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TOPICAL REPORT

**DIPPR PROJECT 871
DETERMINATION OF
IDEAL-GAS ENTHALPIES OF FORMATION
FOR KEY COMPOUNDS
THE 1991 PROJECT RESULTS**

by

W.V. Steele, R.D. Chirico, S.E. Knipmeyer, A. Nguyen and I.R. Tasker

Work performed for the
American Institute of Chemical Engineers
Design Institute for Physical Property Data (DIPPR)

and

Advanced Exploration Research
U.S. Department of Energy
Under Cooperative Agreement DE-FC22-83FE60149

National Institute for Petroleum and Energy Research
IIT Research Institute • P. O. Box 2128
Bartlesville, Oklahoma 74005-2128 • (918) 336 - 2400

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IIT RESEARCH INSTITUTE
NATIONAL INSTITUTE FOR PETROLEUM AND ENERGY RESEARCH
P.O. BOX 2128
BARTLESVILLE, OKLAHOMA 74005
(918) 336-2400

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EXECUTIVE SUMMARY

This report describes the results obtained in the fifth 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. Nine compounds were selected for study in the fifth year of the project, and the ideal-gas enthalpies of formation of cyclohexene, phthalan (2,5-dihydrobenzo-3,4-furan), isoxazole, phenyl isocyanate, 1,4,5,6-tetrahydropyrimidine, n-octylamine, di-n-octylamine, and tri-n-octylamine are reported here. Liquid-phase densities along the saturation line were measured for phthalan and isoxazole in the temperature range 298 K to 523 K.

Values for the group-additivity parameters $N-(C)(H)_2$, $N-(C)_2(H)$, and $N-(C)_3$, were confirmed. A value for the $N-(C_b)(CO)$ group-additivity parameter was defined. Ring correction terms were derived for cyclohexene and phthalan ring systems. An estimate for the ideal-gas enthalpy of formation of 2,3-dihydrofuran was derived. Also, the results of isoxazole and 1,4,5,6-tetrahydropyrimidine were used to estimate ideal gas enthalpies of formation for substituted compounds.

The results reported continue to establish the validity of the group-contribution approach for the accurate estimation of the enthalpies of formation of organic 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.

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 $\rho/(\text{kg}\cdot\text{m}^{-3})$ rather than " ρ (kg/m^3)" or " ρ kg/m^3 ". Molar values, i.e., intensive functions, are denoted by the subscript m, e.g., $C_{\text{sat},m}$, 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 $\text{g}\cdot\text{mol}^{-1}$

T = temperature in Kelvin

p = pressure in Pascals (Pa)

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

$\Delta_c U_m^\circ$ = molar energy of combustion and $\Delta_c U_m^\circ/M$ = energy of combustion per gram

$\Delta_c H_m^\circ$ = molar enthalpy of combustion

$\Delta_f H_m^\circ$ = molar enthalpy of formation

$\Delta_r H_m^\circ$ = 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

$C_{\text{sat},m}$ = 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

$C_v^{\text{II}}(p = p_{\text{sat}})$ = 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).

DIPPR PROJECT 871
DETERMINATION OF IDEAL-GAS ENTHALPIES OF FORMATION FOR KEY COMPOUNDS
THE 1991 PROJECT RESULTS

W. V. Steele, R. D. Chirico, S. E. Knipmeyer, A. Nguyen, N. K. Smith, and I. R. Tasker IIT Research Institute, National Institute for Petroleum and Energy Research, P. O. Box 2128, Bartlesville, OK 74005.

The results of a study aimed at improvement of group-contribution methodology for estimation of thermodynamic properties of organic 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 cyclohexene, phthalan (2,5-dihydrobenzo-3,4-furan), isoxazole, n-octylamine, di-n-octylamine, tri-n-octylamine, phenyl isocyanate, and 1,4,5,6-tetrahydropyrimidine are reported. Two-phase (liquid + vapor) heat capacities were determined for phthalan, isoxazole, the three octylamines, and phenyl isocyanate. Liquid-phase densities along the saturation line were measured for phthalan and isoxazole in the temperature range 298 K to 425 K. The critical temperature and critical density of n-octylamine were determined from the d.s.c. results and a critical pressure derived from the fitting procedures. Fitting procedures were used to derive critical temperatures, critical pressures, and critical densities for cyclohexene (pressure and density only), phthalan, isoxazole, di-n-octylamine, and phenyl isocyanate. Group-additivity parameters or ring-correction terms useful in the application of group-contribution correlations are derived.

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 fifth 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 1990, and subsequent communications, in which representatives of the DOE Bartlesville Project Office, 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.

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 >1400 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. One reason for the choice of isoxazole as a compound in this study was the report of an explosion in a fine chemicals factory of a drum containing a substituted isoxazole (3). The ideal-gas enthalpy of formation is the thermodynamic property most needed for evaluation of the energy hazard potential of an organic compound. A 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 fifth year of the project, nine compounds were chosen for experimental studies. Results for one of the compounds, benzene sulfonic acid, appear to be erroneous. Research on that compound will continue with results being published at a later date. The molecular structures, trivial and Chemical Abstract (CA) names, and CA Registry Numbers of the compounds studied, are listed in Figure 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 given in Table 1.

Table 1. Outline of the measurements performed in this project ^{a,b}

Compound	$\Delta U_{c,m}^0$	Vap. pres.	Heat cap.
Cyclohexene	x	x	
Phthalan	x	x	x
Isoxazole	x	x	x
n-Octylamine	x	x	x
Di-n-octylamine	x	x	x
Tri-n-octylamine	x	x	x
Phenyl isocyanate	x	x	x
1,4,5,6-Tetrahydro-pyrimidine	x	x	

^a Measurements made are denoted by x

^b In addition, liquid-phase density measurements along the saturation line in the temperature range 298 K to 425 K were made for phthalan and isoxazole, and critical temperatures, pressures and densities derived. Values for the critical temperature and critical density for n-octylamine were determined from the d.s.c. measurements on that compound. Values for the critical temperature and critical pressure for di-n-octylamine and phenyl isocyanate were also derived.

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

Figure 1. Molecular structures, trivial and Chemical Abstract names, and CA Registry Numbers for the compounds studied in this research.

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.

EXPERIMENTAL

In this section, details are given of the apparatus and procedures used in obtaining the experimental data. These have been previously described in the literature and in

various DOE reports. Therefore, details have been kept to a minimum here and the literature referenced for further consultation.

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. All compounds except phthalan were purchased from Aldrich Chemical Company. Capillary gas chromatography (cgc) analyses on the purchased samples gave an average purity of 99.8 mole percent. Phthalan was synthesized and all the compounds were purified by the Oklahoma State University Synthesis and Purification Group under the direction

of Professor E. J. Eisenbraun. Cgc analyses of the calorimetric samples gave purities of at least 99.95 mole percent for each compound. The high purity of each calorimetric sample was confirmed subsequently by the percentage CO₂ recoveries in the combustion calorimetric measurements, and the small differences between the boiling and condensation temperatures in the ebulliometric vapor-pressure measurements (which are described in detail in this report).

All transfers of the samples were made 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 MgSO₄, and distillation at 337 K and 1 kPa pressure. Cgc 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 (4) and the gas constant, $R = 8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, adopted by CODATA (5). 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 ITS-90 (6). Measurements of mass, time, electric resistance, and potential difference were made in terms of standards traceable to calibrations at NIST.

Energy of Combustion Apparatus and Procedures

The apparatus and experimental procedures used in the combustion calorimetry of organic C, H, N, O

compounds, and C, H, S compounds at the National Institute for Petroleum and Energy Research have been described in (7-10) and (11,12), respectively. A rotating-bomb calorimeter (laboratory designation BMR II) (13) and a platinum-lined bomb (laboratory designation Pt-3b) (14) with an internal volume of 0.3934 dm³ were used with rotation in the first series of combustions and without rotation in the remaining series. Flexible borosilicate-glass ampoules (7,15) were used to confine the samples which were liquied at 298 K.

NIST thermochemical benzoic acid (sample 39i) was used for calibration of the calorimeter; its specific energy of combustion is $-(26434.0 \pm 3.0) \text{ J} \cdot \text{g}^{-1}$ under certificate conditions. Conversion to standard states (16) gives $-(26413.7 \pm 3.0) \text{ J} \cdot \text{g}^{-1}$ for $\Delta_c U_m^0/M$, the standard specific energy of the idealized combustion reaction. The combustion measurements were performed in five separate series over a nine month period as the purified compounds became available. 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.

In the first combustion series the energy equivalent of the calorimeter, $\epsilon(\text{calor})$, obtained was $(16784.3 \pm 0.4) \text{ J} \cdot \text{K}^{-1}$ (mean and standard deviation of the mean) for the cyclohexene and phthalan measurements. In the second combustion series $\epsilon(\text{calor})$ was $(16775.7 \pm 0.3) \text{ J} \cdot \text{K}^{-1}$ for the n-octylamine and di-n-octylamine measurements. In the third series the energy equivalent of the calorimeter, $\epsilon(\text{calor})$, obtained was $(16772.4 \pm 1.2) \text{ J} \cdot \text{K}^{-1}$ for the isoxazole measurements, and in the fourth series $(16770.9 \pm 0.6) \text{ J} \cdot \text{K}^{-1}$ for the tri-n-octylamine and phenyl isocyanate measurements. Finally, in the fifth series $\epsilon(\text{calor})$ was (16772.2 ± 0.4) for the 1,4,5,6-tetrahydropyrimidine combustions. The changes in the energy equivalent represented small repairs to the bomb to cure leaking gaskets which develop with age and continual usage.

(The bomb calorimeter Pt-3b is now 40 years old!)

The auxiliary oil (laboratory designation TKL66) had the empirical formula $\text{CH}_{1.913}$. For this material, $\Delta_c U_m^0/M$ was $-(46042.5 \pm 1.8) \text{ J} \cdot \text{g}^{-1}$ (mean and standard deviation). For the cotton fuse, empirical formula $\text{CH}_{1.774}\text{O}_{0.887}$, $\Delta_c U_m^0/M$ was $-16945 \text{ J} \cdot \text{g}^{-1}$. 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 (16) is given in Table 2.

Values of density reported in Table 2 were measured in this laboratory, from measurements of volumes of the ampoules used in the combustion calorimetry, and their enclosed sample masses, for the liquid samples. Values of the heat capacity of each sample at 298.15 K were measured using a differential scanning calorimeter as described later.

Table 2. Physical properties at 298.15 K ^a

Compound	ρ $\text{kg} \cdot \text{m}^{-3}$	$10^7 (\partial V / \partial T)_P$ $\text{m}^3 \cdot \text{K}^{-1}$	C_p/R
Cyclohexene	806.2	1.2	17.9
Phthalan	1082	0.91	22.7
Isoxazole	1071	0.70	13.0
n-Octylamine	796.2	1.53	37.2
Di-n-octylamine	796.0	2.32	61.0
Tri-n-octylamine	810.5	3.63	90.3
Phenyl isocyanate	1081	1.04	22.4
1,4,5,6-Tetrahydro-pyrimidine	1024	(1.2)	19.0

^a Values in parentheses are estimates.

Nitric acid, formed during combustions of isoxazole, the three octylamines, and phenyl isocyanate, was determined by titration with standard sodium hydroxide (17). Carbon dioxide was also recovered from the combustion products of each experiment. Anhydrous lithium hydroxide was used as adsorbent for the CO_2 recoveries (8). 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.

Table 3. Carbon dioxide recoveries

Compound	# of expts	% recovery ^a
Benzoic acid calibration	6	100.009 $\pm$ 0.012
Cyclohexene	6	99.995 $\pm$ 0.004
Phthalan	6	99.993 $\pm$ 0.005
Benzoic acid calibration	6	100.000 $\pm$ 0.005
n-Octylamine	7	99.974 $\pm$ 0.009 ^b
Di-n-octylamine	8	99.995 $\pm$ 0.004
Benzoic acid calibration	6	99.985 $\pm$ 0.007
Isoxazole	6	99.935 $\pm$ 0.018 ^b
Benzoic acid calibration	8	100.000 $\pm$ 0.004
Tri-n-octylamine	6	99.997 $\pm$ 0.006
Phenyl isocyanate	7	99.992 $\pm$ 0.005
Benzoic acid calibration	6	99.992 $\pm$ 0.008
1,4,5,6-Tetrahydro-pyrimidine	6	99.995 $\pm$ 0.010

^a Mean and standard deviation of the mean.

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

Vapor-Pressure Apparatus and Procedures

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:

$$\sigma(p) = (0.001) \{ (dp_{\text{ref}}/dT)^2 + (dp_{\psi}/dT)^2 \}^{1/2}, \quad (1)$$

where p_{ref} is the vapor pressure of the reference substance and p_{ψ} 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.

The equipment for the inclined-piston vapor-pressure 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:

$$\sigma(p) = 1.5 \times 10^{-4} p + 0.2 \text{ Pa.} \quad (2)$$

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 have been outlined in references 25 through 30, inclusive. The major difference between our measurement technique and that used by Mraw et al. (25-27) 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 theoretical background for the determination of heat capacities at vapor-saturation pressure, $C_{\text{sat},m}$, with results obtained with a d.s.c. has been described (28-30). 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 , $C_{x,m}^{\text{II}}$, can be expressed in terms of the temperature derivatives of these quantities:

$$n C_{x,m}^{\text{II}}/T = -n(\partial^2 \mu / \partial T^2)_{\text{sat}} + V_x (\partial^2 p / \partial T^2)_{\text{sat}} + \{(\partial V_x / \partial T)_x (\partial p / \partial T)_{\text{sat}}\}. \quad (3)$$

The third term on the right-hand side of equation (3) includes the thermal expansion of the cell. In this research the thermal expansion of the cells was expressed as:

$$V_x(T) / V_x(298.15 \text{ K}) = 1 + ay + by^2, \quad (4)$$

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

$(\partial p / \partial T)_{\text{sat}}$ can be calculated based on the vapor pressures measured in this research. Therefore, with a minimum of two different filling levels of the cell $(\partial^2 p / \partial T^2)_{\text{sat}}$ and $(\partial^2 \mu / \partial T^2)_{\text{sat}}$ 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 $C_{\text{sat},m}$ 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:

$$\lim_{(n/V_x) \rightarrow \{1/V_m(l)\}} (n C_{v,m}^{\text{II}}/T) = V_m(l)(\partial^2 p / \partial T^2)_{\text{sat}} - n(\partial^2 \mu / \partial T^2)_{\text{sat}}. \quad (5)$$

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

$$\lim_{(n/V_k) \rightarrow \{1/V_m(l)\}} (n C_{v,m}^{II}) = n[C_{sat,m} - \{T(\partial p/\partial T)_{sat} (\partial V_m(l)/\partial T)\}]. \quad (6)$$

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

Densitometry

The vibrating-tube densitometer used in the density measurements at NIPER has been described (31). The densitometer has an upper temperature limit near 550 K (the upper temperature limit at present is set by that attainable by the constant-temperature bath.) The design of the new densitometer is essentially that used successfully by Dr. J. M. Simonson and his colleagues at Oak Ridge National Laboratory (32) for the study of aqueous salt mixtures at high temperatures and pressures.

Water was used for the calibration of the densitometer (31). Vibrational frequencies for the water-filled vibrating tube were determined for each of the temperatures at which values for the compound under study were measured previously.

For each temperature a calibration constant for the densitometer was derived with the equation:

$$(\rho_w - \rho_v) / \rho^0 = K(\tau_w^2 - \tau_v^2) / (\tau^0)^2, \quad (7)$$

where ρ^0 and τ^0 are $1.0 \text{ kg}\cdot\text{m}^{-3}$ and 1.0 s , respectively. ρ_w is the density of water in $\text{kg}\cdot\text{m}^{-3}$ as per reference 33. The density of the vacuum ρ_v was assumed to be zero. τ_w and τ_v are the vibration periods in seconds for water and a vacuum in the densitometer, respectively. Densities were derived with the equation:

$$(\rho_1 - \rho_2) / \rho^0 = K(\tau_1^2 - \tau_2^2) / (\tau^0)^2, \quad (8)$$

where τ_1 is the resonance period of the tube when filled with a fluid of density ρ_1 .

RESULTS

Combustion calorimetry

A typical combustion experiment for each compound studied is summarized in Table 4. It is impractical to list summaries for each combustion, but values of $\Delta_c U_m^0/M$ for all the experiments are reported in Table 5. Values of $\Delta_c U_m^0/M$ in Tables 4 and 5 for the C,H,N,O compounds refer to the general reaction:

For n-octylamine and isoxazole the values of $\Delta_c U_m^0/M$ refer to unit mass of sample derived from the corresponding carbon dioxide analyses of the combustion products (see Table 3). Table 6 gives derived values of the standard molar energy of combustion $\Delta_c U_m^0$; the standard molar enthalpy of combustion $\Delta_c H_m^0$; and the standard molar enthalpy of formation $\Delta_f H_m^0$ for the compounds studied. Values of $\Delta_c U_m^0$ and $\Delta_c H_m^0$ for the C,H,N,O compounds refer to Equation 9. The corresponding values of $\Delta_f H_m^0$ refer to the reaction:

Uncertainties given in Table 6 are the "uncertainty interval" (34). The enthalpies of formation of $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ were taken to be $-(393.51 \pm 0.13)$ and $-(285.830 \pm 0.042) \text{ kJ}\cdot\text{mol}^{-1}$, respectively, as assigned by CODATA (35).

Table 4. Typical combustion experiments at
298.15 K ($p^{\circ} = 101.325$ kPa) ^{a,b}

	A	B
m' (compound) /g	0.695827	0.928005
m'' (oil) /g	0.039755	0.025355
m''' (fuse) /g	0.001000	0.001240
n_1 (H ₂ O) /mol	0.05535	0.05535
m (Pt) /g	19.985	33.318
$\Delta T/K$ ^c	1.99892	2.00403
ϵ (calor) (ΔT) /J	-33550.5	-33636.2
ϵ (cont) (ΔT) /J ^d	-41.0	-41.5
$\Delta U_{ign}/J$	0.75	0.75
ΔU (corr. std. states) /J ^e	11.7	19.1
$-m'' (\Delta_c U_m^{\circ}/M)$ (oil) /J	1830.4	1167.4
$-m''' (\Delta_c U_m^{\circ}/M)$ (fuse) /J	16.9	21.0
$m' (\Delta_c U_m^{\circ}/M)$ (compound) /J	-31731.8	-32469.4
$(\Delta_c U_m^{\circ}/M)$ (compound) /J·g ⁻¹	-45602.9	-34988.5

	C	D
m' (compound) /g	1.375320	0.749225
m'' (oil) /g	0.046818	0.038366
m''' (fuse) /g	0.001009	0.000922
n_1 (H ₂ O) /mol	0.05535	0.05535
m (Pt) /g	32.468	38.820
$\Delta T/K$ ^c	2.09915	2.05146
ϵ (calor) (ΔT) /J	-35207.8	-34414.7
ϵ (cont) (ΔT) /J ^d	-43.1	-37.2
$\Delta U_{ign}/J$	0.75	0.75
ΔU_{dec} (HNO ₃) /J	101.3	53.0
ΔU (corr. std. states) /J ^e	25.3	9.0
$-m'' (\Delta_c U_m^{\circ}/M)$ (oil) /J	2155.6	1766.5
$-m''' (\Delta_c U_m^{\circ}/M)$ (fuse) /J	17.1	15.6
$m' (\Delta_c U_m^{\circ}/M)$ (compound) /J	-32950.9	-32607.1
$(\Delta_c U_m^{\circ}/M)$ (compound) /J·g ⁻¹	-23958.7	-43521.1

	E	F
m' (compound) /g	0.739434	0.720606
m'' (oil) /g	0.034250	0.039359
m''' (fuse) /g	0.001088	0.001067
n_1 (H ₂ O) /mol	0.05535	0.05535
m (Pt) /g	32.230	19.971
$\Delta T/K$ ^c	2.08018	2.06644
ϵ (calor) (ΔT) /J	-34896.5	-34656.1
ϵ (cont) (ΔT) /J ^d	-37.6	-37.1
$\Delta U_{ign}/J$	0.75	0.75
ΔU_{dec} (HNO ₃) /J	39.9	27.9
ΔU (corr. std. states) /J ^e	9.8	10.0
$-m'' (\Delta_c U_m^{\circ}/M)$ (oil) /J	1576.9	1812.2
$-m''' (\Delta_c U_m^{\circ}/M)$ (fuse) /J	18.4	18.1
$m' (\Delta_c U_m^{\circ}/M)$ (compound) /J	-33288.4	-32824.4
$(\Delta_c U_m^{\circ}/M)$ (compound) /J·g ⁻¹	-45018.5	-45551.1

Table 4. Continued

	G	H
m' (compound) /g	1.113733	0.945579
m'' (oil) /g ^g	0.035436	0.082722
m''' (fuse) /g	0.001059	0.001522
n_1 (H ₂ O) /mol	0.05535	0.05535
m (Pt) /g	32.507	19.984
$\Delta T/K$ ^c	1.99876	2.03734
ϵ (calor) (ΔT) /J	-33521.0	-34170.8
ϵ (cont) (ΔT) /J ^d	-37.6	-39.9
$\Delta U_{ign}/J$	0.75	0.75
ΔU_{dec} (HNO ₃) /J	33.2	80.0
ΔU (corr. std. states) /J ^e	19.6	14.6
$-m'' (\Delta_c U_m^{\circ}/M)$ (oil) /J	1631.6	3808.7
$-m''' (\Delta_c U_m^{\circ}/M)$ (fuse) /J	17.9	25.6
$m' (\Delta_c U_m^{\circ}/M)$ (compound) /J	-31855.6	-30280.8
$(\Delta_c U_m^{\circ}/M)$ (compound) /J·g ⁻¹	-28602.5	-32023.8

^a The symbols and abbreviations of this Table are those of reference 16 except as noted.

^b **A** = Cyclohexene; **B** = Phthalan; **C** = Isoxazole; **D** = n-Octylamine; **E** = Di-n-octylamine; **F** = Tri-n-octylamine; **G** = Phenyl isocyanate and **H** = 1,4,5,6-Tetrahydropyrimidine.

^c $\Delta T/K = (T_1 - T_f + \Delta T_{corr})/K$

^d ϵ_1 (cont) ($T_1 - 298.15$ K) + ϵ_f (cont) (298.15 K - $T_f + \Delta T_{corr}$)

^e Items 81 to 85, 87 to 90, 93, and 94 of the computational form of reference 16.

Table 5. Summary of experimental energy of combustion results. $T = 298.15$ K, and $p^{\circ} = 101.325$ kPa. The uncertainties shown are one standard deviation of the mean.

Cyclohexene			
$(\Delta_c U_m^{\circ}/M)$ (compound) / (J·g ⁻¹)			
-45602.9	-45605.3	-45601.8	-45604.9
	-45608.1	-45603.1	
$\langle (\Delta_c U_m^{\circ}/M)$ (compound) / (J·g ⁻¹) $\rangle$ -45604.4±0.9			
Phthalan			
$(\Delta_c U_m^{\circ}/M)$ (compound) / (J·g ⁻¹)			
-34988.5	-34989.0	-34988.8	-34984.4
	-34989.0	-34988.3	
$\langle (\Delta_c U_m^{\circ}/M)$ (compound) / (J·g ⁻¹) $\rangle$ -34988.0±0.7			

Table 5. continued.

Isoxazole			
$\{(\Delta_c U_m^0/M) \text{ (compound)}\} / (J \cdot g^{-1})$			
-23958.7	-23957.3	-23962.4	-23957.1
	-23958.3	-23959.6	
$\langle \{(\Delta_c U_m^0/M) \text{ (compound)}\} / (J \cdot g^{-1}) \rangle$			
			-23958.9±0.8

n-Octylamine			
$\{(\Delta_c U_m^0/M) \text{ (compound)}\} / (J \cdot g^{-1})$			
-43521.1	-43516.4	-43527.0	-43513.4
	-43511.8	-43523.2	-43531.3
$\langle \{(\Delta_c U_m^0/M) \text{ (compound)}\} / (J \cdot g^{-1}) \rangle$			
			-43520.6±2.7

Di-n-octylamine			
$\{(\Delta_c U_m^0/M) \text{ (compound)}\} / (J \cdot g^{-1})$			
-45018.5	-45024.0	-45012.3	-45017.9
-45027.0	-45012.2	-45021.2	-45024.2
$\langle \{(\Delta_c U_m^0/M) \text{ (compound)}\} / (J \cdot g^{-1}) \rangle$			
			-45019.7±1.9

Tri-n-octylamine			
$\{(\Delta_c U_m^0/M) \text{ (compound)}\} / (J \cdot g^{-1})$			
-45551.1	-45578.1	-45570.6	-45557.5
	-45560.7	-45568.3	
$\langle \{(\Delta_c U_m^0/M) \text{ (compound)}\} / (J \cdot g^{-1}) \rangle$			
			-45564.4±4.0

Phenyl isocyanate			
$\{(\Delta_c U_m^0/M) \text{ (compound)}\} / (J \cdot g^{-1})$			
-28602.5	-28605.4	-28612.3	-28600.4
	-28601.5	-28604.9	
$\langle \{(\Delta_c U_m^0/M) \text{ (compound)}\} / (J \cdot g^{-1}) \rangle$			
			-28604.5±1.7

1,4,5,6-Tetrahydropyrimidine			
$\{(\Delta_c U_m^0/M) \text{ (compound)}\} / (J \cdot g^{-1})$			
-32023.5	-32023.8	-32034.5	-32028.6
	-32025.0	-32040.7	
$\langle \{(\Delta_c U_m^0/M) \text{ (compound)}\} / (J \cdot g^{-1}) \rangle$			
			-32029.4±3.0

Table 6. Condensed phase molar thermochemical functions at 298.15 K and $p^0 = 101.325 \text{ kPa}$.^a

	$\Delta_c U_m^0 / \text{kJ} \cdot \text{mol}^{-1}$	$\Delta_c H_m^0 / \text{kJ} \cdot \text{mol}^{-1}$	$\Delta_f H_m^0 / \text{kJ} \cdot \text{mol}^{-1}$
A	-3746.19±0.49	-3752.39±0.49	-37.82±0.82
B	-4203.86±0.54	-4207.57±0.54	-83.83±0.93
C	-1654.67±0.32	-1654.05±0.32	44.78±0.56
D	-5624.84±0.96	-5635.38±0.96	-228.09±1.24
E	-10870.5±1.6	-10890.9±1.6	-407.3±1.9
F	-16115.0±3.6	-16145.4±3.6	-587.5±3.8
G	-3407.45±0.85	-3408.07±0.85	-61.08±1.11
H	-2694.34±0.25	-2696.82±0.25	-20.54±0.29

^a A = Cyclohexene; B = Phthalan; C = Isoxazole; D = n-Octylamine; E = Di-n-octylamine; F = Tri-n-octylamine; G = Phenyl isocyanate and H = 1,4,5,6-Tetrahydropyrimidine.

Vapor-pressure measurements

Note again that all temperatures listed in this report are on the ITS-90 temperature scale. Measured vapor pressures for each of the compounds are listed in Tables 7 and 7A. The results for cyclohexene are those of Forziati et al. (36) obtained using an ebulliometer. The precision in the temperature measurements was given by Forziati et al. (36) as 0.003 K. Following previous practice (19,20), the results obtained in the NIPER 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 phthalan, tri-n-octylamine and 1,4,5,6-tetrahydropyrimidine are also listed in Tables 7 and 7A. For phthalan, the inclined-piston values extend the range of measured values down to 285 K. For tri-n-octylamine and 1,4,5,6-tetra-

hydropyrimidine, compound decomposition prevented appreciable measurements in the ebulliometric vapor pressure region (2 to 270 kPa).

The difference between the boiling and condensation temperatures (ΔT) for di-n-octylamine increased significantly above 590 K. An attempt was made to make a measurement at 143.25 kPa (597.8 K), but ΔT started at approximately 0.08 K and rapidly increased to 0.12 K. This phenomenon is normally indicative of sample decomposition. For phenyl isocyanate (see Table 7), at 445.5 K ΔT started at approximately 0.01 K and rapidly increased to 0.125 K. In this case sample decomposition was also noted in the d.s.c. measurements above 490 K. Similar behavior was noted for tri-n-octylamine, when attempting determination of the boiling and condensation temperatures at 8.0 kPa (549 K) where ΔT started at approximately 0.045 K and rapidly increased by a factor of ten.

Table 7. Summary of vapor pressure results: ip = inclined piston; d. = decane or w. = water refers to which material was used as the standard in the reference ebulliometer, the pressure p was calculated from the condensation temperature of the reference substance, T is the condensation temperature of the sample, $\Delta T = T_{\text{boil}} - T_{\text{cond}}$ is the difference between the boiling and condensation temperatures for the sample, $\Delta p = p_{\text{obs}} - p_{\text{Wagner}}$ (Wagner equation fit) is the difference of the calculated value of pressure from the observed value of pressure (see text), $\sigma(p)$ is the propagated error calculated from Equations (1) or (2).

Mat.	T K	p kPa	Δp kPa	$\sigma(p)$ kPa	ΔT K
Cyclohexene ^a					
R.	285.388	6.417	0.000	0.001	
R.	289.070	7.709	0.000	0.002	
R.	292.285	9.006	-0.002	0.002	
R.	295.210	10.345	0.002	0.002	
R.	297.940	11.734	0.001	0.002	
R.	301.634	13.858	0.001	0.003	
R.	305.845	16.651	-0.002	0.003	
R.	310.137	19.958	-0.006	0.004	
R.	314.115	23.505	0.009	0.004	
R.	319.440	28.990	-0.012	0.005	
R.	324.327	34.940	0.008	0.006	
R.	330.242	43.376	0.000	0.007	
R.	336.334	53.712	0.005	0.009	

Table 7. Continued

Mat.	T K	p kPa	Δp kPa	$\sigma(p)$ kPa	ΔT K
Cyclohexene cont.					
R.	342.842	66.808	-0.006	0.010	
R.	349.899	83.761	0.001	0.012	
R.	354.890	97.655	-0.004	0.014	
R.	355.425	99.248	-0.002	0.014	
R.	355.924	100.746	-0.005	0.014	
R.	356.486	102.470	0.006	0.014	
R.	356.985	104.010	0.006	0.015	
Phthalan					
ip	285.001	0.0287	0.0002	0.0002	
ip	289.997	0.0426	0.0003	0.0002	
ip	294.995	0.0622	0.0002	0.0002	
ip	305.001	0.1272	0.0003	0.0002	
ip	314.994	0.2466	0.0004	0.0002	
ip	324.986	0.4551	0.0004	0.0003	
ip	334.983	0.8044	0.0004	0.0003	
ip	339.986	1.0537	0.0003	0.0004	
ip	344.983	1.3664	-0.0002	0.0004	
ip	349.981	1.7573	0.0001	0.0005	
d.	352.625	2.0000	-0.0002	0.0001	0.077
ip	354.975	2.2404	0.0006	0.0005	
ip	359.976	2.8330	0.0005	0.0006	
d.	367.646	3.9999	0.0004	0.0003	0.036
d.	374.360	5.3330	-0.0011	0.0003	0.025
d.	384.334	7.9989	0.0000	0.0005	0.013
d.	391.822	10.666	0.000	0.001	0.008
d.	397.878	13.332	0.001	0.001	0.006
d.	404.172	16.665	0.001	0.001	0.003
d.	409.401	19.933	0.001	0.001	0.002
d.	416.286	25.023	0.001	0.001	0.000
w.	416.284 ^b	25.023	0.002	0.001	-0.001
w.	423.218	31.177	0.001	0.002	-0.002
w.	430.197	38.565	-0.001	0.002	-0.003
w.	437.222	47.375	-0.002	0.002	-0.004
w.	444.295	57.817	-0.006	0.003	-0.002
w.	451.414	70.120	-0.006	0.003	-0.003
w.	458.579	84.533	-0.004	0.004	-0.003
w.	465.792	101.325	-0.003	0.004	-0.003
w.	473.051	120.79	0.00	0.01	-0.004
w.	480.360	143.25	0.01	0.01	-0.005
w.	487.714	169.02	0.01	0.01	-0.004
w.	495.120	198.49	0.00	0.01	-0.004
w.	502.568	232.02	0.00	0.01	-0.003
w.	510.063	270.02	-0.01	0.01	-0.003
Isoxazole					
d.	313.969	13.332	0.000	0.001	0.007
d.	319.053	16.665	0.000	0.001	0.007
d.	323.275	19.933	0.000	0.001	0.006
d.	328.829	25.023	0.000	0.001	0.006
w.	328.829 ^b	25.023	0.000	0.002	0.006
w.	334.417	31.177	-0.001	0.002	0.005
w.	340.037	38.565	-0.002	0.002	0.006
w.	345.681	47.375	0.010	0.003	0.006
w.	351.372	57.817	-0.004	0.003	0.006
w.	357.087	70.120	-0.003	0.004	0.006
w.	362.834	84.533	0.000	0.004	0.006

Table 7. Continued

Mat.	$\frac{T}{K}$	$\frac{p}{kPa}$	$\frac{\Delta p}{kPa}$	$\frac{\sigma(p)}{kPa}$	$\frac{\Delta T}{K}$
Isoxazole cont.					
w.	368.614	101.325	-0.002	0.005	0.006
w.	374.424	120.79	0.00	0.01	0.006
w.	380.271	143.25	0.00	0.01	0.006
w.	386.143	169.02	0.00	0.01	0.007
w.	392.052	198.49	0.00	0.01	0.007
w.	397.989	232.02	0.00	0.01	0.008
w.	403.959	270.02	0.00	0.01	0.008

n-Octylamine

d.	343.488	2.0000	-0.0001	0.0001	0.024
d.	349.212	2.6660	-0.0001	0.0002	0.021
d.	364.092	5.3330	0.0003	0.0003	0.021
d.	373.587	7.9989	0.0000	0.0005	0.016
d.	380.724	10.666	0.000	0.001	0.016
d.	386.502	13.332	0.002	0.001	0.016
d.	392.515	16.665	0.002	0.001	0.013
d.	397.523	19.933	-0.002	0.001	0.011
d.	404.113	25.023	-0.001	0.001	0.009
w.	404.123 ^b	25.023	-0.009	0.001	0.007
w.	410.764	31.177	-0.008	0.002	0.008
w.	417.457	38.565	-0.006	0.002	0.006
w.	424.202	47.375	-0.004	0.002	0.006
w.	430.999	57.817	-0.001	0.003	0.006
w.	437.847	70.120	0.004	0.003	0.006
w.	444.749	84.527	0.001	0.004	0.007
w.	451.702	101.325	0.010	0.004	0.005
w.	458.706	120.79	0.01	0.01	0.007
w.	465.766	143.25	0.01	0.01	0.006
w.	472.872	169.02	0.00	0.01	0.006
w.	480.032	198.49	-0.01	0.01	0.007
w.	487.240	232.02	-0.02	0.01	0.006
w.	494.496	270.02	-0.04	0.01	0.007

Di-n-octylamine

d.	448.500	2.0000	0.0001	0.0001	0.057
d.	455.571	2.6660	0.0000	0.0002	0.049
d.	466.071	3.9999	-0.0004	0.0002	0.035
d.	473.913	5.3330	-0.0007	0.0003	0.031
d.	485.574	7.9989	0.0007	0.0004	0.019
d.	494.330	10.666	0.001	0.001	0.016
d.	501.416	13.332	0.001	0.001	0.014
d.	508.778	16.665	0.000	0.001	0.026
d.	514.895	19.933	-0.001	0.001	0.024
d.	522.948	25.023	-0.001	0.001	0.022
w.	522.947 ^b	25.023	0.000	0.001	0.037
w.	531.061	31.177	-0.005	0.002	0.037
w.	539.214	38.565	0.003	0.002	0.038
w.	547.431	47.375	0.000	0.002	0.040
w.	555.698	57.817	0.002	0.003	0.045
w.	564.020	70.120	0.001	0.003	0.058
w.	580.812	101.325	0.004	0.004	0.076
w.	589.284	120.79	0.00	0.01	0.079
w.	597.791 ^b	143.25	0.02	0.01	0.102

Phenyl isocyanate

d.	329.643	2.0000	0.0000	0.0001	0.054
d.	344.263	3.9999	-0.0002	0.0003	0.032
d.	350.785	5.3330	0.0003	0.0003	0.022

Table 7. Continued

Mat.	$\frac{T}{K}$	$\frac{p}{kPa}$	$\frac{\Delta p}{kPa}$	$\frac{\sigma(p)}{kPa}$	$\frac{\Delta T}{K}$
Phenyl isocyanate cont.					
d.	360.491	7.9989	-0.0004	0.0005	0.002
d.	367.770	10.666	0.000	0.001	0.010
d.	373.653	13.332	0.001	0.001	0.009
d.	379.765	16.665	0.001	0.001	0.009
d.	384.843	19.933	-0.001	0.001	0.009
d.	391.522	25.023	0.000	0.001	0.009
w.	398.245	31.177	0.000	0.002	0.009
w.	405.008	38.565	-0.001	0.002	0.008
w.	411.810	47.375	0.000	0.002	0.009
w.	418.654	57.817	0.000	0.003	0.007
w.	425.540	70.120	-0.001	0.003	0.009
w.	432.468	84.535	-0.002	0.004	0.012
w.	439.433	101.325	0.002	0.004	0.009
w.	445.480 ^b	120.79	2.83	0.01	0.125

^a Reference 36.^b Point excluded from Wagner-equation fit.

Table 7A. Summary of vapor pressure results: The symbols have the same meaning as in Table 7 except that $\Delta p = p_{\text{obs}} - p_{\text{Antoine}}$ (Antoine equation fit) is the difference of the calculated value of pressure from the observed value of pressure (see text).

Mat.	$\frac{T}{K}$	$\frac{p}{kPa}$	$\frac{\Delta p}{kPa}$	$\frac{\sigma(p)}{kPa}$	$\frac{\Delta T}{K}$
Tri-n-octylamine					
ip	414.967	0.0215	0.0019	0.0002	
ip	424.964	0.0387	0.0023	0.0002	
ip	434.963	0.0674	0.0021	0.0002	
ip	444.957	0.1146	0.0016	0.0002	
ip	454.962	0.1902	0.0003	0.0002	
ip	464.963	0.3086	-0.0011	0.0002	
ip	474.965	0.4895	-0.0028	0.0002	
ip	484.958	0.7594	-0.0043	0.0002	
ip	494.936	1.1534	-0.0043	0.0003	
ip	508.874	1.9996	-0.0012	0.0004	
d.	508.850 ^a	1.9970	-0.0020	0.0005	0.076
d.	516.593	2.6676	0.0012	0.0002	0.061
d.	527.881	3.9857	0.0029	0.0002	0.051
d.	536.501	5.3318	-0.0037	0.0003	0.045

1,4,5,6-Tetrahydropyrimidine

ip	330.000	0.0607	-0.0001	0.0002	
ip	340.000	0.1340	0.0000	0.0002	
ip	350.002	0.2814	-0.0001	0.0002	
ip	359.994	0.5657	0.0003	0.0002	
ip	370.004	1.0906	-0.0001	0.0003	
ip	380.007	2.0260	-0.0004	0.0004	
ip	390.000	3.6358	0.0000	0.0007	
ip	394.999	4.8135	0.0004	0.0009	

^a Point excluded from Antoine-equation fit

Differential Scanning Calorimetry

Table 8 lists the two-phase (liquid + vapor) heat capacities $C_{x,m}^{II}$ determined by d.s.c. for phthalan, isoxazole, n-octylamine, di-n-octylamine, tri-n-octylamine, and phenyl isocyanate for the given cell fillings. Heat-capacities were determined at 20-K intervals with a heating rate of $0.083 \text{ K}\cdot\text{s}^{-1}$ and a 120 s equilibration period between heats.

For each compound extensive sample decomposition precluded attainment of heat-capacity measurements above the highest listed temperatures. For n-octylamine, measurements in the critical region were possible. An abrupt decrease in the heat capacity associated with the conversion from two phases to one phase was observed (see Table 8). In other measurements on n-octylamine, sample decomposition was greatly reduced by employing a single continuous heat at a heating rate of $0.333 \text{ K}\cdot\text{s}^{-1}$. Temperatures at which conversion to the single phase occurred were obtained from those measurements. Table 9 reports the density, obtained from the mass of sample and the cell volume calculated with equation (4), and the measured temperatures at which conversion to a single phase was observed.

Critical temperatures and critical densities were derived graphically for n-octylamine with these results, as seen in Figure 2. Results of measurements on benzene and decane performed as "proof-of-concept measurements" for these procedures have been reported (37). The rapid heating method was used previously for critical-temperature and critical-density determinations for 2-amino-biphenyl (38) and dibenzothiophene (39).

TABLE 8. Two-phase (liquid + vapor) heat capacities. ^{a,b}

($R = 8.31451 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)

T/K	$C_{x,m}^{II}/R$	$C_{x,m}^{II}/R$	$C_{x,m}^{II}/R$
mass / g	0.012420	0.016820	0.024170
V. cell (cm ³)	0.05409	0.05387	0.05570

Phthalan

315.0	23.2	23.3	23.3
335.0	24.1	24.3	24.1
355.0	25.2	24.9	24.9
375.0	26.1	25.8	26.0
395.0	27.4	27.1	26.8
415.0	27.9	27.6	27.6
435.0	28.9	28.9	29.0
455.0	30.2	29.8	29.4
475.0	31.8	31.2	30.4
495.0	32.9	32.1	31.4
515.0	34.0	33.2	32.5
535.0	35.6	34.4	33.7
555.0	37.0	35.4	34.7
575.0	38.7	36.7	35.8
595.0	40.7	37.7	36.6
615.0	43.1	41.0	39.0

T/K	$C_{x,m}^{II}/R$	$C_{x,m}^{II}/R$	$C_{x,m}^{II}/R$
mass / g	0.012144	0.017705	0.025696
V. cell (cm ³)	0.05272	0.05292	0.05272

Isoxazole

305.0	13.1	13.0	13.1
315.0	13.3	13.2	13.3
335.0	13.7	13.9	13.9
355.0	14.8	14.5	14.4
375.0	15.6	15.2	15.0
395.0	16.5	16.0	15.6
415.0	17.5	16.8	16.2
435.0	18.6	17.7	17.0
455.0	19.8	18.7	17.9
475.0	21.3	19.9	19.7

T/K	$C_{x,m}^{II}/R$	$C_{x,m}^{II}/R$	$C_{x,m}^{II}/R$
mass / g	0.010067	0.015345	0.019431
V. cell (cm ³)	0.05339	0.05339	0.05339

n-Octylamine

315.0	38.4	38.2	38.1
335.0	39.6	39.0	38.9
355.0	39.9	39.6	39.9
375.0	41.2	40.6	40.8
395.0	42.8	41.7	41.9
415.0	43.3	42.9	43.0
435.0	45.0	44.1	44.1

TABLE 8. Continued

T/K	$C_{x,m}^{II}/R$	$C_{x,m}^{II}/R$	$C_{x,m}^{II}/R$
mass / g	0.010067	0.015345	0.019431
V. cell (cm ³)	0.05339	0.05339	0.05339

n-Octylamine cont.

455.0	46.5	45.3	45.3
475.0	47.9	46.6	46.3
495.0	49.9	48.1	47.6
515.0	51.5	49.6	49.1
535.0	53.4	50.7	50.2
555.0	54.8	52.4	51.5
575.0	57.0	53.9	53.0
595.0	58.8	55.8	54.7
615.0	59.3	59.0	56.9
655.0 ^b	46.8	46.7	46.3

T/K	$C_{x,m}^{II}/R$	$C_{x,m}^{II}/R$
mass / g	0.008468	0.018758
V. cell (cm ³)	0.05272	0.05272

Di-n-octylamine

315.0	63.2	63.9
335.0	66.3	66.3
355.0	68.0	68.0
375.0	69.1	70.1
395.0	72.6	72.1
415.0	74.6	73.9
435.0	76.7	76.1
455.0	78.0	78.2
475.0	80.8	80.3
495.0	82.7	82.4
515.0	86.1	85.3
535.0	86.9	86.5
555.0	90.1	88.9
575.0	92.5	90.8
595.0	95.0	92.6
615.0	98.8	94.8
635.0	102.4	96.6

T/K	$C_{x,m}^{II}/R$	$C_{x,m}^{II}/R$
mass / g	0.010495	0.017666
V. cell (cm ³)	0.05272	0.05272

Tri-n-octylamine

315.0	93.0	92.8
335.0	95.8	95.6
355.0	98.9	98.9
375.0	101.9	101.7
395.0	105.2	105.1
415.0	108.2	108.3
435.0	111.5	110.5
455.0	114.6	115.0

TABLE 8. Continued

T/K	$C_{x,m}^{II}/R$	$C_{x,m}^{II}/R$
mass / g	0.010495	0.017666
V. cell (cm ³)	0.05272	0.05272

Tri-n-octylamine cont.

475.0	117.6	118.4
495.0	120.4	120.8
515.0	124.2	124.1
535.0	127.9	127.2
555.0	129.4	129.6
575.0	133.3	133.1
595.0	135.8	135.5
615.0	138.9	138.3
635.0	143.1	141.7

T/K	$C_{x,m}^{II}/R$	$C_{x,m}^{II}/R$
mass / g	0.011671	0.016651
V. cell (cm ³)	0.05272	0.05339

Phenyl isocyanate

315.0	22.9	23.0
335.0	23.5	23.5
355.0	24.1	24.2
375.0	24.9	24.9
395.0	25.7	25.7
415.0	26.8	26.7
435.0	27.7	27.5
455.0	29.1	28.4
475.0	30.1	29.6

^a Volume of cell is given at 298.15 K.

^b Values not included in fit. Values are listed to show large drop in heat capacity on passing into the fluid phase.

TABLE 9. Densities and temperatures used to define the two-phase dome near T_c .

$\rho / (\text{kg} \cdot \text{m}^{-3})$	T/K
n-Octylamine	
90.8	618.3
135.1	624.6
176.2	635.7
191.1	639.9
224.0	640.7
282.5	640.3
358.0	630.6

FIGURE 2. Vapor-liquid coexistence in the region of the critical point for n-octylamine. The X axis represents density in units of $\text{kg}\cdot\text{m}^{-3}$. The curve is drawn as an aid to the eye. The crosses span the range of uncertainty.

Densitometry

Measured densities for phthalan and isoxazole in the liquid phase along the saturation line are listed in Table 10. The temperatures are precise to 0.005 K. Measurements of the density of benzene were made between 310 K and 523 K to determine the accuracy of the results obtained with the densitometer (40). Results agreed with the values published by Hales and Townsend (41) within ± 0.1 per cent. The precision of the measurements was approximately 0.05 per cent.

TABLE 10. Measured liquid-phase densities along the saturation line

T/K	$\rho_{\text{obs}}/(\text{kg}\cdot\text{m}^{-3})$	$100(\rho_{\text{obs}} - \rho_{\text{c.s.}})/\rho_{\text{obs}}$
Phthalan		
304.475	1076.2	0.00
324.867	1057.3	-0.04
347.509	1036.3	-0.04
372.253	1013.1	-0.02
400.449	986.1	0.04
424.606	962.4	0.11
Isoxazole		
298.150	1071.6	0.12
323.150	1041.7	0.08
348.150	1010.2	-0.02
373.150	978.6	-0.01
398.150	945.6	0.01

Fitting Procedures

General comments

The main goal of the fitting procedures was to derive accurate enthalpies of vaporization for each compound over as wide a temperature range as possible. Although $\Delta_1^g H_m$ at 298.15 K is the only value necessary to obtain $\Delta_f H_m^o(g, 298.15 \text{ K})$, the benefits of a knowledge of the enthalpy of vaporization over a wide range of temperature was recognized. The exact fitting procedure used for each compound varied depending on the range of measured properties available. Details of each fitting procedure used follows.

n-Octylamine

For n-octylamine the fitting parameters were derived by a simultaneous non-linear least-squares fit of the vapor pressures listed in Table 7 and the two-phase heat capacities $C_{x,m}^{II}$ given in Table 8. The critical temperature and critical density were determined from the d.s.c. measurements, and hence, only the critical pressure p_c was included in the variables.

The Wagner equation (42) in the formulation given by Ambrose (43):

$$\ln(p/p_c) = (1/T_r) [AY + BY^{1.5} + CY^{2.5} + DY^5], \quad (11)$$

where $T_r = T/T_c$, and $Y = (1 - T_r)$ was fitted to the measured vapor pressures (Table 7). The vapor-pressure fitting procedure resembled that used previously, when the Cox vapor-pressure equation was used (20, 24, 44). In fits using the Wagner equation, the sums of the weighted squares in the following expression were minimized (replacing equation 12 of reference 24):

$$\Delta = [\ln(p/p_c) / (1/T_r)] - AY - BY^{1.5} - CY^{2.5} - DY^5. \quad (12)$$

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

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

For fitting the two-phase heat capacities obtained in a cell of volume V_x , the experimental $C_{x,m}^{II}$ values (Table 8) were converted to $C_{v,m}^{II}$, by means of equation (4) for the cell expansion and the vapor-pressure fit for $(\partial p/\partial T)_{sat}$,

$$C_{v,m}^{II} = C_{x,m}^{II} - T/n \{(\partial V_x/\partial T)_x (\partial p/\partial T)_{sat}\}. \quad (14)$$

The values of $C_{v,m}^{II}$ were used to derive functions for $(\partial^2 p/\partial T^2)_{sat}$ and $(\partial^2 \mu/\partial T^2)_{sat}$ [see equation (5) above]. The functional form chosen for variation of the second derivative of the chemical potential with temperature was:

$$(\partial^2 \mu/\partial T^2)_{sat} / (J \cdot K^{-2} \cdot mol^{-1}) = \sum_{i=0}^n b_i (1 - T/T_c)^i. \quad (15)$$

[For compounds where sufficient information was available to evaluate reliably $(\partial^2 \mu/\partial T^2)_{sat}$ [e.g., benzene

(45) and toluene (46)], four terms (i.e., expansion to $n=3$) were required to represent the function. Thus, four terms were used in this research.) In these fits the sum of the weighted squares in the following function was minimized:

$$\Delta = C_{v,m}^{II}/R - \{V_m(l)T/nR\} (\partial^2 p/\partial T^2)_{sat} + (T/R) (\partial^2 \mu/\partial T^2)_{sat}. \quad (16)$$

Within the heat-capacity results, the weighting factors were proportional to the square of the mass of sample used in the measurements. 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.

Estimates of liquid-phase molar volumes $V_m(l)$ for n-octylamine were made with the extended corresponding-states equation of Riedel (47) as formulated by Hales and Townsend (41):

$$(p/p_c) = 1.0 - 0.85Y + (1.692 + 0.986\omega)Y^{1/3} \quad (17)$$

with $Y = (1 - T/T_c)$, p_c = critical density, and ω = acentric factor. The acentric factor is defined as $[-\lg(p/p_c) - 1]$, where p is the vapor pressure at $T/T_c = 0.7$ and p_c is the critical pressure. During each iteration a value of ω was obtained from the vapor-pressure fitting parameters and a corresponding value of p_c derived from the liquid-phase density at 298.15 K listed in Table 2.

Cyclohexene

For cyclohexene a literature value (48, 49) of 560.4 K for the critical temperature was used in a Wagner equation fit to the vapor pressure measurements listed in Table 7. P_c was included in the variables in the fit. The procedure used resembled that of n-octylamine except that no two-phase heat capacity measurements were available. Liquid-phase densities from reference 36 were used to derive p_c in each iteration.

Phthalan, Isoxazole, Di-n-octylamine,
and Phenyl isocyanate

For these four compounds, in the absence of measured values, both T_c and p_c were included in the variables in the fitting procedure. During each iteration a value of ω was obtained from the vapor-pressure fitting parameters and a corresponding value of p_c derived from a least-squares fit of the measured liquid-phase densities listed in Table 10 for phthalan and isoxazole and the liquid-phase density at 298.15 K listed in Table 2 for the other two compounds. For the latter two compounds, di-n-octylamine and phenyl isocyanate, in the fitting procedure equation 15 was truncated at the third term (b_2).

Tri-n-octylamine, and 1,4,5,6-Tetra-
hydropyrimidine

For both these compounds the range of vapor pressure measurements (see Table 7A) was so short that Wagner-equation fits were not attempted. For each compound the Antoine equation (21) in the form:

$$\lg(p/p_{\text{ref}}) = A + B / ((T/K) + C), \quad (18)$$

with $p_{\text{ref}} = 1$ kPa, was fit to the experimental vapor pressures.

Derived Results

General comments

Tables 11 and 11A list the parameters derived using the various fitting procedures outlined above. Details of the fits to the vapor-pressure results are given in Tables 7 and 7A (column 4 labeled Δp). Details of the fits of the measured liquid-phase densities (phthalan and isoxazole) to extended corresponding states using the parameters listed in Table 11 are given in column 3 of Table 10.

TABLE 11. Parameters for equations (11) and (15), critical constants and acentric factors

Cyclohexene					
	A	-9.08102			
	B	5.75488			
	C	-5.17505			
	D	-1.04889			
T_c	560.4 K		p_c	4905 kPa	
ρ_c	276.7 kg·m ⁻³		ω	0.263	
Phthalan					
A	-8.94677		b_0	-0.37089	
B	4.24557		b_1	-0.76695	
C	-4.76533		b_2	1.45375	
D	-2.69939		b_3	-1.60131	
T_c	700 K		p_c	4285 kPa	
ρ_c	337.3 kg·m ⁻³		ω	0.382	
Isoxazole					
A	-7.13862		b_0	-0.13775	
B	1.21982		b_1	-1.13826	
C	-1.60913		b_2	2.71604	
D	-3.10251		b_3	-2.68650	
T_c	590 K		p_c	6100 kPa	
ρ_c	361.7 kg·m ⁻³		ω	0.258	
n-Octylamine					
A	-7.99396		b_0	-0.65693	
B	1.40573		b_1	-0.46021	
C	-2.98188		b_2	0.17534	
D	-6.60435		b_3	-1.20063	
T_c	641 K		p_c	2617 kPa	
ρ_c	250 kg·m ⁻³		ω	0.446	
Di-n-octylamine					
A	-10.82124		b_0	-1.16384	
B	4.52645		b_1	-0.36286	
C	-8.33385		b_2	-0.90846	
D	-4.63027		b_3		
T_c	734 K		p_c	1260 kPa	
ρ_c	221 kg·m ⁻³		ω	0.815	
Phenyl isocyanate					
A	-7.77531		b_0	-0.48738	
B	2.13021		b_1	0.29604	
C	-2.62137		b_2	-0.96124	
D	-2.40783		b_3		
T_c	675 K		p_c	4540 kPa	
ρ_c	348.8 kg·m ⁻³		ω	0.314	

Table 11^a. Antoine equation coefficients. ^a

P _{ref} /kPa	A	B
A	7.01290	9.4934
B	-2736.15	-3229.9
C	-101.205	-28.424
Range/K ^b	415 to 537	330 to 395

^a A = Tri-n-octylamine; and B = 1,4,5,6-Tetrahydropyrimidine.

^b Temperature range of the vapor pressures used in the fit.

For phthalan, isoxazole, n-octylamine, di-n-octylamine, and phenyl isocyanate values of $C_{v,m}^{II}(\rho=p_{sat})$ were derived from the parameters listed in Table 11 and corresponding $C_{sat,m}$ obtained using equation (6). The results for $C_{sat,m}/R$ are reported in Table 12. The estimated uncertainty in these values is 1 per cent.

TABLE 12. Values of $C_{sat,m}/R$
($R = 8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)

T/K	$C_{sat,m}/R$	T/K	$C_{sat,m}/R$
Phthalan			
300.0	22.8	500.0	31.3
320.0	23.7	520.0	32.1
340.0	24.5	540.0	32.9
360.0	25.3	560.0	33.8
380.0	26.1	580.0	34.6
400.0	27.0	600.0	35.5
420.0	27.8	620.0	36.5
440.0	28.7	640.0	37.8
460.0	29.5	660.0	40.0
480.0	30.4	680.0	45.5
Isoxazole			
300.0	13.0	460.0	17.0
320.0	13.4	480.0	17.4
340.0	13.9	500.0	17.6
360.0	14.4	520.0	17.8
380.0	14.9	540.0	18.0
400.0	15.5	560.0	18.7
420.0	16.0	580.0	23.7
440.0	16.6		
n-Octylamine			
300.0	37.3	480.0	46.0
320.0	38.3	500.0	47.2
340.0	39.2	520.0	48.4
360.0	40.2	540.0	49.7
380.0	41.1	560.0	51.2

TABLE 12. Continued.

T/K	$C_{sat,m}/R$	T/K	$C_{sat,m}/R$
n-Octylamine cont.			
400.0	42.0	580.0	53.1
420.0	42.9	600.0	55.5
440.0	43.9	620.0	60.2
460.0	44.9	640.0	134.
Di-n-octylamine			
300.0	61.2	460.0	79.0
320.0	63.8	480.0	80.9
340.0	66.3	500.0	82.7
360.0	68.6	520.0	84.6
380.0	70.9	540.0	86.5
400.0	73.0	560.0	88.4
420.0	75.1	580.0	90.4
440.0	77.0	600.0	92.5
Phenyl isocyanate			
300.0	22.4	500.0	29.6
320.0	23.0	520.0	30.7
340.0	23.6	540.0	32.0
360.0	24.2	560.0	33.5
380.0	24.9	580.0	35.2
400.0	25.5	600.0	37.4
420.0	26.2	620.0	40.1
440.0	26.9	640.0	44.0
460.0	27.7	660.0	52.3
480.0	28.6		

Enthalpies of vaporization

Enthalpies of vaporization $\Delta_1^g H_m$ were derived from the Wagner- and Antoine-equation fits (Tables 11 and 11A) using the Clapeyron equation:

$$dp/dT = \Delta_1^g H_m / (T \Delta_1^g V_m), \quad (19)$$

where $\Delta_1^g V_m$ is the increase in molar volume from the liquid to the real vapor.

Cyclohexene, Phthalan, Isoxazole, n-Octylamine, Di-n-octylamine, and Phenyl isocyanate

For each of these compounds estimates of the liquid-phase volumes were made using equation (17) and the parameters given in Table 11. Vapor-phase volumes were calculated with the virial equation of state truncated at

the third virial coefficient. Second virial coefficients were estimated with the corresponding-states equation of Pitzer and Curl, (50) and third virial coefficients were estimated with the corresponding-states method of Orbey and Vera (51). This formulation for third virial coefficients was applied successfully in analyses of the thermodynamic properties of benzene, toluene, and decane (37). Third virial coefficients are required for accurate calculation of the gas volume for pressures greater than 1 bar. Uncertainties in the virial coefficients were assumed to be 10 per cent.

Tri-n-octylamine and 1,4,5,6-Tetrahydropyrimidine

The absence of critical properties precluded using the methodology outlined for the other compounds listed in the previous section. For these remaining two compounds, liquid-phase volumes were derived using the densities at 298.15 K and the coefficients of expansion listed in Table 2. Second virial coefficients were estimated with the correlation of Scott et al. (52). Since enthalpies of vaporization were not derived for pressures greater than 1 bar, third virials were neglected. Uncertainties in both the liquid-phase molar volumes and virial coefficients were assumed to be 20 per cent.

Derived enthalpies of vaporization are reported in table 13. For $p > 1$ bar the uncertainties in the virial coefficients are the dominant contributions to the uncertainties in the derived enthalpies of vaporization.

TABLE 13. Enthalpies of vaporization obtained from the Wagner or Antoine and Clapeyron equations.^a

T/K	$\Delta_1^g H_m / \text{kJ} \cdot \text{mol}^{-1}$	T/K	$\Delta_1^g H_m / \text{kJ} \cdot \text{mol}^{-1}$
Cyclohexene			
260.0	^b 35.30±0.62	400.0	^b 27.86±0.60
280.0	^b 34.32±0.57	420.0	^b 26.63±0.70
298.15	33.42±0.53	440.0	^b 25.36±0.83
300.0	33.33±0.53	460.0	^b 24.02±1.00
320.0	32.31±0.50	480.0	^b 22.58±1.18
340.0	31.25±0.48	500.0	^b 20.99±1.41
360.0	30.18±0.50	520.0	^b 19.06±1.70
380.0	29.04±0.53	540.0	^b 16.41±2.06
Phthalan			
280.0	^b 55.02±0.45	480.0	41.59±0.47
298.15	53.74±0.42	500.0	40.12±0.58
300.0	53.60±0.40	520.0	^b 38.59±0.72
320.0	52.23±0.38	540.0	^b 36.97±0.88
340.0	50.88±0.35	560.0	^b 35.28±1.06
360.0	49.57±0.32	580.0	^b 33.47±1.28
380.0	48.27±0.30	600.0	^b 31.53±1.51
400.0	46.99±0.30	620.0	^b 29.42±1.80
420.0	45.68±0.30	640.0	^b 27.05±2.10
440.0	44.36±0.33	660.0	^b 24.29±2.48
460.0	42.99±0.38	680.0	^b 20.83±2.96
Isoxazole			
280.0	^b 38.08±0.23	440.0	^b 29.31±0.65
298.15	^b 37.17±0.22	460.0	^b 27.80±0.81
300.0	37.07±0.22	480.0	^b 26.13±1.01
320.0	36.09±0.20	500.0	^b 24.28±1.21
340.0	35.10±0.22	520.0	^b 22.20±1.45
360.0	34.10±0.25	540.0	^b 19.86±1.70
380.0	33.03±0.30	560.0	^b 17.19±1.96
400.0	31.89±0.40	580.0	^b 13.89±2.28
420.0	^b 30.66±0.52		
n-Octylamine			
298.15	^b 54.63±0.47	480.0	38.11±0.72
300.0	^b 54.43±0.45	500.0	36.05±0.90
320.0	^b 52.40±0.42	520.0	^b 33.82±1.13
340.0	^b 50.49±0.37	540.0	^b 31.39±1.38
360.0	48.68±0.33	560.0	^b 28.71±1.65
380.0	46.94±0.32	580.0	^b 25.73±1.95
400.0	45.25±0.33	600.0	^b 22.39±2.28
420.0	43.54±0.37	620.0	^b 18.51±2.64
440.0	41.81±0.43	640.0	^b 12.57±3.13
460.0	40.01±0.57		
Di-n-octylamine			
298.15	^b 87.10±1.33	560.0	58.63±0.68
400.0	^b 86.86±1.30	580.0	56.09±0.85
420.0	^b 74.49±0.72	600.0	53.39±1.06
440.0	72.23±0.65	620.0	^b 50.49±1.33
460.0	70.00±0.60	640.0	^b 47.38±1.65
480.0	67.80±0.57	660.0	^b 43.97±2.01
500.0	65.59±0.53	680.0	^b 40.22±2.43

TABLE 13. Continued

T/K	$\Delta_f^g H_m / \text{kJ}\cdot\text{mol}^{-1}$	T/K	$\Delta_f^g H_m / \text{kJ}\cdot\text{mol}^{-1}$
Di-n-octylamine cont.			
520.0	63.36±0.55	700.0 ^b	35.99±2.93
540.0	61.05±0.58	720.0 ^b	31.06±3.53
Phenyl isocyanate			
298.15 ^b	46.54±0.30	400.0	41.46±0.27
300.0 ^b	46.44±0.30	420.0	40.41±0.30
320.0 ^b	45.43±0.28	440.0 ^b	39.29±0.37
340.0	44.44±0.27	460.0 ^b	38.09±0.45
360.0	43.47±0.25	480.0 ^b	36.79±0.57
380.0	42.48±0.25	500.0 ^b	35.39±0.70
Tri-n-octylamine			
298.15 ^b	110.4±15.0	500.0	81.9±8.2
400.0 ^b	93.9±16.7	520.0	80.0±7.9
420.0	90.9±13.4	540.0 ^b	78.1±7.6
440.0	88.3±11.2	560.0 ^b	76.1±7.5
460.0	86.0±9.8	580.0 ^b	74.0±7.5
480.0	83.9±8.9	600.0 ^b	71.5±7.6
1,4,5,6-Tetrahydropyrimidine			
298.15 ^b	75.6±2.0	400.0	71.4±1.2
300.0 ^b	75.5±2.0	420.0 ^b	70.6±1.4
320.0 ^b	74.5±1.6	440.0 ^b	69.7±1.4
340.0	73.6±1.4	460.0 ^b	68.4±1.8
360.0	72.9±1.3	460.0 ^b	66.6±2.0
380.0	72.1±1.2		

^a Uncertainty intervals are twice the standard deviation of the mean.

^b The value at this temperature was calculated with extrapolated vapor pressures derived from the fitted Wagner- or Antoine-equations.

Ideal-Gas enthalpies of formation

Table 14 summarizes the thermochemical property measurements and derived ideal-gas standard enthalpies of formation for all the compounds of this study. In the next 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.

TABLE 14. Thermochemical properties at 298.15 K and $p^\circ = 101.325 \text{ kPa}$.^a Values are in $\text{kJ}\cdot\text{mol}^{-1}$.

	$\Delta_f H_m^\circ (l)$	$\Delta_f^g H_m$	$\Delta_f H_m^\circ (g)$
A	-37.82±0.82	33.42±0.53	-4.40±0.98
B	-83.83±0.93	53.74±0.42	-30.09±1.02
C	44.78±0.56	37.17±0.22	81.95±0.60
D	-228.09±1.24	54.63±0.47	-173.46±1.33
E	-407.3±1.9	87.10±1.33	-320.2±2.3
F	-587.5±3.8	110.4±15.0	-477.1±15.0
G	-61.08±1.11	46.54±0.30	-14.54±1.15
H	-20.54±0.29	75.6±2.0	55.1±2.1

^a A = Cyclohexene; B = Phthalan; C = Isoxazole; D = n-Octylamine; E = Di-n-octylamine; F = Tri-n-octylamine; G = Phenyl isocyanate and H = 1,4,5,6-Tetrahydropyrimidine.

DISCUSSION

Cyclohexene

Values of the energy of combustion for cyclohexene have been reported in the literature by Labbauf and Rossini (53), and by the NIPER group, Good and Smith (8). However, it was noted that Pedley et al. (54) in their compilation also listed a value for the enthalpy of formation for cyclohexene derived from hydrogenation calorimetry (55) which was $5.7 \text{ kJ}\cdot\text{mol}^{-1}$ more negative than that derived from either combustion study. Since both Labbauf and Rossini and Good and Smith used the same API sample in their combustion studies the possibility of an impurity in the sample could not be discarded. Cyclohexene continues to be used as a standard in hydrogenation reaction calorimetry (56-59) so the enthalpy of the hydrogenation reaction to form cyclohexane needs to be well-defined. Hence, the combustion calorimetry of cyclohexene was repeated in this research using a new sample obtained as described above. The results are compared in Table 15. The result obtained in this research is in excellent agreement with those of both Labbauf and Rossini (53), and Good and Smith (8). Hence, the enthalpy of

hydrogenation [$\Delta_f H_m^\circ = -(112.5 \pm 2.5)$ $\text{kJ} \cdot \text{mol}^{-1}$] obtained by Rodgers and McLafferty (55) for the reaction:

appears to be in error. In a later paper Rodgers and Munoz-Hresko (60) listed values of $-(118.7 \pm 0.1)$ $\text{kJ} \cdot \text{mol}^{-1}$ (61), $-(119.0 \pm 0.3)$ $\text{kJ} \cdot \text{mol}^{-1}$ (62), and $-(118.6 \pm 0.2)$ $\text{kJ} \cdot \text{mol}^{-1}$ in that research. In recent work Rodgers et al. (56-59) have used a value of -119.0 $\text{kJ} \cdot \text{mol}^{-1}$ exactly as a standard from which to calculate other enthalpies of hydrogenation. This research gives a value of $-(118.3 \pm 0.7)$ $\text{kJ} \cdot \text{mol}^{-1}$ using the enthalpy of formation of cyclohexane [$\Delta_f H_m^\circ = -(156.2 \pm 0.6)$ $\text{kJ} \cdot \text{mol}^{-1}$] obtained by Good and Smith (8). Hence, the enthalpies of hydrogenation derived by Rodgers et al (56-59) need revision.

TABLE 15. Comparison of literature values for the energy of combustion of cyclohexene.

Author(s)	$-\Delta_c U_m^\circ (\text{cr}) / \text{kJ/mol}$
Labbauf and Rossini (53)	3745.27 ± 0.50
Good and Smith (8)	3745.94 ± 0.28
This research	3746.19 ± 0.49

Vapor pressures for cyclohexene have also been reported in the literature by Lister (63), Forziati et al (36), Meyer and Hotz (64), and Letcher and Marsicano (65). In this research the ebulliometric vapor pressures obtained at NIST by Forziati et al. (36) were used to derive the thermophysical properties. Figure 3 compares the various literature vapor pressures with values calculated with the Wagner-equation parameters listed in Table 11. Two points obtained by Lister at 228.7 K and 248.3 K are not shown in Figure 3. They are 2 and 6 percent high relative to values obtained using the Wagner equation and the parameters listed in Table 11.

FIGURE 3. Comparison of literature vapor pressures for cyclohexene with those obtained from the Wagner equation and the parameters listed in Table 11.

Δ , Lister (63); $\circ$, Meyer and Hotz (64); $\bullet$, Letcher and Marsicano (65).

Figure 4 compares the various literature liquid-phase saturation densities (36, 65-68) with values calculated by extended corresponding states (equation 17) using the parameters listed in Table 11. Agreement is good except for the values of Letcher and Marsicano (65), which are on average 1.2 percent high.

FIGURE 4. Comparison of literature liquid-phase densities for cyclohexene with those obtained from extended corresponding states using the parameters listed in Table 11. ■, Forziati et al (36); ○, Letcher and Marsicano (65); △, Evans (66); ●, Letcher (67); □, Letcher (68).

Using the group parameters given in references 1 and 2, estimation of a ring correction parameter was made as follows:

2	C-(C) ₂ (H) ₂	-20.72X 2	-41.44
2	C-(C)(C _d)(H) ₂	-19.93X 2	-39.86
2	C _d -(C _d)(C)(H)	35.96X 2	71.92
1	Ring correction	?? X 1	??

$$(\Delta_f H_m^{\circ} \text{C}_6\text{H}_{10}, \text{g } 298.15 \text{ K}) \quad -4.40 \text{ kJ}\cdot\text{mol}^{-1}$$

Hence, a value of 5.0 kJ·mol⁻¹ was derived for the cyclohexene ring-

correction parameter compared with a value of 5.86 kJ·mol⁻¹ listed in reference 2.

Phthalan

For phthalan no vapor pressure or other thermophysical property measurements were found in a search of the literature through 1991. Using the group parameters listed in references 1 and 2:

4	C _b -(C _b) ₂ (H)	13.82 X 4	55.28
2	C _b -(C _b) ₂ (C)	23.07 X 2	46.14
2	C-(C _b)(O)(H) ₂	-33.91X 2	-67.82
1	O-(C) ₂	-97.07X 1	-97.07
1	Ring correction	?? X 1	??

$$(\Delta_f H_m^{\circ} \text{C}_8\text{H}_8\text{O}, \text{g } 298.15 \text{ K}) \quad -30.09 \text{ kJ}\cdot\text{mol}^{-1}$$

Hence, a value of 33.4 kJ·mol⁻¹ was derived for ring-correction parameter in phthalan (a 2,5-dihydrofuran ring).

In the 1988 research program (69) the enthalpy of formation of 2,3-dihydrofuran ($\Delta_f H_m^{\circ} \text{C}_4\text{H}_6\text{O}$, g 298.15 K) (-72.25±0.41) kJ·mol⁻¹ was determined. In that research a ring correction term of 37.3 kJ·mol⁻¹ was derived for a 2,3-dihydrofuran ring. In NIPER-457 (70) the ideal gas enthalpy of formation of 4,5-dihydro-2,3-benzofuran was reported ($\Delta_f H_m^{\circ} \text{C}_8\text{H}_8\text{O}$, g 298.15 K) (-46.48±0.72) kJ·mol⁻¹. Addition of the group-additivity terms for 4,5-dihydro-2,3-benzofuran produces a ring correction term of 27.8 kJ·mol⁻¹. Hence, the ring correction terms appear to be dependent on the molecular structure. Sufficient information is available to make an estimate of the ideal-gas enthalpy of formation of 2,5-dihydrofuran. (Attempts to purify 2,5-dihydrofuran for combustion calorimetry were unsuccessful. The highest purity sample obtained was 98.5 mole percent 2,5-dihydrofuran.) An enthalpy of formation of 2,5-dihydrofuran ($\Delta_f H_m^{\circ} \text{C}_4\text{H}_6\text{O}$, g 298.15 K) (-56±4) kJ·mol⁻¹ is estimated (see below).

Isoxazole

The thermochemistry of both oxazole and isoxazole was studied by McCormick and Hamilton (71). McCormick and Hamilton reported an energy of combustion of $-(23920.7 \pm 2.0) \text{ J} \cdot \text{g}^{-1}$. The corresponding value obtained in this research was $\Delta_c U_m^\circ (\text{c}) = -(23958.9 \pm 0.8) \text{ J} \cdot \text{g}^{-1}$. McCormick and Hamilton noted that the most likely impurity in the isoxazole was water and took precautions to prevent contamination of the sample. Their results are based on sample mass whereas the value obtained here is based on CO_2 analyses, and hence, eliminates the effect of water contamination. The presence of 0.1 mole percent water in the sample studied by McCormick and Hamilton (71) would reconcile the two sets of results.

McCormick and Hamilton (71) measured the enthalpy of vaporization of isoxazole at 298.15 K using an LKB 8721-3 calorimeter. They list a value of $\Delta_1 H_m^\circ (\text{C}_3\text{H}_3\text{NO}, 298.15 \text{ K}) = (36.44 \pm 0.04) \text{ kJ} \cdot \text{mol}^{-1}$ the mean of five determinations. The corresponding value obtained in this research is

$\Delta_1 H_m^\circ (\text{C}_3\text{H}_3\text{NO}, 298.15 \text{ K}) = (37.17 \pm 0.22) \text{ kJ} \cdot \text{mol}^{-1}$ (see table 13). It is not possible to determine the effect of water contamination on the McCormick and Hamilton measured enthalpy of vaporization. These inconsistencies in the thermochemical properties lead to a difference of $3.4 \text{ kJ} \cdot \text{mol}^{-1}$ in the ideal gas enthalpies of formation of isoxazole. McCormick and Hamilton ($\Delta_f H_m^\circ \text{C}_3\text{H}_3\text{NO}, \text{ g } 298.15 \text{ K}) (78.6 \pm 0.5) \text{ kJ} \cdot \text{mol}^{-1}$ c.f., ($\Delta_f H_m^\circ \text{C}_3\text{H}_3\text{NO}, \text{ g } 298.15 \text{ K}) (81.95 \pm 0.60) \text{ kJ} \cdot \text{mol}^{-1}$ obtained in this research.

At this time it is not possible to determine each of the group-additivity terms in isoxazole. There are three unknown terms. There are no individual group-additivity terms listed in references 1 or 2 for either the oxygen, or the nitrogen atoms in the molecular environments shown by the arrows.

In addition, no ring correction term for the isoxazole ring structure is listed. However, this lack of individual group terms does not prevent estimation of the ideal-gas enthalpies of formation of substituted isoxazoles. Such calculations need to start with the isoxazole enthalpy of formation and add or subtract the relevant groups. For example for 4-methylisoxazole:

	ISOXAZOLE	81.95	81.95
1	C _d -(C _d) ₂ (H)	28.93	28.93
1	C _d -(C _d) ₂ (C)	37.18	37.18
1	C-(C _d)(H) ₃	-42.20	-42.20

$$(\Delta_f H_m^\circ \text{C}_4\text{H}_5\text{NO}, \text{g } 298.15 \text{ K}) \quad 48.0 \text{ kJ}\cdot\text{mol}^{-1}.$$

n-Octylamine

No energy of combustion measurements were found for n-octylamine in a search of the literature through 1991. Vapor pressures for n-octylamine were reported by in two papers Ralston et al. (72), and Ralston et al. (73). These measurements, supplemented by results obtained at the turn of the century, were used by TRC (74) to obtain the temperatures at set pressures listed by them in their Tables of thermodynamic properties. Figure 5 compares the results of Ralston et al. (72), Ralston et al. (73) and TRC (74) with those obtained using the Wagner equation and the parameters listed in Table 11.

FIGURE 5. Comparison of literature vapor pressures for n-octylamine with those obtained using the Wagner equation and the parameters listed in Table 11.

●, TRC (74); ○, Ralston et al. (72); △, Ralston et al. (73).

Values for the density of n-octylamine reported in the literature (74-76) are lower than the value for 298.15 K obtained in this research and reported in Table 2 or estimated using extended corresponding states (equation 17) and the parameters listed in Table 11. Table 15 compares the various values.

TABLE 15. Comparison of literature values of the density of n-octylamine with values from corresponding states.

Ref.	T/K	$\rho / (\text{kg}\cdot\text{m}^{-3})$ lit.	$\rho / (\text{kg}\cdot\text{m}^{-3})$ corr. states
75	293.15	781.9	799.5
76	298.15	782.6	796.2
74	293.15	782.8	799.5
74	298.15	779.0	796.2
This Research			
	298.15	796.2	

Using the group-additivity parameters listed in references 1 and 2:

1	C-(C)(H) ₃	-42.20 X 1	-42.2
6	C-(C) ₂ (H) ₂	-20.72 X 6	-124.3
1	C-(N)(C)(H) ₂	-27.6 X 1	-27.6
1	N-(C)(H) ₂	20.1 X 1	20.1

$$(\Delta_f H_m^\circ \text{C}_8\text{H}_{19}\text{N}, \text{g } 298.15 \text{ K}) \quad -174.0 \text{ kJ}\cdot\text{mol}^{-1}.$$

The value determined in this research is: $(\Delta_f H_m^\circ \text{C}_8\text{H}_{19}\text{N}, \text{g } 298.15 \text{ K})$ $-(173.46 \pm 1.33) \text{ kJ}\cdot\text{mol}^{-1}$ (Table 14). The agreement is excellent showing that

no group-additivity parameters need revision.

Di-n-octylamine

Carroll and Wright (77) reported distillation ranges of 571 K to 573 K at 751 mm. Hg and 432 K to 434 K at 10 mm Hg for di-n-octylamine along with a density at 299 K of $796.8 \text{ kg}\cdot\text{m}^{-3}$. TRC (74) report densities of $803.8 \text{ kg}\cdot\text{m}^{-3}$ and $800.3 \text{ kg}\cdot\text{m}^{-3}$ at 293.15 K and 298.15 K, respectively. Table 16 compares the density values.

TABLE 16. Comparison of literature values of the density of di-n-octylamine with values from corresponding states.

Ref.	T/K	$\rho/(\text{kg}\cdot\text{m}^{-3})$ lit.	$\rho/(\text{kg}\cdot\text{m}^{-3})$ corr. states
77	299	796.8	795.5
74	293.15	803.8	799.1
74	298.15	800.3	796.0
		This Research	
	298.15	796.0	

Using the group-additivity parameters listed in references 1 and 2:

2	C-(C)(H) ₃	-42.20 X 2	-84.4
12	C-(C) ₂ (H) ₂	-20.72 X 12	-248.6
2	C-(N)(C)(H) ₂	-27.6 X 2	-55.2
1	N-(C) ₂ (H)	64.5 X 1	64.5

$$(\Delta_f H_m^\circ \text{C}_{16}\text{H}_{35}\text{N}, \text{g } 298.15 \text{ K}) \quad -323.7 \text{ kJ}\cdot\text{mol}^{-1}.$$

The value determined in this research is: $(\Delta_f H_m^\circ \text{C}_{16}\text{H}_{35}\text{N}, \text{g } 298.15 \text{ K})$ $-(320.2 \pm 2.3) \text{ kJ}\cdot\text{mol}^{-1}$ (Table 14). The agreement is very good showing that no group-additivity parameters need revision.

Tri-n-octylamine

Values of the energy of combustion, density, and a boiling point at 2 mm Hg, for tri-n-octylamine

have been reported in the literature by Lebedeva (78). The average value for the energy of combustion obtained by Lebedeva, $\Delta_c U_m^\circ = -(45585 \pm 6) \text{ J}\cdot\text{g}^{-1}$, is in good agreement (0.05 percent) with the value of $-(45564 \pm 4) \text{ J}\cdot\text{g}^{-1}$ obtained in this research. Similarly the density at 298.15 K obtained by Lebedeva, $811.0 \text{ kg}\cdot\text{m}^{-3}$, is in good agreement with the value obtained in this research $810.5 \text{ kg}\cdot\text{m}^{-3}$. Using the Antoine parameters listed in Table 11A, a temperature of 461.8 K was calculated for a pressure 2 mm Hg. This is 8 K above the boiling point (454 K) listed by Lebedeva.

Using the group-additivity parameters listed in references 1 and 2:

3	C-(C)(H) ₃	-42.20 X 3	-126.6
18	C-(C) ₂ (H) ₂	-20.72 X 18	-373.0
3	C-(N)(C)(H) ₂	-27.6 X 3	-82.8
1	N-(C) ₃	102.2 X 1	102.2

$$(\Delta_f H_m^\circ \text{C}_{24}\text{H}_{51}\text{N}, \text{g } 298.15 \text{ K}) \quad -480.2 \text{ kJ}\cdot\text{mol}^{-1}.$$

The value determined in this research is: $(\Delta_f H_m^\circ \text{C}_{24}\text{H}_{51}\text{N}, \text{g } 298.15 \text{ K})$ $-(477.1 \pm 15) \text{ kJ}\cdot\text{mol}^{-1}$ (Table 14). The agreement is excellent showing that no group-additivity parameters need revision.

Phenyl isocyanate

A value for the enthalpy of combustion of phenyl isocyanate, $\Delta_c H_m^\circ = -(3402.4) \text{ kJ}\cdot\text{mol}^{-1}$ has been reported in the literature by Strepikheev et al. (79). No details of the combustion calorimetry or the purity of the sample are given by Strepikheev et al. However, the result compares favorably with the value, $\Delta_c H_m^\circ = -(3408.07 \pm 0.85) \text{ kJ}\cdot\text{mol}^{-1}$ obtained in this research.

Vapor pressures for phenyl isocyanate have been reported by Carothers (80), Korovin and Margolin (81), and by Stull (82), in his 1947 compilation. Figure 6 compares the results given by Carothers, Korovin and

Margolin, and Stull with those obtained using the Wagner equation and the parameters listed in Table 11.

FIGURE 6. Comparison of literature vapor pressures for phenyl isocyanate with those obtained using the Wagner equation and the parameters listed in Table 11. $\square$, Carothers (80); $\bullet$, Stull (82); Δ , Korovin and Margolin (81).

TABLE 17. Comparison of literature values (80) of the density of phenyl isocyanate with values from corresponding states.

T/K	$\rho / (\text{kg} \cdot \text{m}^{-3})$ lit.	$\rho / (\text{kg} \cdot \text{m}^{-3})$ corr. states
273.15	1115.2	1114.6
283.15	1104.9	1104.5
293.15	1094.3	1094.3
303.15	1084.0	1083.9
313.15	1073.6	1073.5
323.15	1063.0	1062.9

Table 17 compares saturation densities for phenyl isocyanate obtained by Carothers (80) with

values calculated using extended corresponding states (equation 17) and the parameters listed in Table 11. Agreement is excellent.

Using the group-additivity parameters given in references 1 and 2 and the new value for the N-(Cb)(CO) parameter derived in the 1989 research (42):

5	C _b -(C _b) ₂ (H)	13.82 X 5	69.10
1	C _b -(C _b) ₂ (N)	-2.1 X 1	-2.1
1	N-(C _b)(CO)	-???.?? X 1	-???.?

$$(\Delta_f H_m^\circ \text{ C}_7\text{H}_5\text{NO, g 298.15 K}) \quad -???.? \text{ kJ} \cdot \text{mol}^{-1}.$$

The value determined in this research is:

$$(\Delta_f H_m^\circ \text{ C}_7\text{H}_5\text{NO, g 298.15 K}) \\ -(14.54 \pm 1.15) \text{ kJ} \cdot \text{mol}^{-1} \text{ (Table 14).}$$

Therefore the N-(Cb)(CO) group parameter is assigned a value of $-81.5 \text{ kJ} \cdot \text{mol}^{-1}$.

1,4,5,6-Tetrahydropyrimidine

No thermochemical or thermo-physical property measurements were found for 1,4,5,6-tetrahydropyrimidine in a search of the literature through 1991.

At this time it is not possible to determine each of the group-additivity terms in 1,4,5,6-tetrahydropyrimidine. There are three unknown terms. There are no individual group-additivity parameters listed in references 1 or 2 for either of the nitrogen atoms in the molecular environments shown by the arrows.

In addition, no ring correction term for the 1,4,5,6-tetrahydropyrimidine

ring structure is listed. However, this lack of individual group terms does not prevent estimation of the ideal-gas enthalpies of formation of substituted 1,4,5,6-tetrahydro-pyrimidines. Such calculations need to start with the 1,4,5,6-tetrahydro-pyrimidine enthalpy of formation and add or subtract the relevant groups (as was illustrated above for substituted isoxazoles).

CONCLUSIONS

REVISED OR NEW GROUPS

The ring correction term for a cyclohexene ring is revised from 5.8 kJ·mol⁻¹ to 5.0 kJ·mol⁻¹.

The ring correction term for phthalan of 33.4 kJ·mol⁻¹ was derived, for 2,3-dihydrofuran the corresponding value is 37.3 kJ·mol⁻¹, for 4,5-dihydro-2,3-benzofuran the corresponding value is 27.8 kJ·mol⁻¹, hence, for 5-membered oxygen-containing rings the ring correction terms appear to be dependent on the molecular structure.

An estimate of the ideal-gas enthalpy of formation of 2,5-dihydrofuran was made.

A new ideal gas enthalpy of formation for isoxazole was determined.

An example of the estimation of the ideal gas enthalpy of formation of a substituted isoxazole was given.

The N-(C)(H)₂ group additivity term was verified.

The N-(C)₂(H) group additivity term was verified.

The N-(C)₃ group additivity term was verified.

The N-(C_b)(CO) group additivity term was derived -81.5 kJ·mol⁻¹.

The ideal gas enthalpy of formation of 1,4,5,6-tetrahydropyrimidine was determined.

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