6.268	5.707	5.271	4.902	4.603	4.355	4.152
α,α-dimethylphenethylamine	8.326	7.387	6.619	5.997	5.5	5.106	4.781
1-decanamine	10.279	9.004	7.994	7.165	6.495	5.947	5.496
trans 2-phenylcyclopropylamine	11.258	9.713	8.506	7.533	6.759	6.128	5.618
1-adamantylamine	11.544	10.111	8.958	8.003	7.225	6.591	6.062

TABLE B-3B. Correlation of Vaporization Enthalpies with Enthalpies of Transfer of Some Primary Amines

Run 5	- slope T/K	intercept	ΔH_{trn}(403 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)
benzylamine	4422.9	10.659	36.77	54.4 ± 0.6	54.2 ± 1.6
(*dl*) α-methylbenzylamine	4569.2	10.832	37.99	55.2 ± 0.4	55.4 ± 1.7
2-phenethylamine	4774.7	11.03	39.7	57.2 ± 0.3	57.2 ± 1.7
α,α-dimethylphenethylamine	5267.8	11.853	43.79		61.5 ± 1.8
1-decanamine	5662.7	12.456	47.08	65.0 ± 0.2	65.0 ± 1.9
trans 2-phenylcyclopropylamine	5256.3	11.527	43.7		61.4 ± 1.8
1-adamantylamine	5098.1	10.965	42.38		60.0 ± 1.8

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.05±0.03)ΔH_{trn}(403 K) + (15.6±1.2) $r^2 = 0.9983$ (B-5)

TABLE B-3C. Experimental Retention Times of Some Simple Aliphatic Amines ($t_o = 60$ s)

Run 6	387.8	392.9	398.1	403.3	408.5	413.6	418.7
				t/t_o			
Hexanes	2.641	2.643	2.652	2.663	2.673	2.683	2.695
benzylamine	4.758	4.464	4.22	4.024	3.859	3.721	3.606
(*dl*) α-methylbenzylamine	5.241	4.867	4.558	4.31	4.101	3.927	3.783
2-phenethylamine	6.264	5.721	5.271	4.911	4.61	4.36	4.153
α,α-dimethylphenethylamine	8.384	7.379	6.616	5.998	5.505	5.112	4.785
1-decanamine	10.276	9.02	7.997	7.175	6.502	5.952	5.498
trans 2-phenylcyclopropylamine	11.251	9.736	8.512	7.547	6.767	6.135	5.621
1-adamantylamine	11.557	10.116	8.957	8.009	7.231	6.596	6.067

TABLE B-3D. Correlation of Vaporization Enthalpies with Enthalpies of Transfer of Some Primary Amines

Run 6	- slope T/K	intercept	ΔH_{trn}(403 K)	$\Delta_l^g H_m$(298 K)	$\Delta_l^g H_m$(298 K)

			kJ·mol^{-1}	kJ·mol^{-1} (lit)	kJ·mol^{-1}(calc)
benzylamine	4420	10.652	36.75	54.4 ± 0.6	54.2 ±1.6
(*dl*) α-methylbenzylamine	4566.2	10.823	37.96	55.2 ± 0.4	55.4 ±1.7
2-phenethylamine	4771.7	11.022	39.67	57.2 ± 0.3	57.2 ±1.7
α,α-dimethylphenethylamine	5288.2	11.902	43.96		61.7 ±1.8
1-decanamine	5661	12.45	47.06	65.0 ± 0.2	65.0 ±1.8
trans 2-phenylcyclopropylamine	5255	11.523	43.69		61.4 ±1.8
1-adamantylamine	5097.7	10.963	42.38		60.1 ±1.7

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.05±0.03)ΔH_{trn}(403 K) + (15.7±1.2) $r^2 = 0.9984$ (B-6)

TABLE B-4A. Experimental Retention Times of Some Simple Aliphatic Amines (t_o = 60 s)

Run 7	453.7	458.7	463.6	468.6	473.5	478.5	483.4
				t/t_o			
Hexanes	2.821	2.832	2.855	2.862	2.887	2.896	2.916
(*dl*) α-methylbenzylamine	3.304	3.269	3.249	3.22	3.213	3.193	3.187
2-phenethylamine	3.446	3.394	3.361	3.319	3.301	3.273	3.259
α,α-dimethylphenethylamine	3.67	3.591	3.534	3.472	3.437	3.393	3.366
trans 2-phenylcyclopropylamine	3.888	3.772	3.685	3.633	3.579	3.519	3.478
1-decanamine	3.888	3.772	3.685	3.599	3.543	3.481	3.441
1-adamantylamine	4.185	4.049	3.943	3.838	3.766	3.689	3.634
1-dodecanamine	5.432	5.089	4.811	4.564	4.375	4.201	4.067
1-tetradecanamine	9.04	8.094	7.328	6.679	6.162	5.716	5.36

TABLE B-4B. Correlation of Vaporization Enthalpies with Enthalpies of Transfer of Some Primary Amines

Run 7	- slope T/K	intercept	ΔH_{trn}(469 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)
(*dl*) α-methylbenzylamine	4274.8	10.151	35.54	55.2 ± 0.4	55.0 ± 2.3
2-phenethylamine	4430.4	10.238	36.83	57.2 ± 0.3	56.7 ± 2.3
α,α-dimethylphenethylamine	4687.5	10.498	38.97		59.7 ± 2.4
trans 2-phenylcyclopropylamine	4637.9	10.169	38.56		59.1 ± 2.4
1-decanamine	5246.8	11.502	43.62	65.0 ± 0.2	66.1 ± 2.5
1-adamantylamine	4741.6	10.143	39.42		60.3 ± 2.4
1-dodecanamine	6058.0	12.396	50.36	75.5 ± 1.8	75.4 ± 2.7

1-tetradecanamine	6902.0	13.389	57.38	85.4 ± 2.0	85.1 ± 2.9

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.38±0.04)ΔH_{trn}(469 K) + (5.95±1.8) r^2 = 0.9975 (B-7)

TABLE B-4C. Experimental Retention Times of Some Simple Aliphatic Amines (t_o = 60 s)

Run 8	453.8	458.7	463.6	468.6	473.5	478.5	483.4
				t/t_o			
hexanes	2.828	2.836	2.853	2.866	2.897	2.905	2.924
(*dl*) α-methylbenzylamine	3.244	3.213	3.195	3.178	3.182	3.168	3.196
2-phenethylamine	3.312	3.272	3.247	3.225	3.223	3.202	3.196
α,α-dimethylphenethylamine	3.454	3.398	3.359	3.324	3.312	3.282	3.268
trans 2-phenylcyclopropylamine	3.678	3.595	3.532	3.477	3.448	3.403	3.376
1-decanamine	3.897	3.776	3.684	3.639	3.59	3.529	3.488
1-adamantylamine	3.897	3.776	3.684	3.603	3.554	3.492	3.451
1-dodecanamine	4.194	4.053	3.941	3.843	3.778	3.7	3.645
1-tetradecanamine	5.443	5.093	4.809	4.569	4.39	4.214	4.079

TABLE B-4D. Correlation of Vaporization Enthalpies with Enthalpies of Transfer of Some Primary Amines

Run 8	- slope T/K	intercept	ΔH_{trn}(469 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)
(*dl*) α-methylbenzylamine	4260.0	10.117	35.42	55.2 ± 0.4	55.0 ± 2.3
2-phenethylamine	4415.2	10.203	36.71	57.2 ± 0.3	56.7 ± 2.3
α,α-dimethylphenethylamine	4675.7	10.47	38.87		59.7 ± 2.4
trans 2-phenylcyclopropylamine	4630.7	10.152	38.50		59.2 ± 2.4
1-decanamine	5235.3	11.476	43.52	65.0 ± 0.2	66.1 ± 2.5
1-adamantylamine	4729.6	10.115	39.32		60.3 ± 2.4
1-dodecanamine	6047.7	12.372	50.28	75.5 ± 1.8	75.4 ± 2.7
1-tetradecanamine	6895.4	13.373	57.33	85.4 ± 2.0	85.1 ± 2.9

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.37±0.04)ΔH_{trn}(469 K) + (6.28±1.8) r^2 = 0.9975 (B-8)

TABLE B-5A. Correlation Between ln(t_o/t_a) and Literature ln(p/p_o) Values For Runs 5 & 6

Runs 5 & 6	ln(t_o/t_a)$_{run 5}$	ln(t_o/t_a)$_{run 6}$	ln(t_o/t_a)$_{avg}$	ln(p/p_o)$_{lit}$	ln(p/p_o)$_{calc}$
benzylamine	-4.175	-4.173	-4.174		-6.453
(*dl*) α-methylbenzylamine	-4.493	-4.492	-4.493	-6.780	-6.776
2-phenethylamine	-4.984	-4.982	-4.983	-7.267	-7.273

α,α-dimethylphenethylamine	-5.815	-5.835	-5.825		-8.125
1-decanamine	-6.537	-6.537	-6.537	-8.847	-8.846
trans 2-phenylcyclopropylamine	-6.103	-6.102	-6.103		-8.406
1-adamantylamine	-6.134	-6.135	-6.134		-8.438

$\ln(p/p_o) = (1.02 \pm 0.005) \ln(t_o/t_a)_{avg} - (2.23 \pm 0.026)$ $r^2 = 0.9999$ (B-9)

TABLE B-5B. Correlation Between $\ln(t_o/t_a)$ and Literature $\ln(p/p_o)$ Values For Runs 7 & 8

Runs 7 & 8	$\ln(t_o/t_a)_{run\ 7}$	$\ln(t_o/t_a)_{run\ 8}$	$\ln(t_o/t_a)_{avg}$	$\ln(p/p_o)_{lit}$	$\ln(p/p_o)_{calc}$
(*dl*) α-methylbenzylamine	-4.187	-4.171	-4.179	-6.780	-6.790
2-phenethylamine	-4.622	-4.606	-4.614	-7.267	-7.258
α,α-dimethylphenethylamine	-5.224	-5.212	-5.218		-7.911
trans 2-phenylcyclopropylamine	-5.387	-5.379	-5.383		-8.088
1-decanamine	-6.096	-6.083	-7.917	-8.847	-8.851
1-adamantylamine	-5.760	-5.748	-5.754		-8.489
1-dodecanamine	-7.923	-7.912	-6.090	-10.833	-10.822
1-tetradecanamine	-9.760	-9.754	-7.917	-12.801	-12.807

$\ln(p/p_o) = (1.079 \pm 0.002) \ln(t_o/t_a)_{avg} - (2.28 \pm 0.015)$ $r^2 = 0.9999$ (B-10)

TABLE B-6 Vapor Pressure Parameters, Normal Boiling Temperatures and Liquid Vapor pressures at T/K = 298.15 from Runs 3 & 4, 5 & 6, and 7 & 8.

	$A\cdot10^{-8}/K^3$	$B\cdot10^{-6}/K^2$	$C\cdot10^{-3}/K$	D	T_b/K calc	$p_{(l)}$/Pa 298.15 K calc
Runs 3 & 4						
1-heptanamine	-7.22	5.039	-16.688	20.657	429	287
(*dl*) α-methylbenzylamine	-4.76	3.083	-11.701	15.743	461	115
2-phenethylamine	-3.693	2.249	-9.737	14.025	473	70
1-octanamine	-5.062	3.353	-12.734	17.217	453	105
α,α-dimethylphenethylamine	-2.379	1.226	-7.383	12.04	488	37
1-adamantylamine	-0.732	-0.093	-3.926	8.506	515	21
1-decanamine	-0.969	0.17	-5.417	11.065	495	15
1-dodecanamine	2.99	-2.901	1.534	5.375	532	2
1-(1-adamantyl)ethylamine	3.275	-3.209	3.224	2.512	566	3
1-tetradecanamine	6.886	-5.917	8.307	-0.081	570	0.3
Runs 5 & 6						
benzylamine	-5.306	3.503	-12.619	16.486	453	160
(*dl*) α-	-4.786	3.106	-11.765	15.8	461	116

methylbenzylamine						
2-phenethylamine	-3.65	2.212	-9.635	13.935	473	70
α,α-dimethylphenethylamine	-2.298	1.192	-7.623	12.7	483	30
trans 2-phenylcyclopropylamine	-1.114	0.219	-4.927	9.86	500	23
1-decanamine	-0.986	0.184	-5.455	11.098	494	15
1-adamantylamine	-0.372	-0.416	-2.947	7.534	517	22
Runs 7 & 8						
(dl) α-methylbenzylamine	-4.749	3.075	-11.693	15.751	461	115
2-phenethylamine	-3.724	2.275	-9.8	14.07	473	71
α,α-dimethylphenethylamine	-2.400	1.248	-7.457	12.12	487	37
trans 2-phenylcyclopropylamine	-1.756	0.730	-6.019	10.521	500	31
1-decanamine	-0.941	0.144	-5.343	10.994	494	15
1-adamantylamine	-0.805	-0.018	-4.190	8.802	514	21
1-dodecanamine	2.99	-2.901	1.542	5.362	532	2.0
1-tetradecanamine	6.878	-5.909	8.279	-0.05	570	0.3

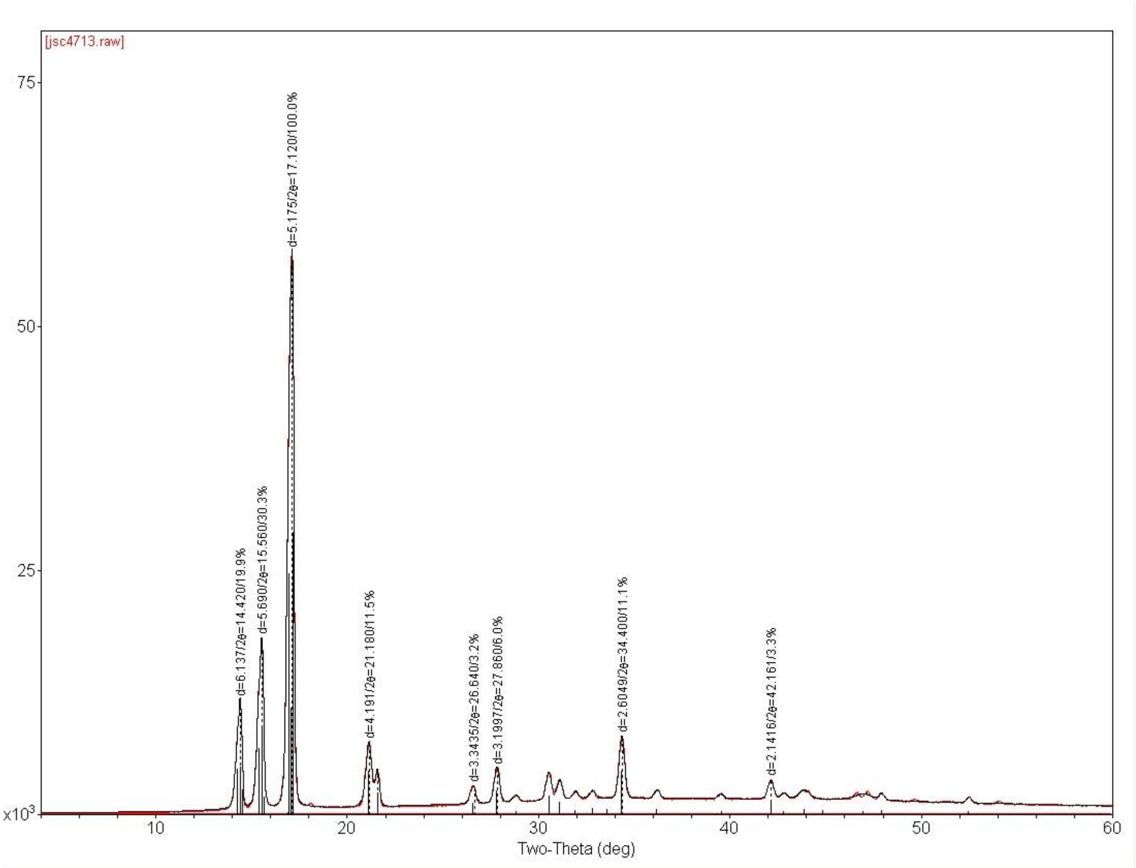

Figure B-1. The powder pattern of 1-adamantylamine

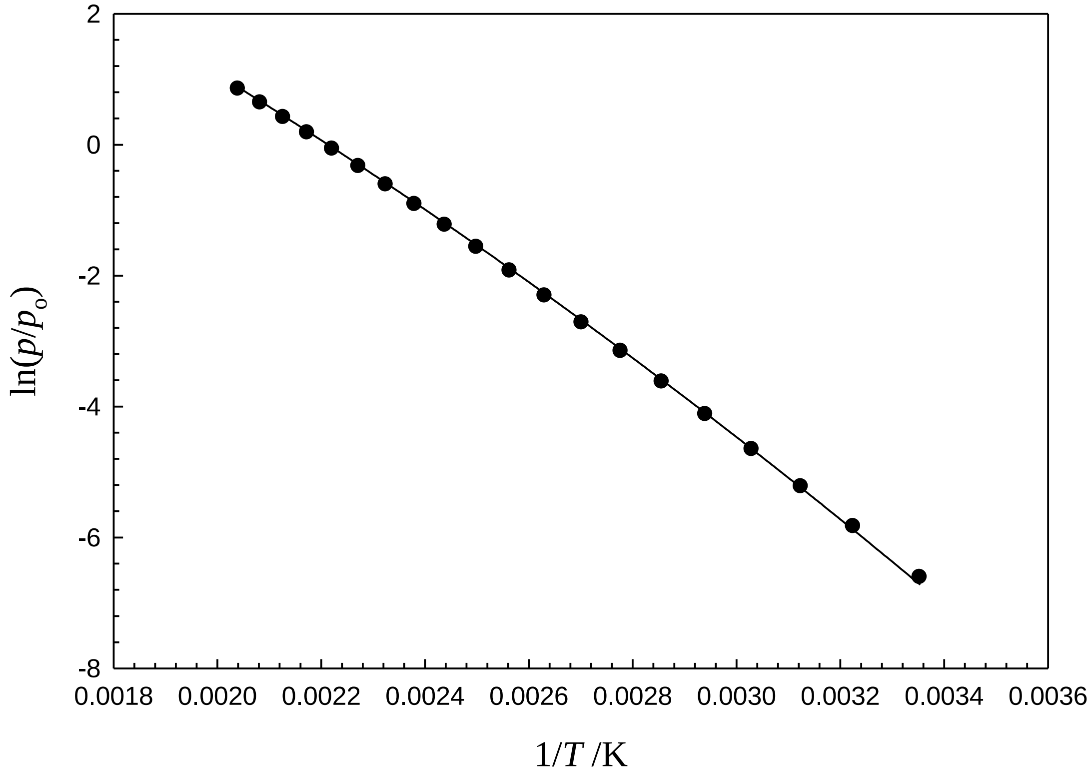

Figure B-2. A comparison of the vapor pressures of 1-octanamine reported by Steele *et al*. (line) and Ralston et al. (•) when fit to the third order polynomial, eq 1-10.

Appendix C

TABLE C1. Solid-Solid Phase Transition and Fusion Enthalpy of Tribenzylamine

mg	$\Delta_{cr}^{cr}H_t(T_t)$/ J·mol^{-1}	T_t/K	$\Delta_{cr}^{l}H_t(T_{fus})$/ J·mol^{-1}	T_{fus}/K
13.51	1073.7	342.1	22535	365.5
14.48	1040.1	342.7	23272	365.7
13.26	1198.5	342.8	23278	365.7
Avg	1104.1±80	342.5±0.4	23028±100	365.6±0.1

TABLE C-2A. Experimental Retention Times of Some Simple Tertiary Amines

Run 1	372.6	377.7	382.8	387.9	393.1	398.2	403.4
t_o = 60 s				t/t_o			
diethyl ether	2.582	2.600	2.616	2.627	2.657	2.677	2.710
triethylamine	2.869	2.854	2.841	2.829	2.837	2.839	2.857
tripropylamine	4.437	4.181	3.969	3.795	3.669	3.559	3.485
N,*N*-dimethylbenzylamine	6.853	6.199	5.66	5.226	4.888	4.600	4.383
triisobutylamine	7.407	6.625	5.986	5.476	5.079	4.746	4.494
N,*N*-dimethyloctylamine	8.779	7.719	6.865	6.187	5.660	5.222	4.889
tri-*n*-butanamine	13.496	11.500	9.907	8.664	7.688	6.890	6.275

TABLE C-2B. Evaluation of the Vaporization Enthalpy of Tri-*n*-butylamine and Triisobutylamine

Run 1	- slope T/K	intercept	ΔH_{trn}(388 K) kJ·mol^{-1}	$\Delta_l^gH_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^gH_m$(298 K) kJ·mol^{-1}(calc)
triethylamine	3262.0	10.009	27.12	35.2±0.2	35.4±1.8
tripropylamine	4263.8	10.833	35.45	46.2±0.1	46.0±2.0
N,*N*-dimethylbenzylamine	4577.9	10.842	38.06	49.7±0.4	49.3±2.0
triisobutylamine	4858.8	11.475	40.39		52.3±2.1
N,*N*-dimethyloctylamine	5104.6	11.885	42.44	54.5±0.5	54.9±2.2
tri-*n*-butylamine	5464.5	12.285	45.43		58.7±2.3

$\Delta_l^gH_m$(298.15 K)/kJ·mol^{-1} = (1.27 ± 0.04)ΔH_{trn}(388 K) + (0.91 ± 1.4) r^2 = 0.9981   (C-1)

TABLE C-3A. Experimental Retention Times of Some Simple Tertiary Amines

Run 2	372.8	377.8	382.8	388	393.1	398.3	403.5
t_o = 60 s				t/t_o			
diethyl ether	2.603	2.616	2.611	2.651	2.669	2.682	2.714
triethylamine	2.893	2.873	2.837	2.854	2.85	2.847	2.862
tripropylamine	4.472	4.209	3.964	3.827	3.686	3.569	3.49
N,*N*-dimethylbenzylamine	6.906	6.238	5.655	5.267	4.908	4.615	4.389
triisobutylamine	7.47	6.67	5.98	5.522	5.102	4.763	4.502
N,*N*-dimethyloctylamine	8.849	7.769	6.856	6.235	5.683	5.24	4.895
tri-*n*-butylamine	13.617	11.585	9.899	8.736	7.723	6.921	6.287

TABLE C-3B. Evaluation of the Vaporization Enthalpy of Tri-*n*-butylamine and Triisobutylamine

Run 2	- slope T/K	intercept	ΔH_{trn}(388 K) kJ·mol^{-1}	$\Delta_l^gH_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^gH_m$(298 K) kJ·mol^{-1}(calc)
triethylamine	3282.7	10.052	27.29	35.2±0.2	35.4±1.8
tripropylamine	4290.7	10.895	35.67	46.2±0.1	46.0±2.0
N,*N*-dimethylbenzylamine	4609	10.916	38.32	49.7±0.4	49.3±2.1
triisobutylamine	4892.4	11.553	40.67		52.3±2.2
N,*N*-dimethyloctylamine	5140.7	11.971	42.74	54.5±0.5	54.9±2.2
tri-*n*-butylamine	5500.2	12.368	45.73		58.7±2.3

$\Delta_l^gH_m$(298.15 K)/kJ·mol^{-1} = (1.26 ± 0.04)ΔH_{trn}(388 K) + (0.98 ± 1.4) $r^2 = 0.9981$ (C-2)

TABLE C-4A. Experimental Retention Times of Some Simple Tertiary Amines

Run 3	424.3	429.3	434.4	439.4	444.3	449.3	454.3
t_o = 60 s				t/t_o			
hexanes	2.687	2.698	2.718	2.733	2.746	2.766	2.788
N,*N*-dimethylbenzylamine	3.59	3.496	3.424	3.362	3.308	3.27	3.240
N,*N*-dimethyloctylamine	3.802	3.670	3.567	3.480	3.405	3.350	3.306
tri-*n*-butylamine	4.454	4.222	4.038	3.884	3.752	3.650	3.566
N,*N*-dimethyldodecylamine	11.502	10.011	8.824	7.869	7.086	6.451	5.931
N,*N*-dimethyl tetradecylamine	26.556	22.015	18.463	15.672	13.436	11.646	10.202

TABLE C-4B. Evaluation of the Vaporization Enthalpy of Tri-*n*-butylamine and *N*,*N*-dimethyltetradecanamime

Run 3	- slope *T*/K	intercept	ΔH_{trn}(439 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)
N,*N*-dimethylbenzylamine	4436.7	10.561	36.89	49.7±0.4	49.9±1.5
N,*N*-dimethyloctylamine	4923.4	11.498	40.93	54.5±0.5	54.2±1.5
tri-*n*-butylamine	5268.0	11.850	43.8		57.3±1.6
N,*N*-dimethyldodecylamine	6621.9	13.435	55.05	69.3±0.3	69.4±1.8
N,*N*-dimethyltetradecylamine	7509.0	14.530	62.43		77.3±1.9

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.07 ± 0.03)ΔH_{trn}(439 K) + (10.4 ± 1.1) r^2 = 0.9995 (C-3)

TABLE C-5A. Experimental Retention Times of Some Simple Tertiary Amines

Run 4	424.3	429.3	434.4	439.3	444.3	449.3	454.3
t_o = 60 s				t/t_o			
hexanes	2.732	2.731	2.723	2.742	2.742	2.767	2.777
N,*N*-dimethylbenzylamine	3.649	3.536	3.433	3.372	3.304	3.270	3.228
N,*N*-dimethyloctylamine	3.865	3.712	3.576	3.490	3.401	3.349	3.294
tri-*n*-butylamine	4.527	4.270	4.049	3.895	3.749	3.649	3.553
N,*N*-dimethyldodecylamine	11.685	10.114	8.853	7.888	7.082	6.446	5.913
N,*N*-dimethyl tetradecylamine	26.948	22.209	18.527	15.698	13.431	11.632	10.171

TABLE C-5B. Evaluation of the Vaporization Enthalpy of Tri-*n*-butylamine and *N*,*N*-dimethyltetradecanamime

Run 4	- slope *T*/K	intercept	ΔH_{trn}(439 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)
N,*N*-dimethylbenzylamine	4544.8	10.804	37.78	49.7±0.4	49.9±1.4
N,*N*-dimethyloctylamine	5035.8	11.75	41.87	54.5±0.5	54.3±1.4
tri-*n*-butylamine	5379.9	12.101	44.73		57.3±1.5
N,*N*-dimethyldodecylamine	6732.9	13.685	55.98	69.3±0.3	69.4±1.7
N,*N*-dimethyltetradecylamine	7613.6	14.766	63.3		77.2±1.8

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.07 ± 0.02)ΔH_{trn}(439 K) + (11.4 ± 0.45) r^2 = 0.9995 (C-4)

TABLE C-6A. Experimental Retention Times of Some Simple Tertiary Amines

Run 5 t_o = 60 s	423.5	429	434	439.2 t/t_o	444.4	449.5	454.7
hexanes	0.552	0.552	0.555	0.557	0.556	0.562	0.568
N,*N*-dimethyloctylamine	1.211	1.128	1.061	1.002	0.949	0.915	0.882
tri-*n*-butylamine	1.609	1.466	1.35	1.249	1.161	1.1	1.043
N,*N*-dimethyldodecylamine	5.409	4.596	3.945	3.411	2.969	2.635	2.343
N,*N*-dimethyl tetradecylamine	13.311	10.914	9.038	7.539	6.329	5.413	4.635
N,*N*-dimethyl hexadecylamine	33.677	26.826	21.545	17.446	14.208	11.786	9.784

TABLE C-6B. Evaluation of the Vaporization Enthalpy of *N*,*N*-Dimethylhexadecylamine

Run 5	- slope T/K	intercept	ΔH_{trn}(439 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)
N,*N*-dimethyloctylamine	4588.7	11.254	38.15	54.5±0.5	54.6±0.8
tri-*n*-butylamine	4949.2	11.633	41.15	58.0±1.9	57.8±0.9
N,*N*-dimethyldodecylamine	6240.3	13.157	51.88	69.3±0.3	69.5±1.0
N,*N*-dimethyltetradecylamine	7084.6	14.185	58.9	77.3±1.9	77.2±1.0
N,*N*-dimethylhexadecylamine	7930.6	15.228	65.93		84.8±1.1

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.09±0.013)ΔH_{trn}(439 K) - (13.0±0.6) r^2 = 0.9997   (C-5)

TABLE C-7A. Experimental Retention Times of Some Simple Tertiary Amines

Run 6 t_o = 60 s	423.6	428.9	434	439.2 t/t_o	444.4	449.5	454.7
hexanes	0.547	0.554	0.551	0.554	0.561	0.563	0.565
N,*N*-dimethyloctylamine	1.199	1.127	1.056	1	0.958	0.915	0.88
tri-*n*-butylamine	1.593	1.463	1.344	1.247	1.172	1.101	1.041
N,*N*-dimethyldodecylamine	5.359	4.581	3.935	3.412	2.993	2.636	2.341
N,*N*-dimethyl tetradecylamine	13.199	10.875	9.02	7.544	6.378	5.416	4.636
N,*N*-dimethyl hexadecylamine	33.443	26.707	21.502	17.451	14.314	11.792	9.788

TABLE C-7B. Evaluation of the Vaporization Enthalpy of *N*,*N*-Dimethylhexadecylamine

Run 6	- slope T/K	intercept	ΔH_{trn}(439 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)
N,*N*-dimethyloctylamine	4521.7	11.103	37.59	54.5±0.5	54.6±0.8
tri-*n*-butylamine	4886.1	11.491	40.62	58.0±1.9	57.8±0.8
N,*N*-dimethyldodecylamine	6181.1	13.023	51.39	69.3±0.3	69.5±0.9
N,*N*-dimethyltetradecylamine	7029.2	14.059	58.44	77.3±1.9	77.2±0.8
N,*N*-dimethyl hexadecylamine	7880.6	15.115	65.52		84.8±0.9

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.07±0.019)ΔH_{trn}(439 K) - (13.0±0.6) $r^2 = 0.9997$ (C-6)

TABLE C-8A. Experimental Retention Times of Some Simple Tertiary Amines

Run 7	484.9	489.9	494.6	500	505.2	510.3	515.5
t_o = 60 s				t/t_o			
methylene chloride	2.975	2.985	3.009	3.021	3.048	3.065	3.08
tri-*n*-butylamine	3.384	3.352	3.342	3.323	3.324	3.316	3.31
N,*N*-dimethyl dodecylamine	4.335	4.179	4.068	3.957	3.883	3.808	3.746
N,*N*-dimethyl tetradecylamine	5.807	5.437	5.151	4.883	4.679	4.498	4.346
N,*N*-dimethyl hexadecylamine	8.797	7.951	7.277	6.669	6.189	5.784	5.447
tri-*n*-octylamine	25.496	21.604	18.514	15.85	13.748	12.056	10.687
tribenzylamine	25.967	22.296	19.346	16.789	14.708	13.013	11.618

TABLE C-8B. Evaluation of the Vaporization Enthalpy of Tri-*n*-octylamine and Tribenzylamine

Run 7	- slope T/K	intercept	ΔH_{trn}(500 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)
tri-*n*-butylamine	4655.4	10.504	38.7	58.0±1.9	58.0±0.9
N,*N*-dimethyldodecylamine	5808.2	11.679	48.29	69.3±0.3	69.5±1.0
N,*N*-dimethyl tetradecylamine	6566.2	12.508	54.59	77.3±1.9	77.1±1.0
N,*N*-dimethyl hexadecylamine	7350.8	13.405	61.11	84.8±1.0	84.9±1.1
tri-*n*-octylamine	8871.4	15.189	73.75		100.1±1.2
tribenzylamine	8091.0	13.559	67.27		92.3±1.2

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.20±0.013)ΔH_{trn}(500 K) + (11.5±0.7) $r^2 = 0.9997$ (C-7)

TABLE C-9A. Experimental Retention Times of Some Simple Tertiary Amines

Run 8	484.9	489.9	494.8	500.1	505.2	510.4	515.5
t_o = 60 s				t/t_o			
methylene chloride	2.971	2.989	2.992	3.025	3.034	3.051	3.076
tri-*n*-butylamine	3.382	3.363	3.331	3.334	3.315	3.307	3.31
N,*N*-dimethyldodecylamine	4.335	4.193	4.057	3.971	3.876	3.803	3.752
N,*N*-dimethyl tetradecylamine	5.802	5.447	5.13	4.889	4.669	4.488	4.35
N,*N*-dimethyl hexadecylamine	8.797	7.956	7.232	6.669	6.171	5.765	5.445
tri-*n*-octylamine	25.512	21.549	18.351	15.818	13.725	12.027	10.66
tribenzylamine	25.972	22.266	19.221	16.738	14.684	12.981	11.592

TABLE C-9B. Evaluation of the Vaporization Enthalpy of Tri-*n*-octylamine and Tribenzylamine

Run 8	- slope T/K	intercept	ΔH_{trn}(500 K) kJ·mol^{-1}	$\Delta_l^gH_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^gH_m$(298 K) kJ·mol^{-1}(calc)
tri-*n*-butylamine	4592.7	10.362	38.18	58.0±1.9	58.1±1.1
N,*N*-dimethyldodecylamine	5731.7	11.516	47.65	69.3±0.3	69.3±1.2
N,*N*-dimethyl tetradecylamine	6522.6	12.418	54.23	77.3±1.9	77±1.3
N,*N*-dimethyl hexadecylamine	7346.4	13.396	61.08	84.8±1.0	85±1.4
tri-*n*-octylamine	8872.4	15.192	73.76		100±1.6
tribenzylamine	8097.3	13.572	67.32		92.4±1.5

$\Delta_l^gH_m$(298.15 K)/kJ·mol^{-1} = (1.18±0.017)ΔH_{trn}(500 K) + (13.2±0.9)   r^2 = 0.9996   (C-8)

TABLE C-10A. Experimental Retention Times of Some Simple Tertiary Amines

Run 9	403.5	408.7	413.8	418.8	424	429.1	434.1
t_o = 60 s				t/t_o			
hexane/diethyl ether	2.673	2.694	2.703	2.718	2.731	2.75	2.78
triisobutylamine	4.439	4.214	4.021	3.857	3.723	3.609	3.545
N,*N*-dimethyloctylamine	4.827	4.535	4.289	4.080	3.913	3.779	3.686
tributylamine	6.206	5.68	5.247	4.879	4.586	4.347	4.175
L- deprenyl	16.55	14.129	12.210	10.638	9.35	8.325	7.546
N,*N*-dimethyl dodecylamine	23.424	19.460	16.386	13.909	11.921	10.353	9.181

TABLE C-10B. Evaluation of the Vaporization Enthalpy of L- Deprenyl

Run 9	- slope T/K	intercept	ΔH_{trn}(419 K) kJ·mol^{-1}	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$(298 K) kJ·mol^{-1} (lit)	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$(298 K) kJ·mol^{-1}(calc)
N,*N*-dimethylbenzylamine	4429.0	10.477	36.82	49.7±0.4	49.9±1.4
N,*N*-dimethyloctylamine	4977.6	11.572	41.38	54.5±0.5	54.5±1.5
tributylamine	5344.6	13.720	56.19	58.0±1.9	57.6±1.5
L- deprenyl	6141.9	11.986	44.43		64.3±1.6
N,*N*-dimethyldodecylamine	6758.5	12.594	51.06	69.3±0.3	69.5±1.7

$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K)/kJ·mol^{-1} = (1.01±0.02)ΔH_{trn}(419 K) + (12.8±1.1) $r^2 = 0.9989$ (C-9)

TABLE C-11A. Experimental Retention Times of Some Simple Tertiary Amines

Run 10	424	429.1	434.1	439.1	444	449	454
t_{o} = 60 s				t/t_{o}			
hexane/diethyl ether	2.727	2.748	2.765	2.783	2.804	2.824	2.84
N,*N*-dimethyl benzylamine	3.687	3.597	3.519	3.456	3.405	3.364	3.325
N,*N*-dimethyloctylamine	3.905	3.775	3.665	3.576	3.505	3.446	3.392
tributylamine	4.573	4.341	4.148	3.99	3.861	3.753	3.658
L- deprenyl	9.3	8.299	7.481	6.815	6.264	5.807	5.42
N,*N*-dimethyl dodecylamine	11.803	10.282	9.061	8.082	7.283	6.628	6.083

TABLE C-11B. Evaluation of the Vaporization Enthalpy of L- Deprenyl

Run 10	- slope T/K	intercept	ΔH_{trn}(439 K) kJ·mol^{-1}	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$(298 K) kJ·mol^{-1} (lit)	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$(298 K) kJ·mol^{-1}(calc)
N,*N*-dimethylbenzylamine	4382.6	10.378	36.44	49.7±0.4	50.1±2.3
N,*N*-dimethyloctylamine	4858.8	11.298	40.39	54.5±0.5	54.2±2.4
tributylamine	5220.4	11.702	43.40	58.0±1.9	57.4±2.5
L- deprenyl	6005.8	12.284	49.93		64.2±2.7
N,*N*-dimethyldodecylamine	6607.9	13.382	54.94	69.3±0.3	69.5±2.8

$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K)/kJ·mol^{-1} = (1.05±0.04)ΔH_{trn}(439 K) + (12.0±1.8) $r^2 = 0.9971$ (C-10)

TABLE C-12A. Experimental Retention Times of Some Simple Tertiary Amines

Run 11 t_o = 60 s	475.6	480.4	485.7	490.5 t/t_o	495.7	500.9	506.2
diethyl ether	2.803	2.79	2.767	2.719	2.67	2.649	2.649
N,*N*-dimethylbenzylamine	3.125	3.082	3.032	2.957	2.884	2.843	2.828
N,*N*-dimethyl dodecylamine	4.555	4.307	4.082	3.851	3.647	3.503	3.404
N,*N*-dimethyl tetradecylamine	6.607	6.026	5.521	5.05	4.647	4.349	4.129
(*S*)-benzphetamine	10.156	9.045	8.088	7.22	6.488	5.934	5.515
N,*N*-dimethyl hexadecylamine	10.955	9.604	8.463	7.454	6.622	5.991	5.515
tribenzylamine	36.263	30.345	25.436	21.227	17.908	15.344	13.373

TABLE C-12B. Evaluation of the Vaporization Enthalpy of (*S*)-Benzphetamine

Run 11	- slope *T*/K	intercept	ΔH_{trn}(491 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)
N,*N*-dimethylbenzylamine	4694.1	11.003	39.02	49.7±0.4	49.7±0.5
N,*N*-dimethyldodecylamine	6689.0	13.508	55.61	69.3±0.3	69.3±0.6
N,*N*-dimethyl tetradecylamine	7498.9	14.436	62.34	77.3±1.9	77.2±0.6
(*S*)-benzphetamine	7493.5	13.766	62.3		77.1±0.6
N,*N*-dimethyl hexadecylamine	8302.2	15.364	69.02	84.8±1.0	85.1±0.6
tribenzylamine	9034.0	15.491	75.11	92.4±1.4	92.3±0.7

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.18±0.01)ΔH_{trn}(491 K) + (3.69±0.4) $r^2 = 0.9999$ (C-11)

TABLE C-13A. Experimental Retention Times of Some Simple Tertiary Amines

Run 12 t_o = 60 s	475.6	480.4	485.7	490.5 t/t_o	495.7	500.9	506.2
diethyl ether	2.803	2.79	2.767	2.719	2.67	2.649	2.649
N,*N*-dimethylbenzylamine	3.125	3.082	3.032	2.957	2.884	2.843	2.828
N,*N*-dimethyl dodecylamine	4.555	4.307	4.082	3.851	3.647	3.503	3.404
N,*N*-dimethyl tetradecylamine	6.607	6.026	5.521	5.05	4.647	4.349	4.129
(*S*)-benzphetamine	10.156	9.045	8.088	7.22	6.488	5.934	5.515
N,*N*-dimethyl hexadecylamine	10.955	9.604	8.463	7.454	6.622	5.991	5.515
tribenzylamine	36.263	30.345	25.436	21.227	17.908	15.344	13.373

TABLE C-13B. Evaluation of the Vaporization Enthalpy of (S)-Benzphetamine

Run 12	- slope T/K	intercept	ΔH_{trn}(419 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)
N,*N*-dimethylbenzylamine	4712.5	11.046	39.18	49.7±0.4	49.6±0.6
N,*N*-dimethyldodecylamine	6752.2	13.645	56.14	69.3±0.3	69.4±0.7
N,*N*-dimethyl tetradecylamine	7569.9	14.59	62.93	77.3±1.9	77.2±0.7
(*S*)-benzphetamine	7563.5	13.918	62.88		77.3±0.7
N,*N*-dimethyl hexadecylamine	8373.4	15.518	69.61	84.8±1.0	85.1±0.7
tribenzylamine	9103.8	15.642	75.69	92.4±1.4	92.1±0.8

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.16±0.01)ΔH_{trn}(419 K) + (3.98±0.5) $r^2 = 0.9998$ (C-12)

TABLE C-14A. Experimental Retention Times of Some Simple Tertiary Amines

Run 13	479	483.9	488.8	493.8	498.9	503.8	508.8
t_o = 60 s	t/t_o						
hexanes	2.908	2.913	2.925	2.942	2.953	2.966	3.021
tri-*n*-butylamine	3.349	3.309	3.281	3.263	3.244	3.23	3.264
N,*N*-dimethyl dodecylamine	4.451	4.261	4.109	3.986	3.877	3.785	3.76
N,*N*-dimethyl hexadecylamine	9.887	8.789	7.917	7.202	6.603	6.107	5.771
Alverine	22.091	18.913	16.389	14.324	12.618	11.209	10.173
tri-*n*-octylamine	31.160	25.914	21.838	18.563	15.923	13.792	12.221

TABLE C-14B. Evaluation of the Vaporization Enthalpy of Alverine

Run 13	- slope T/K	intercept	ΔH_{trn}(494 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)
tri-*n*-butylamine	4871.8	10.997	40.5	58.0±1.9	58.0±0.1
N,*N*-dimethyldodecylamine	6033.6	12.171	50.16	69.3±0.3	69.3±0.1
N,*N*-dimethyl hexadecylamine	7627.9	13.993	63.41	84.8±1.0	84.9±0.2
alverine	8080.2	13.926	67.18		89.3±0.2
tri-*n*-octylamine	9186.8	15.85	76.38	100.1±1.4	100.1±0.2

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.17±0.01)ΔH_{trn}(494 K) + (10.5±0.1) $r^2 = 0.9999$ (C-13)

TABLE C-15A. Experimental Retention Times of Some Simple Tertiary Amines

Run 14	478.9	483.9	488.8	493.8	498.8	503.8	508.7
t_o = 60 s				t/t_o			
hexanes	2.909	2.892	2.898	2.904	2.905	2.92	3.03
tri-*n*-butylamine	3.349	3.284	3.25	3.221	3.192	3.18	3.273
N,*N*-dimethyl dodecylamine	4.45	4.229	4.069	3.934	3.814	3.727	3.77
N,*N*-dimethyl hexadecylamine	9.872	8.726	7.837	7.108	6.496	6.012	5.785
Alverine	22.037	18.768	16.227	14.14	12.413	11.035	10.189
tri-*n*-octylamine	31.08	25.711	21.614	18.321	15.669	13.579	12.234

TABLE C-15B. Evaluation of the Vaporization Enthalpy of Alverine

Run 14	- slope T/K	intercept	ΔH_{trn}(494 K) kJ·mol^{-1}	$\Delta_l^gH_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^gH_m$(298 K) kJ·mol^{-1}(calc)
tri-*n*-butylamine	4908.9	11.083	40.81	58.0±1.9	58.0±0.1
N,*N*-dimethyldodecylamine	6062.7	12.241	50.4	69.3±0.3	69.3±0.1
N,*N*-dimethyl hexadecylamine	7653.0	14.055	63.62	84.8±1.0	84.9±0.1
alverine	8105.5	13.988	67.39		89.3±0.1
tri-*n*-octylamine	9212.8	15.914	76.59	100.1±1.4	100.1±0.1

$\Delta_l^gH_m$(298.15 K)/kJ·mol^{-1} = (1.18±0.01)ΔH_{trn}(494 K) + (10.5±0.1) r^2 = 0.9999 (C-14)

TABLE C-16. Correlations Between $\ln(t_o/t_a)_{avg}$ and liquid $\ln(p/p_o)_{exp}$ at T/K = 298.15 for Runs 5-8

run 5/run 6	-slope/K	intercept	$\ln(t_o/t_a)_{avg}$	$\ln(p/p_o)_{exp}$	$\ln(p/p_o)_{calc}$	p/Pa calc
N,*N*-dimethyl octyl amine	4588.7	11.254				
	4521.7	11.103	-4.099	-7.36	-7.27	71/65
tri-*n*-butylamine	4949.2	11.633				
	4886.1	11.491	-4.931	-8.18[a]	-8.28	26
N,*N*-dimethyl dodecylamine	6240.3	13.157				
	6181.1	13.023	-7.740	-11.69	-11.69	0.83
N,*N*-dimethyl tetradecylamine	7084.6	14.185				
	7029.2	14.059	-9.547	-13.93[a]	-13.93	0.092
N,*N*-dimethyl hexadecylamine	7930.6	15.228				
	7880.6	15.115	-11.344		-16.17	0.01
run 7/run 8						
tri-*n*-butylamine	4655.4	10.504				
	4592.7	10.362	-5.08	-8.18[a]	-8.22	27
N,*N*-dimethyl dodecylamine	5808.0	11.679				
	5731.7	11.516	-7.75	-11.69	-11.65	0.88
N,*N*-dimethyl tetradecylamine	6566.2	12.508				
	6522.6	12.418	-9.49	-13.92[a]	-13.88	0.095
N,*N*-dimethyl hexadecylamine	7350.8	13.405				
	7346.4	13.396	-11.25	-16.10[a]	-16.15	0.01
tri-*n*-octylamine	8871.4	15.189				
	8872.4	15.192	-14.57		-20.41	0.00014
tribenzylamine	8091.0	13.559				
	8097.3	13.572	-13.58		-19.15	0.00049

Run 5 &6: $\ln(p/p_o) = (1.22\pm0.022) \ln(t_o/t_a) - (2.27\pm0.15)$ $r^2 = 0.9993$ (C-15)

Run 7 &8: $\ln(p/p_o) = (1.28\pm0.013)) \ln(t_o/t_a) - (1.69\pm0.1.1)$ $r^2 = 0.9998$ (C-16)

[a] Value based only on runs evaluated as an unknown

Appendix D

TABLE D-1A. Retention times for Run 1

Run 1 $t_o = 60$ s	449.3	454.3	459.2	464.1 t/t_o	469.1	474	479
Hexanes	2.717	2.744	2.765	2.781	2.802	2.823	2.842
N,*N*-Dimethylbenzylamine	3.262	3.237	3.211	3.185	3.17	3.159	3.151
N,*N*-Dimethyloctylamine	3.342	3.303	3.265	3.230	3.206	3.183	3.155
Tributylamine	3.641	3.562	3.490	3.427	3.379	3.340	3.305
N,*N*-Dimethyldodecylamine	6.431	5.920	5.495	5.137	4.844	4.600	4.392
N,*N*-Dimethylhexadecylamine	23.753	19.957	16.954	14.54	12.598	11.026	9.739
Phencyclidine	24.347	20.832	17.984	15.647	13.727	12.139	10.812

TABLE D-1B. Correlation of $\Delta_l^g H_m$(298 K) with $\Delta H_{trn}(T_m)$ for Run 1; Uncertainties are One Standard Deviation; $p_o = 101325$ Pa

Run 1	- slope T/K	intercept	ΔH_{trn}(464 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298.15 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298.15 K) kJ·mol^{-1}(calc)
N,*N*-Dimethylbenzylamine	4134.4±23	9.811±0.05	34.37±0.19	49.7±0.4	49.2±2.8
N,*N*-Dimethyloctylamine	4919.2±113	11.409±0.24	40.90±0.94	54.5±0.5	56.3±3.0
Tributylamine	4999.5±8.3	11.208±0.02	41.56±0.07	58.0±1.9	57.0±3.0
N,*N*-Dimethyldodecylamine	6335.0±19	12.791±0.04	52.67±0.16	69.3±0.3	69.0±3.4
N,*N*-Dimethylhexadecylamine	8084.2±27	14.952±0.06	67.21±0.23	84.8±1.0	84.8±3.9
Phencyclidine	7236.9±20	13.037±0.04	60.16±0.02		77.2±3.7

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.085 ± 0.047)ΔH_{trn}(489 K) + (11.90 ±2.30) $r^2 = 0.9943$ (D-1)

TABLE D-2A. Retention times for Run 2

Run 2 $t_o = 60$ s	449.3	454.3	459.2	464.1 t/t_o	469.1	474	479
Hexanes	2.697	2.731	2.74	2.759	2.785	2.836	2.830
N,*N*-Dimethylbenzylamine	3.238	3.222	3.182	3.161	3.152	3.174	3.138
N,*N*-Dimethyloctylamine	3.318	3.288	3.236	3.205	3.187	3.200	3.143
Tributylamine	3.614	3.546	3.460	3.401	3.359	3.356	3.292
N,*N*-Dimethyldodecylamine	6.385	5.895	5.451	5.099	4.816	4.621	4.374
N,*N*-Dimethylhexadecylamine	23.566	19.87	16.834	14.44	12.527	11.061	9.700
Phencyclidine	24.160	20.740	17.855	15.54	13.647	12.175	10.768

TABLE D-2B. Correlation of $\Delta_l^g H_m$(298 K) with $\Delta H_{trn}(T_m)$ for Run 2; Uncertainties are One Standard Deviation; p_o = 101325 Pa

Run 2	- slope T/K	intercept	ΔH_{trn}(464 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)
N,*N*-Dimethylbenzylamine	4102.4±38	9.746±0.08	34.11±0.31	49.7±0.4	49.3±2.6
N,*N*-Dimethyloctylamine	4861.2±130	11.287±0.28	40.41±1.08	54.5±0.5	56.1±2.7
Tributylamine	4962.2±37	11.132±0.08	41.25±0.31	58.0±1.9	57.0±2.8
N,*N*-Dimethyldodecylamine	6296.6±39	12.713±0.08	52.35±0.32	69.3±0.3	69.1±3.1
N,*N*-Dimethylhexadecylamine	8042.8±38	14.867±0.08	66.86±0.32	84.8±1.0	84.8±3.6
Phencyclidine	7197.8±33	12.958±0.07	59.84±0.28		77.2±3.4

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.086 ± 0.044)ΔH_{trn}(489 K) + (12.23 ±2.10) r^2 = 0.9952 (D-2)

TABLE D-3A. Retention times for Run 3

Run 3	474	478.9	483.8	488.9	493.8	498.8	503.7
t_o = 60 s				t/t_o			
CH_2Cl_2/ hexanes	2.853	2.868	2.889	2.9	2.915	2.94	2.965
Tributylamine	3.377	3.338	3.31	3.285	3.261	3.253	3.256
N,*N*-Dimethyldodecylamine	4.652	4.438	4.263	4.114	3.984	3.887	3.816
N,*N*-Dimethylhexadecylamine	11.15	9.842	8.788	7.917	7.195	6.61	6.151
Phencyclidine	12.273	10.925	9.818	8.888	8.105	7.455	6.938
Trioctylamine	16.572	14.464	12.749	11.326	10.136	9.159	8.377

TABLE D-3B. Correlation of $\Delta_l^g H_m$(298 K) with ΔH_{trn} (T_m) for Run 3; Uncertainties are One Standard Deviation; p_o = 101325 Pa

Run 3	- slope T/K	intercept	ΔH_{trn}(489 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)
Tributylamine	4778.1±70	10.733±0.14	39.72±0.58	58.0±1.9	57.8±0.7
N,*N*-Dimethyldodecylamine	6033.4±49	12.148±0.10	50.16±0.41	69.3±0.3	69.5±0.8
N,*N*-Dimethylhexadecylamine	7696.7±49	14.130±0.10	63.99±0.41	84.8±1.0	85.0±0.9
Phencyclidine	6941.6±41	12.409±0.08	57.71±0.34		78.0±0.8
Trioctylamine	9293.5±51	16.071±0.10	77.26±0.42	100.1±1.4	99.9±1.0

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.122 ± 0.01)ΔH_{trn}(489 K) + (13.21 ±0.60) r^2 = 0.9998 (D-3)

TABLE D-4A. Retention times for Run 4

Run 4 t_o = 60 s	473.7	478.9	483.8	488.9 t/t_o	493.8	498.8	503.7
CH_2Cl_2/ hexanes	2.832	2.849	2.868	2.883	2.905	2.915	2.94
Tributylamine	3.351	3.314	3.288	3.265	3.249	3.229	3.221
N,*N*-Dimethyldodecylamine	4.615	4.405	4.234	4.088	3.968	3.859	3.775
N,*N*-Dimethyl hexadecylamine	11.054	9.768	8.729	7.868	7.161	6.567	6.083
Phencyclidine	12.169	10.845	9.755	8.836	8.065	7.408	6.864
Trioctylamine	37.159	30.738	25.688	21.664	18.427	15.816	13.714

TABLE D-4B. Correlation of $\Delta_l^gH_m$(298 K) with ΔH_{trn} (T_m) for Run 4; Uncertainties are One Standard Deviation; p_o = 101325 Pa

Run 4	- slope T/K	intercept	ΔH_{trn}(489 K) kJ·mol^{-1}	$\Delta_l^gH_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^gH_m$(298 K) kJ·mol^{-1}(calc)
Tributylamine	4811.4±60	10.812±0.12	40.00±0.50	58.0±1.9	57.9±0.5
N,*N*-Dimethyldodecylamine	6020.2±21	12.131±0.04	50.05±0.18	69.3±0.3	69.4±0.5
N,*N*-Dimethylhexadecylamine	7653.1±15	14.050±0.03	63.62±0.13	84.8±1.0	85.0±0.6
Phencyclidine	6899.4±14	12.331±0.03	57.36±0.12		77.8±0.6
Trioctylamine	9224.1±19	15.938±0.04	76.69±0.16	100.1±1.4	100.0±0.7

$\Delta_l^gH_m$(298.15 K)/kJ·mol^{-1} = (1.147 ± 0.01)ΔH_{trn}(489 K) + (11.97±0.42) r^2 = 0.9999 (D-4)

TABLE D-5A. Retention times for Run 5

Run 5 t_o = 60 s	483.5	488.5	493.5	498.5 t/t_o	503.4	508.4	513.5
CH_2Cl_2	0.588	0.582	0.602	0.602	0.604	0.598	0.607
N,*N*-Dimethyldodecylamine	1.363	1.264	1.204	1.138	1.078	1.024	0.988
N,*N*-Dimethyltetradecylamine	2.183	1.963	1.801	1.653	1.52	1.41	1.324
N,*N*-Dimethylhexadecylamine	3.911	3.411	3.012	2.686	2.381	2.159	1.964
Fenpropidin	4.505	3.952	3.505	3.12	2.788	2.513	2.288
Trioctylamine	12.878	10.723	9.003	7.615	6.462	5.561	4.808
Tribenzylamine	13.706	11.562	9.826	8.434	7.217	6.31	5.501

TABLE D-5B. Correlation of $\Delta_l^g H_m$(298 K) with ΔH_{trn} (T_m) for Run 5; Uncertainties are One Standard Deviation; p_o = 101325 Pa

Run 5	- slope T/K	intercept	ΔH_{trn}(498 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)
N,N-Dimethyldodecylamine	5883.9±40	12.429±0.08	48.92±0.33	69.3±0.3	69.4±1.1
N,N-Dimethyltetradecylamine	6629.8±48	13.251±0.10	55.12±0.40	77.3±3.0	76.9±1.2
N,N-Dimethylhexadecylamine	7431.1±71	14.175±0.14	61.78±0.59	84.8±1.0	85.0±1.2
Fenpropidin	7025.6±42	13.170±0.08	58.41±0.35		81.0±1.2
Trioctylamine	8904.9±52	15.915±0.10	74.03±0.43	100.1±1.4	99.9±1.4
Tribenzylamine	8172.3±64	14.336±0.13	67.94±0.53	92.4±1.4	92.5±1.3

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.216 ± 0.014)ΔH_{trn}(498 K) + (9.903 ±0.88) r^2 = 0.9996 (D-5)

TABLE D-6A. Retention times for Run 6

Run 6 t_o = 60 s	483.7	488.5	493.5	498.5	503.4	508.4	513.6
				t/t_o			
CH_2Cl_2	0.579	0.58	0.598	0.586	0.587	0.599	0.606
N,N-Dimethyldodecylamine	1.356	1.263	1.200	1.12	1.064	1.024	0.987
N,N-Dimethyltetradecylamine	2.178	1.964	1.799	1.634	1.509	1.408	1.323
N,N-Dimethylhexadecylamine	3.922	3.422	3.012	2.657	2.384	2.149	1.962
Fenpropidin	4.504	3.950	3.501	3.098	2.779	2.510	2.286
Trioctylamine	12.895	10.736	8.995	7.582	6.471	5.549	4.810
Tribenzylamine	13.755	11.609	9.824	8.373	7.251	6.275	5.507

TABLE D-6B. Correlation of $\Delta_l^g H_m$(298 K) with ΔH_{trn} (T_m) for Run 6; Uncertainties are One Standard Deviation; p_o = 101325 Pa

Run 6	- slope T/K	intercept	ΔH_{trn}(499 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)
N,N-Dimethyl dodecylamine	5915.1±52	12.490±0.10	49.18±0.43	69.3±0.3	69.3±1.8
N,N-Dimethyl tetradecylamine	6672.2±61	13.334±0.12	55.47±0.50	77.3±3.0	76.9±1.9
N,N-Dimethyl hexadecylamine	7510.5±82	14.332±0.16	62.44±0.68	84.8±1.0	85.3±2.0
Fenpropidin	7058.5±60	13.235±0.12	58.68±0.50		80.8±2.0
Trioctylamine	8940.9±79	15.986±0.16	74.33±0.65	100.1±1.4	99.7±2.2
Tribenzylamine	8234.3±92	14.458±0.18	68.46±0.76	92.4±1.4	92.6±2.1

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.211 ± 0.023)ΔH_{trn}(499 K) + (9.76 ±1.44) r^2 = 0.9989 (D-6)

TABLE D-7. A Summary of Vaporization Enthalpies (p_o = 101 325 Pa) and Vapor Pressures Evaluated From Correlation of $\ln(t_o/t_a)_{avg}$ with $\ln(p/p_o)_{lit}$; Uncertainties are One Standard Deviation

	$\Delta_l^g H_m$ (298.15)/kJ·mol^{-1}				$10^2 \cdot p_{298.15\ K}$/Pa
Targets	Run 1/2	Run 3/4	Run 5/6	Avg	
Phencyclidine	77.2±3.7	78.0±0.8			3.1±0.7
	77.2±3.4	77.8±0.6		77.6±2.1	2.8±0.3
Fenpropidin			81.0±1.2		
			80.8±2.0	80.9±1.6	1.6±0.4
Standards					
N,N-Dimethylbenzylamine	49.2±2.8				18800±2900
	49.3±2.6			49.3±2.7	
N,N-Dimethyloctylamine	56.3±3.0				
	56.1±2.7			56.2±2.9	5470±900
Tri-*n*-butylamine	57.0±3.0	57.8±0.7			3050±520
	57.0±2.8	57.9±0.5		57.4±1.8	2790±200
N,N-Dimethyldodecylamine					91±20
	69.0±3.4	69.5±0.8	69.4±1.1		90±10, 86±18
	69.1±3.1	69.4±0.5	69.3±1.8	69.3±1.8	
N,N- Dimethyl tetradecylamine			76.9±1.2		9.6±2.3
			76.9±1.9	76.9±1.6	
N,N-Dimethylhexadecylamine					1.0±0.2
	84.8±3.9	85.0±0.9	85.0±1.2		1.0±0.1, 1.0±0.2
	84.8±3.6	85.0±0.6	85.3±2.0	85.0±2.0	
Tri-*n*-octylamine		99.9±1.0	99.9±1.4		0.015±0.0016
		100.0±0.7	99.7±2.2	99.9±1.3	0.016±0.0046
Tribenzylamine			92.5±1.3		
			92.6±2.1	92.6±1.7	0.05±0.01

Total Phase Change Entropy, ΔS_{tpce}

Phencyclidine consists of three rings, two saturated six-membered ring and an aromatic ring. The following equation is has been developed to estimate the contributions of a molecule that contains saturated rings along with an aromatic ring and various other substituents:

$\Delta S_{tpce}/\ J\cdot mol^{-1}\cdot K^{-1} = [\Delta S_{tpce}/\ J\cdot mol^{-1}\cdot K^{-1}]_{sat\ ring} + \Sigma n_i\, G_i$

$\Delta S_{tpce}/\ J\cdot mol^{-1}\cdot K^{-1} = [\Delta S_{tpce}/\ J\cdot mol^{-1}\cdot K^{-1}]_{sat\ ring} + (C_2{>}NC)_{cyc} + (C_2{>}CC)_{cyc} + 5(=CH)_{arom} + (=CC)_{arom}$

$[\Delta S_{tpce}/\ J\cdot mol^{-1}\cdot K^{-1}]_{sat\ ring} = (33.4)\cdot R + 3.7\cdot [N - 3R] = (33.4)\cdot 2 + 3.7\cdot [12 - 6] = 89$

$\Delta S_{tpce}/\ J\cdot mol^{-1}\cdot K^{-1} = (89) + (-19.3) + (-34.6) + 5(7.4) + (-9.6) = 62.5$

R represents the number of non-aromatic rings and N refers to the total number of ring atoms. The $[\Delta S_{tpce}]_{sat\ ring}$ term calculates the entropy for two cyclohexane rings. The additional groups adjusts $[\Delta S_{tpce}]_{sat\ ring}$ for the presence of a cyclic tertiary sp^3 hybridized nitrogen, a cyclic quaternary sp^3 hybridized carbon, five aromatic C-H carbons and one aromatic quaternary carbon attached to a saturated carbon.[1]

(1) Chickos, J. S.; Acree Jr., W. E. Total phase change entropies and enthalpies. An update on fusion enthalpies and their estimation. *Thermochim. Acta* **2009**, *495*, 5-13.

Appendix E

TABLE E-1A. Experimental Retention Times of Various Tertiary Amines

Run 1	453.6	458.6	463.5	468.5	473.4	478.4	483.3
t_o = 60 s				t/t_o			
Methylene Chloride	0.464	0.464	0.466	0.472	0.472	0.480	0.476
N,*N*-Dimethyldodecylamine	1.921	1.716	1.551	1.411	1.289	1.195	1.106
N,*N*-Dimethyl tetradecylamine	3.807	3.281	2.861	2.507	2.211	1.974	1.770
N,*N*-Dimethyl hexadecylamine	8.049	6.726	5.684	4.822	4.123	3.562	3.099
Alverine	22.110	18.141	15.053	12.509	10.481	8.850	7.523
Terbinafine	32.614	26.396	21.506	17.618	14.546	12.104	10.150
Tribenzylamine	33.800	27.504	22.538	18.559	15.394	12.865	10.830

TABLE E-1B. Enthalpies of Transfer and Vaporization Enthalpies Used to Evaluate Vaporization Enthalpy of Terbinafine

Run 1	- slope T/K	intercept	ΔH_{trn}(468 K) kJ·mol^{-1}	$\Delta_l^gH_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^gH_m$(298 K) kJ·mol^{-1}(calc)
N,*N*-Dimethyl dodecylamine	6197.7±23	13.291±0.05	51.5±0.19	69.3±0.3	69.4±0.9
N,*N*-Dimethyl tetradecylamine	7016.9±24	14.267±0.05	58.3±0.20	77.3±1.9	77.1±0.9
N,*N*-Dimethyl hexadecylamine	7846.4±28	15.277±0.06	65.2±0.23	84.8±1.0	85.0±1.0
Alverine	8286.7±26	15.199±0.06	68.9±0.22	89.3±0.2	89.1±1.0
Terbinafine	8874.8±32	16.100±0.07	73.8±0.27		94.7±1.1
Tribenzylamine	8639.0±29	15.544±0.06	71.8±0.24	92.4±1.4	92.5±1.0
$\Delta_l^gH_m$(298.15 K)/kJ·mol^{-1} = (1.14±0.01)ΔH_{trn}(493 K) - (10.7±0.70)				r^2 = 0.9997	(E-1)

TABLE E-2A. Experimental Retention Times of Various Tertiary Amines

Run 2	453.6	458.6	463.5	468.5	473.4	478.4	483.3
t_o = 60 s				t/t_o			
Methylene Chloride	0.466	0.472	0.476	0.475	0.476	0.480	0.484
N,*N*-Dimethyldodecylamine	1.924	1.727	1.560	1.415	1.295	1.197	1.114
N,*N*-Dimethyl tetradecylamine	3.815	3.298	2.871	2.511	2.217	1.978	1.777
N,*N*-Dimethyl hexadecylamine	8.064	6.752	5.697	4.828	4.130	3.567	3.103
Alverine	22.150	18.203	15.062	12.526	10.488	8.859	7.530
Terbinafine	32.723	26.437	21.541	17.654	14.560	12.123	10.154
Tribenzylamine	33.887	27.556	22.567	18.587	15.410	12.883	10.840

TABLE E-2B. Enthalpies of Transfer and Vaporization Enthalpies Used to Evaluate Vaporization Enthalpy of Terbinafine

Run 2	- slope T/K	Intercept	ΔH_{trn}(468 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)
N,*N*-Dimethyl dodecylamine	6204.3±23	13.305±0.05	51.6±0.19	69.3±0.3	69.4±0.9
N,*N*-Dimethyl tetradecylamine	7029.6±24	14.293±0.05	58.4±0.20	77.3±1.9	77.1±1.0
N,*N*-Dimethyl hexadecylamine	7866.0±27	15.318±0.06	65.4±0.22	84.8±1.0	85.0±1.0
Alverine	8302.2±28	15.231±0.06	69.0±0.23	89.3±0.2	89.1±1.1
Terbinafine	8892.6±32	16.137±0.07	73.9±0.27		94.7±1.1
Tribenzylamine	8651.3±30	15.569±0.06	71.9±0.25	92.4±1.4	92.4±1.1

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.13±0.01)ΔH_{trn}(493 K) - (10.8±0.73) r^2 = 0.9997 (E-2)

TABLE E-3A. Experimental Retention Times of Various Tertiary Amines

Run 3	478.4	483.3	488.2	493.2	498.2	503.1	508.1
t_o = 60 s				t/t_o			
Methylene Chloride	0.486	0.487	0.489	0.497	0.498	0.471	0.499
N,*N*-Dimethyldodecylamine	1.209	1.121	1.049	0.997	0.941	0.862	0.852
N,*N*-Dimethyltetradecylamine	1.999	1.792	1.624	1.493	1.368	1.228	1.168
N,*N*-Dimethylhexadecylamine	3.609	3.138	2.755	2.452	2.179	1.911	1.749
Alverine	8.947	7.598	6.517	5.653	4.886	4.200	3.695
Tri-*n*-octylamine	12.825	10.606	8.860	7.496	6.327	5.321	4.575
Tribenzylamine	13.144	11.064	9.373	8.042	6.878	5.854	5.047
Naftifine	27.057	22.372	18.630	15.698	13.175	11.049	9.403

TABLE E-3B. Enthalpies of Transfer and Vaporization Enthalpies Used to Evaluate Vaporization Enthalpy of Naftifine

Run 3	- slope T/K	Intercept	ΔH_{trn}(493 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)
N,*N*-Dimethyl dodecylamine	5862.0±53	12.583±0.10	48.7±0.44	69.3±0.3	69.4±1.4
N,*N*-Dimethyl tetradecylamine	6663.8±41	13.520±0.08	55.4±0.34	77.3±1.9	77.1±1.4
N,*N*-Dimethyl hexadecylamine	7474.5±38	14.490±0.08	62.1±0.31	84.8±1.0	84.8±1.5
Alverine	7936.5±39	14.458±0.08	66.0±0.33	89.3±0.2	89.2±1.6
Tri-*n*-octylamine	9034.9±39	16.379±0.08	75.1±0.33	100.1±1.4	99.8±1.7
Tribenzylamine	8327.2±48	14.870±0.10	69.2±0.40	92.4±1.4	93.0±1.6
Naftifine	8923.9±35	15.378±0.07	74.2±0.29		98.7±1.7

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.15±0.02)ΔH_{trn}(493 K) - (13.3±1.07) r^2 = 0.9991 (E-3)

TABLE E-4A. Experimental Retention Times of Various Tertiary Amines

Run 4 t_o = 60 s	478.4	483.3	488.2	493.2 t/t_o	498.2	503.1	508.1
Methylene Chloride	0.488	0.490	0.491	0.499	0.502	0.508	0.510
N,*N*-Dimethyldodecylamine	1.215	1.134	1.057	1.001	0.950	0.908	0.866
N,*N*-Dimethyltetradecylamine	2.010	1.813	1.637	1.499	1.381	1.281	1.189
N,*N*-Dimethylhexadecylamine	3.631	3.176	2.780	2.464	2.200	1.981	1.786
Alverine	9.008	7.693	6.580	5.680	4.933	4.321	3.784
Tri-*n*-octylamine	12.912	10.740	8.959	7.543	6.395	5.473	4.691
Tribenzylamine	13.246	11.203	9.482	8.096	6.959	6.027	5.226
Naftifine	27.263	22.657	18.853	15.808	13.335	11.337	9.649

TABLE E-4B. Enthalpies of Transfer and Vaporization Enthalpies Used to Evaluate Vaporization Enthalpy of Naftifine

Run 4	- slope T/K	Intercept	ΔH_{trn}(493 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)
N,*N*-Dimethyl dodecylamine	5835.33±29	12.519±0.06	48.5±0.24	69.3±0.3	69.5±0.6
N,*N*-Dimethyl tetradecylamine	6597.48±28	13.374±0.06	54.8±0.23	77.3±1.9	77.1±0.6
N,*N*-Dimethyl hexadecylamine	7371.36±32	14.268±0.06	61.3±0.26	84.8±1.0	84.8±0.6
Alverine	7816.03±31	14.201±0.06	65.0±0.26	89.3±0.2	89.3±0.6
Tri-*n*-octylamine	8902.68±38	16.096±0.08	74.0±0.31	100.1±1.4	100.1±0.7
Tribenzylamine	8138.42±33	14.471±0.07	67.7±0.28	92.4±1.4	92.5±0.7
Naftifine	8790.85±33	15.094±0.07	73.1±0.27		99.0±0.7

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.20±0.01)ΔH_{trn}(493 K) - (11.1±0.44) r^2 = 0.9999   (E-4)

TABLE E-5A. Experimental Retention Times of Various Tertiary Amines

Run 5 t_o = 60 s	453.6	458.5	463.4	468.4 t/t_o	473.4	478.3	483.2
Methylene Chloride	0.523	0.522	0.516	0.521	0.531	0.529	0.548
N,*N*-Dimethyldodecylamine	2.192	1.952	1.743	1.580	1.457	1.338	1.274
N,*N*-Dimethyl tetradecylamine	4.347	3.732	3.215	2.811	2.496	2.216	2.037
Tri-*n*-hexylamine	4.842	4.136	3.546	3.085	2.724	2.406	2.200
N,*N*-Dimethyl hexadecylamine	9.182	7.644	6.386	5.411	4.648	4.005	3.562
Alverine	25.265	20.680	16.959	14.092	11.843	9.988	8.657
Amitriptyline	30.548	24.907	20.349	16.860	14.109	11.856	10.235
Tribenzylamine	38.970	31.608	25.634	21.102	17.554	14.660	12.569

TABLE E-5B. Enthalpies of Transfer and Vaporization Enthalpies Used to Evaluate Vaporization Enthalpy of Tri-*n*-hexylamine and Amitriptyline

Run 5	- slope *T*/K	Intercept	ΔH_{trn}(468 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)
N,*N*-Dimethyl dodecylamine	6202.9±100	13.175±0.21	51.6±0.83	69.3±0.3	69.4±0.9
N,*N*-Dimethyl tetradecylamine	7022.4±102	14.154±0.22	58.4±0.85	77.3±1.9	77.1±0.9
Tri-*n*-hexylamine	7154.9±102	14.324±0.22	59.5±0.85		78.4±0.9
N,*N*-Dimethyl hexadecylamine	7850.8±106	15.164±0.23	65.3±0.88	84.8±1.0	85.0±1.0
Alverine	8292.0±99	15.086±0.21	68.9±0.83	89.3±0.2	89.2±1.0
Amitriptyline	8407.0±100	15.146±0.21	69.9±0.83		90.2±1.0
Tribenzylamine	8640.2±101	15.413±0.21	71.8±0.84	92.4±1.4	92.5±1.0

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.14±0.01)ΔH_{trn}(493 K) - (10.6±0.67) r^2 = 0.9997 (E-5)

TABLE E-6A. Experimental Retention Times of Various Tertiary Amines

Run 6	453.6	458.5	463.4	468.4	473.4	478.3	483.2
t_o = 60 s				t/t_o			
Methylene Chloride	0.514	0.514	0.520	0.508	0.522	0.535	0.537
N,*N*-Dimethyldodecylamine	2.143	1.908	1.727	1.562	1.442	1.346	1.245
N,*N*-Dimethyl tetradecylamine	4.253	3.650	3.182	2.789	2.477	2.225	1.991
Tri-*n*-hexylamine	4.739	4.047	3.508	3.061	2.703	2.414	2.149
N,*N*-Dimethyl hexadecylamine	8.983	7.483	6.312	5.377	4.620	4.014	3.480
Alverine	24.721	20.279	16.774	14.041	11.784	9.993	8.465
Amitriptyline	29.903	24.430	20.140	16.808	14.053	11.868	10.012
Tribenzylamine	38.305	31.019	25.461	21.136	17.571	14.736	12.334

TABLE E-6B. Enthalpies of Transfer and Vaporization Enthalpies Used to Evaluate Vaporization Enthalpy of Tri-*n*-hexylamine and Amitriptyline

Run 6	- slope *T*/K	Intercept	ΔH_{trn}(468 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)
N,*N*-Dimethyl dodecylamine	6103.3±48	12.977±0.10	50.7±0.40	69.3±0.3	69.3±0.7
N,*N*-Dimethyl tetradecylamine	6938.1±49	13.987±0.10	57.7±0.41	77.3±1.9	77.2±0.8
Tri-*n*-hexylamine	7077.4±49	14.172±0.01	58.8±0.41		78.5±0.8
N,*N*-Dimethyl hexadecylamine	7771.7±52	15.008±0.01	64.6±0.43	84.8±1.0	85.0±0.8
Alverine	8219.9±43	14.944±0.01	68.3±0.36	89.3±0.2	89.2±0.8
Amitriptyline	8333.1±44	15.000±0.01	69.3±0.37		90.3±0.8
Tribenzylamine	8556.3±49	15.241±0.01	71.1±0.41	92.4±1.4	92.4±0.9

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.13±0.01)ΔH_{trn}(493 K) - (12.0±0.57) r^2 = 0.9998 (E-6)

TABLE E-7A. Experimental Retention Times of Various Tertiary Amines[a]

Run 7	494.0	499.0	504.0	508.9	514.0	519.0	524.0
t_o = 60 s				t/t_o			
Methylene Chloride	3.103	3.089	3.109	3.132	3.147	3.161	3.178
Tri-*n*-butylamine	3.441	3.393	3.386	3.384	3.378	3.372	3.372
N,*N*-Dimethyldodecylamine	4.202	4.054	3.968	3.898	3.833	3.776	3.731
N,*N*-Dimethyl hexadecylamine	7.586	6.901	6.398	5.980	5.622	5.319	5.066
Tri-*n*-octylamine	19.526	16.619	14.435	12.656	11.187	9.975	8.977
Tribenzylamine	20.388	17.570	15.419	13.640	12.153	10.902	9.858
Cyproheptadine	26.890	22.931	19.937	17.457	15.387	13.653	12.207

[a] Experiment conducted on a 30m column.

TABLE E-7B. Enthalpies of Transfer and Vaporization Enthalpies Used to Evaluate Vaporization Enthalpy of Cyproheptadine

Run 7	- slope T/K	Intercept	ΔH_{trn}(509 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)
Tri-*n*-butylamine	4768.6±41	10.744±0.08	39.6±0.34	58.0±1.9	58.0±0.2
N,*N*-Dimethyl dodecylamine	5896.4±44	11.849±0.09	49.0±0.37	69.3±0.3	69.4±0.2
N,*N*-Dimethyl hexadecylamine	7429.1±51	13.548±0.10	61.8±0.42	84.8±1.0	84.8±0.2
Tri-*n*-octylamine	8945.9±55	15.321±0.11	74.4±0.46	100.1±1.4	100.1±0.3
Tribenzylamine	8168.5±51	13.695±0.10	67.9±0.42	92.4±1.4	92.3±0.2
Cyproheptadine	8320.1±53	13.683±0.11	69.2±0.44		93.8±0.2

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.21±0.003)ΔH_{trn}(493 K) - (9.8±0.16) r^2 = 1.0000 (E-7)

TABLE E-8A. Experimental Retention Times of Various Tertiary Amines[a]

Run 8	494.0	499.0	504.0	508.9	514.0	519.0	524.0
t_o = 60 s				t/t_o			
Methylene Chloride	3.055	3.074	3.083	3.096	3.102	3.110	3.132
Tri-*n*-butylamine	3.389	3.377	3.358	3.347	3.330	3.319	3.324
N,*N*-Dimethyldodecylamine	4.141	4.034	3.936	3.855	3.779	3.717	3.678
N,*N*-Dimethyl hexadecylamine	7.481	6.863	6.346	5.914	5.546	5.239	4.995
Tri-*n*-octylamine	19.276	16.531	14.319	12.514	11.038	9.832	8.853
Tribenzylamine	20.135	17.475	15.294	13.489	11.991	10.744	9.725
Cyproheptadine	26.528	22.812	19.775	17.259	15.184	13.458	12.040

[a] Experiment conducted on a 30m column.

TABLE E-8B. Enthalpies of Transfer and Vaporization Enthalpies Used to Evaluate Vaporization Enthalpy of Cyproheptadine

Run 8	- slope T/K	Intercept	ΔH_{trn}(509 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)
Tri-*n*-butylamine	4834.4±18	10.884±0.04	40.2±0.15	58.0±1.9	58.0±0.2
N,*N*-Dimethyl dodecylamine	5943.9±25	11.954±0.05	49.4±0.21	69.3±0.3	69.3±0.2
N,*N*-Dimethyl hexadecylamine	7469.7±34	13.639±0.07	62.1±0.28	84.8±1.0	84.8±0.2
Tri-*n*-octylamine	8992.5±41	15.423±0.08	74.8±0.34	100.1±1.4	100.2±0.3
Tribenzylamine	8215.9±38	13.799±0.07	68.3±0.31	92.4±1.4	92.3±0.3
Cyproheptadine	8361.4±36	13.776±0.07	69.5±0.30		93.8±0.3
$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.22±0.003)ΔH_{trn}(493 K) - (9.0±0.17)				r^2 = 1.0000	(E-8)

TABLE E-9A. Experimental Retention Times of Various Tertiary Amines

Run 9	438.8	443.7	448.6	453.6	458.4	463.4	468.3
t_o = 60 s				t/t_o			
Methylene Chloride	0.549	0.551	0.554	0.556	0.552	0.561	0.555
N,*N*-Dimethyldodecylamine	3.379	2.954	2.603	2.314	2.052	1.861	1.683
N,*N*-Dimethyl-1-naphthylamine	3.728	3.285	2.917	2.610	2.326	2.116	1.919
N,*N*-Dimethyl tetradecylamine	7.468	6.299	5.349	4.584	3.921	3.424	2.991
Tri-*n*-hexylamine	8.432	7.082	5.984	5.103	4.345	3.775	3.281
9-Methylcarbazole	12.420	10.532	8.975	7.716	6.594	5.744	5.009
9-Ethylcarbazole	14.028	11.821	10.024	8.583	7.287	6.312	5.480
N,*N*-Dimethyl hexadecylamine	17.296	14.153	11.660	9.695	8.038	6.798	5.765
Triphenylamine	28.037	23.024	19.038	15.887	13.149	11.108	9.416

TABLE E-9B. Enthalpies of Transfer and Vaporization Enthalpies Used to Compare Aliphatic and Aromatic Tertiary Amines with Alphatic Amines Used as Standards[a]

Run 9	- slope T/K	Intercept	ΔH_{trn}(454 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)
N,*N*-Dimethyl dodecylamine	6417.5±32	13.588±0.07	53.4±0.27	69.3±0.3	69.4±1.6
N,*N*-Dimethyl-1-naphthylamine	5901.5±30	12.296±0.07	49.1±0.25	66.9±0.2	64.8±1.6
N,*N*-Dimethyl tetradecylamine	7280.8±34	14.662±0.08	60.5±0.28	77.3±1.9	77.1±1.7
Tri-*n*-hexylamine[b]	7406.7±34	14.819±0.07	61.6±0.28	78.5±1.0	78.3±1.8
9-Methylcarbazole	6840.3±33	13.117±0.07	56.9±0.28	79.5±3.2	73.2±1.7
9-Ethylcarbazole	7024.3±37	13.410±0.08	58.4±0.31	83.9±0.5	74.8±1.7
N,*N*-Dimethyl hexadecylamine	8143.8±38	15.746±0.08	67.7±0.32	84.8±1.0	84.9±1.7
Triphenylamine[c]	7898.6±40	14.691±0.09	65.7±0.33	90.2±1.2	82.3±1.8

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.08±0.02)ΔH_{trn}(454 K) - (11.8±1.2) $r^2 = 0.9997$ (E-9)

[a] Literature values for *N*,*N*-dimethyldodecylamine, *N*,*N* –dimethyltetradecylamine and *N*,*N* –dimethylhexadecylamine only were used as standards. [b] Tri-*n*-hexylamine was left as an unknown to verify validity of alphatic correlations. [c] Literature value of triphenylamine is unreliable as it was determined through correlation using standard compounds with dissimilar functional groups.

TABLE E-9C. Enthalpies of Transfer and Vaporization Enthalpies Used to Compare Aliphatic and Aromatic Tertiary Amines with Aromatic Amines Used as Standards[a]

Run 9	- slope T/K	Intercept	ΔH_{trn}(454 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)
N,*N*-Dimethyl dodecylamine	6417.5±32	13.588±0.07	53.4±0.27	69.3±0.3	74.3±13.3
N,*N*-Dimethyl-1-naphthylamine	5901.5±30	12.296±0.07	49.1±0.25	66.9±0.2	66.7±12.8
N,*N*-Dimethyl tetradecylamine	7280.8±34	14.662±0.08	60.5±0.28	77.3±1.9	86.9±14.2
Tri-*n*-hexylamine	7406.7±34	14.819±0.07	61.6±0.28	78.5±1.0	88.7±14.3
9-Methylcarbazole	6840.3±33	13.117±0.07	56.9±0.28	79.5±3.2	80.4±13.7
9-Ethylcarbazole	7024.3±37	13.410±0.08	58.4±0.31	83.9±0.5	83.1±13.9
N,*N*-Dimethyl hexadecylamine	8143.8±38	15.746±0.08	67.7±0.32	84.8±1.0	99.4±15.1
Triphenylamine[b]	7898.6±40	14.691±0.09	65.7±0.33	90.2±1.2	95.9±14.8

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.75±0.17)ΔH_{trn}(454 K) - (-19.3±9.5) $r^2 = 0.9903$ (E-10)

[a] Literature values for *N*,*N* -dimethyl-1-naphthylamine, 9-Methylcarbazole and 9-Ethylcarbazole only were used as standards. [b] Literature value of triphenylamine is unreliable as it was determined through correlation using standard compounds with dissimilar functional groups.

TABLE E-10A. Experimental Retention Times of Various Tertiary Amines

Run 10	438.8	443.7	448.6	453.6	458.4	463.4	468.3
t_o = 60 s				t/t_o			
Methylene Chloride	0.531	0.540	0.545	0.550	0.554	0.545	0.554
N,*N*-Dimethyldodecylamine	3.266	2.874	2.541	2.263	2.029	1.809	1.650
N,*N*-Dimethyl-1-naphthylamine	3.603	3.198	2.848	2.552	2.298	2.058	1.880
N,*N*-Dimethyl tetradecylamine	7.221	6.119	5.217	4.478	3.869	3.331	2.922
Tri-*n*-hexylamine	8.157	6.880	5.839	4.987	4.287	3.673	3.205
9-Methylcarbazole	12.011	10.227	8.750	7.523	6.504	5.594	4.885
9-Ethylcarbazole	13.561	11.483	9.771	8.353	7.181	6.149	5.341
N,*N*-Dimethyl hexadecylamine	16.710	13.739	11.359	9.455	7.925	6.618	5.622
Triphenylamine	27.119	22.376	18.548	15.464	12.960	10.831	9.169

TABLE E-10B. Enthalpies of Transfer and Vaporization Enthalpies Used to Compare Aliphatic and Aromatic Tertiary Amines with Alphatic Amines Used as Standards[a]

Run 10	- slope T/K	Intercept	ΔH_{trn}(454 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)
N,*N*-Dimethyl dodecylamine	6373.8±20	13.519±0.04	53.0±0.17	69.3±0.3	69.4±1.4
N,*N* -Dimethyl-1-naphthylamine	5857.2±24	12.225±0.05	48.7±0.20	66.9±0.2	64.7±1.3
N,*N*-Dimethyl tetradecylamine	7233.7±19	14.585±0.04	60.1±0.16	77.3±1.9	77.2±1.5
Tri-*n*-hexylamine[b]	7359.2±19	14.740±0.04	61.2±0.16	78.5±1.0	78.3±1.6
9-Methylcarbazole	6788.4±22	13.029±0.05	56.4±0.18	79.5±3.2	73.1±1.4
9-Ethylcarbazole	6974.0±20	13.326±0.04	58.0±0.17	83.9±0.5	74.8±1.4
N,*N*-Dimethyl hexadecylamine	8085.1±16	15.643±0.04	67.2±0.14	84.8±1.0	84.9±1.5
Triphenylamine[c]	7847.0±18	14.603±0.04	65.2±0.15	90.2±1.2	82.7±1.5

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.09±0.02)ΔH_{trn}(454 K) - (11.6±1.0) r^2 = 0.9998   (E-11)

[a] Literature values for *N*,*N*-dimethyldodecylamine, *N*,*N* –dimethyltetradecylamine and *N*,*N* –dimethylhexadecylamine only were used as standards. [b] Tri-*n*-hexylamine was left as an unknown to verify validity of alphatic correlations. [c] Literature value of triphenylamine is unreliable as it was determined through correlation using standard compounds with dissimilar functional groups.

TABLE E-10C. Enthalpies of Transfer and Vaporization Enthalpies Used to Compare Aliphatic and Aromatic Tertiary Amines with Aromatic Amines Used as Standards[a]

Run 10	- slope T/K	Intercept	ΔH_{trn}(454 K) kJ·mol^{-1}	$\Delta_l{}^gH_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l{}^gH_m$(298 K) kJ·mol^{-1}(calc)
N,*N*-Dimethyl dodecylamine	6373.8±20	13.519±0.04	53.0±0.17	69.3±0.3	74.3±13.0
N,*N*-Dimethyl-1-naphthylamine	5857.2±24	12.225±0.05	48.7±0.20	66.9±0.2	66.7±12.5
N,*N*-Dimethyl tetradecylamine	7233.7±19	14.585±0.04	60.1±0.16	77.3±1.9	86.9±13.8
Tri-*n*-hexylamine	7359.2±19	14.740±0.04	61.2±0.16	78.5±1.0	88.8±14.0
9-Methylcarbazole	6788.4±22	13.029±0.05	56.4±0.18	79.5±3.2	80.4±13.4
9-Ethylcarbazole	6974.0±20	13.326±0.04	58.0±0.17	83.9±0.5	83.1±13.6
N,*N*-Dimethyl hexadecylamine	8085.1±16	15.643±0.04	67.2±0.14	84.8±1.0	99.4±14.8
Triphenylamine[b]	7847.0±18	14.603±0.04	65.2±0.15	90.2±1.2	96.0±14.5

$\Delta_l{}^gH_m$(298.15 K)/kJ·mol^{-1} = (1.77±0.17)ΔH_{trn}(454 K) - (-19.2±9.3) $r^2 = 0.9908$ (E-12)

[a]Literature values for *N*,*N* -dimethyl-1-naphthylamine, 9-Methylcarbazole and 9-Ethylcarbazole only were used as standards. [b]Literature value of triphenylamine is unreliable as it was determined through correlation using standard compounds with dissimilar functional groups.

TABLE E-11. Correlations Between $\ln(t_o/t_a)_{avg}$ and $\ln(p/p_o)_{exp}$ at T/K = 298.15 for Runs 3/4[a]

run 3/run 4	-slope/K	Intercept	$\ln(t_o/t_a)_{avg}$	$\ln(p/p_o)_{exp}$	$\ln(p/p_o)_{calc}$	$p\cdot10^3$/Pa calc/lit
			run 3/ run 4			
N,*N*-Dimethyl dodecylamine	5862.04	12.583				
	5835.33	12.519	-7.065	-11.694	-11.696	844/850[b]
N,*N*-Dimethyl tetradecylamine	6663.80	13.520				
	6597.48	13.374	-8.791	-13.917	-13.897	93.4/92[c]
N,*N*-Dimethyl hexadecylamine	7474.48	14.489				
	7371.36	14.268	-10.516	-16.079	-16.097	10.4/11.0[c]
Alverine	7936.54	14.458				
	7816.03	14.201	-12.085	-18.112	-18.098	1.4/1.4[c], 4.5[d], 3.3[e]
Tri-*n*-octylamine	9034.94	16.379				
	8902.68	16.096	-13.841	-20.383	-20.337	0.149/0.132[f]
Tribenzylamine	8327.16	14.870				
	8138.42	14.471	-12.935	-19.121	-19.182	0.473/0.50[c], 2.6[g]
Naftifine	8923.87	15.378				
	8790.85	15.094	-14.468		-21.137	0.067/NA[h]

Run 3/4: $\ln(p/p_o) = (1.275\pm0.007)\ln(p/p_o) - (2.686\pm0.079)$ $r^2 = 0.9999$ (E-13)

[a] Run 3and 4: slope and intercept measured at a mean temperature of T_m/K = 493. [b] Ref 4. [c] Ref 3. [d] Estimated, Ref 6. [e] Estimated, Ref 7. [f] Extrapolated value, Ref 3. [g] Estimated vapor pressure of the sub-cooled liquid, Ref 8. [h] Not Available.

TABLE E-12. Correlations Between $\ln(t_o/t_a)_{avg}$ and $\ln(p/p_o)_{exp}$ at T/K = 298.15 for Runs 5/6[a]

run 5/run 6	-slope/K	Intercept	$\ln(t_o/t_a)_{avg}$	$\ln(p/p_o)_{exp}$	$\ln(p/p_o)_{calc}$	$p\cdot10^3$/Pa calc/lit
			run 5/ run 6			
N,*N*-Dimethyl dodecylamine	6202.87	13.175				
	6103.25	12.977	-7.559	-11.694	-11.685	853/850[b]
N,*N*-Dimethyl tetradecylamine	7022.37	14.154				
	6938.08	13.987	-9.340	-13.917	-13.911	92.1/92[c]
Tri-*n*-hexylamine	7154.93	14.324				
	7077.41	14.172	-9.618		-14.259	65.1/NA[d]
N,*N*-Dimethyl hexadecylamine	7850.84	15.164				
	7771.73	15.008	-11.112	-16.079	-16.126	10.1/11.0[c]
Alverine	8291.95	15.086				
	8219.89	14.944	-12.674	-18.112	-18.079	1.4/1.4[c], 4.5[e], 3.3[f]
Amitriptyline	8406.99	15.146				
	8333.14	15.000	-12.999		-18.485	0.95/NA[d]
Tribenzylamine	8640.22	15.413				
	8556.29	15.241	-13.510	-19.121	-19.124	0.50/0.50[c], 2.6[g]

Run 5/6: $\ln(p/p_o) = (1.250\pm0.007) \ln(p/p_o) - (2.236\pm0.077)$ $r^2 = 0.9999$ (E-14)

[a]Run 5and 6: slope and intercept measured at a mean temperature of T_m/K = 468. [b]Ref 4. [c]Ref 3. [d]Not Available. [e]Estimated, Ref 6. [f]Estimated, Ref 7. [g]Estimated vapor pressure of the sub-cooled liquid, Ref 8.

TABLE E-13. Correlations Between $\ln(t_o/t_a)_{avg}$ and $\ln(p/p_o)_{exp}$ at T/K = 298.15 for Runs 7/8[a]

run 7/run 8	-slope/K	Intercep	$\ln(t_o/t_a)_{avg}$	$\ln(p/p_o)_{exp}$	$\ln(p/p_o)_{calc}$	$p{\cdot}10^3$/Pa calc/lit
			run 7/ run 8			
Tri-*n*-butylamine	4768.61	10.744				
	4834.43	10.884	-5.290	-8.183	-8.207	27626/21000[b], 20000[c], (21000,54000)[c,d]
N,*N*-Dimethyl dodecylamine	5896.38	11.849				
	5943.92	11.954	-7.954	-11.694	-11.652	882/850[e]
N,*N*-Dimethyl hexadecylamine	7429.1	13.548				
	7469.69	13.639	-11.392	-16.079	-16.096	10.4/11.0[f]
Tri-*n*-octylamine	8945.93	15.321				
	8992.51	15.423	-14.710	-20.383	-20.386	0.14/0.132[d]
Tribenzylamine	8168.51	13.695				
	8215.91	13.799	-13.729	-19.121	-19.118	0.51/0.50[f], 2.6[g]
Cyproheptadine	8320.1	13.683				
	8361.39	13.776	-14.245		-19.785	0.26/NA[h]
Run 7/8: $\ln(p/p_o) = (1.293\pm0.004) \ln(p/p_o) - (1.368\pm0.043)$					$r^2 = 1.0000$ (E-14)	

[a] Run 7and 8: slope and intercept measured at a mean temperature of T_m/K = 509. [b] Estimated, Ref 6. [c] Estimated, Ref 7. [d] Extrapolated value, Ref 3. [e] Ref 4. [f] Ref 3. [g] Estimated vapor pressure of the sub-cooled liquid, Ref 8. [h] Not Available.

TABLE E-14. Evaluation of the Constants of Eq 3-2 for New Compounds in Runs 1-8[a]

	A	B
Terbinafine	19.068	-11475.79
Naftifine	19.018	-11972.94
Tri-*n*-hexylamine	17.515	-9472.11
Amitriptyline	18.121	-10914.28
Cyproheptadine	18.289	-11351.83

[a] Values of Constant C for all compounds = 0.

Appendix F

TABLE F-1A. Retention Times on a Poly(dimethyl siloxane) Capillary Column

Run 1 T/K	516.8	521	526.8	531.4	537	542	547.1
				t/60 s			
Methanol/CH_2Cl_2	1.833	1.826	1.859	1.860	1.875	1.892	1.904
Dimethyl phthalate	2.384	2.330	2.318	2.278	2.260	2.246	2.231
Diethyl phthalate	2.661	2.577	2.536	2.471	2.433	2.400	2.369
Di-*n*-butyl phthalate	4.250	3.968	3.742	3.524	3.358	3.214	3.089
Eicosane	4.656	4.305	4.014	3.746	3.539	3.361	3.209
Methyl octadecanoate	5.760	5.251	4.814	4.430	4.127	3.869	3.649
Ethyl octadecanoate	6.597	5.961	5.409	4.932	4.554	4.233	3.962
Docosane	6.890	6.210	5.615	5.107	4.702	4.358	4.069
Methyl eicosanoate	8.851	7.865	6.998	6.272	5.691	5.200	4.791
Butyl benzyl phthalate	8.977	8.037	7.209	6.500	5.933	5.444	5.034
Tetracosane	10.813	9.510	8.348	7.401	6.637	5.994	5.463
Methyl heneicosanoate	11.184	9.822	8.614	7.623	6.828	6.158	5.606
Pentacosane	13.773	11.959	10.372	9.078	8.037	7.170	6.455
Bis(2-ethylhexyl) phthalate	14.338	12.488	10.86	9.527	8.455	7.552	6.810
Hexacosane	17.661	15.169	12.992	11.242	9.835	8.668	7.715
Di-*n*-octyl phthalate	22.442	19.183	16.361	14.087	12.253	10.725	9.482
Octacosane	29.537	24.843	20.815	17.647	15.098	13.013	11.327

TABLE F-1B. Correlation of Vaporization Enthalpies With Enthalpies of Transfer (Poly(dimethyl siloxane) Column)^{a}

Run 1	slope T/K	intercept	ΔH_{trn}(532 K) kJ·mol^{-1}	$\Delta_l^gH_m$(298 K) kJ·mol^{-1} (Lit)	$\Delta_l^gH_m$(298 K) kJ·mol^{-1}(Calc)
Eicosane	-7147.1	12.803	59.42	101.81±0.5	101.8±0.7
Docosane	-7856.6	13.595	65.32	111.9±2.7	111.8±0.7
Tetracosane	-8567.8	14.398	71.23	121.9±2.8	121.9±0.8
Pentacosane	-8924.0	14.804	74.19	126.8±2.9	126.9±0.8
Hexacosane	-9270.9	15.194	77.07	131.7±3.2	131.8±0.8
Octacosane	-9968.2	15.985	82.87	141.9±4.9	141.7±0.8
$\Delta_l^gH_m$(298.15 K)/kJ·mol^{-1} = (1.703±0.007)·ΔH_{trn}(532 K) + (0.590±0.541); r^2 = 0.9999 (F-1)					
Methyl octadecanoate	-7509.0	13.175	62.43	105.87±1.4	106.0±4.1
Ethyl octadecanoate	-7769.2	13.485	64.59	109.6±4.4	109.6±4.1
Methyl eicosanoate	-8223.0	13.997	68.36	116.43±1.5	116.1±4.2
Methyl heneicosanoate	-8579.2	14.380	71.32	120.9±2.5	121.1±4.3
$\Delta_l^gH_m$(298.15 K)/kJ·mol^{-1} = (1.705±0.044)·ΔH_{trn}(532 K) - (0.490±2.97); r^2 = 0.9986 (F-2)					
Dimethyl phthalate	-4830.3	9.952	40.16	77.0±1.2	76.9±0.4
Diethyl phthalate	-5343.5	10.537	44.42	82.1±0.5	82.2±0.4
Di-*n*-butyl phthalate	-6598.1	11.896	54.85	95.0±1.1	95.2±0.5
Butyl benzyl phthalate	-7638.6	12.828	63.50	106.2±2.4	106.0±0.5
bis(2-Ethylhexyl) phthalate	-8659.4	14.245	71.99	116.7±0.5	116.6±0.5
Di-*n*-octyl phthalate	-9251.7	15.194	76.92	122.6±1.4	122.7±0.5
$\Delta_l^gH_m$(298.15 K)/kJ·mol^{-1} = (1.247±0.006)·ΔH_{trn}(532 K) + (26.78±0.34); r^2 = 0.9999 (F-3)					

^{a}Uncertainties represent 1 standard deviation.

TABLE F-1C. Correlation of Vaporization Enthalpies With Enthalpies of Transfer (Poly(dimethyl siloxane) Column) Using Mono-Esters as Standards[a]

Run 1	slope T/K	intercept	ΔH_{trn}(532 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}	
					(Calc)	(Lit)
Eicosane	-7147.1	12.803	59.42		100.8±4.0	101.81±0.5
Docosane	-7856.6	13.595	65.32		110.9±4.1	111.9±2.7
Tetracosane	-8567.8	14.398	71.23		121.0±4.3	121.9±2.8
Pentacosane	-8924.0	14.804	74.19		126.0±4.4	126.8±2.9
Hexacosane	-9270.9	15.194	77.07		130.9±4.5	131.7±3.2
Octacosane	-9968.2	15.985	82.87		140.8±4.7	141.9±4.9
Methyl octadecanoate	-7792.9	13.705	64.79	105.87±1.4	106.0±4.1	
Ethyl octadecanoate	-8067.1	14.043	67.07	109.6±4.4	109.6±4.1	
Methyl eicosanoate	-8541.4	14.576	71.01	116.43±1.5	116.1±4.2	
Methyl heneicosanoate	-8913.6	15.01	74.1	120.9±2.5	121.1±4.3	
Dimethyl phthalate	-4830.3	9.952	40.16		68.0±3.5	77.0±1.2
Diethyl phthalate	-5343.5	10.537	44.42		75.3±3.6	82.1±0.5
Di-*n*-butyl phthalate	-6598.1	11.896	54.85		93.0±3.8	95.0±1.1
Butyl benzyl phthalate	-7638.6	12.828	63.50		107.8±4.1	106.2±2.4
bis(2-Ethylhexyl) phthalate	-8659.4	14.245	71.99		122.3±4.4	116.7±0.5
Di-*n*-octyl phthalate	-9251.7	15.194	76.92		130.7±4.5	122.6±1.4

$$\Delta_l^g H_m(298.15\ \text{K})/\text{kJ·mol}^{-1} = (1.705\pm0.044)\cdot\Delta H_{trn}(532\ \text{K}) - (0.489\pm2.97);\quad r^2 = 0.9986 \qquad \text{(F-4)}$$

[a]Uncertainties represent 1 standard deviation.

TABLE F-2A. Retention Times on a Poly(dimethyl siloxane) Capillary Column

Run 2 T/K	516.8	521	526.8	531.4	537	542	547.1
				t/60 s			
Methanol/CH_2Cl_2	1.852	1.859	1.858	1.884	1.892	1.905	1.916
Dimethyl phthalate	2.410	2.366	2.321	2.308	2.281	2.263	2.246
Diethyl phthalate	2.691	2.614	2.541	2.503	2.455	2.418	2.385
Di-*n*-butyl phthalate	4.297	4.010	3.761	3.568	3.389	3.239	3.111
Eicosane	4.712	4.349	4.039	3.794	3.573	3.390	3.233
Methyl octadecanoate	5.826	5.295	4.849	4.484	4.166	3.901	3.677
Ethyl octadecanoate	6.673	6.006	5.451	4.992	4.598	4.269	3.992
Docosane	6.973	6.258	5.664	5.170	4.748	4.396	4.101
Methyl eicosanoate	8.954	7.915	7.062	6.347	5.745	5.245	4.827
Butyl benzyl phthalate	9.076	8.090	7.269	6.576	5.985	5.488	5.070
Tetracosane	10.949	9.560	8.441	7.491	6.703	6.049	5.508
Methyl heneicosanoate	11.315	9.879	8.700	7.714	6.894	6.213	5.651
Pentacosane	13.937	12.029	10.485	9.186	8.118	7.237	6.510
bis(2-Ethylhexyl) phthalate	14.489	12.547	10.970	9.637	8.536	7.618	6.861
Hexacosane	17.875	15.256	13.150	11.384	9.942	8.752	7.782
Di-*n*-octyl phthalate	22.671	19.277	16.530	14.247	12.371	10.824	9.560
Octacosane	29.934	25.008	21.102	17.869	15.259	13.145	11.433

TABLE F-2B. Correlation of Vaporization Enthalpies With Enthalpies of Transfer (Poly(dimethyl siloxane) Column)[a]

Run 2	slope T/K	intercept	ΔH_{trn}(532 K) kJ·mol^{-1}	$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298 K) kJ·mol^{-1} (Lit)	$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298 K) kJ·mol^{-1}(Calc)
Eicosane	-7142.8	12.785	59.38	101.81±0.5	101.8±0.6
Docosane	-7854.3	13.580	65.32	111.9±2.7	111.8±0.7
Tetracosane	-8567.0	14.386	71.22	121.9±2.8	121.9±0.7
Pentacosane	-8918.9	14.784	74.15	126.8±2.9	126.9±0.7
Hexacosane	-9266.7	15.175	77.04	131.7±3.2	131.8±0.7
Octacosane	-9976.8	15.99	82.94	141.9±4.9	141.8±0.8
$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K)/kJ·mol^{-1} = (1.70±0.007)·ΔH_{trn}(532 K) + (0.920±0.504); r^2 = 0.9999 (F-5)					
Methyl octadecanoate	-7505.1	13.158	62.39	105.87±1.4	105.9±3.9
Ethyl octadecanoate	-7766.1	13.470	64.56	109.6±4.4	109.6±3.9
Methyl eicosanoate	-8221.2	13.964	68.35	116.43±1.5	116.1±4.0
Methyl heneicosanoate	-8575.7	14.363	71.29	120.9±2.5	121.1±4.1
$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K)/kJ·mol^{-1} = (1.704±0.042)·ΔH_{trn}(532 K) - (0.38±2.82); r^2 = 0.9988 (F-6)					
Dimethyl phthalate	-4838.7	9.957	40.23	77.0±1.2	76.9±0.4
Diethyl phthalate	-5348.8	10.537	44.47	82.1±0.5	82.2±0.4
Di-*n*-butyl phthalate	-6598.5	11.888	54.86	95.0±1.1	95.2±0.4
Butyl benzyl phthalate	-7641.3	12.824	63.53	106.2±2.4	106.1±0.4
bis(2-Ethylhexyl) phthalate	-8650.2	14.219	71.914	116.7±0.5	116.6±0.5
Di-*n*-octyl phthalate	-9238.0	14.858	76.801	122.6±1.4	122.7±0.5
$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K)/kJ·mol^{-1} = (1.25±0.005)·ΔH_{trn}(532 K) + (26.46±0.30); r^2 = 0.9999 (F-7)					

[a] Uncertainties represent 1 standard deviation.

TABLE F-2C. Correlation of Vaporization Enthalpies With Enthalpies of Transfer (Poly(dimethyl siloxane) Column) Using Mono-Esters as Standards[a]

Run 2	slope T/K	intercept	ΔH_{trn}(532 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}	
					(Calc)	(Lit)
Eicosane	-7142.8	12.785	59.38		100.8±3.8	101.81±0.5
Docosane	-7854.3	13.58	65.3		110.9±3.9	111.9±2.7
Tetracosane	-8567	14.386	71.22		121.0±4.1	121.9±2.8
Pentacosane	-8918.9	14.784	74.15		126.0±4.2	126.8±2.9
Hexacosane	-9266.7	15.175	77.04		130.9±4.3	131.7±3.2
Octacosane	-9976.8	15.99	82.94		141.0±4.5	141.9±4.9
Methyl octadecanoate	-7505.1	13.158	62.39	105.87±1.4	105.9±3.9	
Ethyl octadecanoate	-7766.1	13.47	64.56	109.6±4.4	109.6±3.9	
Methyl eicosanoate	-8221.2	13.964	68.35	116.43±1.5	116.1±4.0	
Methyl heneicosanoate	-8575.7	14.363	71.29	120.9±2.5	121.1±4.1	
Dimethyl phthalate	-4838.7	9.957	40.23		68.2±3.3	77.0±1.2
Diethyl phthalate	-5348.8	10.537	44.47		75.4±3.4	82.1±0.5
Di-*n*-butyl phthalate	-6598.5	11.888	54.86		93.1±3.7	95.0±1.1
Butyl benzyl phthalate	-7641.3	12.824	63.53		107.9±3.9	106.2±2.4
bis(2-Ethylhexyl) phthalate	-8650.2	14.219	71.91		122.2±4.1	116.7±0.5
Di-*n*-octyl phthalate	-9238	14.858	76.8		130.5±4.3	122.6±1.4

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.704±0.042)·ΔH_{trn}(532 K) - (0.38±2.82); r^2 = 0.9988 (F-8)

[a] Uncertainties represent 1 standard deviation.

TABLE F-3A. Retention Times on a Poly(dimethyl siloxane) Capillary Column

Run 3 T/K	501.2	506.1	511.3	516.4	521.4	526.2	531.6
				t/60 s			
Hexanes/CH_2Cl_2	1.814	1.819	1.838	1.848	1.861	1.858	1.883
Dimethyl phthalate	2.584	2.514	2.468	2.421	2.383	2.333	2.320
Diethyl phthalate	3.000	2.877	2.788	2.703	2.633	2.553	2.517
Methyl palmitate	5.189	4.738	4.380	4.068	3.810	3.569	3.399
Di-*n*-butyl phthalate	5.518	5.036	4.651	4.315	4.034	3.773	3.585
Eicosane	6.273	5.648	5.148	4.719	4.364	4.043	3.805
Methyl octadecanoate	8.163	7.227	6.477	5.841	5.317	4.854	4.500
Ethyl octadecanoate	9.638	8.447	7.491	6.689	6.030	5.454	5.009
Docosane	10.145	8.869	7.840	6.979	6.273	5.659	5.181
Methyl eicosanoate	13.655	11.758	10.232	8.969	7.940	7.060	6.365
Tetracosane	17.256	14.686	12.632	10.945	9.576	8.419	7.499
Methyl heneicosanoate	17.939	15.251	13.096	11.333	9.900	8.692	7.732
Pentacosane	22.771	19.161	16.274	13.927	12.034	10.453	9.192
bis(2-Ethylhexyl) phthalate	23.464	19.829	16.914	14.527	12.593	10.966	9.667
Hexacosane	30.221	25.158	21.125	17.865	15.257	13.108	11.383

TABLE F-3B. Correlation of Vaporization Enthalpies With Enthalpies of Transfer (Poly(dimethyl siloxane) Column)[a]

Run 3	slope T/K	intercept	ΔH_{trn}(516 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (Lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(Calc)
Eicosane	-7390.7	13.258	61.44	101.81±0.5	101.9±0.3
Docosane	-8137.5	14.124	67.65	111.9±2.7	111.9±0.4
Tetracosane	-8880.6	14.99	73.83	121.9±2.8	121.8±0.4
Pentacosane	-9250.8	15.423	76.91	126.8±2.9	126.8±0.4
Hexacosane	-9619.4	15.855	79.97	131.7±3.2	131.7±0.4
$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.61±0.004)·ΔH_{trn}(516 K) + (2.70±0.26); r^2 = 0.9999 (F-9)					
Methyl hexadecanoate	-7032.5	12.822	58.47	96.84±0.63	96.5±3.0
Methyl octadecanoate	-7783.1	13.688	64.71	105.87±1.4	106.3±3.2
Ethyl octadecanoate	-8057.4	14.027	66.99	109.6±4.4	109.9±3.2
Methyl eicosanoate	-8532.3	14.56	70.93	116.43±1.5	116.4±3.3
Methyl heneicosanoate	-8904.9	14.995	74.03	120.9±2.5	120.9±3.4
$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.56±0.034)·ΔH_{trn}(516 K) + (5.07±2.29); r^2 = 0.9986 (F-10)					
Dimethyl phthalate	-4976.4	10.195	41.37	77.0±1.2	76.8±0.6
Diethyl phthalate	-5513.3	10.835	45.84	82.1±0.5	82.2±0.6
Di-*n*-butyl phthalate	-6831.1	12.327	56.79	95.0±1.1	95.2±0.7
bis(2-Ethylhexyl) phthalate	-8983.8	14.858	74.69	116.7±0.5	116.6±0.8
$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.19±0.009)·ΔH_{trn}(516 K) + (27.46±0.48); r^2 = 0.9999 (F-11)					

[a] Uncertainties represent 1 standard deviation.

TABLE F-3C. Correlation of Vaporization Enthalpies With Enthalpies of Transfer (Poly(dimethyl siloxane) Column) Using Mono-Esters as Standards[a]

Run 3	slope T/K	intercept	ΔH_{trn}(516 K) kJ·mol^{-1}	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$(298 K) kJ·mol^{-1} (lit)	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$(298 K) kJ·mol^{-1}	
					(Calc)	(Lit)
Eicosane	-7390.7	13.258	61.44		101.2±3.1	101.81±0.5
Docosane	-8137.5	14.124	67.65		110.9±3.2	111.9±2.7
Tetracosane	-8880.6	14.99	73.83		120.6±3.4	121.9±2.8
Pentacosane	-9250.8	15.423	76.91		125.4±3.5	126.8±2.9
Hexacosane	-9619.4	15.855	79.97		130.2±3.6	131.7±3.2
Methyl hexadecanoate	-7032.5	12.822	58.47	96.84±0.63	96.5±3.0	
Methyl octadecanoate	-7783.1	13.688	64.71	105.87±1.4	106.3±3.2	
Ethyl octadecanoate	-8057.4	14.027	66.99	109.6±4.4	109.9±3.2	
Methyl eicosanoate	-8532.3	14.56	70.93	116.43±1.5	116.0±3.3	
Methyl heneicosanoate	-8904.9	14.995	74.03	120.9±2.5	120.9±3.4	
Dimethyl phthalate	-4976.4	10.195	41.37		69.8±2.7	77.0±1.2
Diethyl phthalate	-5513.3	10.835	45.84		76.8±2.8	82.1±0.5
Di-*n*-butyl phthalate	-6831.1	12.327	56.79		93.9±3.0	95.0±1.1
bis(2-Ethylhexyl)phthalate	-8983.8	14.858	74.69		121.9±3.4	116.7±0.5

$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}(298.15\ \mathrm{K})/\mathrm{kJ\cdot mol^{-1}} = (1.564\pm0.034)\cdot\Delta H_{\mathrm{trn}}(516\ \mathrm{K}) + (5.07\pm2.29);\ r^2 = 0.9986$ (F-12)

[a] Uncertainties represent 1 standard deviation.

TABLE F-4A. Retention Times on a Poly(dimethyl siloxane) Capillary Column

Run 4 T/K	501.2	506.1	511.3	516.4	521.4	526.2	531.6
				t/60 s			
Hexanes/CH_2Cl_2	1.824	1.832	1.844	1.849	1.868	1.878	1.888
Dimethyl phthalate	2.598	2.529	2.477	2.424	2.392	2.357	2.325
Diethyl phthalate	3.016	2.894	2.798	2.707	2.642	2.578	2.522
Methyl hexadecanoate	5.210	4.758	4.394	4.075	3.821	3.596	3.404
Di-*n*-butyl phthalate	5.540	5.058	4.667	4.323	4.046	3.801	3.591
Eicosane	6.294	5.668	5.163	4.727	4.376	4.070	3.810
Methyl octadecanoate	8.190	7.251	6.497	5.852	5.331	4.884	4.506
Ethyl octadecanoate	9.668	8.473	7.514	6.702	6.045	5.485	5.015
Docosane	10.175	8.891	7.862	6.992	6.288	5.689	5.187
Methyl eicosanoate	13.695	11.786	10.263	8.988	7.960	7.093	6.372
Tetracosane	17.296	14.716	12.666	10.965	9.595	8.452	7.504
Methyl heneicosanoate	17.986	15.283	13.135	11.356	9.927	8.729	7.739
Pentacosane	22.834	19.191	16.316	13.953	12.06	10.487	9.198
bis(2-Ethylhexyl) phthalate	23.527	19.872	16.965	14.558	12.626	11.008	9.675
Hexacosane	30.300	25.192	21.177	17.897	15.289	13.144	11.39

TABLE F-4B. Correlation of Vaporization Enthalpies With Enthalpies of Transfer (Poly(dimethyl siloxane) Column)[a]

Run 4	slope T/K	intercept	ΔH_{trn}(516 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (Lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(Calc)
Eicosane	-7401.8	13.278	61.54	101.81±0.5	101.9±0.4
Docosane	-8147.9	14.142	67.74	111.9±2.7	111.9±0.4
Tetracosane	-8890.8	15.008	73.91	121.9±2.8	121.8±0.4
Pentacosane	-9262.3	15.444	77.00	126.8±2.9	126.8±0.5
Hexacosane	-9631.2	15.876	80.07	131.7±3.2	131.8±0.5
$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.61±0.004)·ΔH_{trn}(516 K) + (2.60±0.31); r^2 = 0.9999 (F-13)					
Methyl hexadecanoate	-7044.3	12.842	58.56	96.84±0.6	96.5±3.0
Methyl octadecanoate	-7792.9	13.705	64.79	105.87±1.4	106.3±3.2
Ethyl octadecanoate	-8067.1	14.043	67.07	109.6±4.4	109.9±3.2
Methyl eicosanoate	-8541.4	14.576	71.01	116.43±1.5	116.0±3.3
Methyl heneicosanoate	-8913.6	15.01	74.10	120.9±2.5	120.9±3.4
$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.57±0.034)·ΔH_{trn}(516 K) + (4.78±2.27); r^2 = 0.9986 (F-14)					
Dimethyl phthalate	-4997.7	10.233	41.55	77.0±1.2	76.9±0.5
Diethyl phthalate	-5530.3	10.864	45.98	82.1±0.5	82.2±0.5
Di-*n*-butyl phthalate	-6841.1	12.343	56.87	95.0±1.1	95.2±0.6
bis(2-Ethylhexyl) phthalate	-8993.3	14.874	74.77	116.7±0.5	116.6±0.7
$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.197±0.007)·ΔH_{trn}(516 K) + (27.13±0.41); r^2 = 0.9999 (F-15)					

[a] Uncertainties represent 1 standard deviation.

TABLE F-4C. Correlation of Vaporization Enthalpies With Enthalpies of Transfer (Poly(dimethyl siloxane) Column) Using Mono-Esters as Standards[a]

Run 4	slope T/K	intercept	ΔH_{trn}(516 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (Calc)	 (Lit)
Eicosane	-7401.8	13.278	61.54		101.2±3.1	101.81±0.5
Docosane	-8147.9	14.142	67.74		110.9±3.2	111.9±2.7
Tetracosane	-8890.8	15.008	73.91		120.6±3.4	121.9±2.8
Pentacosane	-9262.3	15.444	77.00		125.4±3.5	126.8±2.9
Hexacosane	-9631.2	15.876	80.07		130.2±3.5	131.7±3.2
Methyl hexadecanoate	-7044.3	12.842	58.56	96.84±0.63	96.5±3.0	
Methyl octadecanoate	-7792.9	13.705	64.79	105.87±1.4	106.3±3.2	
Ethyl octadecanoate	-8067.1	14.043	67.07	109.6±4.4	109.9±3.2	
Methyl eicosanoate	-8541.4	14.576	71.01	116.43±1.5	116.0±3.3	
Methyl heneicosanoate	-8913.6	15.010	74.10	120.9±2.5	120.9±3.4	
Dimethyl phthalate	-4997.7	10.233	41.55		69.9±2.7	77.0±1.2
Diethyl phthalate	-5530.3	10.864	45.98		76.8±2.8	82.1±0.5
Di-*n*-butyl phthalate	-6841.1	12.343	56.87		93.9±3.0	95.0±1.1
bis(2-Ethylhexyl) phthalate	-8993.3	14.874	74.77		121.9±3.4	116.7±0.5

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.567±0.034)·ΔH_{trn}(516 K) + (4.78±2.27); r^2 = 0.9986 (F-16)

[a] Uncertainties represent 1 standard deviation.

TABLE F-5. Summary of Tables 1B-4B Using Appropriate Alkane, Ester and Diester Standards at T = 298.15 K, p_o = 101325 Pa[a]

	Run 1	Run 2	Run 3	Run 4	$\Delta_l^g H_m$(298.15 K) kJ·mol^{-1}	
					(Avg)	(Lit)
Eicosane	101.8±0.7	101.8±0.6	101.9±0.3	101.9±0.4	101.9±0.5	101.81±0.5
Docosane	111.8±0.7	111.8±0.7	111.9±0.4	111.9±0.4	111.9±0.6	111.9±2.7
Tetracosane	121.9±0.8	121.9±0.7	121.8±0.4	121.8±0.4	121.9±0.6	121.9±2.8
Pentacosane	126.9±0.8	126.9±0.7	126.8±0.4	126.8±0.5	126.9±0.6	126.8±2.9
Hexacosane	131.8±0.8	131.8±0.7	131.7±0.4	131.8±0.5	131.8±0.6	131.7±3.2
Octacosane	141.7±0.8	141.8±0.8			141.8±0.8	141.9±4.9
Methyl hexadecanoate			96.5±3.0	96.5±3.0	96.5±3.0	96.5±3.0
Methyl octadecanoate	106.0±4.1	105.9±3.9	106.3±3.2	106.3±3.2	106.1±3.6	105.87±1.4
Ethyl octadecanoate	109.6±4.1	109.6±3.9	109.9±3.2	109.9±3.2	109.8±3.6	109.6±4.4
Methyl eicosanoate	116.1±4.2	116.1±4.0	116.4±3.3	116.0±3.3	116.2±3.7	116.43±1.5
Methyl heneicosanoate	121.1±4.3	121.1±4.1	120.9±3.4	120.9±3.4	121.0±3.8	120.9±2.5
Dimethyl phthalate	76.9±0.4	76.9±0.4	76.8±0.6	76.9±0.5	76.9±0.5	77.0±1.2
Diethyl phthalate	82.2±0.4	82.2±0.4	82.2±0.6	82.2±0.5	82.2±0.5	82.1±0.5
Di-*n*-butyl phthalate	95.2±0.5	95.2±0.4	95.2±0.7	95.2±0.6	95.2±0.6	95.0±1.1
Butyl benzyl phthalate	106.0±0.5	106.1±0.4			106.1±0.5	106.2±2.4
bis(2-Ethylhexyl) phthalate	116.6±0.5	116.6±0.5	116.6±0.8	116.6±0.7	116.6±0.6	116.7±0.5
Di-*n*-octyl phthalate	122.7±0.5	122.7±0.5			122.7±0.5	122.6±1.4

[a] Uncertainties represent 1 standard deviation.

TABLE F-6. A Summary of Vaporization Enthalpies by C-GC only Using Methyl Octadecanoate and Methyl Eicosanoate as Standards, p_o = 101325 Pa[a]

	Run 1	**Run 2**	**Run 3**	**Run 4**	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}		
					(Avg)	(Lit)	(Lit-Avg)
Eicosane	100.5±2.9	100.5±2.9	100.3±2.9	100.4±2.9	100.4±2.9	101.81±0.5	1.4
Docosane	111.0±0.1	111.0±0.1	110.9±0.1	110.9±0.1	111.0±0.1	111.9±2.7	1
Tetracosane	121.5±2.9	121.5±2.9	121.4±2.9	121.4±2.9	121.5±2.9	121.9±2.8	0.5
Pentacosane	126.8±4.4	126.7±4.4	126.6±4.3	126.6±4.3	126.7±4.4	126.8±2.9	0.1
Hexacosane	131.9±5.8	131.8±5.7	131.8±5.7	131.8±5.7	131.8±5.7	131.7±3.2	-0.1
Octacosane	142.3±8.6	142.3±8.6			142.3±8.6	141.9±4.9	-0.4
Methyl hexadecanoate			95.3±4.3	95.3±4.3	95.3±4.3		1.5
Ethyl octadecanoate	109.7±0.3	109.7±0.3	109.7±0.4	109.7±0.3	109.7±0.3	109.6±4.4	-0.1
Methyl heneicosanoate	121.7±2.9	121.6±2.9	121.7±3.0	121.7±2.9	121.7±2.9		-0.8
Dimethyl phthalate	66.2±12	66.6±12	66.2±12	66.4±12	66.4±12	77.0±1.2	10.7
Diethyl phthalate	73.8±10	74.1±10	73.8±10	73.9±10	73.9±10	82.1±0.5	8.2
Di-n-butyl phthalate	92.4±5.1	92.5±5.1	92.4±5.1	92.4±5.1	92.4±5.1	95.0±1.1	2.6
Butyl benzyl phthalate	107.8±0.9	107.9±0.8			107.9±0.9	106.2±2.4	-1.6
bis(2-Ethylhexyl) phthalate	122.9±3.3	122.7±3.2	122.8±3.2	122.8±3.3	122.8±3.3	116.7±0.5	-6.1
Di-n-octyl phthalate	131.7±5.7	131.4±5.6			131.6±5.7	122.6±1.4	-9

[a] Uncertainties represent 1 standard deviation.

TABLE F-7. Vaporization Enthalpies at T/K = 298.15 Using All Monoesters as Standards (Tables 1C-4C), p_o = 101325 Pa[a]

	Run 1 kJ·mol^{-1}	Run 2 kJ·mol^{-1}	Run 3 kJ·mol^{-1}	Run 4 kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}		
					(Avg)	(Lit)	(Lit - Avg)
Eicosane	100.8±4.0	100.8±3.8	101.2±3.1	101.2±3.1	101.0±3.5	101.81±0.5	0.8±3.6
Docosane	110.9±4.1	110.9±3.9	110.9±3.2	110.9±3.2	110.9±3.6	111.9±2.7	1.0±4.6
Tetracosane	121.0±4.3	121.0±4.1	120.6±3.4	120.6±3.4	120.8±3.8	121.9±2.8	1.1±4.8
Pentacosane	126.0±4.4	126.0±4.2	125.4±3.5	125.4±3.5	125.7±3.9	126.8±2.9	1.1±4.4
Hexacosane	130.9±4.5	130.9±4.3	130.2±3.6	130.2±3.5	130.6±4.0	131.7±3.2	1.1±5.2
Octacosane	140.8±4.7	141.0±4.5			140.9±4.6	141.9±4.9	1.0±6.2
Dimethyl phthalate	68.0±3.5	68.2±3.3	69.8±2.7	69.9±2.7	69.0±3.1	77.0±1.2	8.0±3.4
Diethyl phthalate	75.3±3.6	75.4±3.4	76.8±2.8	76.8±2.8	76.1±3.2	82.1±0.5	6.0±3.3
Di-n-butyl phthalate	93.0±3.8	93.1±3.7	93.9±3.0	93.9±3.0	93.5±3.4	95.0±1.1	1.5±3.6
Butyl benzyl phthalate	107.8±4.1	107.9±3.9			107.9±4.0	106.2±2.4	-1.7±4.7
bis(2-Ethylhexyl) phthalate	122.3±4.4	122.2±4.1	121.9±3.4	121.9±3.4	122.1±3.8	116.7±0.5	-5.4±3.8
Di-n-octyl phthalate	130.7±4.5	130.5±4.3			130.6±4.4	122.6±1.4	-8.0±4.6

[a] Uncertainties represent 1 standard deviation.

TABLE F-8. A Comparison of the Ratio of Literature Vapor Pressures, p_{lit}, to Those Evaluated by C-GC, p_{calc}, Using Mono-Esters as Standards at T/K = 298.15 K, p_o = 101325 Pa[a]

	$p_{\mathrm{lit}}/p_{\mathrm{calc}}$ **Run 1**	$p_{\mathrm{lit}}/p_{\mathrm{calc}}$ **Run 2**	$p_{\mathrm{lit}}/p_{\mathrm{calc}}$ **Run 3**	$p_{\mathrm{lit}}/p_{\mathrm{calc}}$ **Run 4**	$p_{\mathrm{lit}}/p_{\mathrm{calc}}$ Avg	p_{lit}/Pa
Eicosane	0.54	0.89	0.87	0.87	0.80±0.17	20.9
Docosane	0.4	0.7	0.69	0.69	0.62±0.14	2.15
Tetracosane	0.32	0.59	0.57	0.57	0.51±0.13	0.24
Pentacosane	0.29	0.55	0.53	0.54	0.48±0.12	0.081
Hexacosane	0.26	0.51	0.5	0.5	0.44±0.12	0.028
Octacosane	0.2	0.42			0.31±0.16	0.0032
Methyl hexadecanoate			1.15	1.15	1.15±0.002	71.4
Ethyl octadecanoate	1.1	1.1	1.1	1.1	1.1±0.002	4.3
Methyl heneicosanoate	0.84	0.84	0.84	0.84	0.84±0.001	0.32
Dimethyl phthalate	0.18	0.25	0.24	0.25	0.23±0.04	3042
Diethyl phthalate	0.23	0.34	0.34	0.34	0.31±0.05	988
Di-n-butyl phthalate	0.32	0.51	0.5	0.5	0.45±0.09	38.7
Butyl benzyl phthalate	0.39	0.69			0.54±0.021	2.0
bis (2-ethylhexyl phthalate	0.55	1.01	1.01	1.01	0.90±0.23	0.23
Di-n-octyl phthalate	0.47	1.3			0.89±0.59	0.055

[a] Uncertainties represent 1 standard deviation.

TABLE F-9A. Retention Times on a Poly(5% diphenyl/95% dimethyl siloxane) Capillary Column

Run 5 T/K	494.8	499.8	504.8	510	515	520.1	525.2
				t/60 s			
Methanol/CH_2Cl_2	0.507	0.495	0.509	0.51	0.492	0.523	0.523
Dimethyl phthalate	1.001	0.949	0.912	0.881	0.827	0.821	0.794
Diethyl phthalate	1.282	1.193	1.125	1.068	0.991	0.966	0.922
Methyl hexadecanoate	2.643	2.343	2.1	1.901	1.703	1.577	1.447
Di-*n*-butyl phthalate	3.062	2.708	2.42	2.183	1.951	1.797	1.642
Methyl octadecanoate	4.652	4.015	3.497	3.079	2.695	2.418	2.163
Ethyl octadecanoate	**5.662**	**4.846**	**4.182**	**3.649**	**3.17**	**2.816**	**2.497**
Docosane	**5.662**	**4.846**	**4.182**	**3.649**	**3.17**	**2.816**	**2.497**
Methyl eicosanoate	8.484	7.157	6.08	5.223	4.476	3.906	3.409
Butyl benzyl phthalate	9.313	7.928	6.789	5.871	5.068	4.444	3.897
Tetracosane	10.543	8.823	7.433	6.33	5.388	4.657	4.031
Methyl heneicosanoate	11.542	9.633	8.094	6.875	5.837	5.03	4.341
Pentacosane	14.34	11.881	9.907	8.352	7.041	6.017	5.152
bis (2-Ethylhexyl) phthalate	16.602	13.769	11.499	9.702	8.186	6.991	5.987
Hexacosane	19.551	16.042	13.253	11.058	9.238	7.811	6.622
Di-*n*-octyl Phthalate	28.968	23.692	19.486	16.174	13.449	11.274	9.51
Octacosane	36.416	29.36	23.835	19.502	16.026	13.289	11.075

TABLE F-9B. Results on the Effects of Retention Time Coincidence on Vaporization Enthalpy ((Poly(5% diphenyl/95% dimethyl siloxane) Column, p_o = 101325)[a]

Run 5	- slope T/K	intercept	ΔH_{trn}(510 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (Lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(Calc)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (Lit)
Docosane	**8191.5**	**14.921**	**68.10**		**111.4±1.5**	**111.9±2.7**
Tetracosane	8968.8	15.827	74.56	121.9±2.8	121.8±1.5	
Pentacosane	9338.2	16.253	77.63	126.8±2.9	126.8±1.6	
Hexacosane	9713.0	16.691	80.75	131.7±3.2	131.8±1.6	
Octacosane	10453.8	17.555	86.91	141.9±4.9	141.8±1.7	
$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.62±0.015)·ΔH_{trn}(510 K) + (1.033±1.13); r^2 = 0.9998						(F-17)
Methyl hexadecanoate	7153.1	13.701	59.47	96.84±0.63	96.6±3.4	
Methyl octadecanoate	7914.5	14.579	65.80	105.87±1.4	106.4±3.5	
Ethyl octadecanoate	**8191.5**	**14.921**	**68.10**		**109.9±3.6**	**109.6±4.4**
Methyl eicosanoate	8674.8	15.462	72.12	116.43±1.5	116.1±3.7	
Methyl heneicosanoate	9053.7	15.904	75.27	120.9±2.5	121.0±3.8	
$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.54±0.037)·ΔH_{trn}(510 K) + (4.96±2.5); r^2 = 0.9988						(F-18)
Dimethyl phthalate	5153.3	11.111	42.84	77.0±1.2	76.8±0.5	
Diethyl phthalate	5699.0	11.768	47.38	82.1±0.5	82.1±0.5	
Di-*n*-butyl phthalate	7045.3	13.304	58.57	95.0±1.1	95.3±0.6	
Butyl benzyl phthalate	8187.6	14.378	68.07	106.2±2.4	106.4±0.6	
bis(2-Ethylhexyl) phthalate	9215.4	15.853	76.61	116.7±0.5	116.5±0.7	
Di-*n*-octyl phthalate	9842.0	16.549	81.82	122.6±1.4	122.6±0.7	
$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.175±0.007)·ΔH_{trn}(510 K) + (26.47±0.43); r^2 = 0.9999						(F-19)

[a] Uncertainties represent 1 standard deviation.

TABLE F-10A. Retention Times on a (Poly(5% diphenyl/95% dimethyl siloxane) Capillary Column

Run 6 T/K	494.8	499.8	504.8	510	515	520.1	525.2
				t/60 s			
Methanol/CH_2Cl_2	0.497	0.517	0.505	0.52	0.515	0.518	0.527
Dimethyl phthalate	1.001	0.986	0.915	0.881	0.851	0.824	0.798
Diethyl phthalate	1.283	1.239	1.128	1.068	1.015	0.969	0.926
Methyl hexadecanoate	2.644	2.409	2.106	1.903	1.729	1.583	1.453
Di-*n*-butyl phthalate	3.063	2.775	2.426	2.185	1.978	1.803	1.649
Methyl octadecanoate	4.656	4.079	3.507	3.082	2.725	2.427	2.17
Ethyl octadecanoate	**5.666**	**4.905**	**4.193**	**3.653**	**3.2**	**2.827**	**2.505**
Docosane	**5.666**	**4.905**	**4.193**	**3.653**	**3.2**	**2.827**	**2.505**
Methyl eicosanoate	8.494	7.2	6.097	5.229	4.508	3.92	3.42
Butyl benzyl phthalate	9.323	7.964	6.808	5.88	5.102	4.46	3.909
Tetracosane	10.555	8.855	7.459	6.342	5.425	4.675	4.044
Methyl heneicosanoate	11.561	9.663	8.121	6.885	5.873	5.049	4.354
Pentacosane	14.37	11.904	9.939	8.369	7.083	6.039	5.168
bis (2-Ethylhexyl) phthalate	16.643	13.786	11.538	9.717	8.228	7.02	6.004
Hexacosane	19.586	16.054	13.301	11.072	9.28	7.841	6.643
Di-*n*-octyl Phthalate	29.138	23.692	19.521	16.199	13.502	11.327	9.533
Octacosane	36.521	29.316	23.897	19.571	16.101	13.35	11.105

TABLE F-10B. Results on the Effects of Retention Time Coincidence on Vaporization Enthalpy ((Poly(5% diphenyl/95% dimethyl siloxane) Column, p_o = 101325 Pa)[a]

Run 6	- slope T/K	intercept	ΔH_{trn}(510 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (Lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(Calc)
Docosane	**8204.7**	**14.943**	**68.21**	**111.9±2.7**	**111.8±1.1**
Tetracosane	8952.2	15.792	74.43	121.9±2.8	113.9±1.1
Pentacosane	9323.7	16.222	77.51	126.8±2.9	117.7±1.1
Hexacosane	9694.9	16.653	80.6	131.7±3.2	121.5±1.2
Octacosane	10430.1	17.506	86.71	141.9±4.9	129.0±1.2
$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.618±0.0076)·ΔH_{trn}(510 K) + (22.52±0.49); r^2 = 0.9998 (F-20)					
Methyl hexadecanoate	7227.6	13.841	60.09	96.84±0.63	96.6±2.8
Methyl octadecanoate	7941.9	14.628	66.03	105.87±1.4	106.2±3.0
Ethyl octadecanoate	**8204.7**	**14.943**	**68.21**	**109.6±4.4**	**109.8±3.0**
Methyl eicosanoate	8669.4	15.449	72.07	116.43±1.5	116.0±3.1
Methyl heneicosanoate	9042.6	15.88	75.18	120.9±2.5	121.0±3.2
$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.615±0.031)·ΔH_{trn}(510 K) - (0.434±2.14); r^2 = 0.9989 (F-21)					
Dimethyl phthalate	5341.3	11.47	44.41	77.0±1.2	77.0±0.6
Diethyl phthalate	5845.7	12.048	48.6	82.1±0.5	82.2±0.6
Di-*n*-butyl phthalate	7106.1	13.418	59.08	95.0±1.1	95.0±0.7
Butyl benzyl phthalate	8177.2	14.355	67.98	106.2±2.4	106.0±0.7
bis(2-Ethylhexyl) phthalate	-9202.2	15.825	76.5	116.7±0.5	116.4±1.1
Di-*n*-octyl phthalate	9841.5	16.546	81.82	122.6±1.4	123.0±1.2
$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.227±0.0076)·ΔH_{trn}(510 K) + (22.52±0.49); r^2 = 0.9998 (F-22)					

[a]Uncertainties represent 1 standard deviation.

TABLE F-11. A Comparison of the Vaporization Enthalpy Results From Tables 1B-4B and 9B-10B on Poly(dimethyl siloxane) and Poly(5% diphenyl 95% dimethyl siloxane) Columns by C-GC With Literature Values at T/K = 298.15; Enthalpies in kJ·mol^{-1}[a]

	Run 5	**Run 6**	$\text{Avg}_{\text{runs 5\&6}}$	$\text{Avg}_{\text{runs 1-4}}$	Lit
Docosane	**111.7±1.6**	**111.8±1.1**	111.8±1.1	111.9±0.6	111.9±2.7
Tetracosane	122.0±1.6	121.9±1.1	122.0±1.3	121.9±0.6	121.9±2.8
Pentacosane	126.9±1.7	126.9±1.1	126.9±1.4	126.9±0.6	126.8±2.9
Hexacosane	131.9±1.7	131.9±1.2	131.9±1.5	131.8±0.6	131.7±3.2
Octacosane	141.7±1.8	141.8±1.2	141.8±1.5	141.8±0.8	141.9±4.9
Methyl hexadecanoate	96.5±3.0	96.6±2.8	96.4±2.9	96.5±3.0	96.84±0.63
Methyl octadecanoate	106.3±3.1	106.2±3.0	106.3±3.1	106.1±3.6	105.87±1.4
Ethyl octadecanoate	**109.9±3.2**	**109.8±3.0**	109.9±3.1	109.8±3.6	109.6±4.4
Methyl eicosanoate	116.0±3.3	116.0±3.1	116.0±3.2	116.2±3.7	116.43±1.5
Methyl heneicosanoate	120.9±3.4	121.0±3.2	121.0±3. 3	121.0±3.8	120.9±2.5
Dimethyl phthalate	76.8±0.5	77.0±0.6	76.9±0.6	76.9±0.5	77.0±1.2
Diethyl phthalate	82.1±.05	82.2±0.6	82.2±0.6	82.2±0.5	82.1±0.5
Di-*n*-butyl phthalate	95.3±0.6	95.0±0.7	95.2±0.7	95.2±0.6	95.0±1.1
Butyl benzyl phthalate	106.4±0.6	106.0±0.7	106.2±0.7	106.1±0.5	106.2±2.4
bis(2-Ethylhexyl) phthalate	116.5±0.7	116.4±1.1	116.5±0.9	116.6±0.6	116.7±0.5
Di-*n*-octyl phthalate	122.6±0.7	123.0±1.2	122.8±1.0	122.7±0.5	122.6±1.4

[a] Uncertainties represent 1 standard deviation.

Uncertainty in boiling temperatures (σ) were evaluated by setting $\ln(p/p_o) = 0$ and solving the third order polynomial (S23) for the real (versus imaginary) value of $T_{\mathrm{B}.}$ Uncertainties in the coefficients were evaluated using Sigma Plot. The uncertainty in T_B was evaluated using eq F-24.

$$\ln(p/p_o) = \mathrm{A}\cdot T^{3} + \mathrm{B}\cdot T^{2} + \mathrm{C}\cdot T + \mathrm{D} \qquad \text{(F-23)}$$

$$[\sigma(T_\mathrm{B})]^2 = \left(\frac{\partial T_\mathrm{B}}{\partial A}\right)^2\cdot\left(\frac{\sigma A}{A}\right)^2 + \left(\frac{\partial T_\mathrm{B}}{\partial B}\right)^2\cdot\left(\frac{\sigma B}{B}\right)^2 + \left(\frac{\partial T_\mathrm{B}}{\partial C}\right)^2\cdot\left(\frac{\sigma C}{C}\right)^2 + \left(\frac{\partial T_\mathrm{B}}{\partial D}\right)^2\cdot\left(\frac{\sigma D}{D}\right)^2 \qquad \text{(F-24)}$$

The derivatives of $\left(\frac{\partial T_\mathrm{B}}{\partial A}\right)$, $\left(\frac{\partial T_\mathrm{B}}{\partial B}\right)$, $\left(\frac{\partial T_\mathrm{B}}{\partial C}\right)$, and $\left(\frac{\partial T_\mathrm{B}}{\partial D}\right)$ were solved using Mathcad.

Appendix G

1.) Fatty Acids

TABLE G-1. Names of the Acids

CAS #	Molecular Formula	Chemical Name (Common name)
544-63-8	$C_{14}H_{28}O_2$	tetradecanoic acid (myristic acid (c))
373-49-9	$C_{16}H_{30}O_2$	(9Z)-hexadecenoic acid (palmitoleic acid (l))
57-10-3	$C_{16}H_{32}O_2$	*n*-hexadecanoic acid (palmitic acid, (c))
60-33-3	$C_{18}H_{32}O_2$	(9Z,12Z)-octadecadienoic acid (linoleic acid, (l))
593-39-5	$C_{18}H_{34}O_2$	(6Z)-octadecenoic acid (petroselinic acid, (c))
112-80-1	$C_{18}H_{34}O_2$	(9Z)-octadecenoic acid (oleic acid (l))
506-32-1	$C_{20}H_{32}O_2$	(5Z,8Z,11Z,14Z)-eicosatetraenoic acid (l) (arachidonic acid)
5561-99-9	$C_{20}H_{38}O_2$	(11Z)-eicosenoic acid (gondoic acid, (c))
506-30-9	$C_{20}H_{40}O_2$	*n*-eicosanoic acid (arachidic acid, (c))
6217-54-5	$C_{22}H_{36}O_2$	(4Z,7Z,10Z,13Z,16Z,19Z)-docosahexenoic acid (cervonic acid, (l))
112-86-7	$C_{22}H_{42}O_2$	(13Z)-docosenoic acid (erucic acid, (c))
112-85-6	$C_{22}H_{44}O_2$	*n*-docosanoic acid (behenic acid, (c))
506-37-6	$C_{24}H_{46}O_2$	(15Z)-tetracosenoic acid (nervonic acid, (c))
557-59-5	$C_{24}H_{48}O_2$	*n*-tetracosanoic acid (lignoceric acid, (c))
506-46-7	$C_{26}H_{52}O_2$	*n*-hexacosanoic acid (cerotic acid, (c))

TABLE G-2A. Carboxylic Acid Retention times for Run 1

Run 1	*T*/K	474.7	479.8	484.8	489.7	494.6	499.6	504.7
					t/min			
CH_2Cl_2		0.255	0.184	0.262	0.27	0.262	0.267	0.252
tetradecanoic acid		1.896	1.529	1.373	1.191	1.044	0.918	0.808
hexadecanoic acid		3.479	2.78	2.37	1.997	1.708	1.444	1.245
(9Z)-hexadecenoic acid		3.941	3.159	2.674	2.243	1.908	1.598	1.375
(9Z)-octadecenoic acid		7.101	5.636	4.622	3.793	3.158	2.582	2.179
eicosanoic acid		11.958	9.367	7.499	6.033	4.926	3.96	3.285
arachidonic acid		18.277	14.255	11.326	9.069	7.36	5.87	4.839
docosanoic acid		25.084	19.38	15.122	11.936	9.587	7.377	6.102

TABLE G-2B. Correlation Results for Run 1

Run 1	-slope T/K	intercept	ΔH_{trn} (490 K) kJ·mol^{-1}	$\Delta_l^g H$ (298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H$ (298 K) kJ·mol^{-1} (calc)
tetradecanoic acid	8683.5	17.806	72.19	111.3±2.2	110.6±6.6
hexadecanoic acid	9442.1	18.728	78.5	120.7±2.3	121.9±6.8
(9Z)-hexadecenoic acid	9549.0	18.816	79.39		123.5±6.8
(9Z)-octadecenoic acid	10185.6	19.538	84.68		132.9±7.1
eicosanoic acid	10848.7	20.399	90.19	143.6±2.5	142.8±7.3
arachidonic acid	10984.5	20.254	91.32		144.8±7.3
docosanoic acid	11668.7	21.372	97.01	154.7±7.3	155.0±7.6

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.79 ± 0.06) ΔH_{trn} (490 K) - (18.4±1.1); $r^2 = 0.9978$ (G-1)

TABLE G-3A. Carboxylic Acid Retention times for Run 2

Run 2 T/K	475	479.9	484.9	489.9	494.8	499.7	504.7
				t/min			
CH_2Cl_2	0.328	0.35	0.364	0.381	0.348	0.397	0.398
tetradecanoic acid	2.439	2.189	1.949	1.695	1.465	1.326	1.188
hexadecanoic acid	4.46	3.878	3.354	2.82	2.396	2.077	1.814
(9Z)-hexadecenoic acid	4.998	4.35	3.735	3.13	2.653	2.288	1.992
(9Z)-octadecenoic acid	9.057	7.667	6.463	5.29	4.404	3.69	3.14
eicosanoic acid	15.436	12.72	10.566	8.475	6.933	5.677	4.742
arachidonic acid	23.784	19.346	15.977	12.733	10.347	8.409	6.959
docosanoic acid	31.559	25.239	20.499	16.045	13.028	10.323	8.495

TABLE G-3B. Correlation Results for Run 2

Run 2	-slope T/K	intercept	ΔH_{trn} (490 K) kJ·mol^{-1}	$\Delta_l^g H$ (298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H$ (298 K) kJ·mol^{-1} (calc)
tetradecanoic acid	8051.6	16.175	66.94	111.3±2.2	110.8±5.6
hexadecanoic acid	8772.3	17.025	72.93	120.7±2.3	121.7±5.8
(9Z)-hexadecenoic acid	8819.0	17.000	73.32		122.4±5.9
(9Z)-octadecenoic acid	9467.9	17.745	78.71		132.2±6.1
eicosanoic acid	10164.1	18.666	84.5	143.6±2.5	142.7±6.3
arachidonic acid	10362.4	18.647	86.15		145.7±6.3
docosanoic acid	10980.3	19.665	91.29	154.7±7.3	155.1±6.5

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.81 ± 0.05) ΔH_{trn} (490 K) - (10.9±4.3); $r^2 = 0.9982$ (G-2)

TABLE G-4A. Carboxylic Acid Retention times for Run 3

Run 3 *T*/K	486	491	495.9	500.9	505.8	510.9	516
				t/min			
CH_2Cl_2	0.235	0.261	0.257	0.250	0.260	0.271	0.271
n-hexadecanoic acid	2.299	1.965	1.652	1.412	1.226	1.082	0.959
(6Z)-octadecenoic acid	4.336	3.591	2.965	2.474	2.093	1.789	1.539
(9Z,12Z)-octadecadienoic acid	5.128	4.224	3.455	2.873	2.397	2.048	1.751
n-eicosanoic acid	7.252	5.860	4.734	3.880	3.196	2.683	2.257
(11Z)-eicosenoic acid	7.920	6.393	5.154	4.225	3.463	2.910	2.445
(13Z)-docosenoic acid	14.207	11.258	8.931	7.185	5.785	4.763	3.927
n-tetracosanoic acid	25.075	19.346	14.947	11.819	9.125	7.506	6.025
(15Z)-tetracosenoic acid	27.320	21.162	16.291	12.902	9.889	8.184	6.568
cervonic acid	27.910	21.843	17.094	13.588	10.738	8.750	7.096
n-hexacosanoic acid	42.445	32.574	25.094	19.571	15.227	12.162	9.700

TABLE G-4B. Correlation Results for Run 3

Run 3	-slope *T*/K	intercept	ΔH_{trn} (501 K) kJ·mol^{-1}	$\Delta_l^g H$ (298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H$ (298 K) kJ·mol^{-1} (calc)
n-hexadecanoic acid	9239.2	18.293	76.81	120.7±2.3	120.7±2.3
(6Z)-octadecenoic acid	9842.6	18.848	81.83		130.9±2.3
(9Z,12Z)-octadecadienoic acid	10043.8	19.086	83.59	134.1±10.3	134.3±2.4
n-eicosanoic acid	10578.9	19.829	87.95	143.6±2.5	143.3±2.4
(11Z)-eicosenoic acid	10589.8	19.760	88.04		143.5±2.4
(13Z)-docosenoic acid	11245.4	20.512	93.49	154.5±7.3	154.6±2.5
n-tetracosanoic acid	12266.8	22.042	101.98		171.9±2.6
(15Z)-tetracosenoic acid	12260.4	21.941	101.93		171.8±2.6
cervonic acid	11745.5	20.857	97.65		163.1±2.6
n-hexacosanoic acid	12570.9	22.134	104.51		177.0±2.7

$$\Delta_l^g H_m(298.15\ \mathrm{K})/\mathrm{kJ{\cdot}mol^{-1}} = (2.04 \pm 0.02)\ \Delta H_{trn}\ (501\ \mathrm{K}) - (36.0 \pm 1.6);\quad r^2 = 0.9998 \qquad \text{(G-3)}$$

TABLE G-5A. Carboxylic Acid Retention times for Run 4

Run 4							
T/K	484.7	489.6	494.5	499.3	504.1	508.9	513.6
				t/min			
CH_2Cl_2	0.259	0.253	0.261	0.258	0.260	0.254	0.260
n-hexadecanoic acid	2.313	1.932	1.656	1.414	1.223	1.063	0.955
(6Z)-octadecenoic acid	4.333	3.549	2.949	2.461	2.077	1.765	1.539
(9Z,12Z)-octadecadienoic acid	5.123	4.176	3.446	2.863	2.4	2.022	1.764
n-eicosanoic acid	7.232	5.822	4.713	3.865	3.19	2.652	2.277
(11Z)-eicosenoic acid	7.908	6.359	5.135	4.213	3.468	2.878	2.478
(13Z)-docosenoic acid	14.173	11.214	8.869	7.156	5.782	4.717	3.989
n-tetracosanoic acid	25.062	19.526	14.898	11.872	9.372	7.449	6.308
(15Z)-tetracosenoic acid	27.247	21.306	16.239	12.952	10.189	8.076	6.877
cervonic acid	27.759	21.725	16.942	13.502	10.751	8.653	7.24
n-hexacosanoic acid	42.443	32.583	24.943	19.503	15.248	12.092	9.907

TABLE G-5B. Correlation Results for Run 4

Run 4	-slope *T*/K	intercept	ΔH_{trn} (499 K) kJ·mol^{-1}	$\Delta_l^g H$ (298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H$ (298 K) kJ·mol^{-1} (calc)
n-hexadecanoic acid	9380.5	18.641	77.99	120.7±2.3	120.8±1.7
(6Z)-octadecenoic acid	10019.6	19.275	83.3		131.4±1.8
(9Z,12Z)-octadecadienoic acid	10179	19.427	84.62	134.1±10.3	134.0±1.8
n-eicosanoic acid	10753	20.251	89.4	143.6±2.5	143.5±1.9
(11Z)-eicosenoic acid	10747.8	20.148	89.35		143.4±1.9
(13Z)-docosenoic acid	11431.7	20.961	95.04	154.5±7.3	154.6±1.9
n-tetracosanoic acid	12332.9	22.245	102.53		169.5±2.0
(15Z)-tetracosenoic acid	12323.8	22.14	102.46		169.4±2.0
cervonic acid	11917	21.281	99.07		162.6±2.0
n-hexacosanoic acid	12803.1	22.682	106.44		177.3±2.0

$\Delta_l^g H_m(298.15\ K)/kJ\cdot mol^{-1} = (1.98 \pm 0.014)\ \Delta H_{trn}\ (499\ K) - (33.9 \pm 1.3)$; $r^2 = 0.9999$ (G-4)

TABLE G-6. Fusion Enthalpies of Some Fatty Acids

	Sample mg	T_t/K (onset)	$\Delta_{cr}^{cr}H_m(T_{tran})$ kJ·mol^{-1}	T_{fus}/K (onset)	$\Delta_{cr}^{l}H_m(T_{fus})$ kJ·mol^{-1}	$\Delta_{tpce}H_m(T_{fus})$ kJ·mol^{-1}
(15Z)-tetracosenoic acid (nervonic acid)	7.02			315.4	60.0	
	9.08			315.2	60.9	
	5.27			314.9	60.0	
average				315±0.3	60.3±0.5	60.3±0.5
tetracosanoic acid	8.64	346/350	4.82	356.3	84.4	
	7.61	346/350	4.95	356.4	84.4	
	10.59	346/350	5.03	356.7	85.1	
average		346/350	4.94±0.1	356.5±0.2	84.5±0.5	89.4±0.5
hexacosanoic acid (cerotic acid)	4.68	354.3		358.6		87.8
	11.72	354.2		359.1		89.7
	11.9	354.3		358.5		88.1
average		354.3±0.1[a]		358.8±0.3		88.5±1.0[b]
naphthalene	23.51			353.7/353.7[c]	19.07/19.06[c]	

[a] An observed peak that was not base line separated from the fusion peak. [b] The sum of the fusion peak and the peak at *T*/K = 354.3. [c] Sabbah, R.; An, X.; Chickos, J. S.; Planas Leitao, M. L.; Roux, M. V.; Torres, L. A. Reference material for calorimetry and differential calorimetry. *Thermochim. Acta* **1999**, *331*, 93-204.

TABLE G-7. Temperature Adjustments of the Vaporization Enthalpies of the C_5-C_{20} Fatty acids and A comparison of Vaporization Enthalpies with Literature Values

	$\Delta_l^gH_m(T)$ kJ·mol^{-1}	T_m/K	$Cp(l)^a$ J·mol^{-} ·K^{-1}	$\Delta C_p\Delta T$ kJ·mol^{-1}	$\Delta_l^gH_m$(298.15 K) kJ·mol^{-1}		
					Ref [b]	By Correlation	By Estimation[e]
pentanoic acid	66.9±2.0	257.8	218	-2.71±0.6	64.2±2.1		65.3±3.3
hexanoic acid	76.1±1.0	271.5	249.9	-2.01±0.4	74.1±1.1		69.9±3.6
heptanoic acid	73.8±1.0	282.3	281.8	-1.33±0.3	72.5±1.0		74.6±3.7
octanoic acid	83.3±1.0	293.8	313.7	-0.44±0.1	82.9±1.0		79.3±4.0
nonanoic aci	85.3±2.0	304..0	345.6	0.59±0.1	85.9±2.0		84.0±4.2
decanoic acid	88.6±2.0	313.8	377.5	1.70±0.2	90.3±2.0		88.7±4.4
undecanoic acid	90.7±2.0	322.9	409.4	2.88±0.4	93.6±2.0		93.4±4.7
dodecanoic acid	95.7±2.0	331.8	441.3	4.22±0.5	99.9±2.1		98.1±4.9
tridecanoic acid	100.4±2.0	340.5	473.2	5.66±0.7	106.1±2.1		102.8±5.1
tetradecanoic acid	104.1±2.0	348.6	505.1	7.2±0.8	111.3±2.2	110.7±6.1[c]	107.5±5.4
pentadecanoic acid	108.4±2.0	357.1	537	8.8±0.9	117.2±2.2	116.6±9.2[d]	112.2±5.6
hexadecanoic acid	110.2±2.0	364.1	568.9	10.5±1.1	120.7±2.3	121.3±4.2[c]	116.8±5.8
heptadecanoic acid	112.7±2.0	372	600.8	12.3±1.2	125.0±2.3	127.3±9.9[d]	121.5±6.1
octadecanoic acid	118.9±2.0	379	632.7	14.2±1.3	133.1±2.4	132.6±8.6[d]	126.2±6.3
nonadecanoic acid	121.8±2.0	386.1	664.6	16.1±1.4	137.9±2.4	138.0±6.8[d]	130.9±6.5
eicosanoic acid	125.5±2.0	392.5	696.5	18.1±1.5	143.6±2.5	143.2±4.5[c]	135.6±6.8
henicosanoic acid						149.2±7.1[d]	140.3±7.0
docosanoic acid						154.7±7.3[d]	145.0±7.2
tetracosanoic acid						170.7±2.3[c]	154.4±7.0
hexacosanoic acid						177.2±2.4[c]	163.7±8.2

[a] C_p(l)/J·mol^{-1}·K^{-1} Group values: CH_3-: 34.9; -CH_2-, 31.9; -CO_2H: 87.4 J·mol^{-1}·K^{-1}. [b] De Kruif, C. G.; Oonk, H. A. Enthalpies of vaporization and vapour pressures of seven aliphatic carboxylic acids. *J. Chem. Thermodyn.* **1979**, *11*, 287-90; De Kruif, C. G.; Oonk, H. A. Enthalpies of vaporization and vapour pressures of seven aliphatic carboxylic acids. *J. Chem. Thermodyn.* **1979**, *11*, 287-90. [c] This work. [d] Wilson, J. ; Chickos, J. S.; Vapor Pressures and Vaporization, Sublimation, and Fusion Enthalpies of Some Fatty Acids. *J. Chem. Eng. Data* **2013**, *58*, 322-33. [e] Chickos J. S. in Computational Thermochemistry Prediction and Estimation of Molecular Thermodynamics, Irikura, K. K.; Frurip, D. J. ACS Symposium Series 677, ACS: Washington DC, 1996. Chapter 4.

TABLE G-8. Parameters of the Clark and Glew Equation: $R\cdot\ln(p/p^{o}) = -\Delta G°(\theta)/\theta + \Delta H°(\theta)(1/\theta - 1/T) + \Delta Cp(\theta)\{\theta/T - 1 + \ln(T/\theta)\}$ Where p^{o}/Pa = 1 and θ is a Reference Temperature and of the Third Order Polynomial: $\ln(p/p^{o}) = A\cdot T^{-3} + B\cdot T^{-2} + C\cdot T^{-1} + D$ Where p_{o}/Pa = 101325

	$\Delta G(\theta)$ $J\cdot mol^{-1}$	$\Delta H(\theta)$ $J\cdot mol^{-1}$	$\Delta Cp(\theta)$ $J\cdot mol^{-1}\cdot K^{-1}$	$p(\theta)$/Pa	(θ)	$\ln(p/p_{o})$ 298.15 K
hexanoic acid[a]	-17740	64890	-75	427	352.36	-9.63
heptanoic acid[a]	-14580	69390	-79	151	349.61	-10.76
octanoic acid[a]	-17070	72300	-96	256	370.18	-11.95
nonanoic acid[a]	-15710	76260	-106	156	374.26	-13.09
decanoic acid[a]	-17160	78920	-111	200	389.39	-14.21
undecanoic acid[a]	-16660	82180	-122	158	395.8	-15.29
dodecanoic acid[a]	-17150	84950	-131	160	406.24	-16.41
tridecanoic acid[a]	-17610	87740	-142	162	416.13	-17.54
Saturated acids	$A\cdot10^{-8}/K^{3}$	$B\cdot10^{-6}/K^{2}$	$C\cdot10^{-3}/K$	D		$\ln(p/p_{o})$ 298.15 K
tetradecanoic acid[c]	4.396	-4.863	4.705	3.659		-18.681
pentadecanoic acid[b]	4.526	-5.029	4.81288	3.623		-19.726
hexadecanoic acid[c]	4.809	-5.293	5.115	3.450		-20.824
heptadecanoic acid[b]	4.883	-5.424	5.134	3.493		-21.883
octadecanoic acid[b]	5.056	-5.617	5.282	3.443		-22.955
nonadecanoic acid[b]	5.279	-5.858	5.615	3.167		-23.980
eicosanoic acid[c]	5.418	-6.046	5.816	3.029		-24.900
heneicosanoic acid[b]	5.422	-6.120	5.696	3.189		-26.095
docosanoic acid[b]	5.650	-6.373	6.003	2.975		-27.266
tetracosanoic acid[c]	5.942	-6.772	6.159	3.251		-29.853
hexacosanoic acid[c]	6.303	-7.147	6.797	2.494		-31.327
Mono-unsaturated acids						
(9Z)-hexadecenoic acid[c]	4.805	-5.317	5.139	3.345		-21.102
(9Z)-octadecenoic acid[c]	5.110	-5.680	5.528	3.051		-23.024
(6Z)-octadecenoic acid[c]	5.213	-5.749	5.748	2.805		-22.920
arachidonic acid[c]	5.664	-6.313	6.515	2.01		-25.786
11Z-eicosenoic acid[c]	5.506	-6.126	6.043	2.703		-25.168
(15Z)-tetracosenoic acid[c]	6.031	-6.851	6.391	2.912		-29.967
Polyunsaturated acids						
(9E)-octadecenoic acid[b]	5.204	-5.742	5.586	3.088		-23.127
γ-linolenic acid[b]	5.597	-6.104	6.409	2.218		-23.832
α-linolenic acid[b]	5.587	-6.099	6.288	2.345		-24.093
(9Z,12Z)-octadecadienoic acid[c]	5.305	-5.682	5.884	2.688		-21.480
(13Z)-docosenoic acid[c]	5.802	-6.493	6.373	2.518		-27.258
cervonic acid[c]	6.256	-6.978	7.231	1.494		-29.147

[a] De Kruif, C. G.; Schaake, R. C. F.; Van Miltenburg, J. C.; Van Der Klaw, K.; Blok, J. G. Thermodynamic properties of the normal carboxylic acids III. Enthalpies of vaporization and vapour pressures of 13 normal alkanoic acids. *J. Chem. Thermodyn.* **1982**, *14*, 791-98. [b] Wilson, J.; Chickos, J. S.; Vapor Pressures and Vaporization, Sublimation, and Fusion Enthalpies of Some Fatty Acids. *J. Chem. Eng. Data* **2013**, *58*, 322-33. [c] This work.

TABLE G-9. Sublimation Enthalpies and a Summary of Both Solid and Liquid Vapor Pressures of Fatty Acids at T/K = 298.15 Evaluated by Correlation

Saturated Fatty Acids	#C	$\Delta_{cr}{}^{g}H_m$(298 K) kJ·mol^{-1}	$p_{cr}{}^{298}$/Pa	$p_{cr}{}^{Tfus}$/Pa (T/K)	$p_l{}^{298}$/Pa
tetradecanoic acid[a]	14	154.1±2.3	$1.6\cdot10^{-4}$		$7.8\cdot10^{-4}$
pentadecanoic acid[a]	15	164.5±2.3	$5.4\cdot10^{-5}$		$2.7\cdot10^{-4}$
hexadecanoic acid[a]	16	171.1±2.5	$8.5\cdot10^{-6}$	$2.6\cdot10^{-8}$ (275.2)	$9.2\cdot10^{-5}$
heptadecanoic acid[a]	17	180.4±2.5	$2.8\cdot10^{-6}$		$3.2\cdot10^{-5}$
octadecanoic acid[a]	18	190.0±2.7	$4.5\cdot10^{-7}$	$3.9\cdot10^{-8}$ (289.4)	$1.1\cdot10^{-5}$
nonadecanoic acid[a]	19	200.4±2.7	$4.8\cdot10^{-7}$		$3.9\cdot10^{-6}$
eicosanoic acid[a]	20	207.6±3.0	$2.4\cdot10^{-8}$	$1.3\cdot10^{-8}$ (296.5)	$6.3\cdot10^{-6}$
heneicosanoic acid[a]	21	211.9±8.0	$1.0\cdot10^{-8}$		$5.0\cdot10^{-7}$
docosanoic acid[a]	22	218.4±7.5	$2.3\cdot10^{-9}$		$15\cdot10^{-8}$
tetracosanoic acid[b]	24	253±3.2	$4.0\cdot10^{-11}$		$1.1\cdot10^{-8}$
hexacosanoic acid[b]	26	257.8±3.5	$8.0\cdot10^{-12}$		$2.5\cdot10^{-9}$
Mono-unsaturated					
(9Z)-hexadecenoic acid[c]	16	152.1±6.4		$1.2\cdot10^{-6}$ (275.2)	$69.4\cdot10^{-6}$
(6Z)-octadecenoic acid[b]	18	(178.2/190.7)±2.1	$(8.5, 7.8)\cdot10^{-6}$		$11.3\cdot10^{-6}$
(9Z)- octadecenoic acid[d]	18	189±6.6		$2.0\cdot10^{-6}$ (289.4)	$10.1\cdot10^{-6}$
(9*E*)-octadecenoic acid[a]	18	189.8±10.3	$2.2\cdot10^{-6}$		$9.3\cdot10^{-6}$
(11Z)-eicosenoic acid[e]	20	192.9±2.2		$9.5\cdot10^{-7}$ (296.5)	$1.18\cdot10^{-6}$
(13Z)-docosenoic acid[b]	22	207.5±7.3	$7.8\cdot10^{-8}$		$14.7\cdot10^{-8}$
(15Z)-tetracosenoic acid[b]	24	228.9±2.4	$2.7\cdot10^{-9}$		$1.1\cdot10^{-8}$

[a] Wilson, J. ; Chickos, J. S.; Vapor Pressures and Vaporization, Sublimation, and Fusion Enthalpies of Some Fatty Acids. *J. Chem. Eng. Data* **2013**, *58*, 322-33. [b] This work. [c] At T/K = 275.2. [d] At T_{fus}/K = 289.4. [e] At T_{fus}/K = 296.5

TABLE G-10. Adjustment of the Sublimation Enthalpies of Davies and Malpass[a] to T/K = 298.15

	$\Delta_{cr}{}^{g}H_m(T_m)$ kJ·mol^{-1}	T_m/K	C_p(cr)[b] J·mol^{-1}·K^{-1}	ΔC_p(cr)ΔT kJ·mol^{-1}	$\Delta_{cr}{}^{g}H_m$(298 K) kJ·mol^{-1}	p_{cr}/Pa*10^8 298.15 K DM[a]/TW[c]
tetradecanoic acid	139.7±3.8	318.7	412.5	1.3±0.4	141.0±3.8	25800/ 16000
hexadecanoic acid	154.4±4.2	326.5	466.3	2.0±0.6	156.4±4.2	1900/9100
octadecanoic acid	166.5±4.2	335.7	520.1	3.0±0.9	169.5±4.3	138/45
eicosanoic acid	199.6±7.5	351/5	573.9	3.8±1.1	203.3±7.6	4.1/2.4
docosanoic acid	193.3±7.9	348.3	627.7	4.8±1.4	198.1±8.1	0.74/0.23

[a] Davies, M.; Malpass, V. E. Heats of Sublimation of Straight Chain Monocarboxylic Acids. *J. Chem. Soc.* **1961**, 1048-55. [b] C_p(cr)/J·mol^{-1}·K^{-1} Group values: CH_3-: 36.6; -CH_2-, 26.9; -CO_2H: 53.1 J·mol^{-1}·K^{-1}. [c] Wilson, J. ; Chickos, J. S.; Vapor Pressures and Vaporization, Sublimation, and Fusion Enthalpies of Some Fatty Acids. *J. Chem. Eng. Data* **2013**, *58*, 322-33.

2.) Lactones

TABLE G-11A. Retention times for Run 1

Run 1	418.8	423.9	428.9	434	439	444	448.8
t_o = 60 s				t_o/t			
methanol	0.666	0.668	0.642	0.664	0.682	0.69	0.678
γ-hexanolactone	1.508	1.406	1.298	1.248	1.205	1.16	1.103
γ-octanolactone	2.984	2.65	2.36	2.158	1.99	1.84	1.701
δ-octanolactone	3.356	2.966	2.629	2.388	2.19	2.014	1.856
γ-nonanolactone	4.513	3.916	3.422	3.052	2.75	2.487	2.261
δ -nonanolactone	5.133	4.432	3.856	3.42	3.064	2.756	2.497
γ-decanolactone	7.046	5.985	5.134	4.477	3.945	3.492	3.124
δ-decanolactone	8.000	6.773	5.787	5.022	4.408	3.882	3.465
γ-undecanolactone	11.204	9.34	7.876	6.729	5.813	5.046	4.441
δ-undecanolactone	12.763	10.606	8.911	7.583	6.527	5.642	4.958
γ-dodecanolactone	18.023	14.769	12.262	10.294	8.73	7.447	6.448
δ-dodecanolactone	20.555	16.796	13.903	11.631	9.837	8.358	7.225

TABLE G-11B. Correlation Results for Run 1

Run 1	- slope T/K	intercept	ΔH_{trn}(434 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)
γ-hexanolactone	-4254.4	10.338	35.37	57.2±0.3	57.5±3.6
γ-octanolactone	-5115.1	11.381	42.52		65.9±3.9
δ-octanolactone	-5169.5	11.362	42.98	67.0±0.2	66.5±3.9
γ-nonanolactone	-5555.6	11.927	46.19	70.3±0.3	70.3±4.0
δ-nonanolactone	-5624.2	11.941	46.76	70.7±0.4	70.9±4.1
γ-decanolactone	-6003.5	12.49	49.91	75.6±0.3	74.7±4.2
δ-decanolactone	-6063.8	12.495	50.41	74.2±0.3	75.2±4.2
γ-undecanolactone	-6450.8	13.057	53.63		79.1±4.4
δ-undecanolactone	-6513.9	13.07	54.15		79.7±4.4
γ-dodecanolactone	-6896.6	13.622	57.34		83.4±4.6
δ-dodecanolactone	-6961.5	13.641	57.88		84.1±4.6

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.18±0.062)ΔH_{trn}(434 K) + (15.62±2.8) r^2 = 0.9890 (G-5)

TABLE G-12A. Retention times for Run 2

Run 2 t_o = 60 s	418.8	423.9	428.9	434 t_o/t	439	444	448.8
methanol	0.666	0.668	0.642	0.664	0.682	0.69	0.678
γ-hexanolactone	1.508	1.406	1.298	1.248	1.205	1.16	1.103
γ-octanolactone	2.984	2.65	2.36	2.158	1.99	1.84	1.701
δ-octanolactone	3.356	2.966	2.629	2.388	2.19	2.014	1.856
γ-nonanolactone	4.513	3.916	3.422	3.052	2.75	2.487	2.261
δ -nonanolactone	5.133	4.432	3.856	3.42	3.064	2.756	2.497
γ-decanolactone	7.046	5.985	5.134	4.477	3.945	3.492	3.124
δ-decanolactone	8.000	6.773	5.787	5.022	4.408	3.882	3.465
γ-undecanolactone	11.204	9.34	7.876	6.729	5.813	5.046	4.441
δ-undecanolactone	12.763	10.606	8.911	7.583	6.527	5.642	4.958
γ-dodecanolactone	18.023	14.769	12.262	10.294	8.73	7.447	6.448
δ-dodecanolactone	20.555	16.796	13.903	11.631	9.837	8.358	7.225

TABLE G-12B. Correlation Results for Run 2

Run 2	- slope T/K	intercept	ΔH_{trn}(434 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(calc)
γ-hexanolactone	-4279.8	10.387	35.58	57.2±0.3	57.2±3.7
γ-octanolactone	-5137.4	11.424	42.71		66.1±3.9
δ-octanolactone	-5192.6	11.407	43.17	67.0±0.2	66.6±4.0
γ-nonanolactone	-5574.8	11.962	46.35	70.3±0.3	70.6±4.1
δ-nonanolactone	-5641.8	11.974	46.9	70.7±0.4	71.3±4.1
γ-decanolactone	-6018.1	12.513	50.03	75.6±0.3	75.2±4.3
δ-decanolactone	-6080.4	12.526	50.55	74.2±0.3	75.8±4.3
γ-undecanolactone	-6462.2	13.075	53.72		79.7±4.4
δ-undecanolactone	-6527.5	13.094	54.27		80.4±4.5
γ-dodecanolactone	-6905.9	13.64	57.41		84.3±4.6
δ-dodecanolactone	-6969.5	13.655	57.94		85.0±4.7

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.19±0.063)ΔH_{trn}(434 K) + (15.12±2.9) r^2 = 0.9889 (G-6)

TABLE G-13. Correlation of $\ln(t_o/t_a)$ with $\ln(p/p_o)_{exp}$ at T = 298.15 K for Run 2

	$\ln(t_o/t_a)$	$\ln(p/p_o)_{exp}$	$\ln(p/p_o)_{calc}$	p/Pa_{lit}	p/Pa_{calc}
γ-hexanolactone	-3.97	-8.46	-8.41±0.25	21.6	22.5±6.5
γ-octanolactone	-5.81		-10.5±0.29		2.78±0.93
δ-octanolactone	-6.01	-10.74	-10.73±0.29	2.2	2.21±0.75
γ-nonanolactone	-6.74	-11.51	-11.56±0.31	1.01	0.97±0.35
δ-nonanolactone	-6.95	-11.67	-11.8±0.31	0.87	0.76±0.28
γ-decanolactone	-7.67	-12.61	-12.62±0.33	0.34	0.33±0.13
δ-decanolactone	-7.87	-12.99	-12.85±0.34	0.23	0.27±0.11
γ-undecanolactone	-8.6		-13.68±0.35		0.12±0.05
δ-undecanolactone	-8.8		-13.91±0.36		0.09±0.04
γ-dodecanolactone	-9.52		-14.73±0.38		0.04±0.019
δ-dodecanolactone	-9.72		-14.95±0.38		0.03±0.015

$\ln(p/p_o)_{calc}$ = (1.137±0.033) $\ln(p/p_o)_{exp}$ - (3.90±0.22) r^2 = 0.9967   (G-7)

TABLE G-14. The slope, intercept and vaporization enthalpy at T = 298.15 K calculated from correlations of $\ln(t_o/t_a)$ with $\ln(p/p_o)_{exp}$ for Run 2 from T = (298.15 to 350) K

	A	B	$\Delta_l^gH_m(T_m)^a$ kJ·mol^{-1}	$C_{p(298\ K)}(l)$ J·mol^{-1}·K^{-1}	$\Delta_l^gH_m(298.15\ K)$ kJ·mol^{-1}	
					calc	lit^a
γ-hexanolactone	14.14	-6719.3	55.9±0.2	206.6	57.5±0.5	57.2±0.3^b
γ-octanolactone	15.32	-7695	64.0±0.3	270.4	66.1±0.5	66.0±3.9^c
δ-octanolactone	15.30	-7757.9	64.5±0.3	264.4	66.6±0.5	67.0±0.2^b
γ-nonanolactone	15.94	-8192.6	68.1±0.3	302.3	70.4±0.5	70.3±0.3^b
δ-nonanolactone	15.95	-8268.9	68.7±0.3	296.3	71.0±0.5	70.7±0.4^b
γ-decanolactone	16.57	-8696.9	72.3±0.4	334.2	74.8±0.6	75.6±0.3^b
δ-decanolactone	16.58	-8767.8	72.9±0.4	328.2	75.4±0.6	74.2±0.3^b
γ-undecanolactone	17.21	-9202.2	76.5±0.4	366.1	79.2±0.6	79.4±4.4^c
δ-undecanolactone	17.23	-9276.5	77.1±0.4	360.1	79.8±0.6	80.1±4.5^c
γ-dodecanolactone	17.85	-9706.9	80.7±0.4	398	83.7±0.6	84.3±4.6^c
δ-dodecanolactone	17.87	-9779.4	81.3±0.4	392	84.2±0.6	85.6±4.7^c

$^a T_m$ = 324 K. ^{b}Ref 17,18. ^{c}This work.

TABLE G-15. A comparison of the literature vapor pressures with this work using equation G-8 (Run 2)

	p/Pa 298.15 K lit[a]	p/Pa 298.15 K this work		p/Pa 298.15 K $\mathrm{EPI_{est}}$[b]	p/Pa 293.15 K lit[c]	p/Pa 293.15 K this work[d]
		eq G-8	eq G-9			
γ-hexanolactone	21.6	22.5±6.4	22.9±3.3	22	80.0	15.6±2.3
γ-octanolactone		2.8±0.9	2.8±0.5	8.46	5.47	1.82±0.3
δ-octanolactone	2.2	2.2±0.8	2.2±0.4	3.63	2.29	1.43±0.3
γ-nonanolactone	1.01	1.0±0.4	1.0±0.2	1.57	0.97	0.62±0.1
δ-nonanolactone	0.87	0.76±0.3	0.77±0.2	1.45	0.89	0.48±0.1
γ-decanolactone	0.34	0.33±0.1	0.34±0.1	0.683	0.42	0.21±0.05
δ-decanolactone	0.23	0.27±0.1	0.27±0.1	0.633	0.39	0.16±0.04
γ-undecanolactone		0.12±0.05	0.12±0.03	0.545	0.34	0.070±0.02
δ-undecanolactone		0.09±0.04	0.095±0.02	0.261	0.14	0.056±0.01
γ-dodecanolactone		0.04±0.02	0.042±0.01	0.141	0.08	0.024±0.006
δ-dodecanolactone		0.03±0.02	0.033±0.01	0.132	0.08	0.019±0.005

$\ln(p/p_o)_{calc} = (1.134\pm0.033)\ln(p/p_o)_{exp} - (3.95\pm0.22)$ $r^2 = 0.9967$ (G-8)

$\ln(p/p_o) = A + B/(T/K)$ (G-9)

[a] From references 17,18 unless noted otherwise. [b] From reference 17,18. Calculated using the EPI Suite. The EPI Suite is available as a download from http://www.epa.gov/oppt/exposure/pubs/episuitedl.htm; accessed 6/10/13. [c] MSDS sheet, http://bedoukian.com/products/searchflavor.asp, accessed 8/29/13 [d] Using equation G-9 and the constants of Table 6B.

3.) Insect Pheromones

TABLE G-16A. Retention Times on a 5% Poly(dimethylphenyl siloxane) Capillary Column

Run 1							
T/K	434.8	439.9	444.7	449.8	454.9	459.9	464.8
				t/60 s			
CH_2Cl_2	0.540	0.56	0.555	0.552	0.572	0.568	0.572
Methyl decanoate	1.965	1.791	1.617	1.476	1.378	1.274	1.191
Methyl dodecanoate	4.193	3.644	3.16	2.769	2.466	2.193	1.974
Z 8-Dodecenyl acetate	5.784	4.952	4.235	3.659	3.207	2.813	2.495
Z 4-Tridecen-1-yl acetate	8.136	6.872	5.802	4.947	4.27	3.699	3.236
Methyl tetradecanoate	9.733	8.148	6.822	5.768	4.934	4.241	3.681
Methyl pentadecanoate	15.019	12.383	10.212	8.499	7.155	6.055	5.171

TABLE G-16B. Correlation of Vaporization Enthalpies With Enthalpies of Transfer (p_o/Pa =101325)[a]

Run 1	- slope T/K	intercept	ΔH_{trn}(450 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (Lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(Calc)
Methyl decanoate	5606.9±30	12.544±0.06	46.61±0.22	66.10±0.17	66.6±4.8
Methyl dodecanoate	6450.7±30	13.544±0.06	53.63±0.23	76.59±0.41	75.9±5.1
Z 8-Dodecenyl acetate	6756.1±30	13.885±0.07	56.17±0.26		79.3±5.3
Z 4-Tridecen-1-yl acetate	7058.6±30	14.210±0.07	58.68±0.27		82.6±5.4
Methyl tetradecanoate	7303.9±40	14.584±0.08	60.72±0.29	85.94±0.76	85.3±5.5
Methyl pentadecanoate	7727.7±40	15.104±0.08	64.24±0.31	89.29±0.79	90.0±5.6
$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.328±0.065)·ΔH_{trn}(450 K) + (4.72±3.7); r^2 = 0.9951					(G-10)

[a] Uncertainties represent 1 standard deviation; all vaporization enthalpies of the standards from reference [G-1].

TABLE G-17A. Retention Times on a 5% Poly(dimethylphenyl siloxane) Capillary Column

Run 2							
T/K	434	438.9	443.8	448.7	453.7	458.5	463.4
				t/60 s			
CH_2Cl_2	0.544	0.568	0.565	0.568	0.577	0.58	0.598
Methyl decanoate	1.981	1.811	1.640	1.501	1.390	1.293	1.227
Methyl dodecanoate	4.225	3.682	3.200	2.807	2.492	2.227	2.021
Z 8-Dodecenyl acetate	5.836	5.006	4.289	3.709	3.244	2.857	2.551
Z 4-Tridecen-1-yl acetate	8.209	6.946	5.874	5.013	4.325	3.755	3.301
Methyl tetradecanoate	9.821	8.242	6.906	5.848	5.006	4.308	3.754
Methyl pentadecanoate	15.153	12.511	10.327	8.609	7.254	6.144	5.264

TABLE G-17B. Correlation of Vaporization Enthalpies With Enthalpies of Transfer (p_o/Pa =101325)[a]

Run 2	- slope T/K	intercept	ΔH_{trn}(449 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (Lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(Calc)
Methyl decanoate	5665.7±17	12.695±0.04	47.10±0.14	66.10±0.17	66.6±5.0
Methyl dodecanoate	6512.1±19	13.705±0.04	54.14±0.16	76.59±0.41	75.9±5.4
Z 8-Dodecenyl acetate	6825.2±21	14.064±0.05	56.74±0.17		79.3±5.5
Z 4-Tridecen-1-yl acetate	7134.4±22	14.406±0.05	59.31±0.18		82.7±5.6
Methyl tetradecanoate	7379.0±24	14.779±0.05	61.35±0.20	85.94±0.76	85.3±5.7
Methyl pentadecanoate	7810.7±26	15.320±0.06	64.94±0.21	89.29±0.79	90.0±5.9

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.312±0.068)·ΔH_{trn}(449 K) + (4.84±3.9); r^2 = 0.9947 (G-11)

[a] Uncertainties represent 1 standard deviation; all vaporization enthalpies of the standards from reference [G-1].

TABLE G-18A. Retention Times on a 5 % Poly(dimethylphenyl siloxane) Capillary Column

Run 3 *T*/K	473.5	478.4	483.3	488.2	493.2	498.2	503.1
				t/60 s			
CH_2Cl_2	0.539	0.534	0.536	0.539	0.538	0.528	0.544
Methyl tetradecanoate	2.627	2.32	2.073	1.868	1.692	1.535	1.425
E 11-Tetradecenyl acetate	3.324	2.899	2.556	2.274	2.034	1.824	1.671
Methyl pentadecanoate	3.568	3.102	2.728	2.419	2.157	1.929	1.761
E, *E* 9,11-tetradecadienyl acetate	4.022	3.476	3.038	2.679	2.375	2.112	1.917
S-Hydropene[a]	4.258	3.677	3.209	2.823	2.498	2.22	2.008
Kinoprene[b]	6.019	5.116	4.396	3.808	3.319	2.905	2.586
Methyl octadecanoate	9.66	8.064	6.799	5.776	4.94	4.249	3.703
Z 13-Octadecen-1-yl acetate	12.429	10.31	8.626	7.261	6.161	5.265	4.541
Methyl eicosanoate	19.323	15.762	12.979	10.777	9.005	7.567	6.433
Methyl henicosanoate	27.426	22.128	18.035	14.815	12.246	10.187	8.563

[a] *S* Ethyl (2*E*,4*E*)-3,7,11-trimethyl-2,4-dodecadienoate. [b] *R,S* 2-Propynyl (2*E*, *E*)-3,7,11-trimethyl-2,4-dodecadienoate.

TABLE G-18B. Correlation of Vaporization Enthalpies With Enthalpies of Transfer (p_o/Pa =101325)[a]

Run 3	- slope *T*/K	intercept	ΔH_{trn}(449 K) kJ·mol^{-1}	$\Delta_l{}^gH_m$(298 K) kJ·mol^{-1} (Lit)	$\Delta_l{}^gH_m$(298 K) kJ·mol^{-1}(Calc)
Methyl tetradecanoate	6929.4±41	13.906±0.08	57.61±0.34	85.94±0.76	85.2±3.5
E 11-Tetradecenyl acetate	7265.2±43	14.327±0.09	60.40±0.35		89.6±3.5
Methyl pentadecanoate	7321.9±43	14.363±0.09	60.87±0.36	89.29±0.79	90.3±3.5
E,*E* 9,11-Tetradecadienyl acetate	7480.7±43	14.506±0.09	62.19±0.36		92.3±3.6
S-Hydropene[b]	7487.1±43	15.783±0.09	70.80±0.36		92.4±3.6
Kinoprene[c]	7927.4±46	15.049±0.1	65.90±0.39		98.1±3.7
Methyl octadecanoate	8516.0±49	15.783±0.1	62.24±0.41	105.87±1.37	105.7±3.8
Z-13-Octadecen-1-yl acetate	8757.9±49	16.029±0.1	72.81±0.41		108.8±3.9
Methyl eicosanoate	9317.2±54	16.754±0.1	77.46±0.45	116.43±1.5	116.0±4.0
Methyl henicosanoate	9717.2±56	17.241±0.1	80.78±0.47	120.9±1.8	121.2±4.1

$\Delta_l{}^gH_m(298.15\ K)/kJ\cdot mol^{-1} = (1.552\pm0.038)\cdot\Delta H_{trn}(449\ K) + (4.21\pm2.67);\ r^2 = 0.9982$ (G-12)

[a] Uncertainties represent 1 standard deviation; reference for the vaporization enthalpy of methyl henicosanoate: [G-2]; all others from reference [G-1]. [b] *S* Ethyl (2*E*,4*E*)-3,7,11-trimethyl-2,4-dodecadienoate. [c] *R*,*S* 2-Propynyl (2*E*,*E*)-3,7,11-trimethyl-2,4-dodecadienoate.

TABLE G-19A. Retention Times on a 5% Poly(dimethylphenyl siloxane) Capillary Column

Run 4							
T/K	473.4	478.4	483.3	488.3	493.3	498.2	503.2
				t/60 s			
CH_2Cl_2	0.516	0.515	0.521	0.525	0.518	0.517	0.528
Methyl tetradecanoate	2.550	2.258	2.024	1.825	1.645	1.500	1.388
E 11-Tetradecenyl acetate	3.228	2.822	2.495	2.221	1.977	1.782	1.628
Methyl pentadecanoate	3.465	3.021	2.663	2.363	2.098	1.884	1.716
E,*E* 9,11-tetradecadienyl acetate	3.905	3.386	2.966	2.616	2.310	2.063	1.867
S-Hydropene[a]	4.140	3.584	3.134	2.758	2.431	2.168	1.957
Kinoprene[b]	5.849	4.984	4.292	3.719	3.230	2.836	2.520
Methyl octadecanoate	9.399	7.862	6.640	5.642	4.810	4.145	3.611
Z 13-Octadecen-1-yl acetate	12.127	10.063	8.425	7.098	6.001	5.132	4.434
Methyl eicosanoate	18.797	15.359	12.677	10.526	8.772	7.379	6.271
Methyl henicosanoate	26.657	21.574	17.615	14.466	11.937	9.935	8.349

[a] *S* Ethyl (2*E*,4*E*)-3,7,11-trimethyl-2,4-dodecadienoate. [b] *R*, *S* 2-Propynyl (2E,E)-3,7,11-trimethyl-2,4-dodecadienoate.

TABLE G-19B. Correlation of Vaporization Enthalpies With Enthalpies of Transfer (p_o/Pa =101325)[a]

Run 4	- slope *T*/K	intercept	ΔH_{trn}(488 K) kJ·mol^{-1}	$\Delta_l^g H_m$(298 K) kJ·mol^{-1} (Lit)	$\Delta_l^g H_m$(298 K) kJ·mol^{-1}(Calc)
Methyl tetradecanoate	6883.3±22	13.834±0.05	57.22±0.2	85.94±0.76	85.2±3.4
E 11-Tetradecenyl acetate	7220.3±23	14.258±0.05	60.03±0.2		89.6±3.5
Methyl pentadecanoate	7275.7±23	14.292±0.05	60.49±0.2	89.29±0.79	90.3±3.5
E,*E* 9,11-tetradecadienyl acetate	7431.2±23	14.481±0.05	61.78±0.2		92.3±3.5
S-Hydropene [b]	7445.0±23	14.443±0.05	61.89±0.2		92.5±3.6
Kinoprene [c]	7877.6±26	14.971±0.05	65.49±0.2		98.1±3.6
Methyl octadecanoate	8468.9±30	15.711±0.06	70.41±0.3	105.87±1.37	105.8±3.8
Z 13-Octadecen-1-yl acetate	8721.4±36	15.977±0.07	72.51±0.3		109.0±3.8
Methyl eicosanoate	9262.2±32	16.665±0.07	77.00±0.3	116.43±1.54	116.1±4.0
Methyl henicosanoate	9655.0±32	17.137±0.07	80.27±0.3	120.9±1.8	121.1±4.1

$\Delta_l^g H_m$(298.15 K)/kJ·mol^{-1} = (1.56±0.038)·ΔH_{trn}(488 K) + (4.11±2.65); $r^2 = 0.9982$ (G-13)

[a] Uncertainties represent 1 standard deviation. [b] *S* Ethyl (2*E*,4*E*)-3,7,11-trimethyl-2,4-dodecadienoate. [c] *R*,*S* 2-Propynyl (2E,E)-3,7,11-trimethyl-2,4-dodecadienoate.

TABLE G-20. Constants for the Third Order Polynomial Eq G-14 for Runs 1/2 and Runs 3/4[a]

Targets: **Runs1/2**	A	B(K)	$10^{-6}\cdot C(K^2)$	$10^{-6}\cdot D(K^3)$
Z 8-Dodecenyl acetate	4.8377±0.1147	1722.17±132.54	-2.906±0.050	245.180±6.315
Z 4-Tridecenyl acetate	4.3471±0.1292	2162.00±149.37	-3.137±0.057	266.067±7.116
Standards: **Runs 1/2**				
Methyl decanoate	6.1270±0.0806	518.51±93.16	-2.189±0.035	4.439±0.001
Methyl dodecanoate	5.2594±1.027	1337.83±118.73	-2.693±0.045	226.274±5.657
Methyl tetradecanoate	4.5807±0.1177	2005.92±136.04	-3.152±0.052	264.130±6.481
Methyl pentadecanoate	4.2738±0.1240	2313.29±143.34	-3.371±0.055	22.056±6.829
Targets: **Runs 3/4**				
E 11-Tetradecenyl acetate	4.5304±0.1307	2111.77±151.09	-3.301±0.057	276.766±7.198
E,*E* 9,11-tetradecadienyl acetate	4.2442±0.1298	2434.36±149.96	-3.476±0.057	291.272±7.145
S- Hydroprene[b]	4.0327±0.1359	2602.9±157.1	-3.540±0.06	298.134±7.485
Kinoprene[c]	3.6966±0.1261	3069.85±145.71	-3.828±0.055	320.001±6.942
Z 13-Octadecen-1-yl acetate	2.9275±0.1111	4061.90±128.36	-4.415±0.049	365.763±6.116
Standards: **Runs 3/4**				
Methyl tetradecanoate	4.7543±0.1394	1779.07±161.14	-3.089±0.061	261.033±7.677
Methyl pentadecanoate	4.366±0.1333	2265.61±154.03	-3.372±0.059	283.371±7.338
Methyl octadecanoate	3.2869±0.1114	3666.53±128.69	-4.205±0.049	348.125±6.131
Methyl eicosanoate	2.6172±0.0951	4562.68±109.91	-4.746±0.042	389.800±5.237
Methyl heneicosanoate	2.2867±0.0870	5006.33±100.49	-5.015±0.038	410.458±4.788

[a] Uncertainties are standard errors. [b] *S* Ethyl (2*E*,4*E*)-3,7,11-trimethyl-2,4-dodecadienoate. [c] *R*,*S* 2-Propynyl (2E,E)-3,7,11-trimethyl-2,4-dodecadienoate.

TABLE G-21. Individual Vapor pressures (p/Pa) Obtained by Correlation From Runs 1/2 as a Function of Temperature (p_o/Pa) = 101323); Uncertainties are One Standard Deviation[a]

T/K	Z 8-DA[b]	Z 4-TA[c]	T/K	Z 8-DA[b]	Z 4-TA[c]
			Pa		
298.15	0.27±0.076	0.12±0.035	400	560±23	340±15
310	0.91±0.20	0.42±0.097	410	930±45	570±30
320	2.3±0.41	1.1±0.21	420	1500±80	930±54
330	5.6±0.8	2.8±0.40	430	2300±130	1500±90
340	13±1.3	6.5±0.69	440	3500±190	2200±140
350	27±1.9	14±1.1	450	5100±260	3300±200
360	53±2.5	29±1.5	460	7300±340	4800±260
370	100±3.2	58±1.9	470	10000±400	6900±320
380	190±5.0	110±3.0	480	14000±480	9600±380
390	330±11	200±6.8	490	19000±680	13000±480
			500	25000±1300	18000±780

[a] Vapor pressures rounded to 2 significant figures. [b] *Z* 8-Dodecenyl acetate. [c] *Z* 4-Tridecen-1-yl acetate.

TABLE G-22. Individual Vapor pressures (Pa) Obtained by Correlation From Runs 3/4 as a Function of Temperature (p_o/Pa) = 101323); Uncertainties are One Standard Deviation[a]

T/K	LBAM(1)[b]	LBAM(2)[c]	S-Hydroprene	Kinoprene	*Z* 13-ODA[d]
			Pa		
298.15	0.028±0.008	0.015±0.0043	0.014±0.0039	0.0042±0.0012	0.00041±0.00013
310	0.11±0.026	0.063±0.015	0.057±0.014	0.019±0.0048	0.0022±0.00061
320	0.32±0.07	0.19±0.042	0.17±0.038	0.061±0.014	0.0082±0.0021
330	0.86±0.18	0.51±0.11	0.47±0.10	0.18±0.040	0.027±0.066
340	2.1±0.44	1.3±0.28	1.2±0.026	0.49±0.11	0.083±0.020
350	4.9±1.0	3.1±0.67	2.9±0.62	1.2±0.028	0.23±0.057
360	11±2.3	7.0±1.5	6.5±1.4	2.9±0.66	0.61±0.15
370	22±4.7	15±3.2	14±2.9	6.5±1.5	1.5±0.37
380	44±9.1	30±6.3	28±5.9	14±3.0	3.4±0.83
390	84±17	58±12	54±11	28±6.0	7.4±1.8
400	150±29	110±21	100±20	53±11	15±3.5
410	270±48	190±36	180±33	98±19	30±6.6
420	450±77	330±58	300±54	170±32	56±12
430	730±117	540±90	500±84	290±52	100±20
440	1200±170	870±130	810±120	490±80	180±33
450	1800±240	1400±190	1300±180	780±120	300±52
460	2700±330	2100±260	1900±250	1200±170	480±77
470	3900±430	3000±350	2800±330	1800±230	760±110
480	5600±540	4400±440	4100±410	2700±300	1200±150
490	7800±650	6200±530	5800±500	3900±370	1700±200
500	11000±760	8600±620	8000±590	5500±440	2500±260

[a] Vapor pressures rounded to 2 significant figures. [b] *E* 11-Tetradecenyl acetate. [c] *E,E* 9,11-Tetradecadienyl acetate. [d] *Z* 13-Octadecenyl acetate.

Error Estimations in Boiling Temperatures

Vapor pressures as a function of temperature from *T*/K = (298.15 - 500) were fit to a third order polynomial using Sigma Plot. The coefficients of eq G-14 and their uncertainty, σ, were provided by the software

$$\ln(p/p_o) = A + B(K)\cdot T + C(K^2)\cdot T^{2} + D(K^3)\cdot T^{3} \qquad \text{(G-14)}$$

The uncertainty in T_B was evaluated by setting $\ln(p/p_o) = 0$ and solving the third order polynomial for the real value of T_B. The uncertainty in T_B was evaluated as follows:

$$\sigma(T_B)^2 = \left(\frac{\partial T_B}{\partial A}\right)^2\sigma_A^2 + \left(\frac{\partial T_B}{\partial B}\right)^2\sigma_B^2 + \left(\frac{\partial T_B}{\partial C}\right)^2\sigma_C^2 + \left(\frac{\partial T_B}{\partial D}\right)^2\sigma_D^2 \qquad \text{(G-15)}$$

The derivatives of eq $(\mathrm{G}-14)$, $\left(\frac{\partial T_B}{\partial A}\right), \left(\frac{\partial T_B}{\partial B}\right), \left(\frac{\partial T_B}{\partial C}\right)$, and $\left(\frac{\partial T_B}{\partial D}\right)$, were solved by Mathcad. They were too large to be displayed.

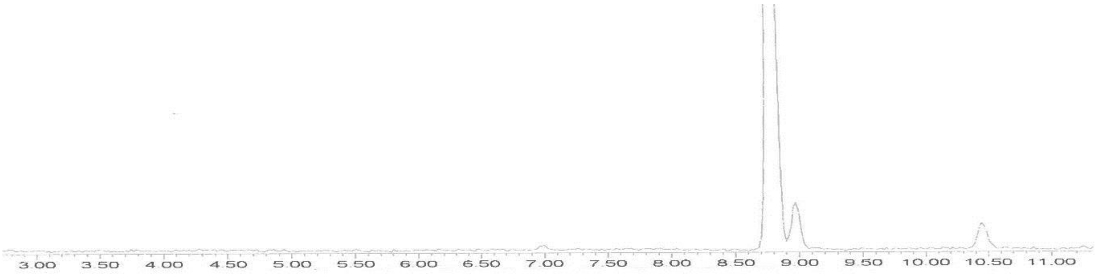

Figure G-1. GCMS trace of the LBAM pheromone using total ion current at T/K = 483, solvent not shown.

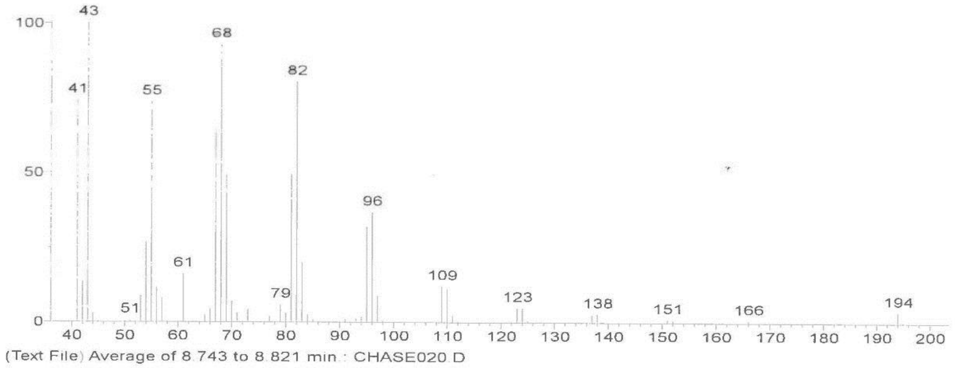

Figure G-2. Mass spectrum of the major component identified as *trans* 11-tetradecenyl acetate.

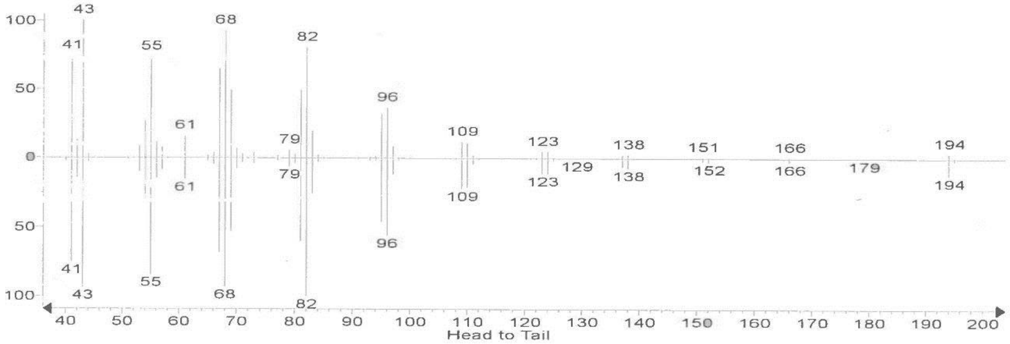

Figure G-3. Comparison of the major component to library spectrum of *trans* 11-tetradecenyl acetate.

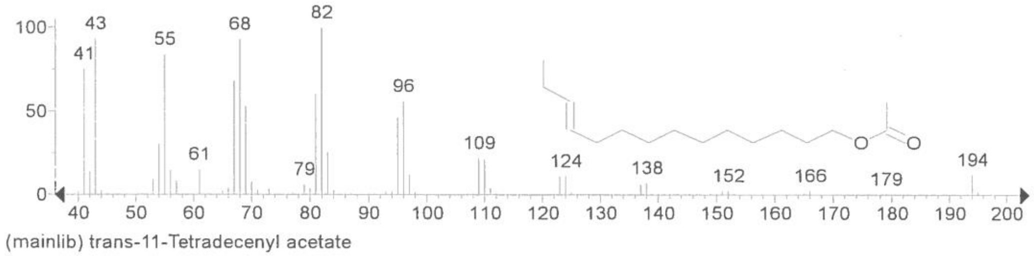

Figure G-4. Library spectrum of *trans* 11-tetradecenyl acetate.

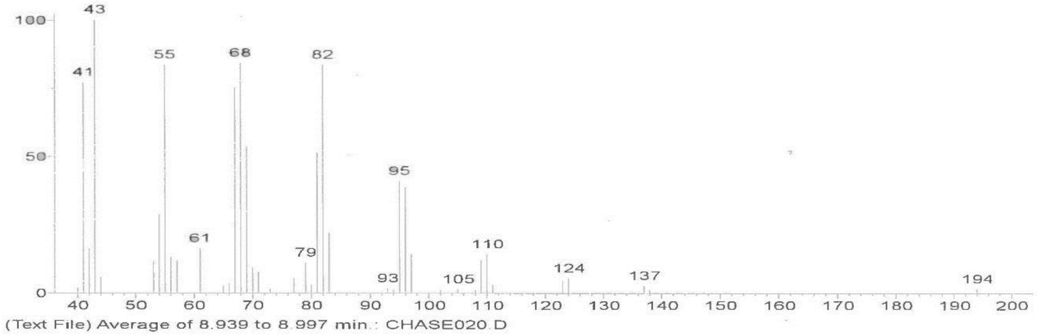

Figure G-5. Minor peak misidentified as *trans* 11-tetradecenyl acetate.

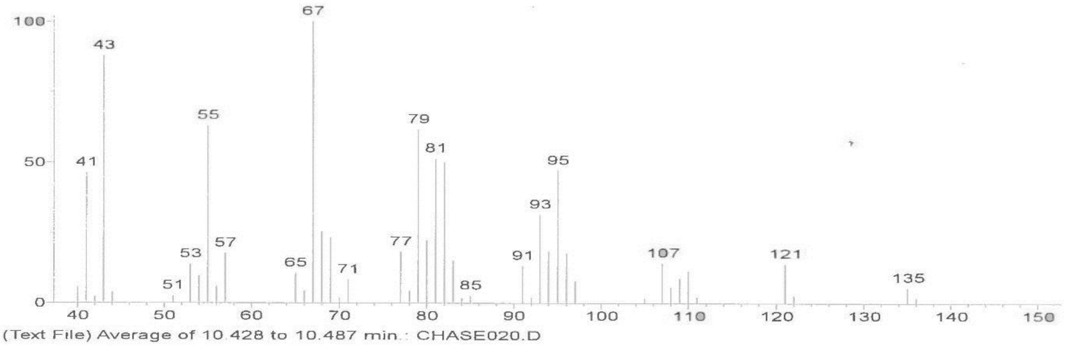

Figure G-6. *E*, *E* 9,11-tetradecadienyl acetate misidentified as Z,E 9.12-tetradecadienyl acetate

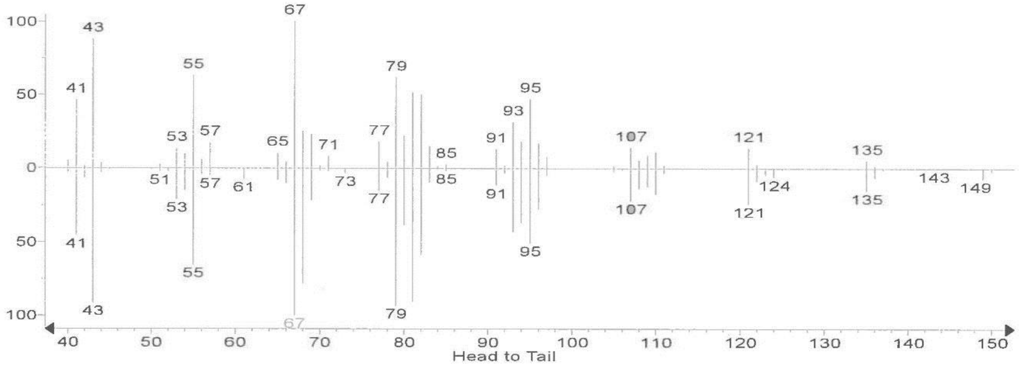

Figure G-7. Comparison of *E*, *E* 9,11-tetradecadienyl acetate and Z,E 9.12-tetradecadienyl acetate

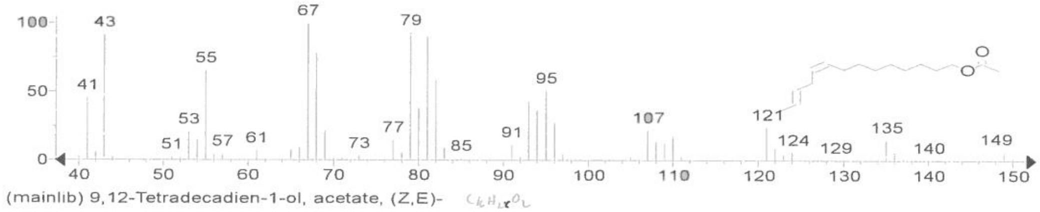

Figure G-8. Library spectrum of Z,E 9.12-tetradecadienyl acetate.

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