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Determination of Ideal-Gas Enthalpies of Formation for Key Compounds
The 1989 Project Results

Topical Report

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EXECUTIVE SUMMARY

This report describes the results obtained in the third year of a project whose goal is the improvement of group-contribution methodology for estimation of thermodynamic data.

It has long been recognized that it is impractical to carry out experimental measurements of the thermodynamic properties of the multitude of organic substances that are of importance in an area such as the processing of alternate fuel sources, or for those chemicals which are of major importance in modern industry. Experimental measurements on a restricted number of carefully selected molecules can be used to relate thermodynamic properties to molecular structure and serve as the foundation for estimation of properties for great numbers of related molecules. The most successful methodology used for this structure/property correlation is the "group-contribution" approach as applied by numerous researchers. The empirical nature of this approach requires data of unassailable quality for the foundation of the correlation. The need for such high-quality data is the basis for this project.

Representatives of the Department of Energy (Bartlesville Project Office), the Design Institute for Physical Property Data (DIPPR), and the National Institute for Petroleum and Energy Research (NIPER) agreed on a list of compounds for which the determination of the enthalpy of formation in the ideal-gas state would be of benefit to all the participants. Eight compounds were selected for study in the third year of the project, and the ideal-gas enthalpies of formation of (±)-butan-2-ol, tetradecan-1-ol, hexan-1,6-diol, methacrylamide, benzoyl formic acid, naphthalene-2,6-dicarboxylic acid dimethyl ester, and tetraethylsilane are reported here. A crystalline-phase enthalpy of formation at 298.15 K was determined for naphthalene-2,6-dicarboxylic acid which decomposed at 695 K before melting.

The results show that the $C-(C)_2(H)_2$ group-additivity parameter (or the CH_2 increment) is significantly smaller in alkanols than in alkanes. New values for the group parameters $CO-(C_d)(N)$, $C_b-(C_b)_2(O)$, and $O-(CO)(C)$ are defined: assignments for the $Si-(C)_4$ and $C-(Si)(C)(H)_2$ group-additivity parameters are made.

The results reported continue to establish the validity of the group-contribution approach for the accurate estimation of the enthalpies of formation of organic and organometallic compounds. They will extend the range of applicability of group-contribution methods open to the chemical engineer concerned with estimation of the energy hazard potential of new chemical processes. The applicability will be broad, covering such areas as fatty acid/ester manufacture through to the development of new fuels from alcohols.

ABSTRACT

The results of a study aimed at improvement of group-contribution methodolgy for estimation of thermodynamic properties of organic and organosilicon substances are reported. Specific weaknesses where particular group-contribution terms were unknown, or estimated because of lack of experimental data, are addressed by experimental studies of enthalpies of combustion in the condensed phase, vapor-pressure measurements, and differential scanning calorimetric (d.s.c.) heat-capacity measurements. Ideal-gas enthalpies of formation of (±)-butan-2-ol, tetradecan-1-ol, hexan-1,6-diol, methacrylamide, benzoyl formic acid, naphthalene-2,6-dicarboxylic acid dimethyl ester, and tetraethylsilane are reported. A crystalline-phase enthalpy of formation at 298.15 K was determined for naphthalene-2,6-dicarboxylic acid, which decomposed at 695 K before melting. The combustion calorimetry of tetraethylsilane used the proven fluorine-additivity methodology. Critical temperature and critical density were determined for tetraethylsilane with the d.s.c. and the critical pressure was derived. Group-additivity parameters useful in the application of group-contribution correlations are derived.

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The authors acknowledge Professor E. J. "Pete" Eisenbraun and his research group at Oklahoma State University for purification of six of the eight samples, and the assistance of Jane Thomson in the gas-liquid chromatographic analyses. The authors also acknowledge the helpful discussions with members of the DIPPR Research Project 871 Committee, especially the Chairman Dennis Jones, and Bill Peters of the U.S. Department of Energy Bartlesville Project Office. We gratefully acknowledge the financial support of the U.S. Department of Energy (DOE) and the Design Institute for Physical Property Data (DIPPR). This research was funded within the Supplemental Government Program (SGP) at NIPER as part of the cooperative agreement with the U. S. Department of Energy DE-FC22-83FE60149.

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GLOSSARY

This report is written with close adherence to the style adopted by The Journal of Chemical Thermodynamics. A complete description of the style can be found in any January issue of the Journal of Chemical Thermodynamics. This glossary attempts to summarize the main points, especially with respect to the symbol usage.

Throughout this report only SI units are used in reporting thermodynamic values. Most values are given in dimensionless units i.e., physical quantity = number X unit; for example $\rho/(\mathrm{kg\cdot m^{-3}})$ rather than " ρ $(\mathrm{kg/m^3})$" or " ρ $\mathrm{kg/m^3}$". Molar values, i.e., intensive functions, are denoted by the subscript m, e.g., $C_{\mathrm{sat,m}}$, whereas extensive functions do not have the subscript. In addition, since thermodynamic values are pressure dependent they are reported in terms of a standard pressure, p°, which in this report is 101.325 kPa (the standard atmosphere in the days before SI units).

M = molar mass in $\mathrm{g\cdot mol^{-1}}$

T = temperature in Kelvin

p = pressure in Pascals (Pa)

ρ = density in $\mathrm{kg\cdot m^{-3}}$

$\Delta_c U^{\circ}_m$ = molar energy of combustion and $\Delta_c U^{\circ}_m/M$ = energy of combustion per gram

$\Delta_c H^{\circ}_m$ = molar enthalpy of combustion

$\Delta_f H^{\circ}_m$ = molar enthalpy of formation

$\Delta_r H^{\circ}_m$ = molar enthalpy of reaction

$\Delta_c^l H_m$ = molar enthalpy of fusion, hence the subscript c (for crystalline solid) and superscript l (for liquid)

$\Delta_l^g H_m$ = molar enthalpy of vaporization, hence the subscript l (for liquid) and superscript g (for gas)

$\Delta_c^g H_m$ = molar enthalpy of sublimation, hence the subscript c (for crystalline solid) and superscript g (for gas)

$\Delta_l^g V_m$ = the change in molar volume going from the liquid to the real vapor

$C_{V,m}$ = molar heat capacity at constant volume

$C_{p,m}$ = molar heat capacity at constant pressure

$C_{\mathrm{sat,m}}$ = molar heat capacity at saturated pressure

μ = chemical potential

n = number of moles of substance

V_x = volume of d.s.c. cell at a temperature T/K.

C_x^{II} = two-phase heat capacity at cell volume V_x

C_V^{II} = two-phase heat capacity at constant volume

C_V^{II} ($\rho = \rho_{sat}$) = two-phase heat capacity along the saturation line

V_l = molar volume of the liquid

T_c = critical temperature

p_c = critical pressure

ρ_c = critical density

T_r = reduced temperature = T/T_c

p_r = reduced pressure = p/p_c

ρ_r = reduced density = ρ/ρ_c

ρ_{cs} = density calculated using extended corresponding states

lg = $\log_{10}$

ω = acentric factor = $[-\lg (p_X/p_c) - 1.000]$ where p_X is the vapor pressure at $T_r = 0.700$.

To avoid listing units in the heat-capacity measurement tables, the heat capacities are reported as divided by the gas constant R. Units of time are s (seconds) or h (hours).

1. INTRODUCTION

This research was funded jointly by the U. S. Department of Energy (DOE) through the Office of Fossil Energy's Advanced Exploratory Research program and the Design Institute for Physical Property Data (DIPPR)* of the American Institute of Chemical Engineers through some of its member industrial organizations. The work performed in the third year of this project, (DIPPR Research Project 871: Determination of Pure Compound Ideal-Gas Enthalpies of Formation), represents the outcome of a meeting in late 1988, and subsequent communications, in which representatives of the DOE Bartlesville Project Office, the Design Institute for Physical Property Data (DIPPR), and the National Institute for Petroleum and Energy Research (NIPER) agreed on a list of compounds for which the determination of the enthalpy of formation in the ideal-gas state would be of benefit to all the participants.

Research programs funded by DOE Fossil Energy at NIPER share a common goal: the accurate estimation of both the thermochemical and thermophysical properties for a range of organic compounds which are important in the processing of alternate fuel sources. Our research has shown that there are a number of key "small" organic compounds for which thermochemical and thermophysical properties are incomplete, in question, or just completely unknown. Data on these compounds will greatly enhance the application of group-contribution methodology (1,2)** as a property-estimation tool. In particular, the determination of the ideal-gas enthalpies of formation of a series of simple ring systems is a necessary forerunner to the development of a scheme for the accurate estimation of data for large molecules which contain these structural entities.

DIPPR's goal is to develop, organize, maintain, and make available reliable physical, thermodynamic, and transport property data for industrially important chemical compounds. Work is in progress compiling data on >1000 compounds important to industry. Where no data exist, estimation is attempted. These estimations require a strong base of accurate and precise data on basic molecular structures.

The evaluation of chemical plant safety has never been as important as it is today. The ideal-gas enthalpy of formation is the thermodynamic property most needed for evaluation of the energy hazard potential of an organic compound. A subcommittee of ASTM E27 has written the computer program CHETAH (Chemical Thermodynamic and Energy Release Evaluation) which estimates gas–phase thermochemical data for organic

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* DIPPR was formed in 1978 under the auspices of the American Institute of Chemical Engineers (AIChE), and consists of 45 industrial organizations and several government agencies.

** Underlined numbers in parentheses refer to items in the references at the end of the text.

materials using a second-order group-contribution method. The second-order group-contribution methodology for the calculation of thermodynamic properties has been outlined in detail by Benson (1). However, this text lacks parameters for a number of important groups and correction terms for several important ring structures. Parameters for some structural groups were derived from data which have since been shown to be incorrect. In the absence of data, application of the methodology for the estimation of thermochemical properties for some important organic compound types is impossible.

Whereas the condensed–phase enthalpy of formation of a compound is of greatest interest in the calculation of energy balances for a given chemical process, the enthalpy of formation for the ideal–gas state is of greatest interest in the general case, where the answer can be used to derive a group parameter or correction factor. In the latter case, this single value can give sufficient information to enable estimations for a large group of compounds containing that molecular entity.

In summary, the objective of this project is to expand the group-additivity method of calculation of thermodynamic properties by determining thermochemical data on compounds containing unique groups or atomic environments.

In the third year of the project, eight compounds were chosen for experimental studies. These compounds and their molecular structures are listed in Table 1.[§] The derivation of ideal-gas standard enthalpies of formation for each of the compounds required experimental measurements in addition to the determination of the standard enthalpies of combustion. A listing of the required auxiliary measurements for each of the compounds is also given in Table 1.

The purity of the sample employed in a measurement of a thermodynamic property can significantly affect the accuracy of the measurement. The degree of inaccuracy introduced by the presence of impurities depends on a number of factors. In the case of the measurement of enthalpies of combustion, the presence of small amounts (less than 0.1 percent) of isomeric impurities usually will not have a significant effect on the result. However, this rule of thumb must be used with care, especially if the major impurity is an isomer with increased stability due to resonance or instability due to steric interactions.

[§] All tables appear at the end of this report.

2. EXPERIMENTAL

MATERIALS

To minimize errors due to impurities, care was taken to ensure only samples of high purity (>99.9 mole percent purity) were subjected to the calorimetric measurements. With the exceptions of naphthalene-2,6-dicarboxylic acid and naphthalene-2,6-dicarboxylic acid dimethyl ester all compounds were purchased from Aldrich Chemical Company. Gas-liquid chromatographic (glc) analyses on the purchased samples gave an average purity of 99.8 mole percent. The compounds were purified by the Oklahoma State University Synthesis and Purification Group under the direction of Professor E. J. Eisenbraun. Glc analyses of the calorimetric samples gave purities of at least 99.95 mole percent for each compound. The samples of naphthalene-2,6-dicarboxylic acid and naphthalene-2,6-dicarboxylic acid dimethyl ester were supplied (purity >99.95 mole percent) by an industrial participant in the project. The high purity of each calorimetric sample was confirmed subsequently by the percentage CO_2 recoveries in the combustion calorimetric measurements, the small differences between the boiling and condensation temperatures in the ebulliometric vapor-pressure measurements, and in the enthalpy-of-fusion measurements in the d.s.c. studies (all of which are described in detail in this report).

All transfers of the calorimetric samples were done under nitrogen, helium, or by vacuum distillation. The water used as a reference material in the ebulliometric vapor-pressure measurements was deionized and distilled from potassium permanganate. The n-decane used as a reference material for the ebulliometric measurements was purified by urea complexation, two recrystallizations of the complex, decomposition of the complex with water, extraction with ether, drying with $MgSO_4$, and distillation at 337 K and 1 kPa pressure. Glc analysis of the n-decane sample failed to show any impurity peaks.

PHYSICAL CONSTANTS

Molar values are reported in terms of the 1981 relative atomic masses (3) and the gas constant, $R = 8.31451\ J \cdot K^{-1} \cdot mol^{-1}$, adopted by CODATA (4). The platinum resistance thermometers used in these measurements were calibrated by comparison with standard thermometers whose constants were determined at the National Institute for Standards and Technology (NIST), formerly the National Bureau of Standards (NBS). All temperatures are reported in terms of the IPTS-68 (5). Measurements of mass, time, electric resistance, and potential difference were made in terms of standards traceable to calibrations at NIST.

COMBUSTION CALORIMETRY

The apparatus and experimental procedures used in the combustion calorimetry of organic C,H,N,O compounds at the National Institute for Petroleum and Energy Research have been described (6-9). (The combustion calorimetry of tetraethylsilane is a special case and details follow in the next section.) A rotating-bomb calorimeter (laboratory designation BMR II) (10) and a platinum-lined bomb (laboratory designation Pt-3b) (11) with an internal volume of 0.3934 dm^3 were used without rotation. Each experiment was started at 296.15 K and, by judicious choice of sample and auxiliary masses, completed very close to 298.15 K. Flexible borosilicate-glass ampoules (6,12) were used to confine the butan-2-ol sample.

NBS benzoic acid (sample 39i) was used for calibration of the calorimeter; its specific energy of combustion is $-(26434.0\pm3.0)$ $J\cdot g^{-1}$ under certificate conditions. Conversion to standard states (13) gives $-(26413.7\pm3.0)$ $J\cdot g^{-1}$ for $\Delta_c U^o_m/M$, the standard specific energy of the idealized combustion reaction. The combustion measurements were performed in two separate series. Calibration experiments were interspersed with each series of measurements. Nitrogen oxides were not formed in the calibration experiments due to the high purity of the oxygen used and preliminary bomb flushing. The energy equivalent of the calorimeter, ε(calor), obtained for each calibration series was (16768.3 ± 0.4) $J\cdot K^{-1}$ (mean and standard deviation of the mean) for the butan-2-ol, tetradecan-1-ol, hexan-1,6-diol, methacrylamide, and benzoyl formic acid measurements, and (16768.4 ± 0.6) $J\cdot K^{-1}$ for the naphthalene-2,6-dicarboxylic acid and naphthalene-2,6-dicarboxylic acid dimethyl ester measurements.

The auxiliary oil (laboratory designation TKL66) had the empirical formula $CH_{1.913}$. For this material, $\Delta_c U^o_m/M$ was $-(46042.5\pm1.8)$ $J\cdot g^{-1}$(mean and standard deviation). For the cotton fuse, empirical formula $CH_{1.774}O_{0.887}$, $\Delta_c U^o_m/M$ was -16945 $J\cdot g.^{-1}$ Information necessary for reducing apparent mass measured in air to mass, converting the energy of the actual bomb process to that of the isothermal process, and reducing to standard states (13) is given in Table 2. Values of density reported in Table 2 were measured in this laboratory, either from measurements of volumes of the ampoules used in the combustion calorimetry, and their enclosed sample masses, for the liquid, butan-2-ol, or from the dimensions of a pellet of known mass for the remaining compounds which were crystalline solids at 298.15 K. Values of the heat capacity of each sample at 298.15 K were measured using a differential scanning calorimeter as described later.

Nitric acid, formed during the nitrogen-containing compound (methacrylamide) combustions, was determined by titration with standard sodium hydroxide (14). Carbon dioxide was also recovered from the combustion products of each experiment. Anhydrous lithium hydroxide was used as adsorbent (7). The combustion products were checked for unburned carbon and other products of incomplete combustion, but none was detected. Summaries of the carbon dioxide recoveries for each calibration series and the corresponding compound energy determinations are listed in Table 3.

TETRAETHYLSILANE COMBUSTION MEASUREMENTS

The rotating-bomb procedure for the combustion of silicon compounds in oxygen using a fluorine auxiliary to promote the combustion and form a well-defined final solution of fluorosilicic acid in excess hydrofluoric acid was first devised by Good et al. (15). The calorimetric procedure devised by Good et al. was used in the study of tetraethylsilane reported here. Benzotrifluoride was selected as the fluorine-containing solvent for tetraethylsilane because of availability and previous energy-of-combustion determination in the laboratory (15). To mix accurately weighed amounts of the two volatile liquids the tetraethylsilane was first sealed in a small container of polyester film that also contained a piece of platinum with a serrated edge. This container then was sealed with the benzotrifluoride in a larger container of polyester film. By weighing at appropriate stages, the masses of tetraethylsilane, benzotrifluoride, polyester film, and platinum were determined individually. The two liquids were mixed intimately by rupturing the inner container with the platinum and manipulating the outer container.

For the benzotrifluoride, molecular formula $C_7H_5F_3$, $\Delta_c U^o_m/M$ was determined previously (15) $-(23051.4\pm1.7)\mathrm{J\cdot g^{-1}}$. The value for $\Delta_c U^o_m/M$ obtained for the polyester film, empirical formula $C_{10}H_8O_4$, was a function of the relative humidity (RH) in the laboratory during weighings (16):

$$\{(\Delta_c U^o_m/M)/(\mathrm{J\cdot g^{-1}})\} = -22912.0 - 1.0560(\mathrm{RH}) \ . \qquad (1)$$

Auxiliary information, necessary for reducing weights measured in air to masses, converting the energy of the actual bomb process to that of the isothermal process, and reducing to standard states (15,17), was taken from reference 15 for all the materials used except tetraethylsilane. For tetraethylsilane the values used are reported in Table 2.

Comparison experiments (17) were used to minimize errors from inexact reduction to standard states caused by a lack of values necessary to correct for such effects as the solubility and enthalpy of solution of CO_2 in solutions of HF and H_2SiF_6. In the comparison experiments the sample burned was the thermochemical standard benzoic acid. The amount of benzoic acid used was selected so that the energy evolved and the CO_2 produced in the comparison experiment were nearly the same as in the companion combustion experiment. The bomb initially contained an aqueous mixture of HF and H_2SiF_6, which upon dilution with the water formed by the combustion of the benzoic acid, gave a solution of nearly the same amount and concentration as in the combustion experiment.

EBULLIOMETRIC VAPOR-PRESSURE MEASUREMENTS

The essential features of the ebulliometric equipment and procedures for vapor-pressure measurements are described in the literature (18-20). The ebulliometers were used to reflux the substance under study with a standard of known vapor pressure under a common helium atmosphere. The boiling and condensation temperatures of the two substances were determined, and the vapor pressure was derived using the condensation temperature of the standard (20).

The precision in the temperature measurements for the ebulliometric vapor-pressure studies was 0.001 K. Uncertainties in the pressures are adequately described by:

$$\sigma(p) = (0.001) \{ (dp_{ref}/dT)^2 + (dp_{\Xi}/dT)^2 \}^{1/2} , \qquad (2)$$

where p_{ref} is the vapor pressure of the reference substance and p_{Ξ} is the vapor pressure of the sample under study. Values of dp_{ref}/dT for the reference substances were calculated from fits of the Antoine equation (21) to vapor pressures of the reference materials (decane and water) reported in reference 20.

INCLINED PISTON VAPOR-PRESSURE MEASUREMENTS.

The equipment for these measurements has been described by Douslin and McCullough, (22) and Douslin and Osborn (23). Recent revisions to the equipment and procedures have been reported (24). The low pressure range of the inclined-piston measurements, 10 to 3500 Pa, necessitated diligent outgassing of the sample prior to introduction into the apparatus. Also, prior to the sample introduction, all parts of the cell in contact with the sample were baked at 623 K under high vacuum ($< 10^{-4}$ Pa). The thoroughly outgassed samples were placed in the apparatus, and additional outgassing was performed prior to commencing measurements. Finally, prior to each measurement, a small amount of sample was pumped off. Measurements were made as a function of time to extrapolate the pressure to the time when the pumping valve was closed; i.e., to the time when insignificant amounts of light gas had leaked into the system or diffused out of the sample.

Uncertainties in the pressures determined with the inclined-piston apparatus, on the basis of estimated precision of measuring the mass, area, and angle of inclination of the piston, are adequately described by the expression:

$$\sigma(p) = 1.5\times10^{-4}\,p + 0.2\ \text{Pa}. \qquad (3)$$

The uncertainties in the temperatures are 0.001 K.

DIFFERENTIAL SCANNING CALORIMETRY

The technique and methodology used in the differential scanning calorimetric (d.s.c.) measurement has been outlined in references 25 through 27. The major difference between our measurement technique and that used by Mraw et al. is the substitution of specially designed cells (28) for the aluminum "volatile sample cells." These cells, designed and manufactured at NIPER, are made of 17-4 PH stainless steel and can withstand both high pressures (to 7.6 MPa) and high temperatures (to 900 K). The d.s.c. was used to determine the enthalpies of fusion and heat capacities of each compound (except butan-2-ol) over a range of temperature. In normal operation (26), correction is made for the enthalpy involved in the vaporization of small amounts of the sample under study into the vapor space of the sealed cells.

The theoretical background for the determination of heat capacities at vapor-saturation pressure, $C_{\mathrm{sat,m}}$, with results obtained with a d.s.c. has been described (28,29). If two phases are present and the liquid is a pure substance, then the vapor pressure p and the chemical potential μ are independent of the amount of substance n and the cell volume V_x, and are equal to p_{sat} and μ_{sat}. The two-phase heat capacities at cell volume V_x, $C^{\mathrm{II}}_{x,\mathrm{m}}$, can be expressed in terms of the temperature derivatives of these quantities:

$$n\,C^{\mathrm{II}}_{x,\mathrm{m}}/T = -n(\delta^2\mu/\delta T^2)_{\mathrm{sat}} + V_x\,(\delta^2 p/\delta T^2)_{\mathrm{sat}} + \{(\delta V_x/\delta T)_x\,(\delta p/\delta T)_{\mathrm{sat}}\}. \qquad (4)$$

The third term on the right-hand side of equation (4) includes the thermal expansion of the cell. In this research the thermal expansion of the cells was expressed as:

$$V_x(T)\,/\,V_x(298.15\ \text{K}) = 1 + ay + by^2, \qquad (5)$$

where, $y = (T - 298.15)$ K, $a = 3.216 \times 10^{-5}\ \text{K}^{-1}$, and $b = 5.4 \times 10^{-8}\ \text{K}^{-2}$.

$(\delta p/\delta T)_{sat}$ can be calculated based on the vapor pressures measured in this research. Therefore, with a minimum of two different filling levels of the cell $(\delta^2 p/\delta T^2)_{sat}$ and $(\delta^2 \mu/\delta T^2)_{sat}$ can be determined. In practice normally three cell fillings spanning a range of density (0.6 to 1.4 times ρ_c) are used. To obtain the saturation heat capacity $C_{sat,m}$ at vapor pressures greater than 0.1 MPa, the limit where the cell is full of liquid is required; i.e., $(n/V_x) = \{1/V_m(l)\}$ where $V_m(l)$ is the molar volume of the liquid:

$$\lim_{(n/V_x) \to \{1/V_m(l)\}} (n C^{II}_{V,m}/T) = V_m(l)(\delta^2 p/\delta T^2)_{sat} - n(\delta^2 \mu/\delta T^2)_{sat}. \qquad (6)$$

$C_{sat,m}$ is obtained using the expression:

$$\lim_{(n/V_x) \to \{1/V_m(l)\}} (n C^{II}_{V,m}) = n[C_{sat,m} - \{T(\delta p/\delta T)_{sat}\,(dV_m(l)/dT)\}]. \qquad (7)$$

Thus, reliable liquid density values are also required to determine $C_{sat,m}$.

3. RESULTS

A typical combustion experiment for each C,H,N,O compound studied is summarized in Table 4. It is impractical to list summaries for each combustion, but values of $\Delta_c U^o_m/M$ for all the experiments are reported in Table 5. Values of $\Delta_c U^o_m/M$ in Tables 4 and 5 for the C,H,N,O compounds refer to the general reaction:

$$C_aH_bN_cO_d \text{ (cr or l)} + \left(a + \frac{b}{4} - \frac{d}{2}\right)O_2 \text{ (g)} = a\, CO_2 \text{ (g)} + \frac{b}{2} H_2O \text{ (l)} + \frac{c}{2} N_2 \text{ (g)}. \qquad (8)$$

For the compounds, hexan-1,6-diol, methacrylamide, and naphthalene-2,6-dicarboxylic acid the values of $\Delta_c U^o_m/M$ refer to unit mass of sample derived from the corresponding carbon dioxide analysis of the combustion products. Table 6 gives derived values of the standard molar energy of combustion $\Delta_c U^o_m$; the standard molar enthalpy of combustion $\Delta_c H^o_m$; and the standard molar enthalpy of formation $\Delta_f H^o_m$ for the compounds studied. Values of $\Delta_c U^o_m$ and $\Delta_c H^o_m$ for the C,H,N,O compounds refer to Equation **8**. The corresponding values of $\Delta_f H^o_m$ refer to the reaction:

$$aC\text{(cr, graphite)} + \frac{b}{2} H_2 \text{ (g)} + \frac{c}{2} N_2 \text{ (g)} + \frac{d}{2} O_2 \text{ (g)} = C_aH_bN_cO_d \text{ (cr or l)}. \qquad (9)$$

Uncertainties given in Table 6 are the "uncertainty interval" (30). The enthalpies of formation of CO_2(g) and H_2O(l) were taken to be −(393.51 ± 0.13) and −(285.830 ± 0.042) kJ·mol^{-1}, respectively, as assigned by CODATA (31).

Results from a typical combustion and its companion comparison experiment for tetraethylsilane are summarized in Table 4A. Six successful combustions and corresponding comparison experiments were made and the results are summarized in Table 5. The measured values for the energy of combustion and subsequent solution of the silicon dioxide or silicon tetrafluoride formed can, on average, be represented by the following equation:

$$\begin{aligned} &C_8H_{20}Si\ (l) + 14\ O_2\ (g) + 15.15_5\ HF{\cdot}413H_2O \rightarrow \\ &\qquad 8CO_2\ (g) + H_2SiF_6{\cdot}9.15_5HF{\cdot}425H_2O. \end{aligned} \qquad (10)$$

The thermochemical cycle used to calculate the enthalpy of formation of tetraethylsilane is given in Table 6A. The footnote to Table 6A lists the sources of the auxiliary thermochemical values (31-33) required to determine the values reported in Table 6.

Measured vapor pressures for butan-2-ol; tetradecan-1-ol; hexan-1,6-diol; benzoyl formic acid; naphthalene-2,6-dicarboxylic acid dimethyl ester; and tetraethylsilane are listed in Table 7. Following previous practice (19), the results obtained in the ebulliometric measurements were adjusted to common pressures. The common pressures, the condensation temperatures, and the difference between the condensation and boiling temperatures for the samples are reported. The small differences between the boiling and condensation temperatures in the ebulliometric measurements indicated correct operation of the equipment and the high purity of the samples studied. Inclined-piston vapor-pressure measurements for naphthalene-2,6-dicarboxylic acid dimethyl ester and benzoyl formic acid are also listed in Table 7. For the ester the inclined-piston values extend the range of measured values down to 465 K. For benzoyl formic acid, sample decomposition at 429 K, (p>3.2 kPa), (see below) prevented determination of ebulliometric vapor pressures. Liquid-phase inclined-piston vapor-pressure measurements are reported in the temperature range 338.9 K (melting point) to 420 K.

The difference between the boiling and condensation temperatures (ΔT) for tetradecan-1-ol increased significantly above 569 K (see Table 7). An attempt was made to make a measurement at 169 kPa (593.5 K), but ΔT started at approximately 0.06 K and rapidly increased by several tenths of a degree. This phenomenon is indicative of sample decomposition. Similar behavior was observed for naphthalene-2,6-dicarboxylic acid dimethyl ester, where at 641.4 K (84 kPa) ΔT started at approximately 0.08 K and rapidly increased to 0.5 K.

All attempts to measure the vapor pressure of naphthalene-2,6-dicarboxylic acid in the solid phase were unsuccessful. At 523 K (the upper temperature limit of the apparatus at present) the vapor pressure was below the lower detection limit of the inclined piston, 10 Pa. The sample decomposed with a large pressure build-up before melting (695 K) preventing any attempt at obtaining liquid-phase measurements.

Previous studies by Scott and Osborn (34) have shown that the Cox equation (35) can adequately represent measured vapor pressures from the triple-point pressure to 0.3 MPa. The Cox equation in the form:

$$\ln(p/p_{\mathrm{ref}}) = \{1 - (T_{\mathrm{ref}}/T)\}\exp\{A + B(T/\mathrm{K}) + C(T/\mathrm{K})^2\}\ , \qquad (11)$$

was fit to the experimental vapor pressures with p_{ref} being chosen to be 101.325 kPa so that T_{ref} was the normal boiling temperature. In those fits, the sums of the weighted squares in the following function were minimized:

$$\Delta = \ln\{\ln(p/p_{\mathrm{ref}})/(1 - T_{\mathrm{ref}}/T)\} - A - B(T/\mathrm{K}) - C(T/\mathrm{K})^2\ . \qquad (12)$$

The weighting factors W are the reciprocals of the variance in Δ derived from the propagation of errors in the temperature and pressure determinations. W is defined as:

$$W = [(\delta\Delta/\delta T)_p^2\ \{\sigma(T)\}^2 + (\delta\Delta/\delta p)_T^2\ \{\sigma(p)\}^2\ ]^{-1}. \qquad (13)$$

Parameters derived from the fits are given in Table 8. For benzoyl formic acid the normal boiling point was fixed at 532.0 K. Details of the Cox equation fits are given in Table 7.

Enthalpies of vaporization $\Delta_l^g H_m$ were derived from the Cox equation fits using the Clapeyron equation:

$$dp/dT = \Delta_l^g H_m\ /\ (\ T\Delta_l^g V_m)\ , \qquad (14)$$

where $\Delta_l^g V_m$ is the increase in molar volume from the liquid to the real vapor. Estimates of second virial coefficients were made with the extended corresponding-states equation of Pitzer and Curl (36). Liquid-phase densities were also derived from corresponding-states using the formulation of Hales and Townsend (37):

$$(\rho/\rho_c) = 1.0 + 0.85\{1.0 - (T/T_c)\} + (1.692 + 0.986\omega)\{1.0 - (T/T_c)\}^{1/3}. \qquad (15)$$

Third virial coefficients were estimated with the corresponding-states method of Orbey and Vera (38). This formulation for the third virial coefficient was applied successfully in analyses of the thermodynamic properties of benzene, toluene, and decane (39). The third virial coefficient is required for accurate calculation of the gas volume for pressures greater than one bar. Parameters (40,41) used to estimate the second and third virial coefficients for each compound are listed in Table 9A. Derived enthalpies of vaporization and entropies of compression are reported in Table 9.

Table 10 lists the experimental two-phase heat capacities $C^{II}_{x,m}$ determined by d.s.c. for tetradecan-1-ol, hexan-1,6-diol, benzoyl formic acid, naphthalene-2,6-dicarboxylic acid, naphthalene-2,6-dicarboxylic acid dimethyl ester, and tetraethylsilane obtained for the given cell fillings. Heat-capacities were determined at 20-K intervals with a heating rate of $0.083\ \mathrm{K \cdot s^{-1}}$ and a 120 s equilibration period between heats. For each compound the upper temperature bound of the measurements was set by sample decomposition.

For tetraethylsilane sample decomposition was greatly reduced by employing a single continuous heat at a heating rate of $0.333\ \mathrm{K \cdot s^{-1}}$, and the abrupt decrease in heat capacity associated with the conversion from the two-phases to one-phase was observed. Temperatures at which conversion to the single phase occurred were measured for five cell fillings. Table 11 reports the density, obtained from the mass of sample and the cell volume calculated with equation **5**, and the measured temperatures at which conversion to a single phase was observed. A critical temperature of (606±1) K and a corresponding critical density of $(246 \pm 5)\ \mathrm{kg \cdot m^{-3}}$ were derived graphically for tetraethylsilane with these results, as seen in figure **1**. Results of measurements on benzene and decane performed as "proof-of-concept measurements" for these procedures have been reported (29). The rapid heating method was used previously for critical temperature and critical density determinations for dibenzothiophene (42).

The critical pressure for tetraethylsilane was not measured directly, but was estimated by means of simultaneous non-linear least-squares fits using the vapor pressures listed in Table 7 and the $C^{II}_{x,m}$ values given in Table 10. $C_{sat,m}$ values were derived using results of the fit and equation (7). Experimental $C^{II}_{x,m}$ were converted to $C^{II}_{v,m}$ values by means of equation (5) for the cell expansion and the vapor-pressure fit described below for $(\delta p/\delta T)_{sat}$. The values of $C^{II}_{v,m}$ were used to derive functions for $(\delta^2 p/\delta T^2)_{sat}$ and $(\delta^2 \mu/\delta T^2)_{sat}$. The Cox equation (35) was used to represent the vapor pressures in the form:

$$\ln(p/p_c) = (1 - 1/T_r)\ \exp\ (A + BT_r + CT_r^2)\ , \qquad (16)$$

with $T_r = T/T_c$, where T_c and p_c are the critical temperature and critical pressure. The critical pressure was included as a variable in the non-linear least-squares analysis.

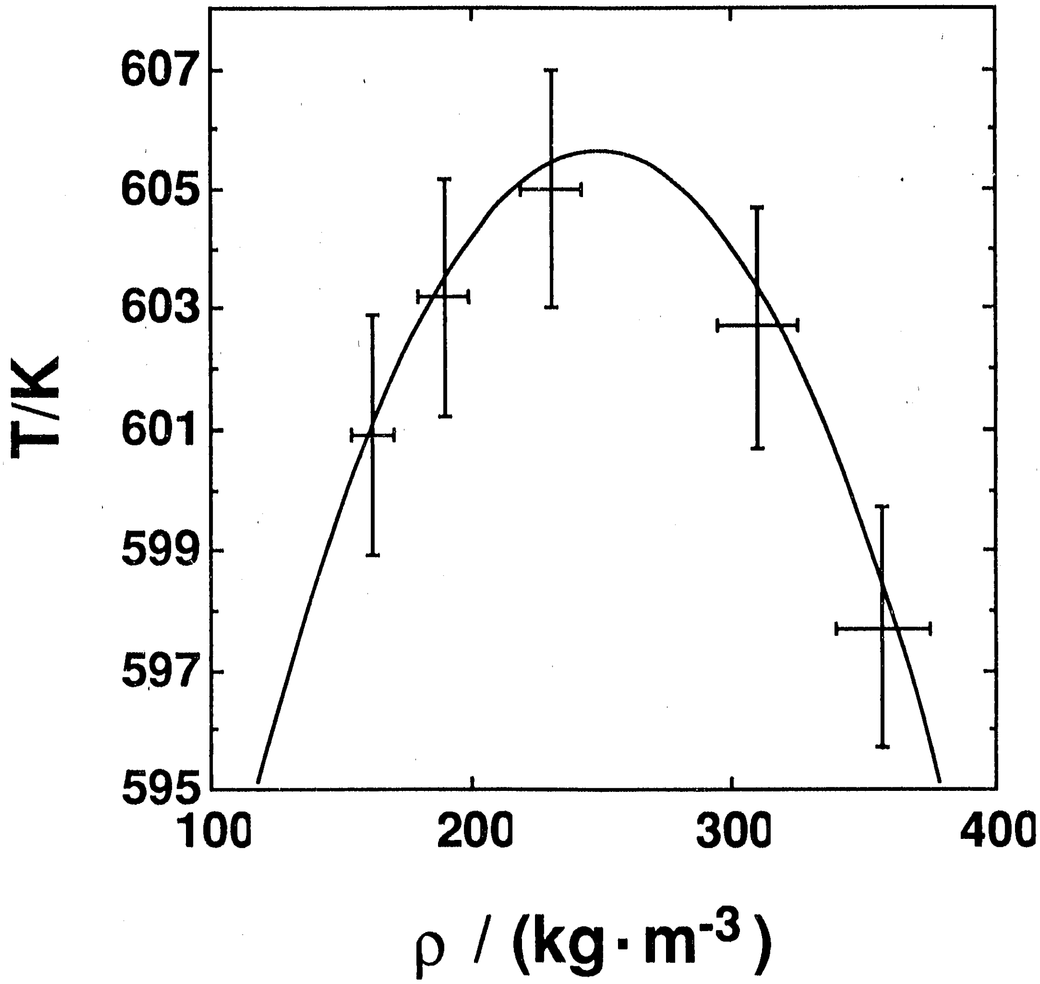


FIGURE 1. Vapor-liquid coexistence region for tetraethylsilane. The crosses span the range of uncertainty.

The functional form chosen for variation of the second derivative of the chemical potential with temperature was:

$$(\delta^2\mu/\delta T^2)_{sat} = \sum_{i=0}^{n} b_i(1 - T/T_c)^i. \tag{17}$$

[For compounds where sufficient information was available to evaluate reliably $(\delta^2\mu/\delta T^2)_{sat}$ {e.g., benzene (43), toluene (44)}, four terms (i.e, expansion to n=3) were required to represent the function. Three terms were used in this research.] In these fits the sum of the weighted squares in the following function was minimized:

$$\Delta = C^{II}_{V,m}/R - \{V_m(l)T/nR\}(\delta^2p/\delta T^2)_{sat} + (T/R)(\delta^2\mu/\delta T^2)_{sat}. \qquad (18)$$

For the vapor-pressure fits, the functional forms of the weighting factors used have been reported (20). Within the heat-capacity results, the weighting factors were proportional to the square of the mass of sample used in the measurements. Table 12 lists the coefficients determined in the non-linear least-squares fit. A weighting factor of 20 was used to increase the relative weights of the vapor-pressure measurements in the fit. The weighting factor reflects the higher precision of the vapor-pressure values relative to the experimental heat capacities.

Values of $C_{sat,m}$ for tetraethylsilane were derived from $C^{II}_{V,m}(\rho=\rho_{sat})$ with densities obtained from equation **15** using $\rho_c = 246\ kg\cdot m^{-3}$, $T_c = 606$ K, and the acentric factor $\omega = 0.401$. The acentric factor is defined as $\{-lg(p/p_c) - 1\}$, where p is the vapor pressure at $T_r = 0.7$ and p_c is the critical pressure. The Cox equation coefficients given in Table 8 were used to calculate p. The results for $C^{II}_{V,m}(\rho = \rho_{sat})/R$ and $C_{sat,m}/R$ are reported in Table 13. The estimated uncertainty in these values is 1 per cent.

By judicious choice of starting temperature, the melting endotherms during the d.s.c. enthalpy measurements occurred in the center of a heating cycle. The measured enthalpies during those particular heating cycles contained the enthalpy of fusion plus enthalpies for raising the solid from the initial temperature to the melting point and for raising the liquid from the melting point to the final temperature. Figure **2** shows the thermochemical cycle used to "correct" the enthalpy of fusion of the compound at its melting point to the corresponding value at the standard temperature of 298.15 K. Details of the derived enthalpies of fusion for tetradecan-1-ol, hexan-1,6-diol, benzoyl formic acid, and naphthalene-2,6-dicarboxylic acid dimethyl ester at their melting points and the corresponding values at 298.15 K are reported in Table 10. Equations (representing the heat capacities for both the liquid and solid phases for each compound) which were used in the "correction" to 298.15 K are also reported in Table 10. [Note the heat-capacity equations should only be used to derive values within the temperature ranges specified in Table 10; extrapolation outside the temperature range will produce erroneous values. As an extreme example, extrapolation of the reported solid-phase heat capacity equation for tetradecan-1-ol by 100 K gives a negative heat capacity.]

$$\begin{tikzcd}
\text{(C) Melting Point} \arrow[r] \arrow[d] & \text{(l) Melting Point} \\
\text{(C) 298.15 K} \arrow[r] & \text{(l) 298.15 K} \arrow[u]
\end{tikzcd}$$

$$\Delta_c^l H_m^o(\text{Melting Point/K}) = \int_{\text{Melting Point}}^{298.15\text{ K}} C_{sat}(c)dT + \Delta_c^l H_m^o(298.15\text{ K}) + \int_{298.15}^{\text{Melting Point}} C_{sat}(l)dT$$

FIGURE 2. Thermochemical cycle relating $\Delta_c^l H_m^o$(298.15 K) to $\Delta_c^l H_m^o$(melting point K).

The sample of methacrylamide polymerized at temperatures greater than 392 K. At 390 K its vapor pressure was 2.38 kPa precluding vapor-pressure measurements in the ebulliometer (pressure range 2 to 270 kPa). Inclined-piston vapor-pressure measurements made in the temperature range 325 K to 390 K are reported in Table 14. Subsequent d.s.c. enthalpy measurements, also reported in Table 14, defined the melting point of the sample as 385.1 K. Hence, the two vapor-pressure measurements at 385 K (due to some premelting) and 390 K, were for the liquid phase. Since the sublimation pressure measurements extended only over a 50 K range it was inappropriate to fit any vapor-pressure equation other than the "simple" Clausius Clapeyron;

$$\ln(p/1\text{kPa}) = A + B/(T/K)\ . \tag{19}$$

Results of the fit are given in Table 14. Values of "A" and "B" in Equation 19 were determined also for the liquid phase with the two experimental values that were obtained before polymerization. The corresponding enthalpies of sublimation and vaporization (calculated from the values of B obtained) at the mid-temperature of the data range are also reported in Table 14. The intersection point of the solid- and liquid-phase vapor-pressure curves was 385.1 K, in excellent agreement with the d.s.c. value for the fusion temperature.

4. DISCUSSION

Table 15 summarizes the thermochemical property measurements and derived ideal-gas standard enthalpies of formation for all the compounds of this study. In this section of the report the results obtained for each compound are discussed and compared with previously available literature values and relevant group-contribution parameters derived.

Butan-2-ol

Butan-2-ol is optically active. The results reported here are for the racemic (R,S) mixture. (±)-Butan-2-ol has been the subject of previous combustion calorimetric (45), vapor-pressure (40,46-49), and heat-capacity studies (50,51). The major reason for the inclusion of the compound in this study was to confirm the previous measurements and solidify our knowledge of the value of the –CH_2– group increment in the alcohol series. Sunner and coworkers (52,53) in papers published in the late 1970's drew attention to the "abnormally" low value for the CH_2 group increment in the alcohols. At that time sufficient uncertainty existed, particularly in the enthalpies of vaporization at 298.15 K, to cloud the picture somewhat.

The energy of combustion for (±)-butan-2-ol reported in this research -35827.4±1.2 $J\cdot g^{-1}$ is in excellent agreement with that obtained by Skinner and Snelson (45) –35828.5±6.2 $J\cdot g^{-1}$ in their study on the four isomeric butyl alcohols. Vapor-pressure measurements made on (±)-butan-2-ol by the research group at the National Physical Laboratory (NPL) at Teddington, Middlesex, England have been reported four times in the literature (40,46-48). Biddiscombe et al. (46) reported values obtained in the temperature range 345 K to 380 K; Ambrose and Townsend (40) reported measurements in the temperature range 422 K to 535.95 K (from 474 kPa to the critical pressure 4194 kPa); Ambrose and Sprake (47) reported measurements made on (±)-butan-2-ol (341 K to 380 K), one of a series of selected alcohols from methanol through hexadecan-1-ol; and the same authors (48) also reported results from an ebulliometric study (307 K to 381 K) on the pure optical isomer (+)-butan-2-ol. Figure 3 compares the above vapor-pressure measurements (except those of Ambrose and Townsend (40) which fall outside the range of the measurements reported here) with those obtained in this research. On average the NPL results are slightly lower than those reported here but the agreement remains excellent (±0.15 percent). The results also confirm the statement of Ambrose and Sprake (48) that the vapor pressure of pure "(+)-butan-2-ol is not significantly different from that of (±)-butan-2-ol." Vapor pressure measurements reported by Brown, Foch, and

Smith (49) (323 K to 373 K, 10.6 kPa to 101.3 kPa) are consistently 0.4 percent greater than values calculated using the Cox equation coefficients given in Table 8.

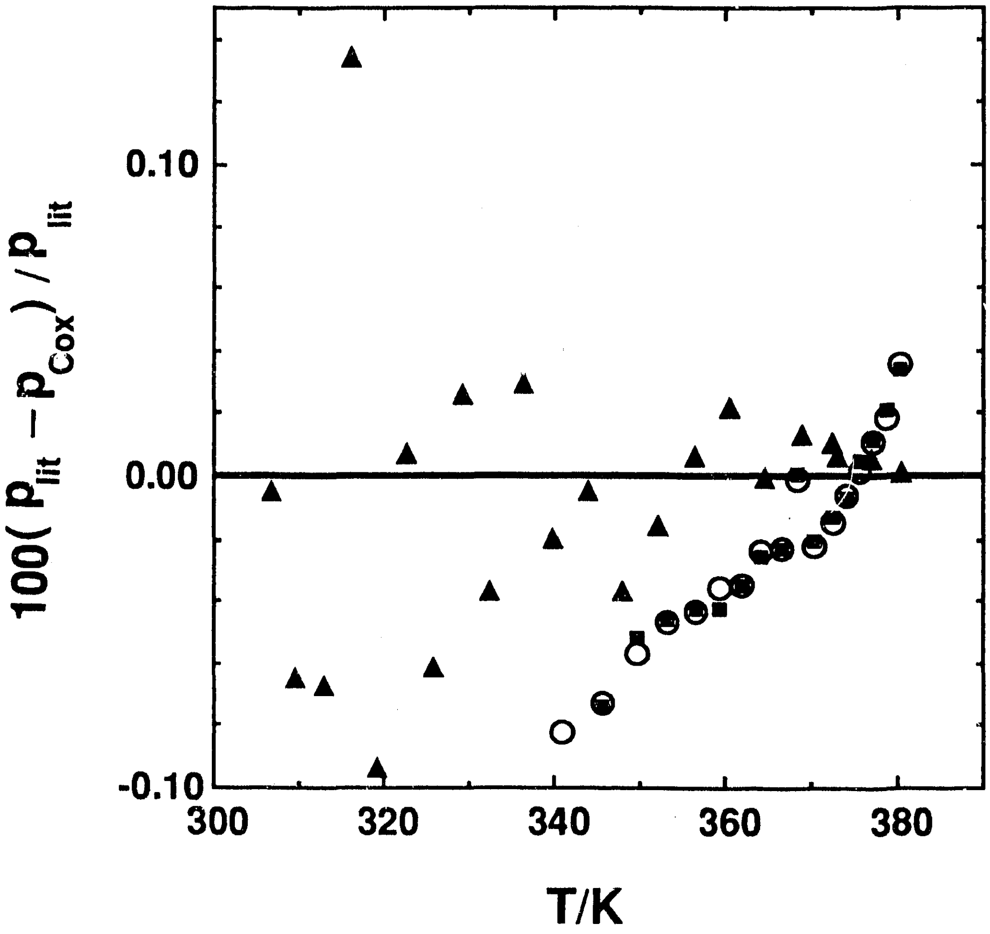


FIGURE 3. Comparison of measured vapor pressures for (±)-butan-2-ol with those obtained previously at NPL. P_{lit} is the literature value of the vapor pressure. ■ Biddiscombe et al. (46); ○ Ambrose and Sprake (47); ▲ Ambrose and Sprake (48).

The derivation of reliable values for the enthalpy of vaporization of (±)-butan-2-ol at temperatures within the range of the vapor-pressure measurements requires accurate values for the difference between the molar volumes of the real gas and the liquid, ($\Delta_l^g V_m$ in equation 14). The method used to calculate values of $\Delta_l^g V_m$ in this research was outlined above and depends on extended corresponding states being applicable over the temperature range under consideration. The estimated second viral coefficients obtained from extended corresponding states were in good agreement (±8 percent) with those measured by Cox (54). Densities for the liquid obtained using equation **15** and the critical constants given in Table 9A are compared with literature values (55-57) in Figure 4. Above 350 K the values reported by Costello and Bowden (55) differ by over 3 percent with those reported by Hales and Ellender (56). The latter agree with those calculated in this research using extended corresponding states to within a few tenths of a percent. Below 350 K, the deviation of extended corresponding states from the experimentally measured densities may be due to the effects of hydrogen bonding. The calculated enthalpies of vaporization of this research are not affected significantly by the uncertainty in the liquid-phase densities.

Figure 5 compares the enthalpies of vaporization derived in this research (Table 9) with values determined experimentally by vaporization calorimetry (51,58,59). With the exception of the single datum point of McCurdy and Laidler (59) the agreement is good, especially above 320 K.

A full discussion of the group parameters used to estimate the ideal-gas enthalpy of formation of (±)-butan-2-ol is given later in this report in the discussion on tetradecan-1-ol. It is, however, worth noting at this stage that the $-CH_2-$ group increment obtained by differencing the enthalpy of formation reported in Table 15 and that for propan-2-ol [as assessed by Pedley, Naylor, and Kirby (60)] is −19.9±0.6 $kJ\cdot mol^{-1}$ compared to the "universal" value of −20.72 $kJ\cdot mol^{-1}$ given by the group-additivity parameters listed in references 1 and 2.

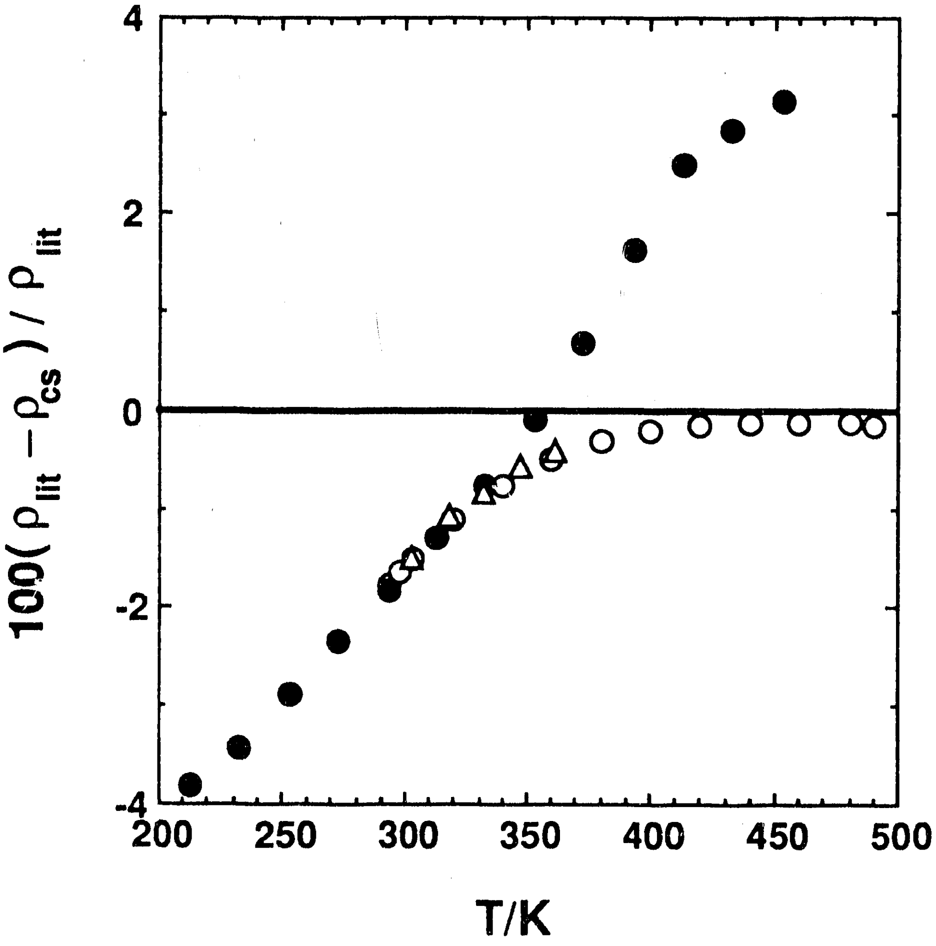


FIGURE 4. Comparison of literature density measurements for (±)-butan-2-ol with those obtained using extended corresponding states. ρ_{cs} = value of the density calculated using equation **15** and the critical properties reported in Table 9A. ● Costello and Bowden; (55); ○ Hales and Ellender (56); △ Thomas and Meatyard (57).

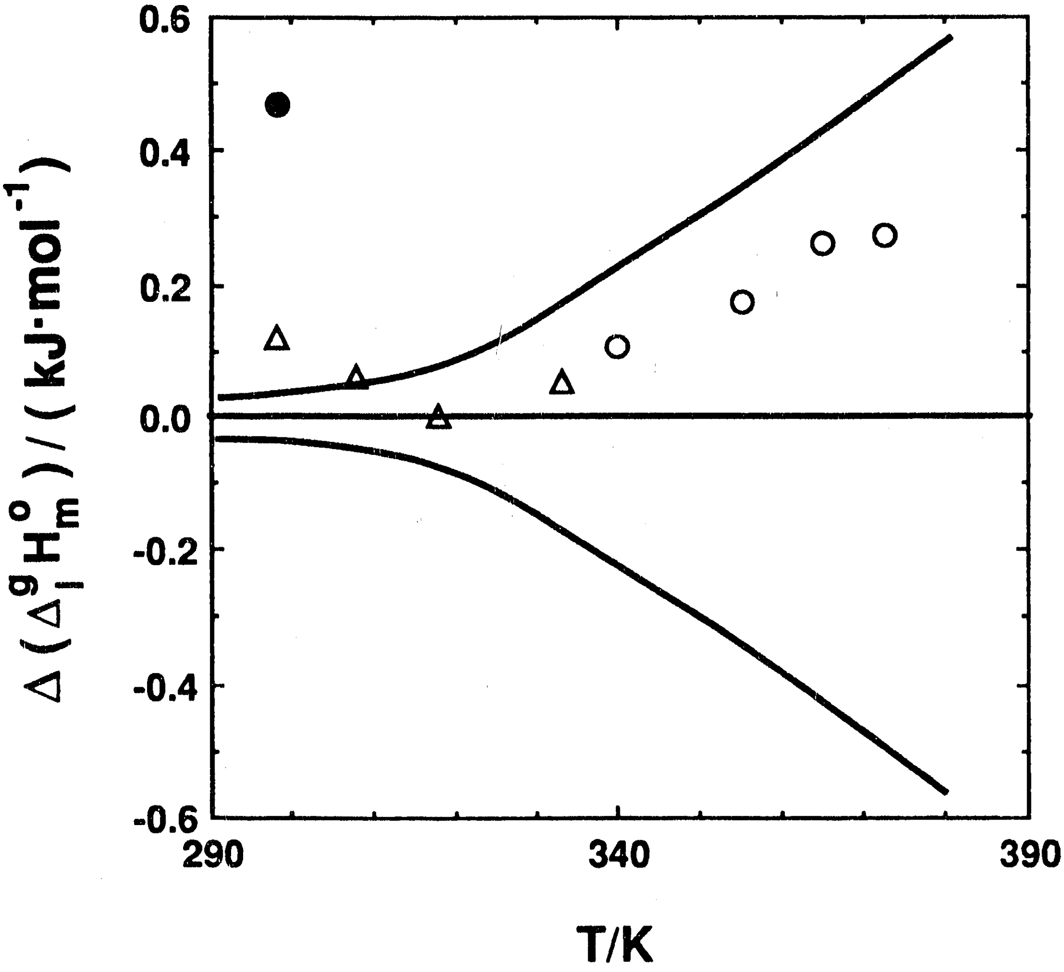


FIGURE 5. Comparison of experimentally measured enthalpies of vaporization for (±)-butan-2-ol with those calculated using the Clapeyron equation. $\Delta(\Delta_l^g H_m^o) = \{\Delta_l^g H_m^o(\text{literature}) - \Delta_l^g H_m^o(\text{this research})\}$. The curves represent the uncertainty limits (approximately two standard deviations) on the enthalpies of vaporization reported in this research. ○ Berkman and McKetta; (51); Δ Polák and Benson (58); ● McCurdy and Laidler (59).

Tetradecan-1-ol

The literature on polymorphism in the higher alkan-1-ols in general and tetradecan-1-ol in particular is large. References 61 through 68 are some examples of studies in this field. Contradictions still exist on the relative stability of the crystal phase present at a given temperature (67,68). The sample of tetradecan-1-ol used in this study exhibited the same properties as that designated as the β form by Mosselman et al. (69).

Mosselman and Decker (70) reported energy of combustion measurements on the C_{12} through the C_{16} alkan-1-ols in which the energy of combustion of tetradecan-1-ol is listed as -9149.6 ± 1.2 $\mathrm{kJ \cdot mol^{-1}}$ for the β form. This is in good agreement with the value -9151.06 ± 1.16 $\mathrm{kJ \cdot mol^{-1}}$ obtained in this research. Mosselman and Decker (70) stated; "Reduction to the vapor phase for the normal primary alkanols as a group is not yet possible, since reliable enthalpies of vaporization are known only for compounds up to and including C_6."

Vapor-pressure measurements on tetradecan-1-ol both above and below its triple point have been reported in the literature by several research groups (71-74). Further discussion of the solid-phase measurements is given later in this report when the enthalpy of sublimation is discussed. The liquid-phase literature data fall into two groups: 1) measurements made close to the triple point (311 K to 350 K); and 2) measurements made at higher temperatures(pressures) in the region 450 K to approximately 600 K. Figures 6 and 7 compare both groups with values obtained using the Cox equation coefficients listed in Table 8.

For the data below 360 K (figure 6) the measured vapor pressures are scattered and, with the exception of one point, are significantly higher than values obtained using the Cox equation coefficients. It must be noted, however, that this represents an appreciable (~100 K) extrapolation and the vapor pressures in this region are small (of the order 0.07 to 4.6 Pa). For the data above 400 K, as shown in Figure 7, with the exception of two points [424.75 K/0.69 kPa (18.3 percent low) and 422.3 K/6.45 kPa (3.6 percent high) not plotted in the figure], the vapor-pressure measurements of Kemme and Kreps (73) are in good agreement with values calculated using the Cox equation coefficients. Ambrose and Walton (74) list values for the critical temperatures, critical pressures, and coefficients for the Wagner equation (75) for the vapor pressures of both the normal alkanes and the alkan-1-ols. The listed coefficients for tetradecan-1-ol were obtained by linear interpolation (see reference 75). The Wagner equation and the coefficients listed by Ambrose and Walton were used to calculate vapor pressures at the temperatures of the measurements reported in this research.

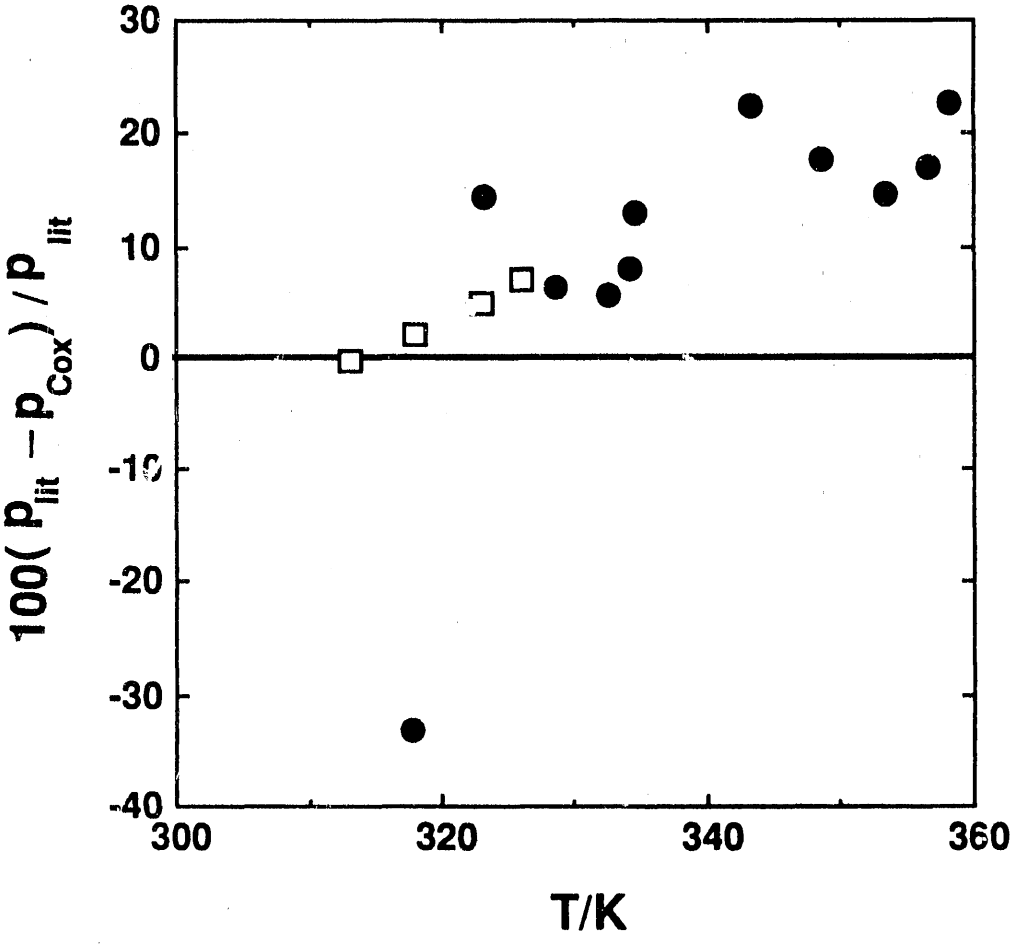


FIGURE 6. Vapor-pressure comparisons for tetradecan-1-ol in the "low" pressure region. Literature vapor-pressure values are compared with those obtained using the Cox equation coefficients listed in Table 8. □; Davies and Kybett (71) ●; Spizzichino (72).

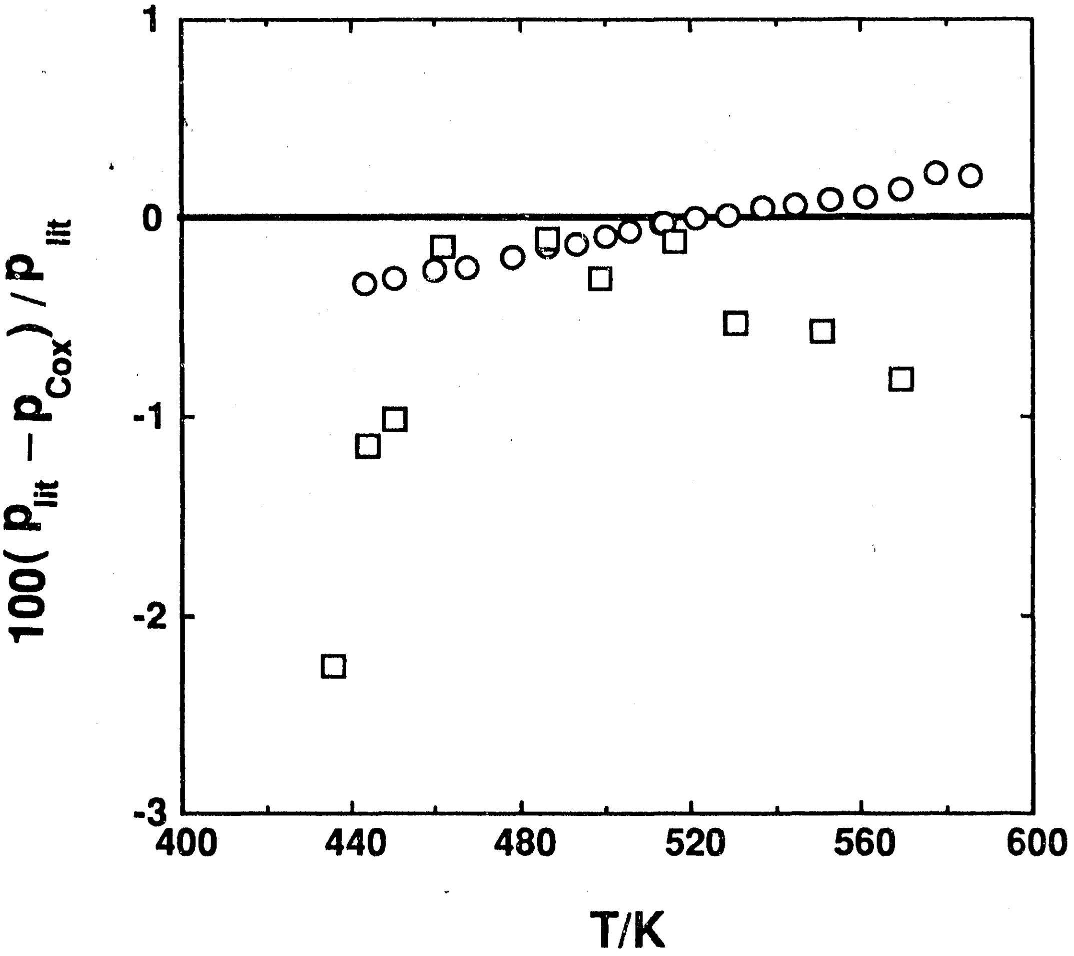


FIGURE 7. Vapor-pressure comparisons for tetradecan-1-ol in the "high" pressure region. Literature vapor-pressure values are compared with those obtained using the Cox equation coefficients listed in Table 8. □; Kemme and Kreps (73) ○; Ambrose and Walton (74).

The percentage deviation between the calculated and observed vapor pressures is shown in figure 7. The maximum deviation is only 0.3 percent for the values derived using the Ambrose and Walton equation! This would seem to attest to the accuracy of the representation of the vapor pressures of the alkan-1-ols derived by Ambrose and Walton.

As noted earlier, the derivation of reliable values for the enthalpy of vaporization within the range of the vapor-pressure measurements requires accurate values for the difference between the molar volumes of the real gas and the liquid, $\Delta_l^g V_m$. The method used to calculate values of $\Delta_l^g V_m$ in this research was outlined above and depends on extended corresponding states being applicable over the temperature range under consideration. Densities for the liquid obtained using equation **15** with the critical constants given in Table 9A are compared with literature values (55,76) in Figure 8. The two literature datasets are in good agreement with each other but those of Matsao and Makita (76) cover only a short temperature range. Over the temperature range 313 K to 573 K the percentage deviations between the observed [Costello and Bowden (55)] and the extended corresponding states values fall on a monotonic curve ranging from +1 percent to −1 percent. Derived enthalpies of vaporization for tetradecan-1-ol are listed in Table 9.

Månnson et al. (77) measured the enthalpy of vaporization at temperatures just above the melting point and, using heat-capacity data from Mosselman et al.(69), corrected the experimental measurements to 298.15 K. They reported a value ($\Delta_l^g H_m^o$ $C_{14}H_{30}O$, 298.15 K) = 102.2±2.3 kJ·mol^{-1} which compares favorably with the value obtained in this research 104.9±1.9 kJ·mol^{-1}. Spizzichino (72) derived an equation to represent the enthalpy of vaporization over the temperature range 313 K to 373 K:

$$\Delta_l^g H_m^o/(\mathrm{kJ \cdot mol^{-1}}) = 174.81 - 0.234\ T\ . \qquad (20)$$

Davis and Kybett (71) derived from their vapor-pressure measurements a value ($\Delta_l^g H_m^o$ $C_{14}H_{30}O$, 320 K) = 104.2±1.7 kJ·mol^{-1} and Kramer (78) reported ($\Delta_l^g H_m^o$ $C_{14}H_{30}O$, 566.2 K) = 66.92 kJ·mol^{-1}. Figure 9 compares the literature values with those derived in this research. No major deviations are apparent except for the value quoted by Kramer.

Since the vapor pressure was below 0.1 MPa over the range of the $C_{x,m}^{II}$ measurements reported in Table 10 no correction for vaporization of the sample into the vapor-space of the d.s.c. cells was made. The saturation heat capacities $C_{sat,m}$ were

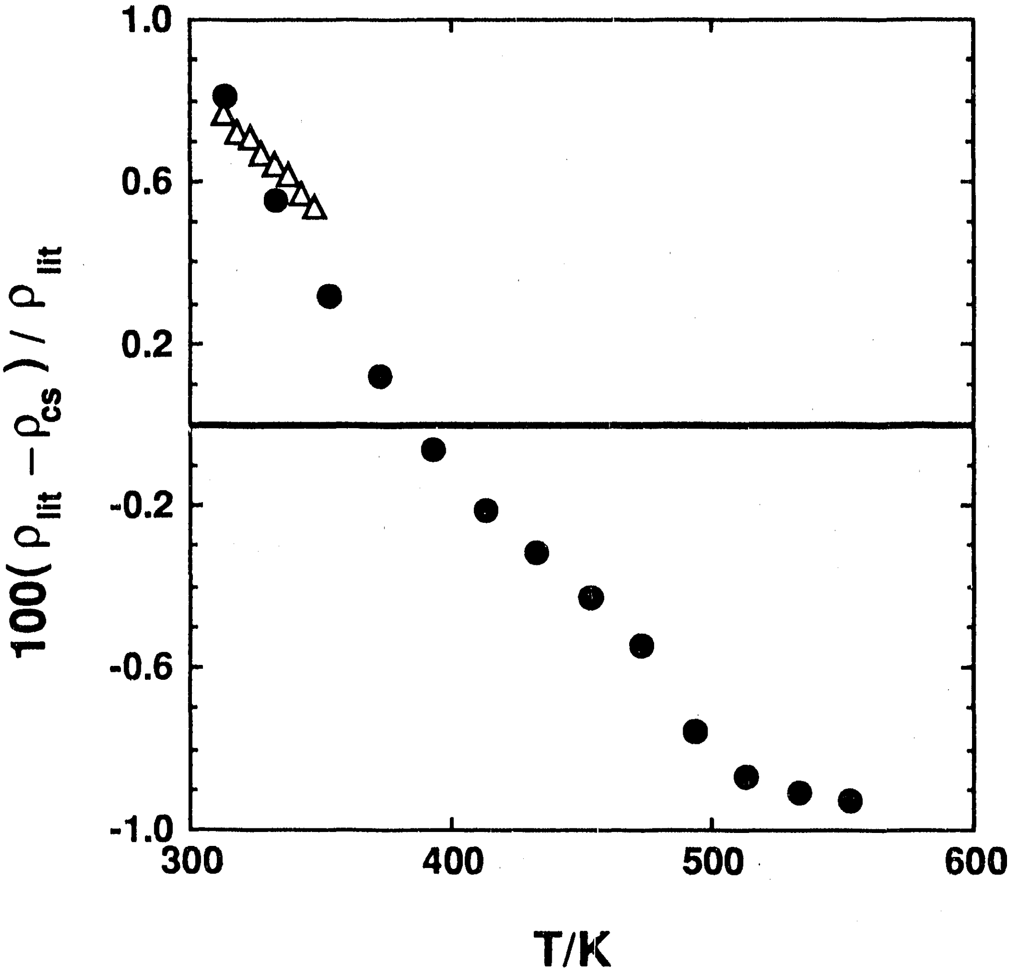


FIGURE 8. Comparison of literature density measurements for tetradecan-1-ol with those obtained by extended corresponding states. ρ_{cs} = value of the density calculated using equation **15** with the critical properties reported in Table 9A. ●; Costello and Bowden; (55); Δ; Matsao and Makita (76).

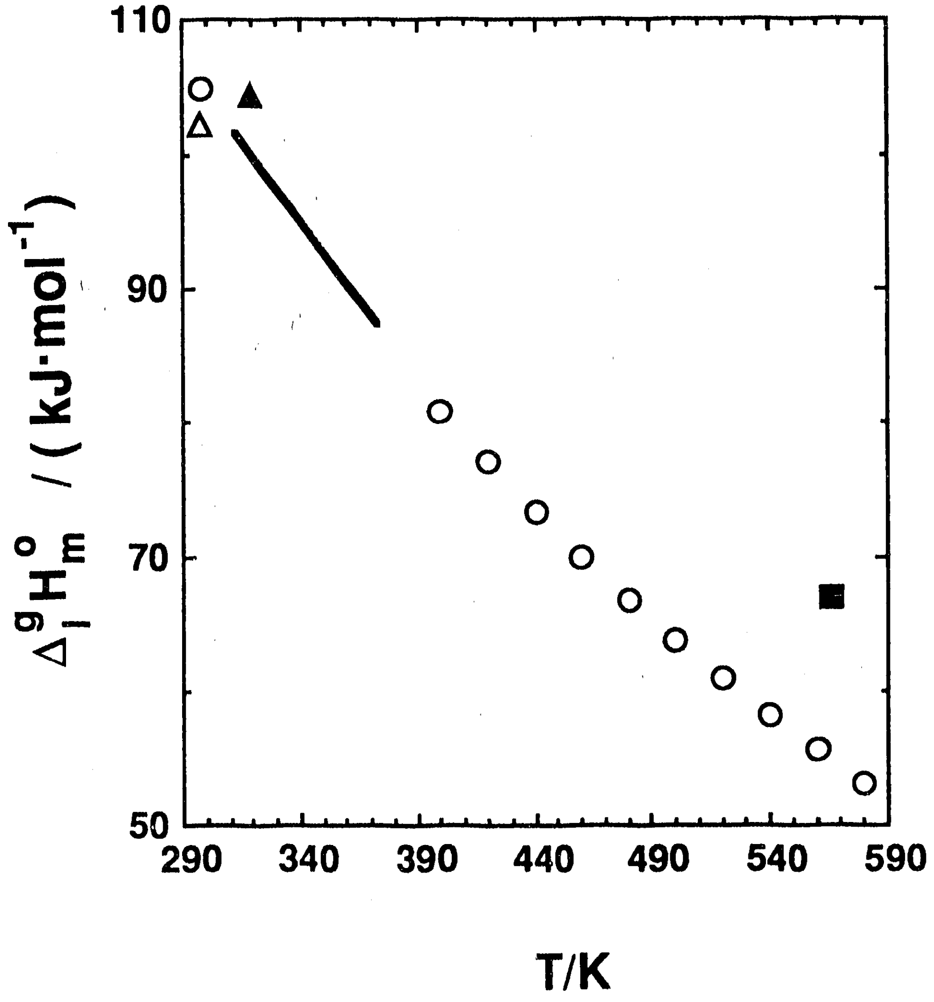


FIGURE 9. Comparison of literature enthalpy of vaporization measurements for tetradecan-1-ol with those obtained in this research. ○; This research, △; Månnson et al. (77), ▲; Davis and Kybett (71), ■; Kramer (78), the solid line; Spizzichino (72).

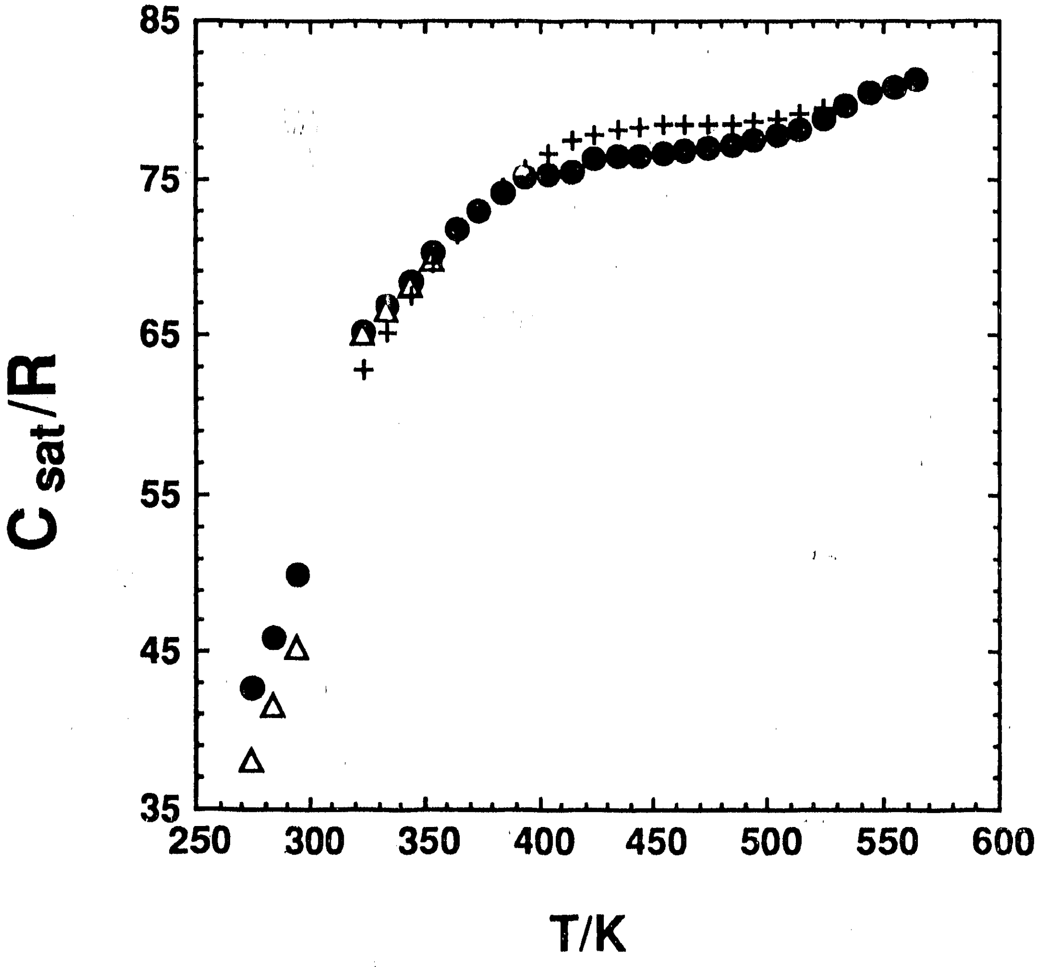


FIGURE 10. Comparison of literature heat-capacity measurements for tetradecan-1-ol with those obtained in this research. ●; This research, Δ; Mosselman, Mourik, and Dekker (69), +; Vasil'ev et al (79) which are the same as Khasanshin et al. (80).

assumed to be the mean of the reported values. Figure 10 compares the $C_{sat,m}$ values with published values (69,79,80). Differences are within the relative uncertainties in the measurements (81).

The enthalpy of fusion, ($\Delta_c^l H_m^o$ $C_{14}H_{30}O$, 311 K) = 49.4±0.4 kJ·mol^{-1}, listed in Table 10 is in good agreement with the value of 49.51±0.42 kJ·mol^{-1} obtained by Mosselman et al. (69) which lends credence to the assignment of the β form to the crystalline state of the sample. Combination of the listed enthalpies of fusion (Table 10) and vaporization at 298.15 K (Table 15) gives a value ($\Delta_c^g H_m^o$ $C_{14}H_{30}O$, 298.15 K) = 153.4±2.1 kJ·mol^{-1}. With solid-phase vapor-pressure measurements Davis and Kyber (71) obtained a value ($\Delta_c^g H_m^o$ $C_{14}H_{30}O$, 300 K) = 143.9±2.1 kJ·mol^{-1}. Hoyer and Peperle (82) using the same procedure, but with a different set of vapor-pressure measurements, reported ($\Delta_c^g H_m^o$ $C_{14}H_{30}O$, 310.7 K) = 159.4 kJ·mol^{-1}. The deviations attest to the difficulty in making accurate vapor-pressure measurements below 10 Pa.

Table 16 lists ideal-gas enthalpies of formation for the alkan-1-ols from ethanol through hexadecan-1-ol. Column 2 of Table 16 lists enthalpies of formation reported by NPL (83) and, in the case of tetradecan-1-ol, this research. Column 3 lists the "Assessed Best" values reported by Pedley, Naylor, and Kirby (60) and column 4 lists values estimated using the updated group-additivity parameters of Benson listed in reference 2. The difference between column 4 and either column 2 or 3 increases monotonically as the size of the alkan-1-ol increases. Column 5 lists the values obtained using the equation;

$$[\Delta_f H_m^o, CH_3(CH_2)_nOH, g\ 298.15\ K]/(kJ\cdot mol^{-1}) = -214.57 - 20.206\,n \qquad (21)$$

for n≥1. The agreement obtained is excellent. The $-CH_2-$ increment {the $[C\text{-}(C)_2(H)_2]$ group-additivity parameter} is then 0.51 kJ·mol^{-1} smaller than the "universal" value of −20.72 kJ·mol^{-1} listed by Benson (1,2). The $-CH_2-$ group increment obtained above for alkan-2-ols, −19.9±0.6 kJ·mol^{-1}, is in excellent agreement with this lower value.

Hexan-1,6-diol

When this research was started, one thermochemical study (84) on hexan-1,6-diol existed in the literature. The reported vapor-pressure results are inconsistent with the equation given failing to reproduce the listed normal boiling point. The "correction" of the derived enthalpy of vaporization at the mid temperature of the vapor-pressure measurements to give a value at 298.15 K also appear inconsistent. Since this research was completed, an energy of combustion, and enthalpies of fusion and sublimation measurements on hexan-1,6-diol have been reported by Knauth and Sabbah (85,86).

The energy of combustion, $\{(\Delta_c U^o_m/M)\}/(J\cdot g^{-1}) = -31916.7\pm1.6$, obtained in this research is lower than either of the two reported values, $-32087\pm41\ J\cdot g^{-1}$ and $-31999\pm37\ J\cdot g^{-1}$ of references 84 and 85, respectively. In neither study was the sample purity sufficient for accurate measurements. Gardner and Hussain (84) list a sample purity of 99.8 mole percent and Knauth and Sabbath (85) state a purity of only 99.38±0.02 mole percent. In contrast glc analysis of the sample used in this research gave a purity of >99.95 percent which was corroborated both by the CO_2 analyses (Table 2) during the combustion measurements and the small differences observed between the boiling and condensation temperatures (Table 7) during the ebulliometric vapor-pressure measurements. The spread of measured energies of combustion observed by Knauth and Sabbah was $-32116\ J\cdot g^{-1}$ to $-31896\ J\cdot g^{-1}$, which encompasses all of the values obtained here where the spread (Table 5) was $-31924\ J\cdot g^{-1}$ to $-31911\ J\cdot g^{-1}$. Gardner and Hussain do not give sufficient details to delineate their spread in values, but from the reported uncertainty interval, the width must have been similar to that of Knauth and Sabbah.

The vapor-pressure equation given by Gardner and Hussain cannot be reconciled with their listed normal boiling point. Consistency is obtained if it is assumed that their constant "B" contains a typographical error and should read 9.37±0.18 instead of 8.37±0.18. Then the equation would read:

$$\lg(p/\text{torr}) = 9.37 - 3405/(T/K) \text{ (in the temperature range 451 K to 525 K)}\ , \qquad (22)$$

where 1 torr = (101.325/760)kPa. Figure 11 compares the vapor pressures calculated using equation **22** with the values reported in Table 7. Gardner and Hussain assigned an uncertainty of ±2 percent on their measurements. Above 480 K the agreement is within their assigned uncertainty limits.

The enthalpy of vaporization at the mid temperature of the vapor-pressure measurements listed by Gardner and Hussain $(\Delta_l^g H^o_m\ C_6H_{14}O_2,\ 488\ K) = 65.2\pm1.2$

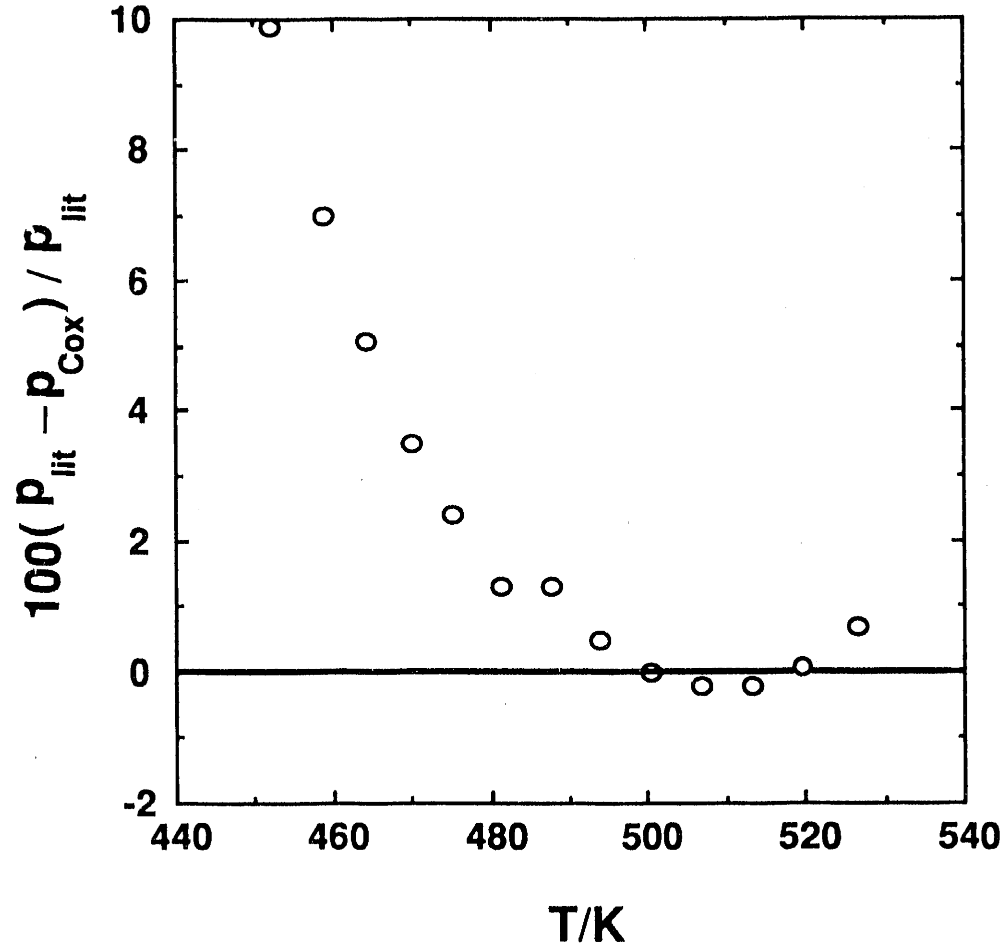


FIGURE 11. Comparison of hexan-1,6-diol vapor-pressure measurements with literature values. The "literature values" are those calculated using the "corrected" (see text and equation **22**) vapor-pressure equation of Gardner and Hussain (84).

kJ·mol^{-1} is in excellent agreement with an interpolated value (see Table 9) of ($\Delta_l^g H_m^o$ $C_6H_{14}O_2$, 488 K) = 65.6±0.3 kJ·mol^{-1}. Gardner and Hussain list a value ($\Delta_l^g H_m^o$ $C_6H_{14}O_2$, 298.15 K) = 83.3±1.7 kJ·mol^{-1} obtained using the Watson equation (87) to convert the 488 K result to 298.15 K. This result is in stark contrast to the value obtained in this research ($\Delta_l^g H_m^o$ $C_6H_{14}O_2$, 298.15 K) = 102.9±1.5 kJ·mol^{-1} (Table 9).

The measured enthalpy of fusion 22.6±0.6 kJ·mol^{-1} of this research (Table 10) is in good agreement with the value reported by Knauth and Sabbah, 22.2±0.3 kJ·mol^{-1} and somewhat lower than that of Gardner and Hussain 25.5±0.3 kJ·mol^{-1}. Knauth and Sabbath measured enthalpies of sublimation and list ($\Delta_c^g H_m^o$ $C_6H_{14}O_2$, 298.15 K) = 112.0±0.4 kJ·mol^{-1} which is somewhat lower than the value ($\Delta_c^g H_m^o$ $C_6H_{14}O_2$, 298.15 K) = 124.5±1.8 kJ·mol^{-1} obtained by addition of the enthalpies of vaporization and fusion reported here in Tables 9, 10, and 15. These differences may be due to the lower purity of the sample used by Knauth and Sabbah.

Addition of the group-additivity parameters (1,2) for hexan-1,6-diol follows:

2	$C-(C)(O)(H)_2$	−33.91 times 2	−67.82	
2	$O-(C)(H)$	−158.68 times 2	−317.36	
4	$C-(C)_2(H)_2$	−20.21 times 4	−80.84	
		($\Delta_f H_m^o$ $C_6H_{14}O_2$, g 298.15 K)	−466.0	kJ·mol^{-1}

using the $C(C)_2(H)_2$ group increment derived above for the alkanols. The value (Table 15) obtained in this research is ($\Delta_f H_m^o$ $C_6H_{14}O_2$, 298.15 K) = −459.4±1.9 kJ·mol^{-1}, which is 6.6 kJ·mol^{-1} more positive than that estimated using the group-additivity parameters. The difference is larger than normal (±4 kJ·mol^{-1}) and could be due to any one or a combination of three effects: 1) misassigned parameter(s), 2) a destabilizing effect within the molecule which is not allowed for in the estimation, or 3) experimental error. Changing the group parameters to fit the experimental result would have a "ripple effect" making the estimation of the alkanols (Table 16) diverge from the present good agreement. Byström and Månsson (88) have noted destabilization effects in other oxygen-containing compounds and intramolecular hydrogen bonding may be present in this case. However, that is pure speculation in the absence of a structural analysis in the gas phase. Experimental error is always possible and may in this case arise in the long extrapolation necessary for the derivation of the enthalpy of vaporization at 298.15 K. However, for tetradecan-1-ol, where a similar extrapolation was necessary, the agreement with literature values was good (loc. cit).

Methacrylamide

Results of a previous study of the thermochemical properties of methacrylamide have been reported in the literature (89). Lebedeva, Gutner, and Kiseleva (89) gave little detail of the measurements made and list an energy of combustion of 27284±6 $J \cdot g^{-1}$ compared to the value 27324.6±2.1 $J \cdot g^{-1}$ (Table 5) obtained in this research. Lebedeva et al. list an enthalpy of fusion of 17.6±0.8 $kJ \cdot mol^{-1}$, which is considerably higher than that obtained in this research $(\Delta_{c}^{l}H^{o}_{m}$ C_4H_7NO, 385.1 K) = 15.0±1.0 $kJ \cdot mol^{-1}$ (Table 14). Polymerization of our sample started at 392 K so the difference may be due to a portion of the enthalpy of polymerization being contained within the fusion measurements made by Lebedeva et al., (89).

Table 17 outlines "correction" of the measured enthalpy of sublimation at 350 K listed in Table 14 to both 385.1 K (the melting point) and 298.15 K using a cycle similar to that shown in Figure 2. In the absence of any experimental measurements the ideal-gas heat capacity for methacrylamide used in Table 17 was obtained by taking the values listed by Stull, Westrum and Sinke (90) for acrylic acid and multiplying them by the ratio of the respective molar masses.

The small difference (0.4 $kJ \cdot mol^{-1}$) between the measured enthalpy of fusion and the value calculated in the thermochemical cycles in Table 17 illustrates the self-consistency of the measurements. This, in turn, gives confidence to the derived enthalpy of sublimation at 298.15 K given in Tables 15 and 17.

The ideal-gas enthalpy of formation at 298.15 K is:

$$(\Delta_f H^{o}_{m}\ C_4H_7NO,\ g\ 298.15\ K) = -157.7 \pm 2.1\ kJ \cdot mol^{-1}\ .$$

Addition of the group-additivity parameters (1,2,91) follows;

$N-(CO)(H)_2$	−67.82	
$CO-(C_d)(N)$	−115.3	
$C_d-(C_d)(C)(CO)$	39.36	
$C-(C_d)(H)_3$	−42.20	
$C_d-(C_d)(H)_2$	26.21	
gives $(\Delta_f H^{o}_{m}$ C_4H_7NO, g 298.15 K)	−154.3	$kJ \cdot mol^{-1}$,

using the $CO-(C_d)(N)$ value derived in 1987 in this research program from the results for acrylamide. In 1987, since the compound polymerized so easily on heating above room temperature, some doubt existed in the accuracy of the literature vapor pressures (92) used to derive the ideal-gas enthalpy of formation of acrylamide. The difference between the experimental and group-additivity estimate, 3.4 $kJ \cdot mol^{-1}$, is within the uncertainty intervals assigned to the measurements. Therefore, the doubt in the accuracy of the literature vapor pressures for acrylamide is erased. Combining the acrylamide and methacrylamide results, an average value of -117 ± 2 kJ·mol^{-1} is recommended for the CO–(C_d)(N) group.

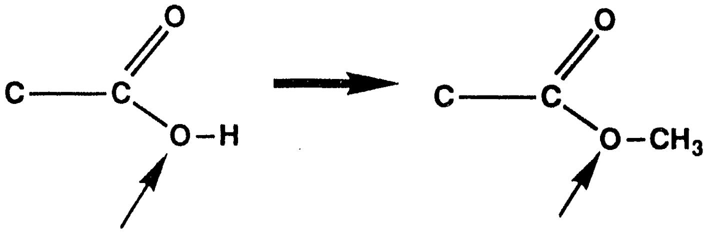
Naphthalene-2,6-dicarboxylic acid dimethyl ester

The discussion of naphthalene-2,6-dicarboxylic acid dimethyl ester follows out of the compound order used so far in this report to set the logic for some modifications of group parameters given in references 1 and 2 before discussing benzoyl formic acid. Throughout this section naphthalene-2,6-dicarboxylic acid dimethyl ester will be denoted as NDCA-2M.

In the literature, reports of the physical and thermodynamic properties of NDCA-2M are rare. Freund and Fleischer (93) in 1913 reported a melting point of 461 K for this compound. More recently (1978) Dozen, Fujishoma, and Shingu (94) measured values of 460-1 K (in a capillary tube) and 464.4 K in a d.s.c. The latter value is in excellent agreement with that observed in this research, 464.5 K (Table 10). Dozen et al. also measured an enthalpy of fusion, 38.4 kJ·mol^{-1}, but state that the sample lost 7.7 percent of its original mass during the measurement. The enthalpy of fusion measured in this research, 53.3 ± 2.0 kJ·mol^{-1}, is 39 percent higher than that reported by Dozen et al. (94).

The thermochemical properties of DNCA-2M at 298.15 K are listed in Table 15. When the group-additivity parameters (1,2) were initially summed for this compound, the estimated ideal-gas enthalpy of formation at 298.15 K obtained, -523.3 kJ·mol^{-1}, was substantially different from that given in Table 15; -555.1 ± 6.1 kJ·mol^{-1}. Further investigation of the various group parameters involved followed.

First, it was noted that the difference between the "assessed" (60) ideal-gas enthalpies of formation for the aliphatic carboxylic acids and the corresponding methyl esters averaged 21.3 ± 2.7 kJ·mol^{-1} (Table 18). The group-additivity parameters listed in references 1 and 2 gave 15.48 kJ·mol^{-1} for the difference:

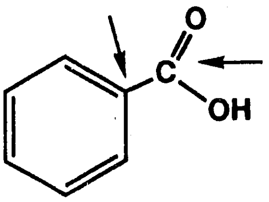


O–(CO)(H) O–(CO)(C) + C(O)$(H)_3$

-243.25 -185.48 + -42.29 kJ·mol^{-1}

It was assumed[§] that the "error" lay in the O–(CO)(C) group parameter. It was assigned a value of −179.7 kJ·mol^{-1} i.e., −185.48 + (21.3−15.48) (previously −185.48 kJ·mol^{-1}). Table 18 lists the enthalpies of formation of the carboxylic acids, their methyl esters, and values for the difference between the respective enthalpies of formation.

Next it was noted that the group parameters listed in references 1 and 2 failed to reproduce the ideal-gas enthalpies of formation at 298.15 K for either benzoic acid (60) or naphthalene-2-carboxylic acid (95): c.f., −294.1±2.2 (60) with -269.6 and −223.1±1.0 (95) with −201.8, respectively (all values in kJ·mol^{-1}). The relevant group parameters were:



$C_b{-}(C_b)_2(CO)$ + $CO{-}(C_b)(O)$

40.61 −136.07 kJ·mol^{-1} .

It was assumed that the "error" lay in the $C_b{-}(C_b)_2(CO)$ group parameter. It was assigned a value of 17.5 kJ·mol^{-1} rather than 40.61 kJ·mol^{-1}. (Then summation of the group parameters gave −292.7 kJ·mol^{-1} and −224.9 kJ·mol^{-1} for benzoic acid and naphthalene-2-carboxylic acid, respectively.)

With the above changes in group parameters, the estimation of the ideal-gas enthalpy of formation of DNCA-2M was repeated with the result as follows:

4	$C_b{-}(C_{bf})(C_b)(H)$	13.82 times 4	55.28
2	$C_b{-}(C_b)_2(H)$	13.82 times 2	27.64
2	$C_{bf}{-}(C_{bf})(C_b)_2$	20.10 times 2	40.20
2	$C_b{-}(C_b)_2(CO)$	17.5 times 2	35.0
2	$CO{-}(C_b)(O)$	−136.07 times 2	−272.14
2	$O{-}(CO)(C)$	−179.7 times 2	−359.4
2	$C{-}(O)(H)_3$	−42.29 times 2	−84.58
	($\Delta_f H^{o}_{m}$ $C_{14}H_{12}O_4$, g 298.15 K)		−558.0 kJ·mol^{-1} .

in excellent agreement with the value determined in this research −555.1±6.1 kJ·mol^{-1} (Table 15).

[§] In the 1990 research program it is hoped to test the validity of the group parameter changes made in this section of the report by studying compounds which contain these groups in the presence of others which are well defined.

Benzoyl formic acid

As evidenced by both the inclined-piston vapor-pressure measurements and the d.s.c. studies, decomposition started at 429 K in the sample of benzoyl formic acid. Hence, the normal boiling point (532 K) listed in Table 8 is an estimate. Hurd and Ratherink (96) in a study of the decomposition of alpha keto acids note that "Claisen and Bouveault found that benzoyl formic acid yielded benzoic acid and benzaldehyde at 473-523 K." Hurd and Ratherink found CO and CO_2 in the reaction products in addition to benzoic acid and benzaldehyde in studies in the temperature range 523 to 573 K. A search of the literature through 1989 failed to find any thermodynamic property data for benzoyl formic acid.

Using the group parameters given in references 1 and 2 and the new value for the $C_b-(C_b)_2(CO)$ parameter, estimation of the ideal-gas enthalpy of formation of benzoyl formic acid was made as follows:

5	$C_b-(C_b)_2(H)$	13.82 times 5	69.1	
1	$C_b-(C_b)_2(CO)$	17.50 times 1	17.5	
1	$CO-(CO)(C_b)$	−112.13 times 1	−112.1	
1	$CO-(CO)(O)$	−122.59 times 1	−122.6	
1	$O-(CO)(H)$	−243.25 times 1	−243.3	
		($\Delta_f H^o_m$ $C_8H_6O_3$, g 298.15 K)	−391.4	$kJ \cdot mol^{-1}$.

The result is in good agreement with the value determined in this research −388.7±1.0 $kJ \cdot mol^{-1}$ (Table 15).

Naphthalene-2,6-dicarboxylic acid

As noted above in the Results section of this report, attempts to measure the vapor pressure of naphthalene-2,6-dicarboxylic acid were unsuccessful. At 523 K the vapor pressure was less than the limit of sensitivity of the inclined-piston apparatus (10 Pa). The sample decomposed at 695 K before melting, and hence, no liquid-phase measurements were possible. This relative inertness probably accounts for the complete lack of thermodynamic property data on this acid in the literature (through 1989).

Some thermodynamic property values (heat capacities and the enthalpy of combustion and formation) are reported here in Tables 4, 5, 6, 10, and 15. With the group-additivity parameters given in references 1 and 2 and the parameter revisions made earlier in this report, the ideal-gas enthalpy of formation at 298.15 K was estimated as follows:

4	$C_b-(C_{bf})(C_b)(H)$	13.82 times 4	55.3	
2	$C_b-(C_b)_2(H)$	13.82 times 2	27.6	
2	$C_{bf}-(C_{bf})(C_b)_2$	20.10 times 2	40.2	
2	$C_b-(C_b)_2(CO)$	17.50 times 2	35.0	
2	$CO-(C_b)(O)$	−136.07 times 2	−272.1	
2	$O-(CO)(H)$	−243.25 times 2	−486.5	
	($\Delta_f H^\circ_m$ $C_{12}H_8O_4$, g 298.15 K)		−570.5	$kJ{\cdot}mol^{-1}$.

The enthalpy of formation of crystalline naphthalene-2,6-dicarboxylic acid derived in this research (Table 15) is -770.25 ± 0.96 $kJ{\cdot}mol^{-1}$. Hence, the enthalpy of sublimation is estimated to be ($\Delta_c^g H^\circ_m$ $C_{12}H_8O_4$, 298.15 K) = 199.8 $kJ{\cdot}mol^{-1}$. This value is considerably higher than the corresponding value for the dimethyl ester ($\Delta_c^g H^\circ_m$ $C_{14}H_{12}O_4$, 298.15 K) = 146.5 ± 6.0 $kJ{\cdot}mol^{-1}$ (Table 15). Listings of enthalpies of vaporization in reference 60 also show the aliphatic acids to have larger values than their corresponding methyl esters (data is available through C_{16} where the methyl esters are all liquids at 298.15 K).

Tetraethylsilane

In contrast to the previous few compounds where little or no thermodynamic property measurements were found in the literature search, tetraethylsilane has an overabundance of determined values. Reference 97 is an excellent review of organosilicon thermochemistry through 1988. Particularly in the area of combustion calorimetric determinations, the literature is rife with contradicting values for tetraethylsilane. References 98 through 105 pertain to the combustion calorimetric results which are summarized in Table 19. All of the pre 1971 measurements (98-102) were made in static-bomb calorimeters where incomplete combustion, facilitated by the formation of the fire retardant silicon dioxide, led to erroneous results.

In 1971 Iseard et al. (103) at the University of Sussex, England reported measurements of the energy of combustion of tetraethylsilane using the fluorine additive technique developed by Good et al. (15) in these laboratories, when the standard enthalpy of formation of crystalline silica (silicon dioxide, SiO_2) was defined. The University of Sussex group subsequently listed, in a data compilation (106), enthalpies of formation for a number of organosilicon compounds all measured using the fluorine additive technique. A firm foundation for the estimation of the thermochemical properties of organosilicons appeared to have been set. However, group-additivity parameters could not be defined: the results were not internally consistent (97). Subsequent work by Steele (107) on tetramethylsilane (one of the compounds listed in reference 106) gave a significantly different value from that obtained under almost identical calorimetric procedures by the University of Sussex group.

References 104 and 105 appear to report the same research. The enthalpy of formation derived (Table 19) differs substantially from that determined by Iseard et al. (103). The Russian research (104,105) used a "high temperature controlled combustion technique" which produced "highly dispersed hydrated amorphous silicon dioxide" as the sole solid reaction product of the combustion. The authors list a thesis for the method of determination of the enthalpy of formation of the silicon dioxide product of the combustions. A copy of the thesis could not be obtained by the authors of this report. In the absence of the thesis, no definitive comparisons could be made. It would appear that the Russian results are as reliable as the ones obtained at the University of Sussex. The existence of these widely differing values was the reason for the study undertaken in this research.

The energy of combustion measurements reported here were made using the technique developed by Good et al. (15). In that research, hexamethyldisiloxane was also studied. In the research reported here, to test the present procedures, two combustions were performed on the *same* sample of hexamethyldisiloxane as that used in the earlier study. The results gave energies of formation within 0.02 percent of the published value (15).

The derived enthalpy of formation (see Tables 4A, 5, 6, 6A, and 15), $\Delta_f H^o_m$ ($C_8H_{20}Si$, l 298.15 K) = -328.6 ± 5.2 $kJ \cdot mol^{-1}$, is different from all the previous values. However the uncertainty intervals for the result reported here and those listed by Voronkov et al. (104,105) (-335.6 ± 5.6 $kJ \cdot mol^{-1}$ and -336.0 ± 4.0 $kJ \cdot mol^{-1}$) overlap. The Russian workers also reproduced the enthalpy of formation for tetramethylsilane reported by Steele (107). The agreement appears to not be serendipitous.

The uncertainty in the energy of combustion measurements on tetraethylsilane is higher than those reported in Table 5 for the C,H,N,O compounds studied in this research. This higher uncertainty [of the same order of magnitude as the earlier study on hexamethyldisiloxane (15)] is the penalty for using a combustion reaction in which only a fraction of the evolved energy is produced by the substance of interest.

Ambrose reported (41) a critical temperature of 603 K and a critical pressure of 2602 kPa for tetraethylsilane with no details of the source of the values. In this research, the corresponding experimentally determined critical temperature was 606±1 K and the derived critical pressure was 2400±24 kPa. Literature values for the density of tetraethylsilane in the temperature range 270 K to 430 K (108-110) are compared in Figure 12 with values estimated by extended corresponding states (Equation **15**) using the critical properties (this research) listed in Table 9A. The agreement between the various literature values and extended corresponding states is good (±1 percent), and is well within the uncertainty interval assigned to the critical density measured in this research namely, 246±5 kg·m^{-3}.

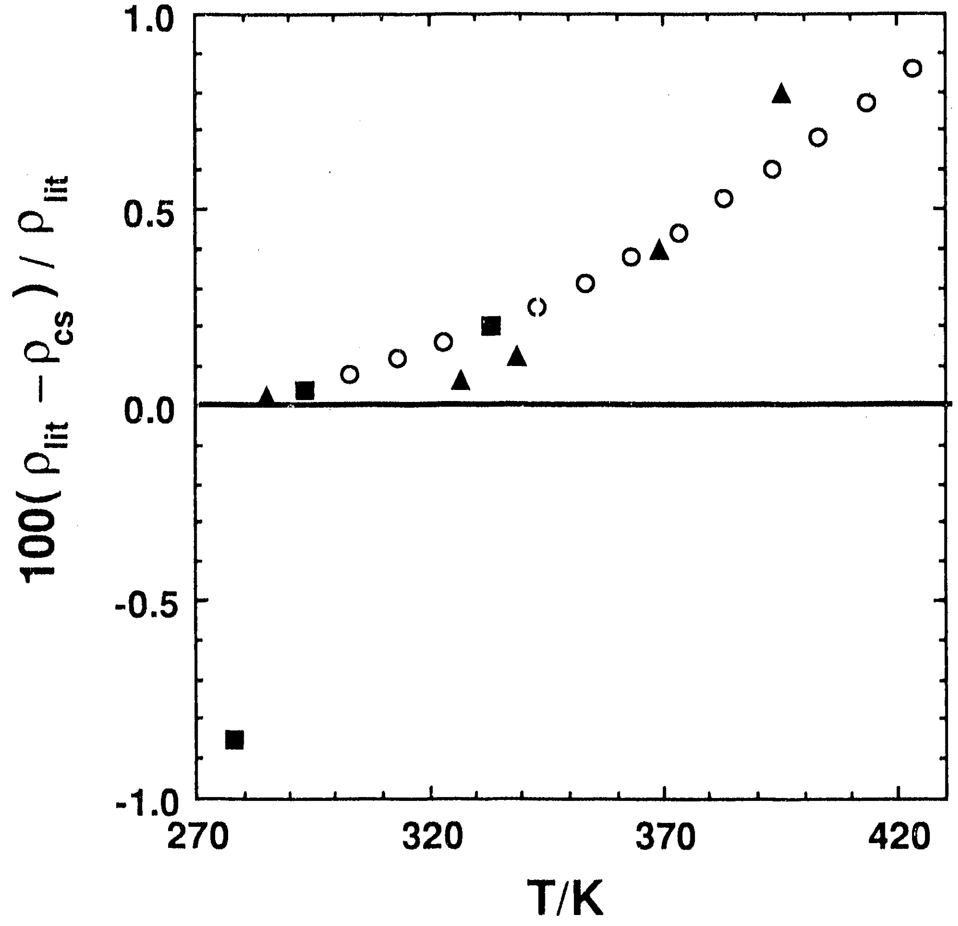


FIGURE 12. Comparison of literature density measurements for tetraethylsilane with those obtained by extended corresponding states. ρ_{cs} = value of the density calculated using equation **15** and the critical properties reported in Table 9A. ○; Brostow et al. (108); ▲; Sugden and Wilkins (109); ■; Whitmore et al. (110).

Iseard et al (103) list $(\Delta_{l}^{g}H_{m}^{o}\ C_8H_{20}Si,\ 298.15\ K) = 39.7\ kJ\cdot mol^{-1}$, quoting reference 110 as the source of the value. However, Whitmore et al. (110) do not give a temperature for their value and state that it was derived from vapor-pressure measurements, only 2 points of which are quoted in the paper although it alludes to many more. Subsequently, Abraham and Irving (111) questioned the value listed by Iseard et al. and using vapor-pressure measurements from the literature (112) derived:

$$(\Delta_{l}^{g}H_{m}^{o}\ C_8H_{20}Si,\ 298.15\ K) = 43.3\ kJ\cdot mol^{-1}.$$

The value obtained by Abraham and Irving (111) is in good agreement with the value obtained in this research:

$$(\Delta_{l}^{g}H_{m}^{o}\ C_8H_{20}Si,\ 298.15\ K) = 44.62\pm0.05\ kJ\cdot mol^{-1}.$$

With the results reported in Table 9, the value of $39.7\ kJ\cdot mol^{-1}$ would correspond to a temperature of 369 K and not 298.15 K .

Figure 13 compares values for the vapor pressure of tetraethylsilane found in the literature (110,112) with those calculated using the Cox equation coefficients reported in Table 8. The percentage deviations are within the probable uncertainty intervals of the literature values.

Group-additivity parameters applicable to tetra-alkyl silanes can be derived using the ideal-gas enthalpies of formation for tetramethylsilane and tetraethylsilane as the anchor points. With the ideal-gas enthalpy of formation at 298.15 K for tetramethylsilane obtained by Steele (107), the Si–(C)$_4$ group can be derived as follows:

4	C–(Si)(H)$_3$	−42.2 times 4	−168.8	assigned as C–(C)(H)$_3$
1	Si–(C)$_4$		?	
	$(\Delta_f H_{m}^{o}\ C_4H_{12}Si,\ g\ 298.15\ K)$		$-233.2\pm3.2\ kJ\cdot mol^{-1}$	

and hence, Si–(C)$_4$ equals $-64.4\ kJ\cdot mol^{-1}$. Then the C–(Si)(C)(H)$_2$ group parameter is derived as follows:

4	C–(C)(H)$_3$	−42.2 times 4	−168.8
4	C–(Si)(C)(H)$_2$	? times 4	
1	Si–(C)$_4$		−64.4

$(\Delta_f H_{m}^{o}\ C_8H_{20}Si,\ g\ 298.15\ K)$ $-284.0\pm5.2\ kJ\cdot mol^{-1}$, and hence, C-(Si)(C)(H)$_2$ equals $-12.7\ kJ\cdot mol^{-1}$.

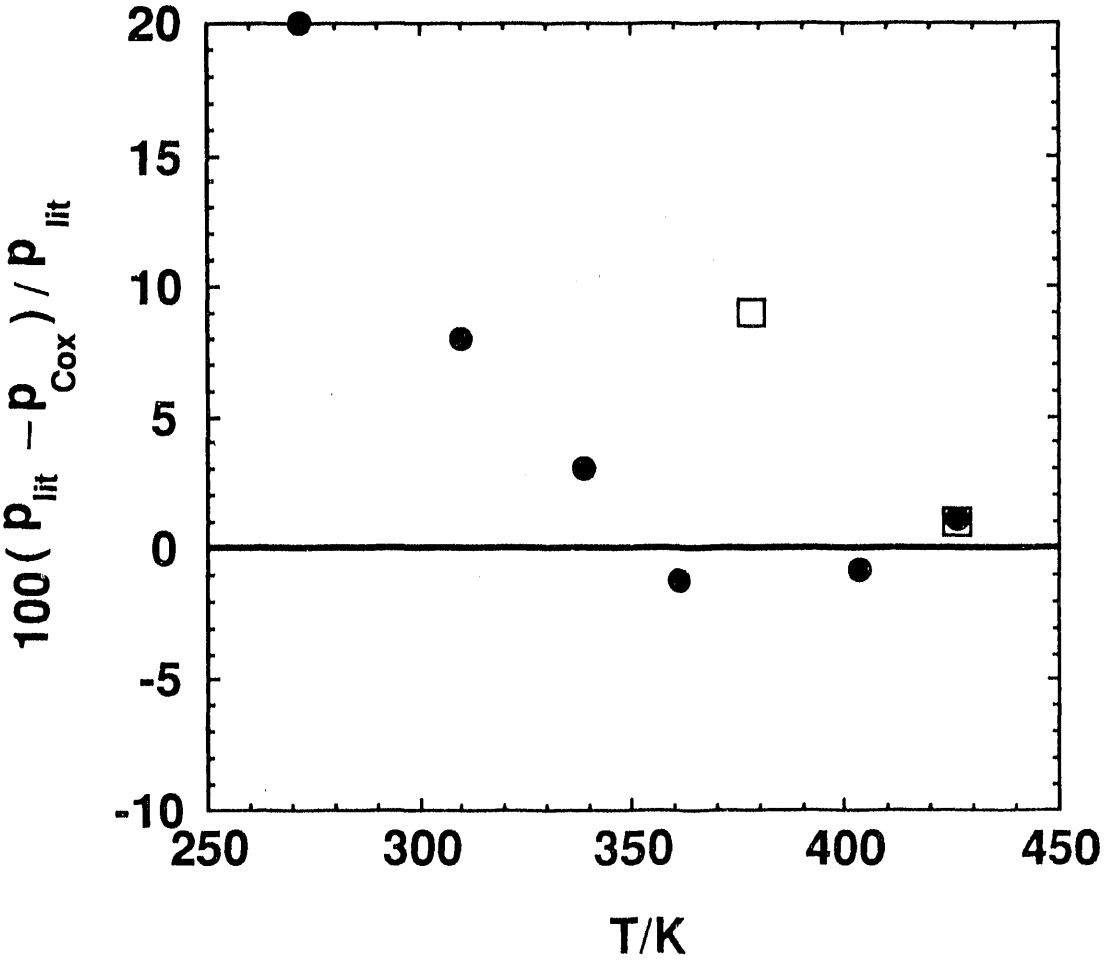


Figure 13. Comparison of literature vapor pressures for tetraethylsilane with values obtained using the Cox equation coefficients reported in Table 8. ●; Stull reference 112; □; Whitmore et al. reference 110.

5. CONCLUSIONS

The group-additivity parameter changes/additions arising from the results reported here can be summarized as follows.

- The C–$(C)_2(H)_2$ group-additivity parameter (or the $-CH_2-$ increment) is significantly smaller in alkanols than in alkanes.
- The CO–(C_d)(N) group-additivity parameter is assigned a value of –117±2 kJ·mol^{-1}.
- The O–(CO)(C) group-additivity parameter is reassigned a value of –179.7 kJ·mol^{-1} from the previous value of –185.5 kJ·mol^{-1}.
- The C_b–$(C_b)_2$(O) group-additivity parameter is reassigned a value of 17.5 kJ·mol^{-1} from the previous value of 40.6 kJ·mol^{-1}.
- The Si–$(C)_4$ group-additivity parameter is assigned a value of –64.4 kJ·mol^{-1}.
- The C–(Si)(C)$(H)_2$ group-additivity parameter is assigned a value of –12.7 kJ·mol^{-1}.

Results for hexan-1,6-diol could not be reconciled with the listed group-additivity parameters (including the reassigned values). Best estimates overestimate the stability of the compound by 6.7 kJ·mol^{-1}. The discrepancy may be due to 1) misassigned parameter(s), 2) a destabilizing effect within the molecule which is not allowed for in the estimation, or 3) experimental error. Study of a further diol will be required to elucidate the truth.

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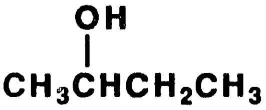
TABLE 1. Outline of sample measurements performed in this project [a]

Compound	$\Delta_c U^o_m$	Vapor pressure	Heat capacity
(±)-Butan-2-ol	x	x	
Tetradecan-1-ol	x	x	x
Hexan-1,6-diol	x	x	x
Methacrylamide	x	x	x
Benzoyl formic acid	x	x	x
Naphthalene-2,6-dicarboxylic acid	x	b	x
Naphthalene-2,6-dicarboxylic acid dimethyl ester	x	x	x
Tetraethylsilane	x	x	x

[a] Measurements made are denoted by **x**

[b] Attempted but not successful. See text.



$CH_3CH(OH)CH_2CH_3$

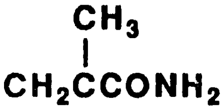
Butan-2-ol

$CH_3(CH_2)_{12}CH_2OH$

Tetradecan-1-ol

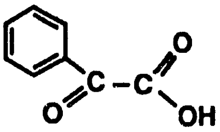
$HOCH_2(CH_2)_4CH_2OH$

Hexan-1,6-diol

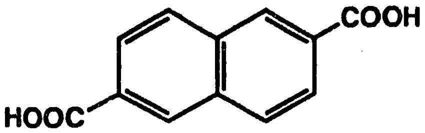


$CH_2C(CH_3)CONH_2$

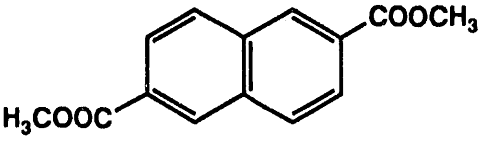
Methacrylamide



Benzoyl formic acid



naphthalene-2,6-dicarboxylic acid



naphthalene-2,6-dicarboxylic acid dimethyl ester

$(CH_3CH_2)_4Si$

Tetraethylsilane

TABLE 2. Physical properties at 298.15 K: values in parentheses are estimates [a]

Compound	$\frac{\rho}{\mathrm{kg \cdot m^{-3}}}$	$\frac{10^7(\delta V_m/\delta T)_p}{\mathrm{m^3 \cdot K^{-1}}}$	$\frac{C_{\mathrm{sat,m}}}{R}$
(±)-Butan-2-ol	802.5	0.96	23.7
Tetradecan-1-ol	949.6	(0.3)	51.3
Hexan-1,6-diol	1079	(0.3)	24.4
Methacrylamide	1080	(0.3)	17.3
Benzoyl formic acid	1340	(0.3)	23.2
Naphthalene-2,6-dicarboxylic acid	1330	(0.3)	27.7
Naphthalene-2,6-dicarboxylic acid dimethyl ester	1321	(0.3)	23.1
Tetraethylsilane	768.3	2.0	35.8

[a] See text for details of the density and heat-capacity measurements (crystalline phase except (±)-butan-2-ol and tetraethylsilane both liquid phase) .

TABLE 3. Carbon dioxide recoveries

Compound	Number of experiments	Percent recovery [a]
benzoic acid calibration	6	99.983±0.018
(±)-Butan-2-ol	6	99.994±0.016
Tetradecan-1-ol	6	99.986±0.024
Hexan-1,6-diol	7	100.021±0.027 [b]
Methacrylamide	6	99.810±0.028 [b]
Benzoyl formic acid	6	99.960±0.031
benzoic acid calibration	6	99.998±0.006
Naphthalene-2,6-dicarboxylic acid	7	99.996±0.008
Naphthalene-2,6-dicarboxylic acid dimethyl ester	7	99.942±0.013 [b]

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[a] Mean and standard deviation of the mean.

[b] Results of combustion study based on percentage CO_2 recovery (See text).

TABLE 4. Typical combustion experiments at 298.15 K. [a,b] (p° = 101.325 kPa)

	A	B	C
m'(compound)/g	0.872314	0.781654	1.040842
m''(oil)/g	0.045762	0.0	0.0
m'''(fuse)/g	0.001652	0.001610	0.001712
$n_i(H_2O)$/mol	0.05535	0.05535	0.05535
m(Pt)/g	19.924	20.804	19.924
$\Delta T/K = (t_i - t_f + \Delta t_{corr})/K$	1.98964	1.98970	1.98162
ε(calor)(ΔT)/J	−33362.9	−33363.9	−33228.5
ε(cont)(ΔT)/J [c]	−36.8	−36.6	−36.9
ΔU_{ign}/J	0.8	0.8	0.8
ΔU(corr. to std. states)/J [d]	11.0	10.3	12.6
$-m''(\Delta_c U^\circ_m/M)$(oil)/J	2107.0	0.0	0.0
$-m'''(\Delta_c U^\circ_m/M)$(fuse)/J	28.0	27.3	29.0
$m'(\Delta_c U^\circ_m/M)$(compound)/J	−31252.9	−33362.1	−33223.0
$(\Delta_c U^\circ_m/M)$(compound)/$J \cdot g^{-1}$	−35827.6	−42681.4	−31919.3

	D	E	F
m'(compound)/g	1.216268	1.390517	1.426682
m''(fuse)/g	0.001701	0.001704	0.001797
$n_i(H_2O)$/mol	0.05535	0.05535	0.05535
m(Pt)/g	19.924	20.804	19.926
$\Delta T/K = (t_i - t_f + \Delta t_{corr})/K$	1.98764	1.94468	2.00666
ε(calor)(ΔT)/J	−33329.3	−32608.9	−33648.5
ε(cont)(ΔT)/J [c]	−37.2	−37.5	−38.0
ΔU_{ign}/J	0.8	0.8	0.8
$\Delta U_{dec}(HNO_3)$/J	80.2	0.0	0.0
ΔU(corr. to std. states)/J [d]	17.9	29.2	31.4
$-m''(\Delta_c U^\circ_m/M)$(fuse)/J	25.9	28.9	30.5
$m'(\Delta_c U^\circ_m/M)$(compound)/J	−33241.7	−32587.5	−33623.8
$(\Delta_c U^\circ_m/M)$(compound)/$J \cdot g^{-1}$	−27331.0	−23435.5	−23568.0

TABLE 4. Continued.

	G
m'(compound)/g	1.261291
m''(fuse)/g	0.001705
$n_i(H_2O)$/mol	0.05535
m(Pt)/g	20.805
$\Delta T/K = (t_i - t_f + \Delta t_{corr})/K$	2.01072
ε(calor)(ΔT)/J	−33716.6
ε(cont)(ΔT)/J [c]	−38.0
ΔU_{ign}/J	0.8
ΔU(corr. to std. states)/J [d]	26.4
$-m''(\Delta_c U^\circ_m/M)$(fuse)/J	28.9
$m'(\Delta_c U^\circ_m/M)$(compound)/J	−33698.5
$(\Delta_c U^\circ_m/M)$(compound)/$J\cdot g^{-1}$	−26717.6

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[a] The symbols and abbreviations of this Table are those of reference 13 except as noted.

[b] **A** = (±)-butan-2-ol; **B** = tetradecan-1-ol; **C** = hexan-1,6-diol; **D** = methacrylamide; **E** = benzoyl formic acid; **F** = naphthalene-2,6-dicarboxylic acid; and **G** = naphthalene-2,6-dicarboxylic acid dimethyl ester.

[c] $\varepsilon_i(\text{cont})(t_i - 298.15\ K) + \varepsilon_f(\text{cont})(298.15\ K - t_f + \Delta t_{corr})$

[d] Items 81 to 85, 87 to 90, 93, and 94 of the computational form of reference 13.

TABLE 4A. Typical combustion and comparison experiments for tetraethylsilane at 298.15 K and 101.325 kPa. [a]

	Combustion expt.	**Comparison expt.**
m(Tetraethylsilane)/g	0.201115	
m(Benzotrifluoride)/g	0.993319	
m(Polyester film)/g	0.101393	
m(Benzoic acid)/g		1.301002
m(fuse)/g	0.001335	0.001753
$n_i(H_2O)$/mol	0.5534	0.52693
$n_i(HF)$/mol		0.011685
$n_i(H_2SiF_6)$/mol		0.001345
m(Pt)/g	20.805	20.805
$\Delta T/K = (t_i - t_f + \Delta t_{corr})/K$	2.05674	2.04660
$\varepsilon(calor)(\Delta T)$/J	−34530.6	−34362.0 [b]
$\varepsilon(cont)(\Delta T)$/J [c]	−114.7	−111.6
ΔU_{ign}/J	0.8	0.8
ΔU(corr. to std. states)/J [d]	41.6	51.1
$-m(\Delta_c U^\circ_m/M)$(fuse)/J	22.6	29.7
$-m(\Delta_c U^\circ_m/M)$(Benzoic acid)/J		−34392.0
$-m(\Delta_c U^\circ_m/M)$(Polyester film)/J	−2328.5	
$-m(\Delta_c U^\circ_m/M)$(Benzotrifluoride)/J	−22898.8	
$\Delta U_{soln.}$/J [e]	3.2	
$(\Delta_c U^\circ_m/M)$(Tetraethylsilane)/J	−9349.8	
$(\Delta_c U^\circ_m/M)$(Tetraethylsilane)/$J \cdot g^{-1}$	−46490	

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[a] The symbols and abbreviations of this Table are those of references 13, 15 and 17 except as noted.

[b] Value used to determine ε(calor) for the corresponding combustion experiment (see text).

[c] $\varepsilon_i(cont)(t_i - 298.15\ K) + \varepsilon_f(cont)(298.15\ K - t_f + \Delta t_{corr})$

[d] Items 81 to 85, 87 to 90, 93, and 94 of the computational form of references 13 and 17; correction to standard states.

[e] Thermochemical correction for the solution of tetraethylsilane in benzotrifluoride: solution of 1 mole of tetraethylsilane in 3 moles of benzotrifluoride was accompanied by the adsorption of 2316 J.

TABLE 5. Summary of experimental energy of combustion results. T = 298.15 K, and p° =101.325 kPa. The uncertainties shown are one standard deviation of the mean.

(±)-Butan-2-ol

$\{(\Delta_c U^\circ_m/M)/(\mathrm{J\cdot g^{-1}})\}$

−35827.6	−35828.5	−35823.2	−35829.9	−35830.5	−35824.6

$\langle\{(\Delta_c U^\circ_m/M)\}/(\mathrm{J\cdot g^{-1}})\rangle$ −35827.4±1.2

Tetradecan-1-ol

$\{(\Delta_c U^\circ_m/M)/(\mathrm{J\cdot g^{-1}})\}$

−42681.4	−42684.0	−42684.4	−42684.6	−42684.9	−42681.7

$\langle\{(\Delta_c U^\circ_m/M)\}/(\mathrm{J\cdot g^{-1}})\rangle$ −42683.5± 0.6

Hexan-1,6-diol

$\{(\Delta_c U^\circ_m/M)/(\mathrm{J\cdot g^{-1}})\}$

−31919.3	−31917.9	−31910.8	−31924.2	−31915.3	−31914.4	−31914.8

$\langle\{(\Delta_c U^\circ_m/M)\}/(\mathrm{J\cdot g^{-1}})\rangle$ −31916.7±1.6

Methacrylamide

$\{(\Delta_c U^\circ_m/M)/(\mathrm{J\cdot g^{-1}})\}$

−27331.0	−27325.0	−27326.2	−27318.7	−27321.9	−27305.2 [a]

$\langle\{(\Delta_c U^\circ_m/M)\}/(\mathrm{J\cdot g^{-1}})\rangle$ −27324.6±2.1

Benzoyl formic acid

$\{(\Delta_c U^\circ_m/M)/(\mathrm{J\cdot g^{-1}})\}$

−23435.5	−23429.9	−23429.7	−23435.1	−23441.2	−23436.3

$\langle\{(\Delta_c U^\circ_m/M)\}/(\mathrm{J\cdot g^{-1}})\rangle$ −23434.7±1.8

Naphthalene-2,6-dicarboxylic acid

$\{(\Delta_c U^\circ_m/M)/(\mathrm{J\cdot g^{-1}})\}$

−23568.0	−23564.5	−23566.7	−23568.5	−23568.8	−23569.8

$\langle\{(\Delta_c U^\circ_m/M)\}/(\mathrm{J\cdot g^{-1}})\rangle$ −23567.7±0.8

TABLE 5. Continued.

Naphthalene-2,6-dicarboxylic acid dimethyl ester					
$\{(\Delta_c U^{\circ}_m/M)/(J\cdot g^{-1})\}$					
−26717.6	−26708.9	−26716.8	−26717.0	−26718.4	−26712.9
$<\{(\Delta_c U^{\circ}_m/M)\}/(J\cdot g^{-1})>$	−26715.2±1.5				
Tetraethylsilane [b]					
$\{(\Delta_c U^{\circ}_m/M)/(J\cdot g^{-1})\}$					
−46490	−46558	−46443	−46467	−46492	−46495
$<\{(\Delta_c U^{\circ}_m/M)\}/(J\cdot g^{-1})>$	−46491±16				

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[a] Value excluded from average (see text).

[b] Value for the following reaction (see text):

$$C_8H_{20}Si\ (l) + 14\ O_2\ (g) + 15.15_5HF\cdot 413H_2O \rightarrow 8CO_2\ (g) + H_2SiF_6\cdot 9.15_5HF\cdot 425H_2O.$$

TABLE 6. Condensed phase molar thermochemical functions at 298.15 K and $p^\circ = 101.325$ kPa.

	$\Delta_c U^\circ_m$/kJ·mol^{-1}	$\Delta_c H^\circ_m$/kJ·mol^{-1}	$\Delta_f H^\circ_m$/kJ·mol^{-1}
(±)-Butan-2-ol (l)	−2655.63±0.18	−2660.59±0.18	−342.60±0.25
Tetradecan-1-ol (c)	−9151.06±1.16	−9168.41±1.16	−628.18±1.46
Hexan-1,6-diol (c)	−3771.81±0.60	−3778.01±0.60	−583.86±0.72
Methacrylamide (c)	−2325.49±0.46	−2327.35±0.46	−247.10±0.50
Benzoyl formic acid (c)	−3518.35±0.70	−3518.35±0.70	−487.22±0.80
Naphthalene-2,6-dicarboxylic acid (c)	−5095.19±0.78	−5095.19±0.78	−770.25±0.96
Naphthalene-2,6-dicarboxylic acid dimethyl ester (c)	−6525.14±1.16	−6527.61±1.16	−696.51±1.34
Tetraethylsilane (l)	−6710.2±4.6[a]	−6725.1±4.6[a]	−328.6±5.2[b]

[a] Value for the following reaction (see text):
$C_8H_{20}Si$ (l) + 14 O_2 (g) + $15.15_5HF\cdot 413H_2O$ →
8CO_2 (g) + $H_2SiF_6\cdot 9.15_5HF\cdot 425H_2O$.

[b] Value for the following reaction (see text):
8C(c, graphite) + 10H_2(g) + Si(c) → $C_8H_{20}Si$ (l).

TABLE 6A Thermochemical cycle for tetraethylsilane

(I) $8CO_2\ (g) + H_2SiF_6 \cdot 9.15_5HF \cdot 425H_2O \rightarrow$

$C_8H_{20}Si\ (l) + 14\ O_2\ (g) + 15.15_5HF \cdot 413H_2O$

$\Delta_rH^o_m = (6725.1 \pm 4.6)\ kJ \cdot mol^{-1}$

(II) $8C(c, graphite) + 8O_2(g) \rightarrow 8CO_2\ (g)$

$\Delta_rH^o_m = -(3148.08 \pm 1.04)\ kJ \cdot mol^{-1}$

(III) $10H_2(g) + 5O_2(g) \rightarrow 10H_2O\ (l)$

$\Delta_rH^o_m = -(2858.3 \pm 0.4)\ kJ \cdot mol^{-1}$

(IV) $Si(c) + O_2(g) \rightarrow SiO_2\ (c, quartz)$

$\Delta_rH^o_m = -(910.7 \pm 0.8)\ kJ \cdot mol^{-1}$

(V) $SiO_2\ (c, quartz) + 15.15_5HF \cdot 423H_2O \rightarrow H_2SiF_6 \cdot 9.15_5HF \cdot 425H_2O$

$\Delta_rH^o_m = -(136.6 \pm 1.0)\ kJ \cdot mol^{-1}$

(VI) $15.15_5HF \cdot 413H_2O + 10H_2O\ (l) \rightarrow 15.15_5HF \cdot 425H_2O$

$\Delta_rH^o_m = -(0.005 \pm 0.001)\ kJ \cdot mol^{-1}$

(VII) $8C(c, graphite) + 10H_2(g) + Si(c) \rightarrow C_8H_{20}Si\ (l)$

$\Delta_fH^o_m = -(328.6 \pm 5.2)\ kJ \cdot mol^{-1}$

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[a] Enthalpies of reaction; **(I)** this research, **(II)** reference 31, **(III)** reference 31, **(IV)** reference 31, **(V)** reference 32, **(VI)** reference 33, and **(VII)** is the sum of reactions **(I)** through **(VI)**.

TABLE 7. Summary of vapor-pressure results; "IP" refers to measurements made with the inclined piston, "decane" or "water" refers to which material was used as the standard in the reference ebulliometer, T is the condensation temperature of the sample, the pressure p was calculated from the condensation temperature of the reference substance, Δp is the difference of the calculated value of pressure (Cox equation fit) from the observed value of pressure ($p-p_{Cox}$), σ(p) is the propagated error calculated from Equations **1**, **2**, and **3**, ΔT is the difference between the boiling and condensation temperatures ($T_{boil}-T_{cond}$) for the sample under study.

Method	$\frac{T}{K}$	$\frac{p}{kPa}$	$\frac{\Delta p}{kPa}$	$\frac{\sigma(p)}{kPa}$	$\frac{\Delta T}{K}$
		(±)-Butan-2-ol			
decane	301.900	3.0000	−0.0001	0.0002	0.033
decane	311.023	5.3330	0.0007	0.0004	0.028
decane	317.901	7.9989	−0.0004	0.0006	0.026
decane	323.029	10.666	−0.001	0.001	0.022
decane	327.157	13.332	0.000	0.001	0.014
decane	331.429	16.665	0.001	0.001	0.014
decane	334.969	19.933	−0.001	0.001	0.011
decane	339.612	25.023	0.001	0.002	0.008
water	339.615 [a]	25.023	−0.003	0.002	0.003
water	344.275	31.177	−0.003	0.002	0.003
water	348.949	38.565	0.001	0.002	0.002
water	353.644	47.375	0.002	0.003	0.002
water	358.361	57.817	0.002	0.003	0.003
water	363.101	70.120	0.002	0.004	0.002
water	367.867	84.533	0.000	0.005	0.002
water	372.666	101.325	−0.023	0.006	0.002
water	377.484	120.79	0.00	0.01	0.004
water	382.343	143.25	−0.01	0.01	0.006
water	387.232	169.02	0.01	0.01	0.010

TABLE 7. Continued

Method	$\frac{T}{K}$		$\frac{p}{kPa}$	$\frac{\Delta p}{kPa}$	$\frac{\sigma(p)}{kPa}$	$\frac{\Delta T}{K}$
			Tetradecan-1-ol			
decane	443.455		2.0000	−0.0003	0.0001	0.098
decane	450.026		2.6660	0.0001	0.0002	0.070
decane	459.817		3.9999	0.0006	0.0002	0.033
decane	467.161		5.3330	0.0002	0.0003	0.025
decane	478.124		7.9989	−0.0002	0.0004	0.018
decane	486.379		10.666	0.000	0.001	0.020
decane	493.079		13.332	−0.001	0.001	0.016
decane	500.053		16.665	−0.001	0.001	0.014
decane	505.863		19.933	−0.002	0.001	0.011
decane	513.524		25.023	0.000	0.001	0.008
water	513.521	[a]	25.023	0.001	0.001	0.013
water	521.256		31.177	0.000	0.002	0.008
water	529.054		38.565	0.002	0.002	0.004
water	536.917		47.375	0.003	0.002	0.006
water	544.843		57.817	0.003	0.003	0.010
water	552.831		70.120	0.003	0.003	0.012
water	560.879		84.533	−0.006	0.004	0.015
water	568.969		101.325	0.003	0.004	0.031
water	577.096	[a]	120.79	0.04	0.01	0.043
water	585.310	[a]	143.25	−0.04	0.01	0.057

TABLE 7. Continued

Method	T/K	p/kPa	Δp/kPa	σ(p)/kPa	ΔT/K
		Hexan-1,6-diol			
decane	422.184	2.0000	0.0001	0.0001	0.124
decane	427.801	2.6660	0.0004	0.0002	0.076
decane	436.124	3.9999	−0.0003	0.0003	0.054
decane	442.321	5.3330	0.0000	0.0003	0.053
decane	451.520	7.9989	0.000	0.001	0.024
decane	458.412	10.666	−0.002	0.001	0.022
decane	463.974	13.332	−0.003	0.001	0.020
decane	469.741	16.665	−0.001	0.001	0.018
decane	474.530	19.933	0.000	0.001	0.017
decane	480.826	25.023	0.003	0.001	0.017
water	480.825 [a]	25.023	0.003	0.001	0.017
water	487.161	31.177	0.004	0.002	0.019
water	493.533	38.565	0.005	0.002	0.022
water	499.942	47.375	0.006	0.002	0.021
water	506.391	57.817	0.007	0.003	0.021
water	512.882	70.120	0.006	0.003	0.021
water	519.417	84.533	−0.003	0.004	0.015
water	525.994	101.325	−0.012	0.004	0.013
water	532.613	120.79	−0.02	0.01	0.014
water	539.277	143.25	−0.02	0.01	0.014
water	545.982	169.02	−0.03	0.01	0.011
water	552.729	198.49	0.01	0.02	0.012
water	559.524	232.02	0.03	0.02	0.013

TABLE 7. Continued

Method	T/K	p/kPa	Δp/kPa	σ(p)/kPa	ΔT/K
		Benzoyl formic acid			
IP	338.900	0.0147	0.0000	0.0002	
IP	340.000	0.0161	0.0000	0.0002	
IP	350.000	0.0343	0.0000	0.0002	
IP	360.000	0.0696	0.0000	0.0002	
IP	370.000	0.1350	0.0000	0.0002	
IP	380.000	0.2508	0.0000	0.0002	
IP	390.000	0.4484	0.0000	0.0003	
IP	400.000	0.7735	0.0000	0.0003	
IP	410.000	1.2912	0.0000	0.0004	
IP	420.000	2.0909	0.0000	0.0005	

TABLE 7. Continued

Method	T/K	p/kPa	Δp/kPa	$\sigma(p)$/kPa	ΔT/K
Naphthalene-2,6-dicarboxylic acid dimethyl ester					
IP	465.011	0.3853	0.0008	0.0003	
IP	469.998	0.4817	0.0002	0.0003	
IP	475.003	0.5992	−0.0005	0.0003	
IP	479.998	0.7428	0.0002	0.0003	
IP	485.003	0.9139	−0.0008	0.0003	
IP	494.998	1.3638	−0.0011	0.0004	
IP	504.999	1.9967	0.0002	0.0005	
IP	510.002	2.3993	0.0014	0.0006	
IP	515.002	2.8676	0.0011	0.0006	
decane	546.383	7.9989	−0.0001	0.0004	0.031
decane	556.096	10.666	−0.001	0.001	0.022
decane	563.933	13.332	−0.001	0.001	0.023
decane	572.051	16.665	0.004	0.001	0.036
decane	578.802	19.933	0.000	0.001	0.029
water	587.668	25.023	−0.001	0.001	0.029
water	596.565	31.177	0.006	0.001	0.043
water	605.522	38.565	−0.002	0.002	0.040
water	614.510	47.375	−0.004	0.002	0.049
water	623.543	57.817	−0.010	0.003	0.056
water	632.598	70.120	0.010	0.003	0.083

TABLE 7. Continued

Method	T/K	p/kPa	Δp/kPa	σ(p)/kPa	ΔT/K
Tetraethylsilane					
decane	318.628	2.0000	−0.0013	0.0001	0.076
decane	324.312	2.6660	−0.0001	0.0002	0.078
decane	332.782	3.9999	0.0010	0.0003	0.059
decane	339.119	5.3330	0.0027	0.0003	0.059
decane	348.579	7.9989	0.0027	0.0005	0.052
decane	355.694	10.666	0.002	0.001	0.048
decane	361.459	13.332	0.001	0.001	0.044
decane	367.458	16.665	−0.002	0.001	0.040
decane	372.449	19.933	−0.005	0.001	0.038
decane	379.027	25.023	−0.008	0.001	0.038
water	379.025 [a]	25.023	−0.006	0.001	0.036
water	385.656	31.177	−0.008	0.002	0.036
water	392.339	38.565	−0.008	0.002	0.035
water	399.074	47.375	−0.006	0.002	0.036
water	405.863	57.817	−0.002	0.003	0.039
water	412.698	70.120	0.021	0.003	0.047
water	419.573 [a]	84.533	0.083	0.004	0.047
water	426.555	101.325	0.023	0.004	0.047
water	433.559	120.79	0.03	0.01	0.053
water	440.623	143.25	0.03	0.01	0.056
water	447.734	169.02	0.01	0.01	0.063
water	454.913	198.49	−0.06	0.01	0.061

[a] Point excluded from Cox equation fitting.

TABLE 8. Cox equation coefficients [a]

	A	**B**	**C**
T_{ref}/K	372.660	568.970	525.990
P_{ref}/kPa	101.325	101.325	101.325
A	3.05809	3.67463	3.62713
10^3B	−1.14891	−3.55062	−2.76856
10^6C	−0.02270	2.69238	1.75082
Range/K [b]	301 to 387	443 to 585	422 to 559
	E	**G**	**H**
T_{ref}/K	532.0 [c]	650.86	426.564
P_{ref}/kPa	101.325	101.325	101.325
A	3.08308	3.12543	2.84003
10^3B	−1.18877	−1.43697	−1.71981
10^6C	0.53278	0.82334	1.5532
Range/K [b]	339 to 420	465 to 633	318 to 455

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[a] **A** = (±)-butan-2-ol; **B** = tetradecan-1-ol; **C** = hexan-1,6-diol: **E** = benzoyl formic acid **G** = naphthalene-2,6-dicarboxylic acid dimethyl ester and **H** = tetraethylsilane.

[b] Temperature range of the vapor pressures used in the fit.

[c] Temperature fixed at 532.0 K in fit.

TABLE 9. Enthalpies of vaporization obtained from the Cox and Clapeyron equations [a]

T/K	$\Delta_l^g H_m$/kJ·mol^{-1}	T/K	$\Delta_l^g H_m$/kJ·mol^{-1}
(±)-Butan-2-ol			
298.15 [b]	49.86±0.03	360.00	42.84±0.23
300.00 [b]	49.68±0.03	380.00 [b]	39.96±0.38
320.00	47.65±0.07	400.00 [b]	36.72±0.57
340.00	45.39±0.12	420.00 [b]	33.17±0.78
Tetradecan-1-ol			
298.15 [b]	104.92±1.85	520.00	61.04±0.35
400.00 [b]	80.81±0.08	540.00	58.32±0.50
420.00 [b]	76.97±0.05	560.00	55.68±0.70
440.00	73.38±0.05	580.00	53.10±0.91
460.00	70.02±0.08	600.00 [b]	50.49±1.18
480.00	66.87±0.15	620.00 [b]	47.82±1.50
500.00	63.88±0.23		
Hexan-1,6-diol			
298.15 [b]	102.92±1.51	480.00	66.98±0.22
360.00 [b]	89.21±0.28	500.00	63.53±0.35
380.00 [b]	85.14±0.13	520.00	60.06±0.52
400.00 [b]	81.26±0.07	540.00	56.51±0.73
420.00	77.53±0.05	560.00	52.89±0.98
440.00	73.94±0.07	580.00 [b]	49.16±1.26
460.00	70.44±0.13	600.00 [b]	45.29±1.58
Benzoyl formic acid			
298.15 [b]	79.12±0.08	380.00	71.98±0.02
300.00 [b]	78.96±0.08	400.00	70.21±0.02
320.00 [b]	77.23±0.05	420.00	68.41±0.03
340.00	75.49±0.02	440.00 [b]	66.57±0.07
360.00	73.73±0.02	460.00 [b]	64.65±0.12

TABLE 9. continued

T/K	$\Delta_l^g H_m$/kJ·mol^{-1}	T/K	$\Delta_l^g H_m$/kJ·mol^{-1}
Naphthalene-2,6-dicarboxylic acid dimethyl ester			
298.15 [b]	99.67±5.15	580.00	71.27±0.57
460.00 [b]	82.61±0.15	600.00	69.31±0.80
480.00	80.69±0.10	620.00	67.25±1.10
500.00	78.80±0.10	640.00 [b]	65.06±1.48
520.00	76.93±0.17	660.00 [b]	62.73±1.96
540.00	75.07±0.27	680.00 [b]	60.21±2.56
560.00	73.19±0.40		
Tetraethylsilane			
298.15 [b]	44.62±0.05	400.00	38.11±0.27
300.00 [b]	44.51±0.05	420.00	36.70±0.37
320.00	43.26±0.03	440.00	35.19±0.52
340.00	42.01±0.07	460.00 [b]	33.56±0.68
360.00	40.76±0.10	480.00 [b]	31.79±0.88
380.00	39.46±0.17	500.00 [b]	29.87±1.10

[a] Uncertainty intervals are twice the standard deviation of the mean.

[b] Values at this temperature were calculated with extrapolated vapor pressures derived from the fitted Cox coefficients.

TABLE 9A. Critical constants. [a]

Compound		T_c/K	P_c/kPa	$\rho_c/(kg\cdot m^{-3})$
(±)-Butan-2-ol	[b]	535.95	4194	275.5
Tetradecan-1-ol	[c]	747	1810	232
Hexan-1,6-diol	[d]	700	2400	294
Benzoyl formic acid	[d]	743	3160	300
Naphthalene-2,6-dicarboxylic acid dimethyl ester		883	2485	350
Tetraethylsilane	[e]	606	2400	246

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[a] Values used in the derivation of the enthalpies of vaporization listed in Table 9. See text.

[b] Reference 40

[c] Reference 41

[d] Estimated using unpublished group-additivity procedures developed in a research program at NIPER funded by DOE Office of Energy Research.

[e] This research.

TABLE 10. Condensed-phase heat capacities and enthalpies of fusion. [a]
(R=8.31451 $J \cdot K^{-1} \cdot mol^{-1}$)

T/K	$C^{II}_{x,m}$ /R	$C^{II}_{x,m}$ /R	Phase
mass / g	0.015414	0.024312	
Vol. cell / cm^3 [b]	0.05292	0.05288	
	Tetradecan-1-ol		
274.0	42.6	42.8	cr
284.0	45.6	46.3	cr
294.0	49.6	50.2	cr
324.0	64.9	65.3	l
334.0	66.5	67.1	l
344.0	68.2	68.7	l
354.0	70.0	70.5	l
364.0	71.4	72.0	l
374.0	72.7	73.2	l
384.0	74.0	74.4	l
394.0	74.9	75.2	l
404.0	75.5	75.0	l
414.0	74.8	76.2	l
424.0	76.0	76.6	l
434.0	76.2	76.7	l
444.0	76.2	76.8	l
454.0	76.3	77.0	l
464.0	76.3	77.2	l
474.0	76.6	77.2	l
484.0	76.8	77.4	l
494.0	77.3	77.7	l
504.0	77.8	77.7	l
514.0	78.1	78.1	l
524.0	78.9	78.7	l
534.0	79.4	80.1	l
544.0	81.1	79.7	l
554.0	81.1	80.4	l
564.0	81.9	80.9	l

Crystalline $C_{sat,m}/R = 0.360\ T - 56.0_6$ (in temperature range 269 to 311 K)

Liquid $C_{sat,m}/R = 0.159\ T + 13.61_8$ (in temperature range 311 to 379 K)

$$\Delta_c^l H_m^o(311\ K) = 49.4 \pm 0.4\ kJ\ mol^{-1}$$

$$\Delta_c^l H_m^o(298.15\ K) = 48.5 \pm 1.0\ kJ\ mol^{-1}$$

TABLE 10. Continued.

T/K	$C^{II}_{x,m}$ /R	$C^{II}_{x,m}$ /R	$C^{II}_{x,m}$ /R	Phase
mass / g	0.017145	0.009932	0.016104	
Vol. cell / cm^3 ^{b}	0.05288	0.05292	0.05292	
Hexan-1,6-diol				
273.0	21.4	21.0		cr
283.0	22.4	22.6		cr
293.0	24.0	23.7		cr
303.0	25.2	25.0		cr
333.0	35.2	35.5		l
353.0	37.5	38.0		l
373.0	40.1	40.2		l
393.0	42.3	42.5		l
413.0	44.1	44.6	44.3	l
433.0	45.9	46.3	45.8	l
453.0	46.8	47.1	47.1	l
473.0	47.9	48.2	47.8	l
493.0	48.4		48.8	l
513.0	49.1		49.4	l
533.0	49.5		49.7	l
553.0	49.5		50.1	l
573.0			50.7	l
593.0			51.1	l
613.0			51.8	l
633.0			52.6	l
653.0			54.2	l
673.0			54.9	l
693.0			56.0	l

Crystalline $C_{sat,m}/R = 0.128\,T - 13.72$ (in temperature range 268 to 315 K)

Liquid $C_{sat,m}/R = 0.1123\,T - 1.91$ (in temperature range 315 to 413 K)

$$\Delta_c^l H_m^o(315\ \mathrm{K}) = 22.6 \pm 0.6\ \mathrm{kJ\,mol^{-1}}$$

$$\Delta_c^l H_m^o(298.15\ \mathrm{K}) = 21.6 \pm 1.0\ \mathrm{kJ\,mol^{-1}}$$

TABLE 10. Continued.

T/K	$C^{II}_{x,m}$ /R	$C^{II}_{x,m}$ /R	Phase
mass / g	0.013491	0.026761	
Vol. cell / cm^3 ^{b}	0.05292	0.05282	
	Benzoyl formic acid		
295.0	23.1	23.2	cr
315.0	23.6	23.7	cr
355.0	32.4	32.2	l
375.0	33.2	32.9	l
395.0	33.9	33.8	l
415.0	34.9	34.6	l

Crystalline $C_{sat,m}/R = 0.025\ T + 15.7_8$ (in temperature range 285 to 338.9 K)

Liquid $C_{sat,m}/R = 0.0411\ T + 17.6_7$ (in temperature range 338.9 to 425 K)

$$\Delta_c^l H_m^o (338.9\ \mathrm{K}) = 21.8 \pm 0.3\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta_c^l H_m^o (298.15\ \mathrm{K}) = 19.4 \pm 0.6\ \mathrm{kJ\ mol^{-1}}$$

TABLE 10. Continued.

T/K	$C^{II}_{x,m}$ /R	$C^{II}_{x,m}$ /R	Phase
mass / g	0.013392	0.018834	
Vol. cell / cm$^{3\ b}$	0.05292	0.05288	
Naphthalene-2,6-dicarboxylic acid dimethyl ester			
320.00	36.3	36.9	cr
340.00	38.3	38.2	cr
360.00	39.7	39.7	cr
380.00	42.1	42.3	cr
400.00	43.9	43.4	cr
420.00	45.9	45.1	cr
440.00	47.7	48.9	cr
480.00	57.4	56.9	l
500.00	58.5	58.0	l
520.00	59.6	59.4	l
540.00	60.1	60.8	l
560.00	61.7	61.6	l
580.00	63.7	63.0	l
600.00	64.7	64.5	l
620.00	66.1	66.2	l
640.00	66.9	67.5	l
660.00	67.6	68.9	l

Crystalline $C_{sat,m}/R = 0.0960\ T + 5.5_1$ (in temperature range 310 to 464.5 K)

Liquid $C_{sat,m}/R = 0.0635\ T + 26.2_9$ (in temperature range 464.5 to 670 K)

$$\Delta_c^l H_m^o(464.5\ \text{K}) = 53.3 \pm 2.0\ \text{kJ mol}^{-1}$$

$$\Delta_c^l H_m^o(298.15\ \text{K}) = 41.7 \pm 3.0\ \text{kJ mol}^{-1}$$

TABLE 10. Continued.

T/K	$C^{II}_{x,m}$ /R	T/K	$C^{II}_{x,m}$ /R
Naphthalene-2,6-dicarboxylic acid [o]			
315.0	28.9	495.0	42.1
335.0	30.4	515.0	44.2
355.0	32.5	535.0	45.0
375.0	33.9	555.0	46.7
395.0	35.1	575.0	49.2
415.0	36.8	595.0	50.4
435.0	38.0	615.0	51.7
455.0	40.0	635.0	55.0
475.0	41.1	655.0	54.5

Crystalline $C_{sat,m}/R = 0.0763\ T + 4.983$ (in temperature range 305 to 665 K)

TABLE 10. Continued.

T/K	$C^{II}_{x,m}$ /R	$C^{II}_{x,m}$ /R	$C^{II}_{x,m}$ /R	Phase
mass / g	0.008712	0.016641	0.023425	
Vol. cell / cm^3 [b]	0.05292	0.05292	0.05288	
		Tetraethylsilane		
315.00	36.8	36.8	36.8	l
335.00	38.2	38.0	38.0	l
355.00	39.7	39.4	39.4	l
375.00	41.4	41.0	40.8	l
395.00	43.2	42.6	42.4	l
415.00	45.2	44.3	44.0	l
435.00	47.3	46.0	45.6	l
455.00	49.5	47.8	47.2	l
475.00	51.6	49.4	48.7	l
495.00	53.7	50.8	49.9	l
515.00	55.8	52.1	50.9	l
535.00	57.7	53.1	51.6	l
555.00	59.6	53.7	51.8	l
575.00	61.4	54.0		l
595.00	63.3			l

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[a] With the exceptions of hexan-1,6-diol and tetraethylsilane, all the heat-capacity measurements were made at saturation pressures of less than 0.1 MPa. Therefore, the reported $C^{II}_{x,m}$ values can be assumed to be equal to $C_{sat,m}$ values.

[b] Volume of cell at 298.15 K.

[c] Values reported for the crystalline phase only due to decomposition at 695 K (see text).

TABLE 11. Densities and temperatures used to define the vapor/liquid curve near T_c for tetraethylsilane

$\rho/(\mathrm{kg \cdot m^{-3}})$	T/K
162.2	600.9
189.7	603.2
230.7	605.0
309.8	602.7
357.2	597.7

TABLE 12. Parameters for equations (**16**) and (**17**), critical constants and acentric factor for tetraethylsilane

A	2.50408	b_0	−0.85739
B	−1.28488	b_1	0.87232
C	0.84442	b_2	−2.24261

T_c	606 K	p_c	2400 kPa	ρ_c	246 $kg \cdot m^{-3}$	ω	0.401

TABLE 13. Values of $C^{\mathrm{II}}_{V,m}(\rho = \rho_{sat})/R$ and $C_{sat,m}/R$ for tetraethylsilane ($R = 8.31451\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$)

T/K	$C^{\mathrm{II}}_{V,m}(\rho = \rho_{sat})/R$	$C_{sat,m}/R$	T/K	$C^{\mathrm{II}}_{V,m}(\rho = \rho_{sat})/R$	$C_{sat,m}/R$
300.0	35.7	35.7	460.0	44.0	44.1
320.0	36.4	36.4	480.0	46.0	46.2
340.0	37.1	37.1	500.0	48.4	48.6
360.0	37.9	37.9	520.0	51.1	51.6
380.0	38.8	38.8	540.0	54.5	55.3
400.0	39.8	39.8	560.0	58.5	60.0
420.0	41.0	41.0	580.0	63.6	66.9
440.0	42.4	42.4	600.0	70.6	86.0

TABLE 14. Vapor-pressure and heat-capacity measurements, derived enthalpies of sublimation, vaporization and fusion for methacrylamide. "IP" refers to measurements made with the inclined piston, Δp is the difference of the calculated value of pressure {ln(p/1kPa) versus 1/(T/K) equation fit} from the observed value of pressure ($p - p_{Fit}$), $\sigma(p)$ is the propagated error calculated from Equation 3.

Method	$\frac{T}{K}$	$\frac{p}{kPa}$	$\frac{\Delta p}{kPa}$	$\frac{\sigma(p)}{kPa}$
IP	325.000	0.0137	0.0001	0.0001
IP	335.000	0.0347	−0.0001	0.0001
IP	345.000	0.0831	−0.0010	0.0001
IP	355.007	0.1929	−0.0009	0.0001
IP	365.000	0.4270	0.0009	0.0002
IP	375.000	0.9030	−0.0042	0.0002
		Triple point	**385.1 K**	
IP	385.003	1.8201		0.0005
IP	390.001	2.3803		0.0006

$\ln(p/1kPa) = 27.136 - 10216/(T/K)$ crystalline → gas phase

$\ln(p/1kPa) = 21.54 - 8061/(T/K)$ liquid → gas phase

$\Delta_c^g H_m^o(350\ K) = 84.9 \pm 0.4\ kJ\ mol^{-1}$ $\Delta_l^g H_m^o(387.5\ K) = 67.0 \pm 0.4\ kJ\ mol^{-1}$

T/K	$C^{II}_{x,m}$ /R	$C^{II}_{x,m}$ /R	Phase
mass / g	0.023179	0.010071	
Vol. cell / cm^3 [a]	0.05288	0.05292	
295.0	17.2	17.3	cr
305.0	17.6	17.5	cr
315.0	18.0	17.9	cr
325.0	18.3	18.4	cr
335.0	18.6	18.6	cr
345.0	19.0	19.0	cr
355.0	19.3	19.3	cr
365.0	19.8	19.7	cr

Crystalline phase $C_{sat,m}/R = 6.82 + 0.0352\ T$ (in temperature range 290 K to 385 K)

$\Delta_c^l H_m^o(385.1\ K) = 15.0 \pm 1.0\ kJ\ mol^{-1}$

TABLE 15. Thermochemical properties at 298.15 K. Values are in kJ·mol^{-1}. (R = 8.31441 J·K^{-1}·mol^{-1} and p° = 101.325 kPa)

Compound	$\Delta_f H^\circ_m(c)$	$\Delta_c^l H^\circ_m$	$\Delta_f H^\circ_m(l)$	$\Delta_l^g H^\circ_m$	$\Delta_f H^\circ_m(g)$
(±)-Butan-2-ol			−342.6±0.3	49.86±0.03	−292.7±0.3
Tetradecan-1-ol	−628.18±1.46	48.5±1.0	−579.7±1.8	104.9±1.9	−474.8±2.6
Hexan-1,6-diol	−583.86±0.72	21.6±1.0	−562.3±1.2	102.9±1.5	−459.4±1.9
Methacrylamide	−247.10±0.50			89.4±2.0 [a]	−157.7±2.1
Benzoyl formic acid	−487.22±0.80	19.4±0.6	−467.8±1.0	79.12±0.08	−388.7±1.0
Naphthalene-2,6-dicarboxylic acid	−770.25±0.96	?.? [b]			
Naphthalene-2,6-dicarboxylic acid dimethyl ester	−696.51±1.34	41.7±3.0	−654.8±3.3	99.67±5.15	−555.1±6.1
Tetraethylsilane			−328.6±5.2	44.62±0.05	−284.0±5.2

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[a] Value for enthalpy of sublimation at 298.15 K; see text and Table 17.

[b] Compound decomposes before the melting point; see text.

TABLE 16. Enthalpies of formation of alkan-1-ols. Comparison of experimental,[a] assessed,[b] and estimated[c] ideal-gas enthalpies of formation at 298.15 K for some alcohols. All values in kJ·mol^{-1}.

Compound	Experimental	Assessed	Benson Groups	Equation **21**
Ethanol		−235.2±0.4	−234.8	−234.8
Propan-1-ol		−255.1±0.5	−255.5	−255.0
Butan-1-ol	−275.28±0.53	−275.0±0.4	−276.2	−275.2
Pentan-1-ol	−295.63±0.74	−294.5±0.5	−297.0	−295.5
Hexan-1-ol		−315.8±0.6	−317.7	−315.6
Heptan-1-ol		−336.4±1.0	−338.4	−335.8
Octan-1-ol	−356.87±1.17	−355.5±0.8	−359.1	−356.0
Nonan-1-ol		−376.3±1.4	−379.8	−376.2
Decan-1-ol		−396.4±1.6	−400.6	−396.4
Dodecan-1-ol		−436.6±1.1	−442.0	−436.8
Tetradecan-1-ol	−474.8±2.6	−478.4±2.4	−483.4	−477.2
Hexadecan-1-ol	−517.5±3.2	−517.0±2.4	−524.9	−517.7

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[a] Reference 83 except for tetradecan-1-ol the value for which was obtained in this research.

[b] Reference 60.

[c] References 1 and 2.

Table 17. Thermochemical cycles for methacrylamide

Sublimation at 298.15 K

$\Delta_c^g H_m^o(350\ \mathrm{K}) =$

$$\int_{350}^{298.15} C_{sat}(c)dT + \Delta_c^g H_m^o(298.15\ \mathrm{K}) + \int_{298.15}^{350} C_{sat}(g)dT$$

$C_{sat}/R = 6.82 + 0.0352\ T$ for crystalline phase (see Table 14)

$C_{sat}/R = 4.13 + 0.0234\ T$ for the gas phase (see text)

$\Delta_c^g H_m^o(350\ \mathrm{K}) = 84.9 \pm 0.4\ \mathrm{kJ \cdot mol^{-1}}$ (see Table 14)

Hence:

$84.9 = -12.8 + \Delta_c^g H_m^o(298.15\ \mathrm{K}) + 8.3$ in $\mathrm{kJ \cdot mol^{-1}}$

and;

$\Delta_c^g H_m^o(298.15\ \mathrm{K}) = 89.4 \pm 2.0\ \mathrm{kJ \cdot mol^{-1}}$

Sublimation at 385.1 K

$\Delta_c^g H_m^o(350\ \mathrm{K}) =$

$$\int_{350}^{385.1} C_{sat}(c)dT + \Delta_c^g H_m^o(385.1\ \mathrm{K}) + \int_{385.1}^{350} C_{sat}(g)dT$$

Hence:

$84.9 = 9.5 + \Delta_c^g H_m^o(385.1\ \mathrm{K}) - 6.2$ in $\mathrm{kJ \cdot mol^{-1}}$

and;

$\Delta_c^g H_m^o(385.1\ \mathrm{K}) = 81.6 \pm 2.0\ \mathrm{kJ \cdot mol^{-1}}$

which compares favorably with sum of the enthalpies of vaporization and fusion reported in Table 14 (67.0 and 15.0 $\mathrm{kJ \cdot mol^{-1}}$).

Table 18. "Assessed" ideal-gas enthalpies of formation for some aliphatic carboxylic acids and the corresponding methyl esters. T = 298.15 K and p° = 101.325 kPa. Values from reference 60. All values in $kJ{\cdot}mol^{-1}$.

Acid	$\Delta_f H_m^o$ Acid	$\Delta_f H_m^o$ Methyl ester	Difference [a]
Formic	-378.7 ± 0.6	-355.5 ± 0.8	23.2 ± 1.0
Acetic	-432.8 ± 1.5	-411.9 ± 1.6	20.9 ± 2.2
Pentanoic	-491.9 ± 3.0	-471.2 ± 0.9	20.7 ± 3.1
Hexanoic	-511.9 ± 2.3	-492.6 ± 1.2	19.3 ± 2.6
Heptanoic	-536.2 ± 2.1	-515.9 ± 1.2	20.3 ± 2.4
Octanoic	-554.3 ± 1.5	-533.8 ± 1.3	20.5 ± 2.0
Nonanoic	-577.3 ± 2.1	-553.9 ± 1.9	23.4 ± 2.8
Decanoic	-594.9 ± 2.3	-573.8 ± 1.8	21.1 ± 2.9
Undecanoic	-614.6 ± 1.6	-593.8 ± 1.4	20.8 ± 2.1
Tridecanoic	-660.2 ± 2.5	-635.4 ± 2.7	24.8 ± 3.7
Pentadecanoic	-699.0 ± 4.5	-680.0 ± 2.8	19.0 ± 5.3

[a] Difference = ($\Delta_f H_m^o$ methyl ester − $\Delta_f H_m^o$ acid)

Table 19. Literature values for the enthalpy of formation of tetraethylsilane (T = 298.15 K and p° = 101.325 kPa. All values in $kJ \cdot mol^{-1}$.)

Reference Number	Year	$\Delta_f H^o_m$
98	1953	$-171.5\pm?$ [a]
99	1956	$-280.0\pm?$ [a]
100	1964	-205.0 ± 8.0
101	1966	-205.0 ± 8.0
102	1970	-221.0 ± 21.0
103	1971	-277.8 ± 18.8
104	1986	-335.6 ± 5.6
105	1988	-336.0 ± 4.0
This research	1989	-328.6 ± 5.2

[a] ? = unknown uncertainty interval due to insufficient detail in the reference.

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