J. Chem. Eng. Data **1996,** *41,* 1269−1284

Thermodynamic Properties and Ideal-Gas Enthalpies of Formation for Cyclohexene, Phthalan (2,5-Dihydrobenzo-3,4-furan), Isoxazole, Octylamine, Dioctylamine, Trioctylamine, Phenyl Isocyanate, and 1,4,5,6-Tetrahydropyrimidine

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, Oklahoma 74005

The results of a study aimed at improvement of the 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 (dsc) heat-capacity measurements. Ideal-gas enthalpies of formation of cyclohexene, phthalan (2,5-dihydrobenzo-3,4-furan), isoxazole, octylamine, dioctylamine, trioctylamine, 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 octylamine were determined from the dsc 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, dioctylamine, and phenyl isocyanate. Group-additivity parameters or ring-correction terms useful in the application of the Benson group-contribution correlations are derived.

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 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 (Benson, 1976; Reid et al., 1987) 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 >1600 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 (Cardillo, 1988). 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 (Benson, 1976). However, Benson's text lacks parameters for a number of important groups and correction terms for several important ring structures. Also, parameters for some structural groups were derived from data which have since been shown to be incorrect. In the absence of experimental values, 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.

[†] Present address: BDM-Oklahoma Inc., National Institute for Petroleum & Energy Research, P.O. Box 2565, Bartlesville, OK 74005-2565.
[‡] Retired.

S0021-9568(96)00093-3 CCC: $12.00

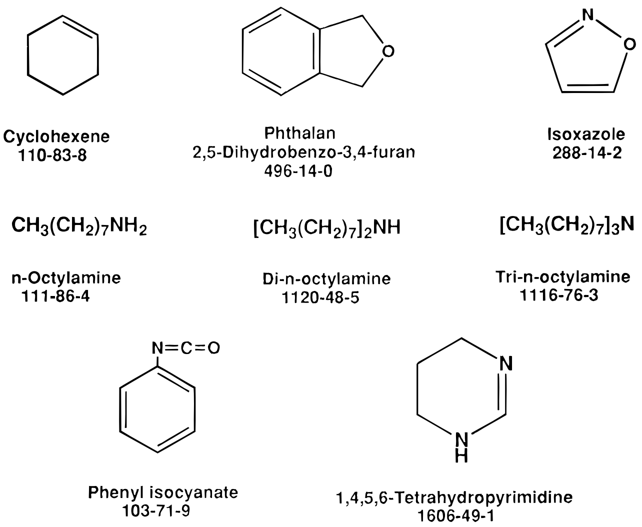


Figure 1. Molecular structures, trivial and Chemical Abstracts names (supplied by the authors), and CA Registry Numbers (supplied by the authors) for the compounds studied in this research.

Table 1. Outline of the Measurements Performed in This Project[a,b]

compound	$\Delta_c U^\circ_m$	vapor pressure	heat capacity
cyclohexene	x		
phthalan	x	x	x
isoxazole	x	x	x
octylamine	x	x	x
dioctylamine	x	x	x
trioctylamine	x	x	x
phenyl isocyanate	x	x	x
1,4,5,6-tetrahydropyrimidine	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 were derived. Values for the critical temperature and critical density for octylamine were determined from the dsc measurements on that compound. Values for the critical temperature and critical pressure for dioctylamine and phenyl isocyanate were also derived.

In the fifth year of the project, nine compounds were chosen for experimental studies. Results for one of the compounds, benzenesulfonic 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 Abstracts Service (CAS) names, and CAS 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.

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%) 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 Section

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 has been referenced for further consultation.

Materials. To minimize errors due to impurities, care was taken to ensure only samples of high purity (>99.9 mol % purity) were subjected to the calorimetric measurements. All compounds except phthalan were purchased from Aldrich Chemical Co. Capillary gas chromatography (cgc) analyses on the purchased samples gave an average purity of 99.8 mol %. 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 mol % for each compound. The high purity of each calorimetric sample was confirmed subsequently by the percentage CO_2 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 paper).

All transfers of the samples were made under nitrogen or 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 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. Cgc analysis of the decane sample failed to show any impurity peaks.

Physical Constants. Molar values are reported in terms of the 1981 relative atomic masses (IUPAC, 1993) and the gas constant, $R = 8.314\ 51\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, adopted by CODATA (Cohen and Taylor, 1988). 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). All temperatures are reported in terms of ITS-90 (Goldberg and Weir, 1990; Mangum et al., 1990). 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 Good (1969, 1972), Good and Smith (1969), and Steele et al. (1988a) and Hubbard et al. (1954) and Waddington et al. (1956), respectively. A rotating-bomb calorimeter (laboratory designation BMR II) (Good et al., 1956) and a platinum-lined bomb (laboratory designation Pt-3b) (Good et al., 1959) with an internal volume of 0.3934 dm^3 were used with rotation in the first series of combustions and without rotation in the remaining series. Flexible borosilicate-glass ampules (Guthrie et al., 1952; Good, 1972) were used to confine the samples which were liquid at 298 K.

NIST thermochemical benzoic acid (sample 39i) was used for calibration of the calorimeter; its specific energy of combustion is $-(26\ 434.0 \pm 3.0)\ \text{J}\cdot\text{g}^{-1}$ under certificate conditions. Conversion to standard states (Hubbard et al.,

Table 2. Physical Properties at 298.15 K[a,b]

compound	ρ/kg·m^{-3}	$10^7(\partial V/\partial T)_p$/ m^3·K^{-1}	C_p/R
cyclohexene	806.2	1.2	17.9
phthalan	1082	0.91	22.7
isoxazole	1071	0.70	13.0
octylamine	796.2	1.53	37.2
dioctylamine	796.0	2.32	61.0
trioctylamine	810.5	3.63	90.3
phenyl isocyanate	1081	1.04	22.4
1,4,5,6-tetrahydropyrimidine	1024	(1.2)	19.0

[a] Value in parentheses is an estimate. [b] Each compound in liquid phase.

1956) gives −(26 413.7 ± 3.0) J·g^{-1} for $\Delta_c U_m^\circ/M$, 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, ϵ(calor), obtained was (16 784.3 ± 0.4) J·K^{-1} (mean and standard deviation of the mean) for the cyclohexene and phthalan measurements. In the second combustion series ϵ(calor) was (16 775.7 ± 0.3) J·K^{-1} for the octylamine and dioctylamine measurements. In the third series the energy equivalent of the calorimeter, ϵ(calor), obtained was (16 772.4 ± 1.2) J·K^{-1} for the isoxazole measurements, and in the fourth series (16 770.9 ± 0.6) J·K^{-1} for the trioctylamine and phenyl isocyanate measurements. Finally, in the fifth series ϵ(calor) was (16 772.2 ± 0.4) J·K^{-1} 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 $CH_{1.913}$. For this material, $\Delta_c U_m^\circ/M$ was −(46 042.5 ± 1.8) J·g^{-1} (mean and standard deviation). For the cotton fuse, empirical formula $CH_{1.774}O_{0.887}$, $\Delta_c U_m^\circ/M$ was −16 945 J·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 (Hubbard et al., 1956) is given in Table 2.

Values of density reported in Table 2 were measured in this laboratory, from measurements of volumes of the ampules 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.

Small amounts of nitric acid, formed during combustions of isoxazole, the three octylamines, and phenyl isocyanate, were determined by titration with standard sodium hydroxide (Good and Moore, 1970). Carbon dioxide was also recovered from the combustion products of each experiment. Anhydrous lithium hydroxide was used as adsorbent for the CO_2 recoveries (Good and Smith, 1969). 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	no. of expts	% recovery[a]
benzoic acid calibration	6	100.009 ± 0.012
cyclohexene	6	99.995 ± 0.004
phthalan	6	99.993 ± 0.005
benzoic acid calibration	6	100.000 ± 0.005
octylamine	7	99.974 ± 0.009[b]
dioctylamine	8	99.995 ± 0.004
benzoic acid calibration	6	99.985 ± 0.007
isoxazole	6	99.935 ± 0.018[b]
benzoic acid calibration	8	100.000 ± 0.004
trioctylamine	6	99.997 ± 0.006
phenyl isocyanate	7	99.992 ± 0.005
benzoic acid calibration	6	99.992 ± 0.008
1,4,5,6-tetrahydropyrimidine	6	99.995 ± 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 (Swietoslawski, 1945; Osborn and Douslin, 1966; Chirico et al., 1989a). The ebulliometers were used to reflux the substance under study with a standard of known vapor pressure under a common helium atmosphere. In the pressure region 25 kPa to 270 kPa, water was used as the standard, and the pressures were derived using the internationally accepted equation of state for ordinary water revised to ITS-90 (Wagner and Pruss, 1993). In the pressure region 2 kPa to 25 kPa, decane (Chirico et al., 1989a) was used as the standard. Pressures were calculated on ITS-90 for those measurements using the equation

$$\ln(p/\mathrm{kPa}) = 7.73165 + (1/T_r)\{-9.98917(1 - T_r) + 5.28411(1 - T_r)^{1.5} - 6.51326(1 - T_r)^{2.5} - 2.68400(1 - T_r)^5\} \quad (1)$$

where $T_r = T/617.650$ K and T denotes the condensation temperature for the decane.

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

$$\sigma(p) = (0.001)\{(\mathrm{d}p_{\mathrm{ref}}/\mathrm{d}T)^2 + (\mathrm{d}p_x/\mathrm{d}T)^2\}^{1/2} \quad (2)$$

where p_{ref} is the vapor pressure of the reference substance and p_x is the vapor pressure of the sample under study.

The equipment for the inclined-piston vapor-pressure measurements has been described by Douslin and McCullough (1963) and Douslin and Osborn (1965). Recent revisions to the equipment and procedures have been reported (Steele et al., 1988a). The low-pressure range of the inclined-piston measurements, 10 Pa 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 sample was 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).

Table 4. Typical Combustion Experiments at 298.15 K for C, H, N, O Compounds ($p^\circ = 101.325$ kPa)[a,b]

	A	B	C	D	E	F	G	H
m'(compound)/g	0.695 827	0.928 005	1.375 320	0.749 225	0.739 434	0.720 606	1.113 733	0.945 579
m''(oil)/g	0.039 755	0.025 355	0.046 818	0.038 366	0.034 250	0.039 359	0.035 436	0.082 722
m'''(fuse)/g	0.001 000	0.001 240	0.001 009	0.000 922	0.001 088	0.001 067	0.001 059	0.001 522
$n_i(H_2O)$/mol	0.055 35	0.055 35	0.055 35	0.055 35	0.055 35	0.055 35	0.055 35	0.055 35
m(Pt)/g	19.985	33.318	32.468	38.820	32.230	19.971	32.507	19.984
ΔT/K[c]	1.998 92	2.004 03	2.099 15	2.051 46	2.080 18	2.066 44	1.998 76	2.037 34
ϵ(calor)(ΔT)/J	−33 550.5	−33 636.2	−35 207.8	−34 414.7	−34 896.5	−34 656.1	−33 521.0	−34 170.8
ϵ(cont)(ΔT)/J[d]	−41.0	−41.5	−43.1	−37.2	−37.6	−37.1	−37.6	−39.9
ΔU_{ign}/J	0.7_5	0.7_5	0.7_5	0.7_5	0.7_5	0.7_5	0.7_5	0.7_5
ΔU(corr std states)/J[e]	11.7	19.1	101.3	53.0	39.9	27.9	33.2	80.0
$\Delta U_{dec}(HNO_3)$/J			25.3	9.0	9.8	10.0	19.6	14.6
$-m''(\Delta_c U^\circ_m/M)$(oil)/J	1830.4	1167.4	2155.6	1766.5	1576.9	1812.2	1631.6	3808.7
$-m'''(\Delta_c U^\circ_m/M)$(fuse)/J	16.9	21.0	17.1	15.6	18.4	18.1	17.9	25.6
$m'(\Delta_c U^\circ_m/M)$(compound)/J	−31 731.8	−32 469.4	−32 950.9	−32 607.1	−33 288.4	−32 824.4	−31 855.6	−30 280.8
$(\Delta_c U^\circ_m/M)$(compound)/J·g^{-1}	−45 602.9	−34 988.5	−23 958.7	−43 521.1	−45 018.5	−45 551.1	−28 602.5	−32023.8

[a] A = cyclohexene, B = phthalan, C = isoxazole, D = octylamine, E = dioctylamine, F = trioctylamine, G = phenyl isocyanate, and H = 1,4,5,6-tetrahydropyrimidine. [b] The symbols and abbreviations of this table are those of Hubbard and Scott (1956) except as noted. [c] $\Delta T/\mathrm{K} = (T_i - T_f + \Delta T_{corr})/\mathrm{K}$. [d] $\epsilon_i(\mathrm{cont})(T_i - 298.15\ \mathrm{K}) + \epsilon_f(\mathrm{cont})(298.15\ \mathrm{K} - T_f + \Delta T_{corr})$. [e] Items 81−85, 87−90, 93, and 94 of the computational form of Hubbard and Scott (1956).

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

$$\sigma(p) = 1.5 \times 10^{-4} p + 0.2\ \mathrm{Pa} \qquad (3)$$

The uncertainties in the temperatures are 0.001 K. The contributions of the temperature uncertainties to $\sigma(p)$ are insignificant in the range of the measurements.

Differential Scanning Calorimetry. The technique and methodology used in the differential scanning calorimetric (dsc) measurements have been outlined in Steele et al. (1988b, 1994), Chirico et al. (1989b), Knipmeyer et al. (1989), Chirico and Steele (1994), and Steele (1995). The major difference between our measurement technique and that used by Mraw and Naas (1979) is the substitution of specially designed cells (Steele et al., 1988b) 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, $C_{sat,m}$, from $C^{II}_{x,m}$ values obtained with a dsc has been described (Steele et al., 1988b, 1994; Chirico et al., 1989b; Knipmeyer et al., 1989; Chirico and Steele, 1994; Steele, 1995). The review (Steele, 1995) is detailed and will be repeatedly referenced throughout the rest of this paper.

Densitometry. Densities, ρ, at saturation pressure for the liquid phase for a range of temperatures were obtained in this research with a vibrating-tube densitometer. The densitometer design is essentially that used successfully by Dr. J. M. Simonson and his colleagues at Oak Ridge National Laboratory for the study of aqueous salt mixtures at high temperatures and pressures (Simonson et al., 1994). The instrument and its operation have been described (Chirico et al., 1993). Test measurements of the density of benzene between $T = 310$ K and $T = 523$ K have been reported (Chirico et al., 1994). Results agreed with the values published by (Hales and Townsend, 1972) within $1 \times 10^{-3}\rho$. The precision of the measurements was approximately $5 \times 10^{-4}\rho$.

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 $\Delta_c U^\circ_m/M$ for all the experiments are reported in Table 5. Values of $\Delta_c U^\circ_m/M$ in Tables 4 and 5 for the C, H, N, O compounds refer to the general reaction

$$C_aH_bN_cO_d(\mathrm{cr\ or\ l}) + \left(a + \frac{b}{4} - \frac{d}{2}\right)O_2(g) = aCO_2(g) + \frac{b}{2}H_2O(l) + \frac{c}{2}N_2(g) \qquad (4)$$

Corrections for the small amounts of nitric acid, formed during combustions of isoxazole, the three octylamines, and phenyl isocyanate, were made during the conversion to standard states (Hubbard et al., 1956) based on a value of −59.7 kJ·mol^{-1} for the energy of fornation of 0.1 mol·dm^{-3} HNO_3(aq) from N_2, O_2, and H_2O(l).

For octylamine and isoxazole the values of $\Delta_c U^\circ_m/M$ refer to the unit mass of the 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 $\Delta_c U^\circ_m$, the standard molar enthalpy of combustion $\Delta_c H^\circ_m$, and the standard molar enthalpy of formation $\Delta_f H^\circ_m$, for the compounds studied. Values of $\Delta_c U^\circ_m$ and $\Delta_c H^\circ_m$ for the C, H, N, O compounds refer to eq 4. The corresponding values of $\Delta_f H^\circ_m$ refer to the reaction

$$a\mathrm{C(cr,\ graphite)} + \frac{b}{2}H_2(g) + \frac{c}{2}N_2(g) + \frac{d}{2}O_2(g) = C_aH_bN_cO_d(\mathrm{cr\ or\ l}) \qquad (5)$$

Uncertainties given in Table 6 are the “uncertainty interval” (Rossini, 1956). 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 (Cox et al., 1989).

Vapor-Pressure Measurements. Measured vapor pressures for each of the compounds are listed in Table 7. The results for cyclohexene are those of Forziati et al. (Forziati et al., 1950) obtained using an ebulliometer, converted to ITS-90. The precision in the temperature measurements was given by Forziati et al. as ±0.003 K. Following previous practice (Osborn and Douslin, 1966; Chirico et al., 1989b), 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

Table 5. Summary of Experimental Energy of Combustion Results ($T = 298.15$ K and $p^\circ = 101.325$ kPa)[a]

Cyclohexene
$\{(\Delta_c U^\circ_m/M)(\text{compound})\}/\text{J}\cdot\text{g}^{-1}$
−45 602.9, −45 605.3, −45 601.8
−45 604.9, −45 608.1, −45 603.1

$\langle\{(\Delta_c U^\circ_m/M)(\text{compound})\}/\text{J}\cdot\text{g}^{-1}\rangle$ −45 604.4 ± 0.9

Phthalan
$\{(\Delta_c U^\circ_m/M)(\text{compound})\}/\text{J}\cdot\text{g}^{-1}$
−34 988.5, −34 989.0, −34 988.8
−34 984.4, −34 989.0, −34 988.3

$\langle\{(\Delta_c U^\circ_m/M)(\text{compound})\}/\text{J}\cdot\text{g}^{-1}\rangle$ −34 988.0 ± 0.7

Isoxazole
$\{(\Delta_c U^\circ_m/M)(\text{compound})\}/\text{J}\cdot\text{g}^{-1}$
−23 958.7, −23 957.3, −23 962.4
−23 957.1, −23 958.3, −23 959.6

$\langle\{(\Delta_c U^\circ_m/M)(\text{compound})\}/\text{J}\cdot\text{g}^{-1}\rangle$ −23 958.9 ± 0.8

Octylamine
$\{(\Delta_c U^\circ_m/M)(\text{compound})\}/\text{J}\cdot\text{g}^{-1}$
−43 521.1, −43 516.4, −43 527.0, −43 513.4
−43 511.8, −43 523.2, −43 531.3

$\langle\{(\Delta_c U^\circ_m/M)(\text{compound})\}/\text{J}\cdot\text{g}^{-1}\rangle$ −43 520.6 ± 2.7

Dioctylamine
$\{(\Delta_c U^\circ_m/M)(\text{compound})\}/\text{J}\cdot\text{g}^{-1}$
−45 018.5, −45 024.0, −45 012.3, −45 017.9
−45 027.0, −45 012.2, −45 021.2, −45 024.2

$\langle\{(\Delta_c U^\circ_m/M)(\text{compound})\}/\text{J}\cdot\text{g}^{-1}\rangle$ −45 019.7 ± 1.9

Trioctylamine
$\{(\Delta_c U^\circ_m/M)(\text{compound})\}/\text{J}\cdot\text{g}^{-1}$
−45 551.1, −45 578.1, −45 570.6
−45 557.5, −45 560.7, −45 568.3

$\langle\{(\Delta_c U^\circ_m/M)(\text{compound})\}/\text{J}\cdot\text{g}^{-1}\rangle$ −45 564.4 ± 4.0

Phenyl Isocyanate
$\{(\Delta_c U^\circ_m/M)(\text{compound})\}/\text{J}\cdot\text{g}^{-1}$
−28 602.5, −28 605.4, −28 612.3
−28 600.4, −28 601.5, −28 604.9

$\langle\{(\Delta_c U^\circ_m/M)(\text{compound})\}/\text{J}\cdot\text{g}^{-1}\rangle$ −28 604.5 ± 1.7

1,4,5,6-Tetrahydropyrimidine
$\{(\Delta_c U^\circ_m/M)(\text{compound})\}/\text{J}\cdot\text{g}^{-1}$
−32 023.5, −32 023.8, −32 034.5
−32 028.6, −32 025.0, −32 040.7

$\langle\{(\Delta_c U^\circ_m/M)(\text{compound})\}/\text{J}\cdot\text{g}^{-1}\rangle$ −32 029.4 ± 3.0

[a] The uncertainties shown are one standard deviation of the mean.

Table 6. Condensed Phase Molar Thermochemical Functions at 298.15 K and $p^\circ = 101.325$ kPa[a,b]

	$\Delta_c U^\circ_m$/kJ·mol^{-1}	$\Delta_c H^\circ_m$/kJ·mol^{-1}	$\Delta_f H^\circ_m$/kJ·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 = octylamine, E = dioctylamine, F = trioctylamine, G = phenyl isocyanate, and H = 1,4,5,6-Tetrahydropyrimidine. [b] The results listed in this table are for the liquid phase for each compound.

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, trioctylamine, and 1,4,5,6-tetrahydropyrimidine are also listed in Table 7A. For phthalan, the inclined-piston values extend the range of measured values down to 285 K. For trioctylamine and 1,4,5,6-tetrahydropyrimidine, 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 dioctylamine 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 dsc measurements above 490 K. Similar behavior was noted for trioctylamine, 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 10.

Differential Scanning Calorimetry. Table 8 lists the two-phase (liquid + vapor) heat capacities $C^{\text{II}}_{x,m}$ determined by dsc for phthalan, isoxazole, octylamine, dioctylamine, trioctylamine, and phenyl isocyanate for the given cell fillings. Heat capacities were determined at 20 K intervals with a heating rate of 0.083 K·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 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 octylamine, sample decomposition was greatly reduced by employing a single continuous heat at a heating rate of 0.333 K·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 eq 6, and the measured temperatures at which conversion to a single phase was observed.

In this research, the thermal expansion of the cells was expressed as

$$V_x(T)/V_x(298.15\ \text{K}) = 1 + ay + by^2 \tag{6}$$

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

Critical temperatures and critical densities were derived graphically for octylamine with these results, as seen in Figure 2. Results of measurements on benzene and toluene performed as "proof-of-concept measurements" for these procedures have been reported (Knipmeyer et al., 1989). The rapid heating method was used previously for critical temperature and critical density determinations for 2-aminobiphenyl (Steele et al., 1991), dibenzothiophene (Chirico et al., 1991), carbazole, phenanthrene, and benzofuran (Steele, 1995).

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.

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 $\Delta_l^g H_m$ at 298.15 K is the only value necessary to obtain $\Delta_f H^\circ_m$ (g, 298.15 K), the benefit 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.

Table 7. Summary of Vapor-Pressure Results[a]

method	T/K	p/kPa	Δp/kPa	σ/kPa	ΔT/K	method	T/K	p/kPa	Δp/kPa	σ/kPa	ΔT/K
Cyclohexene[b]											
Rossini	285.388	6.417	0.000	0.001		Rossini	324.327	34.940	0.008	0.006	
Rossini	289.070	7.709	0.000	0.002		Rossini	330.242	43.376	0.000	0.007	
Rossini	292.285	9.006	−0.002	0.002		Rossini	336.334	53.712	0.005	0.009	
Rossini	295.210	10.345	0.002	0.002		Rossini	342.842	66.808	−0.006	0.010	
Rossini	297.940	11.734	0.001	0.002		Rossini	349.899	83.761	0.001	0.012	
Rossini	301.634	13.858	0.001	0.003		Rossini	354.890	97.655	−0.004	0.014	
Rossini	305.845	16.651	−0.002	0.003		Rossini	355.425	99.248	−0.002	0.014	
Rossini	310.137	19.958	−0.006	0.004		Rossini	355.924	100.746	−0.005	0.014	
Rossini	314.115	23.505	0.009	0.004		Rossini	356.486	102.470	0.006	0.014	
Rossini	319.440	28.990	−0.012	0.005		Rossini	356.985	104.010	0.006	0.015	
Phthalan											
ip	285.001	0.0287	0.0002	0.0002		d	404.172	16.665	0.001	0.001	0.003
ip	289.997	0.0426	0.0003	0.0002		d	409.401	19.933	0.001	0.001	0.002
ip	294.995	0.0622	0.0002	0.0002		d	416.286	25.023	0.001	0.001	0.000
ip	305.001	0.1272	0.0003	0.0002		w	416.284^c	25.023	0.002	0.001	−0.001
ip	314.994	0.2466	0.0004	0.0002		w	423.218	31.177	0.001	0.002	−0.002
ip	324.986	0.4551	0.0004	0.0003		w	430.197	38.565	−0.001	0.002	−0.003
ip	334.983	0.8044	0.0004	0.0003		w	437.22	47.375	−0.002	0.002	−0.004
ip	339.986	1.0537	0.0003	0.0004		w	444.295	57.817	−0.006	0.003	−0.002
ip	344.983	1.3664	−0.0002	0.0004		w	451.414	70.120	−0.006	0.003	−0.003
ip	349.981	1.7573	0.0001	0.0005		w	458.579	84.533	−0.004	0.004	−0.003
d	352.625	2.0000	−0.0002	0.0001	0.077	w	465.792	101.325	−0.003	0.004	−0.003
ip	354.975	2.2404	0.0006	0.0005		w	473.05	120.79	0.00	0.01	−0.004
ip	359.976	2.8330	0.0005	0.0006		w	480.360	143.25	0.01	0.01	−0.005
d	367.646	3.9999	0.0004	0.0003	0.036	w	487.714	169.02	0.01	0.01	−0.004
d	374.360	5.3330	−0.0011	0.0003	0.025	w	495.120	198.49	0.00	0.01	−0.004
d	384.334	7.9989	0.0000	0.0005	0.013	w	502.568	232.02	0.00	0.01	−0.003
d	391.822	10.666	0.000	0.001	0.008	w	510.063	270.02	−0.01	0.01	−0.003
d	397.878	13.322	0.001	0.001	0.006						
Isoxazole											
d	313.969	13.332	0.000	0.001	0.007	w	357.087	70.120	−0.003	0.004	0.006
d	319.053	16.665	0.000	0.001	0.007	w	362.834	84.533	0.000	0.004	0.006
d	323.275	19.933	0.000	0.001	0.006	w	368.614	101.325	−0.002	0.005	0.006
d	328.829	25.023	0.000	0.001	0.006	w	374.424	120.79	0.00	0.01	0.006
w	328.829^c	25.023	0.000	0.002	0.006	w	380.271	143.25	0.00	0.01	0.006
w	334.417	31.177	−0.001	0.002	0.005	w	386.143	169.02	0.00	0.01	0.007
w	340.037	38.565	−0.002	0.002	0.006	w	392.052	198.49	0.00	0.01	0.007
w	345.681	47.375	0.010	0.003	0.006	w	397.989	232.02	0.00	0.01	0.008
w	351.372	57.817	−0.004	0.003	0.006	w	403.959	270.02	0.00	0.01	0.008
Octylamine											
d	343.488	2.0000	−0.0001	0.0001	0.024	w	424.202	47.375	−0.004	0.002	0.006
d	349.212	2.6660	−0.0001	0.0002	0.021	w	430.999	57.817	−0.001	0.003	0.006
d	364.092	5.3330	0.0003	0.0003	0.021	w	437.847	70.120	0.004	0.003	0.006
d.	373.587	7.9989	0.0000	0.0005	0.016	w	444.749	84.527	0.001	0.004	0.007
d	380.724	10.666	0.000	0.001	0.016	w	451.702	101.325	0.010	0.004	0.005
d	386.502	13.332	0.002	0.001	0.016	w	458.706	120.79	0.01	0.01	0.007
d	392.515	16.665	0.002	0.001	0.013	w	465.766	143.25	0.01	0.01	0.006
d	397.523	19.933	−0.002	0.001	0.011	w	472.872	169.02	0.00	0.01	0.006
d	404.113	25.023	−0.001	0.001	0.009	w	480.032	198.49	−0.01	0.01	0.007
w	404.123^c	25.023	−0.009	0.001	0.007	w	487.240	232.02	−0.02	0.01	0.006
w	410.764	31.177	−0.008	0.002	0.008	w	494.496	270.02	−0.04	0.01	0.007
w	417.457	38.565	−0.006	0.002	0.006						
Dioctylamine											
d	448.500	2.0000	0.0001	0.0001	0.057	w	522.947^c	25.023	0.000	0.001	0.037
d	455.571	2.6660	0.0000	0.0002	0.049	w	531.061	31.177	−0.005	0.002	0.037
d	466.071	3.9999	−0.0004	0.0002	0.035	w	539.214	38.565	0.003	0.002	0.038
d	473.913	5.3330	−0.0007	0.0003	0.031	w	547.431	47.375	0.000	0.002	0.040
d	485.574	7.9989	0.0007	0.0004	0.019	w	555.698	57.817	0.002	0.003	0.045
d	494.330	10.666	0.001	0.001	0.016	w	564.020	70.120	0.001	0.003	0.058
d	501.416	13.332	0.001	0.001	0.014	w	580.812	101.325	0.004	0.004	0.076
d	508.778	16.665	0.000	0.001	0.026	w	589.284	120.79	0.00	0.01	0.079
d	514.895	19.933	−0.001	0.001	0.024	w	597.791^c	143.25	0.02	0.01	0.102
d	522.948	25.023	−0.001	0.001	0.022						
Phenyl Isocyanate											
d	329.643	2.0000	0.0000	0.0001	0.054	w	398.245	31.177	0.000	0.002	0.009
d	344.263	3.9999	−0.0002	0.0003	0.032	w	405.008	38.565	−0.001	0.002	0.008
d	350.785	5.3330	0.0003	0.0003	0.022	w	411.810	47.375	0.000	0.002	0.009
d	360.491	7.9989	−0.0004	0.0005	0.002	w	418.654	57.817	0.000	0.003	0.007
d.	367.770	10.666	0.000	0.001	0.010	w	425.540	70.120	−0.001	0.003	0.009
d	373.653	13.332	0.001	0.001	0.009	w	432.468	84.535	−0.002	0.004	0.012
d	379.765	16.665	0.001	0.001	0.009	w	439.433	101.325	0.002	0.004	0.009
d	384.843	19.933	−0.001	0.001	0.009	w	445.480^c	120.79	2.83	0.01	0.125
d	391.522	25.023	0.000	0.001	0.009						

Table 7 (Continued)

method	T/K	p/kPa	Δp/kPa	σ/kPa	ΔT/K	method	T/K	p/kPa	Δp/kPa	σ/kPa	ΔT/K
Trioctylamine[d]											
ip	414.967	0.0215	0.0019	0.0002		ip	484.958	0.7594	−0.0043	0.0002	
ip	424.964	0.0387	0.0023	0.0002		ip	494.936	1.1534	−0.0043	0.0003	
ip	434.963	0.0674	0.0021	0.0002		ip	508.874	1.9996	−0.0012	0.0004	
ip	444.957	0.1146	0.0016	0.0002		d	508.850[e]	1.9970	−0.0020	0.0005	0.076
ip	454.962	0.1902	0.0003	0.0002		d	516.593	2.6676	0.0012	0.0002	0.061
ip	464.963	0.3086	−0.0011	0.0002		d	527.881	3.9857	0.0029	0.0002	0.051
ip	474.965	0.4895	−0.0028	0.0002		d	536.501	5.3318	−0.0037	0.0003	0.045
1,4,5,6-Tetrahydropyrimidine[d]											
ip	330.000	0.0607	−0.0001	0.0002		ip	370.004	1.0906	−0.0001	0.0003	
ip	340.000	0.1340	0.0000	0.0002		ip	380.007	2.0260	−0.0004	0.0004	
ip	350.002	0.2814	−0.0001	0.0002		ip	390.000	3.6358	0.0000	0.0007	
ip	359.994	0.5657	0.0003	0.0002		ip	394.999	4.8135	0.0004	0.0009	

[a] ip denotes inclined piston. Water (w) or decane (d) 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 value of pressure, calculated with eq 7 and the parameters listed in Table 10, from the observed value of pressure. σ is the propagated error calculated from eqs 2 and 3. ΔT is the difference between the boiling and condensation temperature ($T_{\mathrm{boil}} - T_{\mathrm{cond}}$) for the sample. [b] Forziati et al. (1950). [c] Point excluded from Wagner-equation fit. [d] $\Delta p = p_{\mathrm{obs}} - p_{\mathrm{Antoine}}$ (Antoine-equation fit) is the difference of the value of pressure, calculated value of the pressure, from the observed value of pressure (see text). [e] Point excluded from Antoine-equation fit.

Octylamine. For octylamine the fitting parameters were derived by a simultaneous nonlinear least-squares fit of the vapor pressures listed in Table 7 and the two-phase heat capacities $C^{\mathrm{II}}_{\mathrm{x,m}}$ given in Table 8. The critical temperature and critical density were determined from the dsc measurements, and hence, only the critical pressure p_{c} was included in the variables. A summary of the procedure follows.

The Wagner equation (Wagner, 1973) in the formulation given by Ambrose (Ambrose and Walton, 1989),

$$\ln(p/p_{\mathrm{c}}) = (1/T_{\mathrm{r}})[AY + BY^{1.5} + CY^{2.5} + DY^{5}] \qquad (7)$$

where $T_{\mathrm{r}} = T/T_{\mathrm{c}}$ and $Y = (1 - T_{\mathrm{r}})$, was fitted to the measured vapor pressures (Table 1). As noted above, the critical pressure was included in the variables. The vapor-pressure fitting procedure including the minimization equation and the relative weightings is detailed in Steele (1995).

For fitting the two-phase heat capacities obtained in a cell of volume V_{x}, the experimental $C^{\mathrm{II}}_{\mathrm{x,m}}$ values (Table 2) were converted to $C^{\mathrm{II}}_{\mathrm{V,m}}$ by means of eq 6 for the cell expansion and the vapor-pressure fit for $(\partial p/\partial T)_{\mathrm{sat}}$,

$$C^{\mathrm{II}}_{\mathrm{V,m}} = C^{\mathrm{II}}_{\mathrm{x,m}} - T/n\{(\partial V_{\mathrm{x}}/\partial T)_{\mathrm{x}}(\partial p/\partial T)_{\mathrm{sat}}\} \qquad (8)$$

The values of $C^{\mathrm{II}}_{\mathrm{V,m}}$ were used to derive functions for $(\partial^2 p/\partial T^2)_{\mathrm{sat}}$ and $(\partial^2\mu/\partial T^2)_{\mathrm{sat}}$ [see eq 2 of Steele (1995)]. The functional form chosen for variation of the second derivative of the chemical potential with temperature was

$$(\partial^2\mu/\partial T^2)_{\mathrm{sat}}/\mathrm{J{\cdot}K^{-2}{\cdot}mol^{-1}} = \sum_{i=0}^{n} b_i(1 - T/T_{\mathrm{c}})^i \qquad (9)$$

{For compounds where sufficient information was available to evaluate reliably $(\partial^2\mu/\partial T^2)_{\mathrm{sat}}$ [e.g., benzene (Goodwin, 1988) and toluene (Goodwin, 1989)], four terms (i.e., expansion to $n = 3$) were required to represent the function (Steele, 1995). Thus, four terms were used in this research.} Details of the weighting procedures, etc. are given in Steele (1995).

Estimates of liquid-phase molar volumes $V_{\mathrm{m}}(\mathrm{l})$ for each compound were made with the extended corresponding-states equation (Riedel, 1954) as formulated by Hales and Townsend (1972):

$$(\rho/\rho_{\mathrm{c}}) = 1.0 - 0.85Y + (1.6916 + 0.9846\omega)Y^{1/3} \qquad (10)$$

with $Y = (1 - T/T_{\mathrm{c}})$, ρ_{c} = critical density, and ω = acentric factor. The acentric factor, ω, is defined as $[-\log(p/p_{\mathrm{c}}) - 1]$, where p is the vapor pressure at $T/T_{\mathrm{c}} = 0.7$ 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 ρ_{c} derived from the liquid-phase density at 298.15 K listed in Table 2.

Cyclohexene. For cyclohexene a literature value (Ambrose et al., 1960; Ambrose, 1978, 1979) 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 octylamine except that no two-phase heat-capacity measurements were available. Liquid-phase densities (Forziati et al., 1950) were used to derive ρ_{c} in each iteration.

Phthalan, Isoxazole, Dioctylamine, 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 ρ_{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, dioctylamine and phenyl isocyanate, in the fitting procedure eq 9 was truncated at the third term (b_2).

Trioctylamine and 1,4,5,6-Tetrahydropyrimidine. For both these compounds the range of vapor pressure measurements (see Table 7) was so short that Wagner-equation fits were not attempted. For each compound the Antoine equation in the form

$$\log(p/p_{\mathrm{ref}}) = A + B/\{(T/\mathrm{K}) + C\} \qquad (11)$$

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

Derived Results. General Comments. Table 11 lists the parameters derived using the various fitting procedures outlined above. Details of the fits to the vapor-pressure

Table 8. Two-Phase (Liquid + Vapor) Heat Capacities (R = 8.314 51 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$)

T/K	$C^{\rm II}_{\rm X,m}/R$	$C^{\rm II}_{\rm X,m}/R$	$C^{\rm II}_{\rm X,m}/R$
	Phthalan		
mass/g	0.012 420	0.016 820	0.024 170
vol cell/cm^3	0.054 09	0.053 87	0.055 70
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
	Isoxazole		
mass/g	0.012 144	0.017 705	0.025 696
vol cell/cm^3	0.052 72	0.052 92	0.052 72
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
	Octylamine		
mass/g	0.010 067	0.015 345	0.019 431
vol cell/cm^3	0.053 39	0.053 39	0.053 39
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
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	$C^{\rm II}_{\rm X,m}/R$	$C^{\rm II}_{\rm X,m}/R$
	Dioctylamine	
mass/g	0.008 468	0.018 758
vol cell/cm^3	0.052 72	0.052 72
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
	Trioctylamine	
mass/g	0.010 495	0.017 666
vol cell/cm^3	0.052 72	0.052 72
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
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
	Phenyl Isocyanate	
mass/g	0.011 671	0.016 651
vol cell/cm^3	0.052 72	0.053 39
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 the cell is given at 298.15 K. [b] Values not included in fit. Values are listed to show the 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

ρ/(kg·m^{-3})	T/K	ρ/(kg·m^{-3})	T/K
	Octylamine		
90.8	618.3	224.0	640.7
135.1	624.6	282.5	640.3
176.2	635.7	358.0	630.6
191.1	639.9		

results are given in Table 7 (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.

For phthalan, isoxazole, octylamine, dioctylamine, and phenyl isocyanate values of $C^{\rm II}_{\rm V,m}(\rho{=}\rho)_{\rm sat}$ were derived from the parameters listed in Table 11 and corresponding $C_{\rm sat,m}$ obtained using eq 6 of Steele et al. (1995). The results for $C_{\rm sat,m}/R$ are reported in Table 12. The estimated uncertainty in these values is 1%.

Enthalpies of Vaporization. Enthalpies of vaporization $\Delta_{\rm l}^{\rm g}H_{\rm m}$ were derived from the Wagner- and Antoine-equation fits (Table 11A) using the Clapeyron equation:

$${\rm d}p/{\rm d}T = \Delta_{\rm l}^{\rm g}H_{\rm m}/(T\Delta_{\rm l}^{\rm g}V_{\rm m}) \qquad (12)$$

where $\Delta_{\rm l}^{\rm g}V_{\rm m}$ is the increase in molar volume from the liquid to the real vapor.

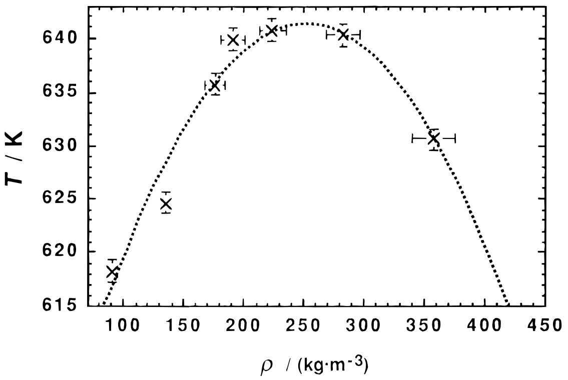


Figure 2. Vapor−liquid coexistence in the region of the critical point for octylamine. The curve is drawn as an aid to the eye. The crosses span the range of uncertainty.

Table 10. Measured Liquid-Phase Densities along the Saturation Line[a]

T/K	ρ_{obs}/kg·m^{-3}	100(ρ_{obs} − $\rho_{c.s.}$)/ρ_{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

[a] $\rho_{c.s.}$ is the density calculated using eq 10 and the parameters listed in Table 11.

Cyclohexene, Phthalan, Isoxazole, Octylamine, Dioctylamine, and Phenyl Isocyanate. For each of these compounds estimates of the liquid-phase volumes were made using eq 10 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 (1957), and third virial coefficients were estimated with the corresponding-states method of Orbey and Vera (1983). This formulation for third virial coefficients was applied successfully in analyses of the thermodynamic properties of benzene and toluene (Chirico et al., 1994). 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%.

Trioctylamine 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. (1950). 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%.

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.

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. In Table 14 the enthalpies of vaporization, $\Delta_l^g H_m$, have been converted to the corresponding values for the ideal

Table 11. Parameters for Eqs 7 and 9, Critical Constants, and Acentric Factors

	Cyclohexene				Phthalan		
A	−9.081 02			A	−8.946 77	b_0	−0.370 89
B	5.754 88			B	4.245 57	b_1	−0.766 95
C	−5.175 05			C	−4.765 33	b_2	1.453 75
D	−1.048 89			D	−2.699 39	b_3	−1.601 31
T_c	560.4 K	p_c	4905 kPa	T_c	700 K	p_c	4285 kPa
ρ_c	276.7 kg·m^{-3}	ω	0.263	ρ_c	337.3 kg·m^{-3}	ω	0.382
	Isoxazole				Octylamine		
A	−7.138 62	b_0	−0.137 75	A	−7.993 96	b_0	−0.656 93
B	1.219 82	b_1	−1.138 26	B	1.405 73	b_1	−0.460 21
C	−1.609 13	b_2	2.716 04	C	−2.981 88	b_2	0.175 34
D	−3.102 51	b_3	−2.686 50	D	−6.604 35	b_3	−1.200 63
T_c	590 K	p_c	6100 kPa	T_c	641 K	p_c	2617 kPa
ρ_c	361.7 kg·m^{-3}	ω	0.258	ρ_c	250 kg·m^{-3}	ω	0.446
	Dioctylamine				Phenyl isocyanate		
A	−10.821 24	b_0	−1.163 84	A	−7.775 31	b_0	−0.487 38
B	4.526 45	b_1	−0.362 86	B	2.130 21	b_1	0.296 04
C	−8.333 85	b_2	−0.908 46	C	−2.621 37	b_2	−0.961 24
D	−4.630 27	b_3		D	−2.407 83	b_3	
T_c	734 K	p_c	1260 kPa	T_c	675 K	p_c	4540 kPa
ρ_c	221 kg·m^{-3}	ω	0.815	ρ_c	348.8 kg·m^{-3}	ω	0.314

Antoine Equation Coefficients

	Trioctylamine	1,4,5,6-Tetrahydropyrimidine
P_{ref}/kPa	1	1
A	7.012 90	9.4934
B	−2736.15	−3229.9
C	−101.205	28.424
range/K[a]	415−537	330−395

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

Table 12. Values of $C_{\mathrm{sat,m}}/R$ (R = 8.314 51 J·K^{-1}·mol^{-1})

T/K	$C_{\mathrm{sat,m}}/R$	T/K	$C_{\mathrm{sat,m}}/R$
	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		
	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
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.
	Dioctylamine		
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		

gas, $\Delta_{\mathrm{l}}^{\mathrm{g}}H^{\circ}_{\mathrm{m}}$, using the following estimates of $(H^{\circ} - H)$ in kJ·mol^{-1} for the real gas at its saturation vapor pressure at 298.15 K:cyclohexene, 0.08; isoxazole, 0.07. The corrections for the less volatile compounds were estimated to be negligibly small. These corrections were calculated using eq 20 of Chirico et al. (1993) and the virial coefficients derived above.

Discussion

Cyclohexene. Values of the energy of combustion for cyclohexene have been reported in the literature (Labbauf and Rossini, 1961), and by the NIPER group (Good and Smith, 1969). However, it was noted that there existed a value for the enthalpy of formation for cyclohexene derived from hydrogenation calorimetry (Rogers and McLafferty, 1971) which was 5.7 kJ·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 (Rogers and Crooks, 1987; Rogers and Dejroongruang, 1988, 1989; Rogers et al., 1992) 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 (1961) and Good and Smith (1969). Hence, the enthalpy of hydrogenation [$\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}} = -(112.5 \pm 2.5)$ kJ·mol^{-1}] obtained by Rogers and McLafferty (1971) for the reaction

$$\text{cyclohexene(l)} + \mathrm{H_2(g)} = \text{cyclohexane(l)}$$

appears to be in error. In a later paper Rogers and Munoz-Hresko (1984) listed a value of $-(118.7 \pm 0.1)$ kJ·mol^{-1}. Using the results obtained in Dolliver et al. (1937) with modern units gives $-(119.0 \pm 0.3)$ kJ·mol^{-1} and Roth and Lennartz (1980) list $-(118.6 \pm 0.2)$ kJ·mol^{-1} for the above hydrogenation reaction. In recent work Rogers et al. (Rogers and Crooks, 1987; Rogers and Dejroongruang, 1988, 1989; Rogers et al., 1992) have used a value of exactly -119.0 kJ·mol^{-1} as a standard from which to calculate other enthalpies of hydrogenation. This research gives a value of $-(118.3 \pm 0.7)$ kJ·mol^{-1} using the enthalpy of formation of cyclohexane [$\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}} = -(156.2 \pm 0.6)$ kJ·mol^{-1}] obtained (Good and Smith, 1969). Hence, the enthalpies of hydrogenation derived by Rogers et al. (Rogers and Crooks, 1987; Rogers and Dejroongruang, 1988, 1989; Rogers et al., 1992) need revision. For further detailed discussion of this topic see Steele and Chirico (1993)

Vapor pressures for cyclohexene have been reported (Lister, 1941; Forziati et al., 1950; Meyer and Hotz, 1973; Letcher and Marsicano, 1974). In this research the ebulliometric vapor pressures obtained at NIST (Forziati et al., 1950) 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 (Lister, 1941) at 228.7 K and 248.3 K are not shown in Figure 3. They are 2 and 6% high relative to values obtained using the Wagner equation and the parameters listed in Table 11.

The various literature liquid-phase saturation densities (Forziati et al., 1950; Letcher and Marsicano, 1974; Evans, 1941; Letcher, 1975, 1977) are compared in Table 16 with values calculated by extended corresponding states eq 10 using the parameters listed in Table 11. Agreement is good except for the values of Letcher and Marsicano (1974), which are on average 1.2% high.

Using the group parameters given in Benson (1976) and Reid et al. (1987), estimation of a ring correction parameter for the Benson scheme was made as follows:

2	C$-$(C)$_2$(H)$_2$	-20.72×2	-41.44
2	C$-$(C)(C$_{\mathrm{d}}$)(H)$_2$	-19.93×2	-39.86
2	C$_{\mathrm{d}}-$(C$_{\mathrm{d}}$)(C)(H)	35.96×2	71.92
1	ring correction		
	$\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$(C$_6H_{10}$, g, 298.15 K)		-4.32 kJ·mol^{-1}

Hence, a value of 5.1 kJ·mol^{-1} was derived for the cyclohexene ring-correction parameter compared with a value of 5.86 kJ·mol^{-1} listed in Reid et al. (1987).

Phthalan. For phthalan no vapor-pressure or other thermophysical property measurements were found in a

Table 13. Enthalpies of Vaporization Obtained from the Wagner or Antoine and Clapeyron Equations[a]

T/K	$\Delta_l^g H_m$/kJ·mol^{-1}	T/K	$\Delta_l^g H_m$/kJ·mol^{-1}	T/K	$\Delta_l^g H_m$/kJ·mol^{-1}	T/K	$\Delta_l^g H_m$/kJ·mol^{-1}
Cyclohexene							
260.0^b	35.30 ± 0.62	320.0	32.31 ± 0.50	400.0^b	27.86 ± 0.60	480.0^b	22.58 ± 1.18
280.0^b	34.32 ± 0.57	340.0	31.25 ± 0.48	420.0^b	26.63 ± 0.70	500.0^b	20.99 ± 1.41
298.15	33.42 ± 0.53	360.0	30.18 ± 0.50	440.0^b	25.36 ± 0.83	520.0^b	19.06 ± 1.70
300.0	33.33 ± 0.53	380.0	29.04 ± 0.53	460.0^b	24.02 ± 1.00	540.0^b	16.41 ± 2.06
Phthalan							
280.0^b	55.02 ± 0.45	380.0	48.27 ± 0.30	500.0	40.12 ± 0.58	620.0^b	29.42 ± 1.80
298.15	53.74 ± 0.42	400.0	46.99 ± 0.30	520.0^b	38.59 ± 0.72	640.0^b	27.05 ± 2.10
300.0	53.60 ± 0.40	420.0	45.68 ± 0.30	540.0^b	36.97 ± 0.88	660.0^b	24.29 ± 2.48
320.0	52.23 ± 0.38	440.0	44.36 ± 0.33	560.0^b	35.28 ± 1.06	680.0^b	20.83 ± 2.96
340.0	50.88 ± 0.35	460.0	42.99 ± 0.38	580.0^b	33.47 ± 1.28		
360.0	49.57 ± 0.32	480.0	41.59 ± 0.47	600.0^b	31.53 ± 1.51		
Isoxazole							
280.0^b	38.08 ± 0.23	340.0	35.10 ± 0.22	420.0^b	30.66 ± 0.52	500.0^b	24.28 ± 1.21
298.15^b	37.17 ± 0.22	360.0	34.10 ± 0.25	440.0^b	29.31 ± 0.65	520.0^b	22.20 ± 1.45
300.0	37.07 ± 0.22	380.0	33.03 ± 0.30	460.0^b	27.80 ± 0.81	540.0^b	19.86 ± 1.70
320.0	36.09 ± 0.20	400.0	31.89 ± 0.40	480.0^b	26.13 ± 1.01	560.0^b	17.19 ± 1.96
						580.0^b	13.89 ± 2.28
Octylamine							
298.15^b	54.63 ± 0.47	380.0	46.94 ± 0.32	480.0	38.11 ± 0.72	580.0^b	25.73 ± 1.95
300.0^b	54.43 ± 0.45	400.0	45.25 ± 0.33	500.0	36.05 ± 0.90	600.0^b	22.39 ± 2.28
320.0^b	52.40 ± 0.42	420.0	43.54 ± 0.37	520.0^b	33.82 ± 1.13	620.0^b	18.51 ± 2.64
340.0^b	50.49 ± 0.37	440.0	41.81 ± 0.43	540.0^b	31.39 ± 1.38	640.0^b	12.57 ± 3.13
360.0	48.68 ± 0.33	460.0	40.01 ± 0.57	560.0^b	28.71 ± 1.65		
Dioctylamine							
298.15^b	87.10 ± 1.33	480.0	67.80 ± 0.57	580.0	56.09 ± 0.85	680.0^b	40.22 ± 2.43
400.0^b	86.86 ± 1.30	500.0	65.59 ± 0.53	600.0	53.39 ± 1.06	700.0^b	35.99 ± 2.93
420.0^b	74.49 ± 0.72	520.0	63.36 ± 0.55	620.0^b	50.49 ± 1.33	720.0^b	31.06 ± 3.53
440.0	72.23 ± 0.65	540.0	61.05 ± 0.58	640.0^b	47.38 ± 1.65		
460.0	70.00 ± 0.60	560.0	58.63 ± 0.68	660.0^b	43.97 ± 2.01		
Phenyl Isocyanate							
298.15^b	46.54 ± 0.30	340.0	44.44 ± 0.27	400.0	41.46 ± 0.27	460.0^b	38.09 ± 0.45
300.0^b	46.44 ± 0.30	360.0	43.47 ± 0.25	420.0	40.41 ± 0.30	480.0^b	36.79 ± 0.57
320.0^b	45.43 ± 0.28	380.0	42.48 ± 0.25	440.0^b	39.29 ± 0.37	500.0^b	35.39 ± 0.70
Trioctylamine							
298.15^b	110.4 ± 15.0	440.0	88.3 ± 11.2	500.0	81.9 ± 8.2	560.0^b	76.1 ± 7.5
400.0^b	93.9 ± 16.7	460.0	86.0 ± 9.88	520.0	0.0 ± 7.9	580.0^b	74.0 ± 7.5
420.0	90.9 ± 13.4	480.0	83.9 ± 8.97	540.0^b	8.1 ± 7.6	600.0^b	71.5 ± 7.6
1,4,5,6-Tetrahydropyrimidine							
298.15^b	75.6 ± 2.0	340.0	73.6 ± 1.4	400.0	71.4 ± 1.2	460.0^b	68.4 ± 1.8
300.0^b	75.5 ± 2.0	360.0	72.9 ± 1.3	420.0^b	70.6 ± 1.4	460.0^b	66.6 ± 2.0
320.0^b	74.5 ± 1.6	380.0	72.1 ± 1.2	440.0^b	69.7 ± 1.4		

[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.

Table 14. Thermochemical Properties at 298.15 K (R = 8.314 51 J·K^{-1}·mol^{-1} and $p°$ = 101.325 kPa)[a]

	$\Delta_f H_m^\circ$(l)/kJ·mol^{-1}	$\Delta_l^g H_m^\circ$/kJ·mol^{-1}	$\Delta_f H_m^\circ$(g)/kJ·mol^{-1}
A	−37.82 ± 0.82	33.50 ± 0.53	−4.32 ± 0.98
B	−83.83 ± 0.93	53.74 ± 0.42	−30.09 ± 1.02
C	44.78 ± 0.56	37.24 ± 0.22	82.02 ± 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 = octylamine, E = dioctylamine, F = trioctylamine, G = phenyl isocyanate, and H = 1,4,5,6-tetrahydropyrimidine.

search of the literature through 1991. Using the group parameters listed in Benson (1976) and Reid et al., (1987)

4	$C_b-(C_b)_2(H)$	13.82 × 4	55.28
2	$C_b-(C_b)_2(C)$	23.07 × 2	46.14
2	$C-(C_b)(O)(H)_2$	−33.91 × 2	−67.82
1	$O-(C)_2$	−97.07 × 1	−97.07
1	ring correction		
	$\Delta_f H_m^\circ(C_8H_8O, g, 298.15\ K)$		−30.09 kJ·mol^{-1}

Table 15. Comparison of Literature Values for the Energy of Combustion of Cyclohexene

author(s)	$-\Delta_c U_m^\circ$/kJ·mol^{-1}
Labbauf and Rossini (1961)	3745.27 ± 0.50
Good and Smith (1969)	3745.94 ± 0.28
this research	3746.19 ± 0.49

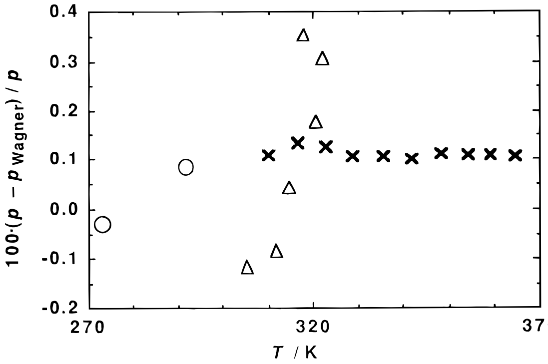
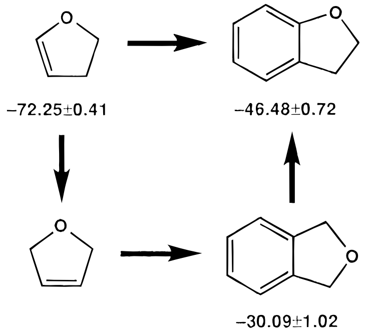


Figure 3. Comparison of literature vapor pressures for cyclohexene with those obtained from the Wagner equation and the parameters listed in Table 11: (○), Lister (1941); (×) Meyer and Hotz (1973); (△) Letcher and Marsicano (1974).

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

In the 1988 research program (Steele et al., 1989) the enthalpy of formation of 2,3-dihydrofuran, ($\Delta_f H^\circ_m$(C_4H_6O, 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 (Steele and Chirico, 1989) the ideal-gas enthalpy of formation of 4,5-dihydro-2,3-benzofuran was reported, $\Delta_f H^\circ_m$(C_8H_8O, 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 mol % 2,5-dihydrofuran.) An enthalpy of formation of 2,5-dihydrofuran of $\Delta_f H^\circ_m$(C_4H_6O, 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 (1978). McCormick and Hamilton reported an energy of combustion of −(23920.7 ± 2.0) J·g^{-1}. The corresponding value obtained in this research was $\Delta_c U^\circ_m$(l) = −(23958.9 ± 0.8) J·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 mol % water in the sample studied (McCormick and Hamilton, 1978) would reconcile the two sets of results.

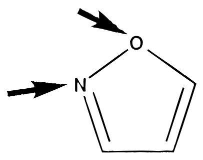
They (McCormick and Hamilton, 1978) measured the enthalpy of vaporization of isoxazole at 298.15 K using an LKB 8721-3 calorimeter. They list a value $\Delta_l^g H_m$(C_3H_3NO, 298.15 K) = (36.44 ± 0.04) kJ·mol^{-1}, the mean of five determinations. The corresponding value obtained in this research is $\Delta_l^g H_m$(C_3H_3NO, 298.15 K) = (37.17 ± 0.22) kJ·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 kJ·mol^{-1} in the ideal gas enthalpies of formation of isoxazole: McCormick and Hamilton ($\Delta_f H^\circ_m$(C_3H_3NO, g, 298.15 K) = (78.6 ± 0.5) kJ·mol^{-1} vs ($\Delta_f H^\circ_m$(C_3H_3NO, g, 298.15 K) = (81.95 ± 0.60) kJ·mol^{-1} obtained in this research.

Table 16. Comparison of Literature Values of the Density with Values from Corresponding States

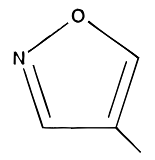
reference	T/K	ρ/kg·m^{-3} lit.	ρ/kg·m^{-3} corr states
	Cyclohexene		
Forziati et al., 1950	293.15	810.96	810.9
Forziati et al., 1950	298.15	806.09	806.2
Forziati et al., 1950	303.15	801.41	801.4
Letcher and Marsicanco, 1974	299.29	814.5	805.1
Letcher and Marsicanco, 1974	307.25	806.7	797.5
Letcher and Marsicanco, 1974	315.28	799.3	789.7
Letcher and Marsicanco, 1974	323.61	790.7	781.5
Evans, 1941	293.15	810.4	810.9
Evans, 1941	323.15	782.3	781.9
Letcher, 1975	298.15	806	806.2
Letcher, 1975	298.15	805.7	806.2
	Octylamine		
Vogel, 1948	293.15	781.9	799.5
Huggins, 1954	298.15	782.6	796.2
TRC, 1990	293.15	782.8	799.5
TRC, 1990	298.15	779.0	796.2
TRC, 1990[a]	299.95	776.9	
this research	298.15	796.2	
	Dioctylamine		
Carill and Wright, 1948	299	796.8	795.5
TRC, 1990	293.15	803.8	799.1
TRC, 1990	298.15	800.3	796.0
TRC, 1990[b]	293.15	806.5	
TRC, 1990[b]	298.15	802.0	
this research	298.15	796.0	
	Phenyl isocyanate		
Carothers, 1923	273.15	1115	1115
Carothers, 1923	283.15	1105	1105
Carothers, 1923	293.15	1094	1094
Carothers, 1923	303.15	1084	1084
Carothers, 1923	313.15	1074	1074
Carothers, 1923	323.15	1063	1063

[a] Listed value and corresponding reference (Eykman, J. F. *Recl. Trav. Chim. Pays-Bas.* **1896**, 12, 268) were obtained in a communication from the Editor. [b] Listed values and corresponding reference (Sudaricov, B. N.; Prolov, U. G.; Ilichev, V. A.; Pushcov, A. A.; Zaharov-Narcissov, O. I.; Ochkin, A. B. *Tr. Inst. Mosk. Khim. Teknol. Inst. im. D. I. Mendeleeva* **1963**, 43, 21) were obtained in a communication from the Editor.

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 Benson (1976) or Reid et al. (1987) 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	82.02	82.02
−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
	($\Delta_f H^\circ_m$(C_4H_5NO, g, 298.15 K)		48.1 kJ·mol^{-1}

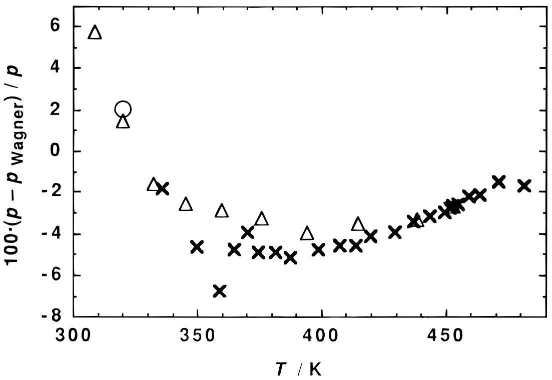


Figure 4. Comparison of literature vapor pressures for octylamine with those obtained using the Wagner equation and the parameters listed in Table 11: (×) TRC (1990); (△) Ralston et al. (1940); (○) Ralston et al. (1942).

Octylamine. No energy of combustion measurements were found for octylamine in a search of the literature through 1991. Vapor pressures for octylamine were reported in two papers (Ralston et al., 1940, 1942). These measurements, supplemented by results obtained at the turn of the century, were used by TRC (TRC, 1990) to obtain the temperatures at set pressures listed by them in their tables of thermodynamic properties. Figure 4 compares the results (Ralston et al., 1940, 1942; TRC, 1990) with those obtained using the Wagner equation and the parameters listed in Table 11.

Values for the density of octylamine reported in the literature (Vogel, 1948, Huggins, 1954; TRC, 1990) are lower than the value for 298.15 K obtained in this research and reported in Table 2 or estimated using extended corresponding states eq 10 and the parameters listed in Table 11. Table 16 compares the various values.

Using the group-additivity parameters listed (Benson, 1976; Reid et al., 1987)

1	C−(C)(H)$_3$	−42.20 × 1	−42.2
6	C−(C)$_2$(H)$_2$	−20.72 × 6	−124.3
1	C−(N)(C)(H)$_2$	−27.6 × 1	−27.6
1	N−(C)(H)$_2$	20.1 × 1	20.1
	($\Delta_f H^\circ_m$(C$_8$H$_{19}$N, g, 298.15 K)		−174.0 kJ·mol^{-1}

The value determined in this research is $\Delta_f H^\circ_m$(C$_8$H$_{19}$N, g, 298.15 K) = −(173.46 ± 1.33) kJ·mol^{-1} (Table 14). The agreement is excellent, showing that no group-additivity parameters need revision.

Dioctylamine. Carroll and Wright (1948) reported distillation ranges of 571 K to 573 K at 751 mmHg and 432 K to 434 K at 10 mmHg for dioctylamine along with a density at 299 K of 796.8 kg·m^{-3}. TRC (TRC, 1990) report densities of 803.8 kg·m^{-3} and 800.3 kg·m^{-3} at 293.15 K and 298.15 K, respectively. Table 16 compares the density values.

Using the group-additivity parameters listed (Benson, 1976; and Reid et al., 1987)

2	C−(C)(H)$_3$	−42.20 × 2	−84.4
12	C−(C)$_2$(H)$_2$	−20.72 × 12	−248.6
2	C−(N)(C)(H)$_2$	−27.6 × 2	−55.2
1	N−(C)$_2$(H)	64.5 × 1	64.5
	($\Delta_f H^\circ_m$(C$_{16}$H$_{35}$N, g, 298.15 K)		−323.7 kJ·mol^{-1}

The value determined in this research is $\Delta_f H^\circ_m$(C$_{16}$H$_{35}$N, g, 298.15 K) = −323.7 kJ·mol^{-1} (Table 14). The agreement is excellent, showing that no group-additivity parameters need revision.

Trioctylamine. Values of the energy of combustion, density, and a boiling point at 2 mmHg, for trioctylamine, have been reported in the literature (Lebedeva, 1966). The average value for the energy of combustion obtained by Lebedeva, $\Delta_c U^\circ_m$(l) = −(45 585 ± 6) J·g^{-1}, is in good agreement with the value of −(45 564 ± 4) J·g^{-1} obtained in this research. Similarly, the density at 298.15 K obtained by Lebedeva, 811.0 kg·m^{-3}, is in good agreement with the value obtained in this research 810.5 kg·m^{-3}. Using the Antoine parameters listed in Table 11A, a temperature of 461.8 K was calculated for a pressure 2 mmHg. This is 8 K above the 2 mmHg boiling point (454 K) listed by Lebedeva.

Using the group-additivity parameters listed in Benson (1976) and Reid et al., (1987)

3	C−(C)(H)$_3$	−42.20 × 3	−126.6
18	C−(C)$_2$(H)$_2$	−20.72 × 18	−373.0
3	C−(N)(C)(H)$_2$	−27.6 × 3	−82.8
1	N−(C)$_3$	102.2 × 1	102.2
	($\Delta_f H^\circ_m$(C$_{24}$H$_{51}$N, g, 298.15 K)		−480.7 kJ·mol^{-1}

The value determined in this research is $\Delta_f H^\circ_m$(C$_{24}$H$_{51}$N, g, 298.15 K) = −(477.1 ± 15) kJ·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, $\Delta_c H^\circ_m$(l) = −(3402.4) kJ·mol^{-1}, has been reported in the literature (Strepikheev et al., 1962). No details of the combustion calorimetry or the purity of the sample are given (Strepikheev et al., 1962). However, the result compares favorably with the value, $\Delta_c H^\circ_m$(l) = −(3408.07 ± 0.85) kJ·mol^{-1}, obtained in this research.

Vapor pressures for phenyl isocyanate have been reported (Carothers, 1923; Korovin and Margolin, 1976; Stull, 1947). Figure 5 compares the results given (Carothers, 1923; Korovin and Margolin, 1976; and Stull, 1947) with those obtained using the Wagner equation and the parameters listed in Table 11.

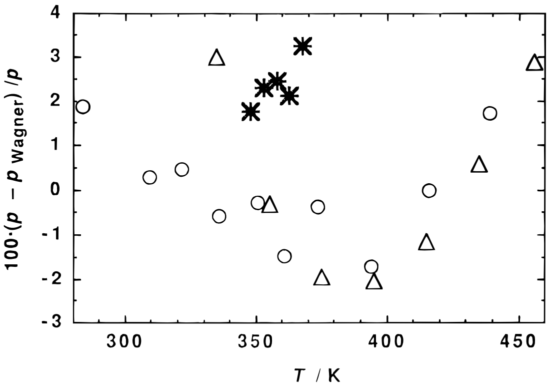


Figure 5. Comparison of literature vapor pressures for phenyl isocyanate with those obtained using the Wagner equation and the parameters listed in Table 11: (✱) Carothers (1923); (○) Stull (1947); (△) Korovin and Margolin (1976).

Table 16 compares saturation densities for phenyl isocyanate obtained (Carothers, 1923) with values calculated using extended corresponding states (eq 10) and the parameters listed in Table 11. Agreement is excellent.

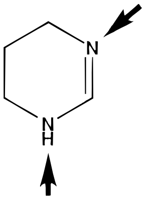
Using the group-additivity parameters given (Benson, 1976; Reid et al., 1987) and the new value for the C$_b$−(C$_b$)$_2$-(N) parameter derived in the 1989 research (Steele et al., 1980)

5	C$_b$−(C$_b$)$_2$(H)	13.82 × 5	69.10
1	C$_b$−(C$_b$)$_2$(N)	−2.1 × 1	−2.1
1	N−(C$_b$)(CO)		
	($\Delta_f H^\circ_m$(C$_7$H$_5$NO, g, 298.15 K)		−14.54 kJ·mol^{-1}

The value determined in this research is $\Delta_f H^\circ_m$(C_7H_5NO, g, 298.15 K) = −(14.54 ± 1.15) kJ·mol^{-1} (Table 14). Therefore the N−(C_b)(CO) group parameter is assigned a value of −81.5 kJ·mol^{-1}.

1,4,5,6-Tetrahydropyrimidine. No thermochemical or thermophysical 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 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-tetrahydropyrimidines. Such calculations need to start with the 1,4,5,6-tetrahydropyrimidine 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 5.9 kJ·mol^{-1} to 5.1 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}, and for 4,5-dihydro-2,3-benzofuran the corresponding value is 27.8 kJ·mol^{-1}; hence, for five-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. For the Benson scheme, the following were verified: the N−(C)$(H)_2$ group-additivity term, the N-$(C)_2$(H) group-additivity term, and the N−$(C)_3$ group-additivity term. 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.

Acknowledgment

Contribution number 337 from the Thermodynamics Research Laboratory at the National Institute for Petroleum and Energy Research (NIPER). The authors acknowledge Professor E. J. “Pete” Eisenbraun and his research group at Oklahoma State University for purification of the compounds used in this research. The authors also acknowledge the helpful discussions with members of the DIPPR Research Project 871 Committee, especially the DIPPR Technical Director, T. B. Selover, Jr., the Committee Chairman, Dennis Jones, and Bill Peters of the U.S. Department of Energy Bartlesville Project Office.

Literature Cited

Ambrose, D. Correlations and Estimations of Vapor-Liquid Critical Properties. I. Critical Temperatures of Organic Compounds. NPL Rep. Chem. 82; National Physical Laboratory, Teddington, England, September **1978**; corrected March 1980.

Ambrose, D. Correlations and Estimations of Vapor-Liquid Critical Properties. II. Critical Pressures and Volumes of Organic Compounds. *NPL Rep. Chem. 98*; National Physical Laboratory, Teddington, England, September 1979.

Ambrose, D.; Cox, J. D.; Townsend, R. The Critical Temperatures of Forty Organic Compounds. *Trans. Faraday Soc.* **1960**, *56*, 1452−1459.

Ambrose, D.; Walton, J. Vapor Pressures up to Their Critical Temperatures of Normal Alkanes and 1-Alkanols. *Pure Appl. Chem.* **1989**, *61*, 1395−1403.

Benson, S. W. *Thermochemical Kinetics*, 2nd ed., Wiley: New York, 1976.

Cardillo, P. Thermal Decomposition of Isoxazoles. *Chem. Ind. (Milan)* **1988**, *70* (6), 90−92.

Carothers, W. H. The Isosterism of Phenyl Isocyanate and Diazobenzene-Imide. *J. Am. Chem. Soc.* **1923**, *45*, 1734−1738.

Carroll, K. K.; Wright, G. F. Catalyzed Nitration of Amines. VI. The Nitration of Dioctylamine. *Can. J. Res.* **1948**, *26B*, 271−283.

Chirico, R. D.; Steele, W. V. Reconciliation Of Calorimetrically And Spectroscopically Derived Thermodynamic Properties at Pressures Greater Than 0.1 MPa for Benzene and Methylbenzene: The Importance of the Third Virial Coefficient. *Ind. Eng. Chem. Res.* **1994**, *33*, 157−167.

Chirico, R. D.; Knipmeyer, S. E.; Nguyen, A.; Steele, W. V. Thermodynamic Properties of Biphenyl. *J. Chem. Thermodyn.* **1989a**, *21*, 1307−1331.

Chirico, R. D.; Nguyen, A.; Steele, W. V.; Strube, M. M.; Tsonopoulos, C. The Vapor Pressure of n-Alkanes Revisited. New Vapor Pressure Data on *n*-Decane, *n*-Eicosane and *n*-Octacosane. *J. Chem. Eng. Data* **1989b**, *34*, 149−156.

Chirico, R. D.; Knipmeyer, S. E.; Nguyen, A.; Steele, W. V. The Thermodynamic Properties of Dibenzothiophene. *J. Chem. Thermodyn.* **1991**, *23*, 431−450.

Chirico, R. D.; Knipmeyer, S. E.; Nguyen, A.; Smith, N. K.; Steele, W. V. The Thermodynamic Properties of 4,5,9,10-Tetrahydropyrene and 1,2,3,6,7,8-Hexahydropyrene. *J. Chem. Thermodyn.* **1993**, *25*, 729−761.

Cohen, E. R.; Taylor, B. N. The 1986 CODATA Recommended Values of the Fundamental Physical Constants. *J. Phys. Chem. Ref. Data* **1988**, *17*, 1795−1803.

Cox, J. D., Wagman, D. D., Medvedev, V. A., Eds. *CODATA Key Values for Thermodynamics*; Hemisphere: New York, 1989.

Dolliver, M. A.; Gresham, T. L.; Kistiakowsky, G. B.; Vaughan, W. E. Heats of Organic Reactions. V. Heats of Hydrogenation of Various Hydrocarbons. *J. Am. Chem. Soc.* **1937**, *59*, 831−841.

Douslin, D. R.; McCullough, J. P. An Inclined-Piston Deadweight Pressure Gage. *Bur. Mines Rep. Invest.* **1963**, No. 6149, 11.

Douslin, D. R.; Osborn, A. G. Pressure Measurements in the 0.01−30 mm Range with an Inclined-Piston Gauge. *J. Sci. Instrum.* **1965**, *42*, 369−373.

Evans, E. B. The Viscosities of Hydrocarbons. Parts IV-VI. *J. Inst. Petrol. Technol.* **1941**, *24*, 321−337.

Forziati, A.; Camin, D. L.; Rossini, F. D. Density, Refractive Index, Boiling Point, and Vapor Pressure of Eight Monoolefin (1-Alkene), Six Pentadiene, and Two Cyclomonoolefin Hydrocarbons. *J. Res. Natl. Bur. Stand.* **1950**, *45*, 406−410.

Goldberg, R. N.; Weir, R. D. Conversion of Temperatures and Thermodynamic Properties to the Basis of the International Temperature Scale of 1990. *Pure Appl. Chem.* **1990**, *64*, 1545−1562.

Good, W. D. The Enthalpies of Combustion and Formation of 11 Isomeric Nonanes. *J. Chem. Eng. Data* **1969**, *14*, 231−235.

Good, W. D. The Enthalpies of Combustion of Nine Organic Nitrogen Compounds Related to Petroleum. *J. Chem. Eng. Data* **1972**, *17*, 28−31.

Good, W. D.; Smith, N. K. The Enthalpies of Combustion of Toluene, Benzene, Cyclohexane, Cyclohexene, Methylcyclopentane, 1-Methylcyclopentene, and n-Hexane. *J. Chem. Eng. Data* **1969**, *14*, 102−106.

Good, W. D.; Moore, R. T. The Enthalpies of Formation of Ethylenediamine, 1,2-Propanediamine, 1,2-Butanediamine, 2-Methyl-1,2-propanediamine, and Isobutylamine. *J. Chem. Eng. Data* **1970**, *15*, 150−154.

Good, W. D.; Scott, D. W.; Waddington, G. Combustion Calorimetry of Organic Fluorine Compounds by a Rotating-Bomb Method. *J. Phys. Chem.* **1956**, *60*, 1080−1089.

Good, W. D.; Douslin, D. R.; Scott, D. W.; George, A.; Lacina, J. L.; Dawson, J. P.; Waddington, G. Thermochemistry and Vapor Pressure of Aliphatic Fluorocarbons. A Comparison of the C-F and C-H Thermochemical Bond Energies. *J. Phys. Chem.* **1959**, *63*, 1133−1138.

Goodwin, R. D. Benzene Thermophysical Properties from 279 to 900 K at Pressures to 1000 Bar. *J. Phys. Chem. Ref. Data* **1988**, *17*, 1541−1636.

Goodwin, R. D. Toluene Thermophysical Properties from 178 to 800 K at Pressures to 1000 Bar. *J. Phys. Chem. Ref. Data* **1989**, *18*, 1565−1636.

Guthrie, G. B.; Scott, D. W.; Hubbard, W. N.; Katz, C.; McCullough, J. P.; Gross, M. E.; Williamson, K. D.; Waddington, G. Thermodynamic Properties of Furan. *J. Am. Chem. Soc.* **1952**, *74*, 4662−4669.

Hales, J. L.; Townsend, R. Liquid Densities from 293 to 490 K of Nine Aromatic Hydrocarbons. *J. Chem. Thermodyn.* **1972**, *4*, 763−772.

Hubbard, W. N.; Scott, D. W.; Waddington, G. Reduction to Standard States (at 25 °C) of Bomb Calorimetric Data for Compounds of Carbon, Hydrogen, Oxygen and Sulfur. *J. Phys. Chem.***1954**, *58*, 152−162.

Hubbard, W. N.; Scott, D. W.; Waddington, G. Standard States and Corrections for Combustions in a Bomb at Constant Volume. In *Experimental Thermochemistry*; Rossini, F. D., Ed.; Interscience: New York, 1956, Chapter 5, pp 75−128.

Huggins, M. L. Densities and Optical Properties of Organic Compounds in the Liquid State. IV. The Densities of α-Substituted Normal Alkanes. *J. Am. Chem. Soc.* **1954**, *76*, 845−847.

IUPAC Commission on Atomic Weights and Isotopic Abundances. Atomic Weights of the Elements 1991. *J. Phys. Chem. Ref. Data* **1993**, *22*, 1571−1584.

Knipmeyer, S. E.; Archer, D. G.; Chirico, R. D.; Gammon, B. E.; Hossenlopp, I. A.; Nguyen, A.; Smith, N. K.; Steele, W. V.; Strube, M. M. High Temperature Enthalpy and Critical Property Measurements using a Differential Scanning Calorimeter. *Fluid Phase Equilib.* **1989**, *52*, 185−192.

Korovin, A. I.; Margolin, L. N. Thermodynamic Functions of Phenyl Isocyanate. *Russ. J. Phys. Chem.* **1976**, *50*, 1735−1736.

Labbauf, A.; Rossini, F. D. Heats of Combustion, Formation, and Hydrogenation of 14 Selected Cyclomonoolefin Hydrocarbons. *J. Phys. Chem.* **1961**, *65*, 476−480.

Lebedeva, N. D. Heats of Combustion and Formation of Aliphatic Tertiary Amine Homologues. *Russ. J. Phys. Chem.* **1966**, *40*, 1465−1467.

Letcher, T. M. The Excess Volumes of Some Mixtures of Saturated and Unsaturated C_6 Hydrocarbons *J. Chem. Thermodyn.* **1975**, *7*, 205.

Letcher, T. M. The Excess Volumes of Some Mixtures of Saturated and Unsaturated C_6 Hydrocarbons. Part II. *J. Chem. Thermodyn.* **1977**, *9*, 661−664.

Letcher, T. M.; Marsicano, F. Vapour Pressures and Densities of Some Unsaturated C_6 Acyclic and Cyclic Hydrocarbons Between 300 and 320 K. *J. Chem. Thermodyn.* **1974**, *6*, 509−514.

Lister, M. A. Heats of Organic Reactions. X. Heats of Bromination of Cyclic Olefins. *J. Am. Chem. Soc.* **1941**, *63*, 143−149.

Mangum, B. W.; Furukawa, G. T. Guidelines for Realizing the International Temperature Scale of 1990 (ITS-90). NIST Technical Note 1265; National Institute of Standards and Technology: Gaithersburgh, MD, 1990.

McCormick, D. G.; Hamilton, W. S. The Enthalpies of Combustion and Formation of Oxazole and Isoxazole. *J. Chem. Thermodyn.* **1978**, *10*, 275−278.

Meyer, E. F.; Hotz, R. D. High-Precision Vapor-Pressure Data for Eight Organic Compounds. *J. Chem. Eng. Data* **1973**, *18*, 359−362.

Mraw, S. C.; Naas, D. F. The Measurement of Accurate Heat Capacities by Differential Scanning Calorimetry. Comparison of dsc Results on Pyrite (100 to 800 K) with Literature Values from Precision Adiabatic Calorimetry. *J. Chem. Thermodyn.* **1979**, *11*, 567−584.

Orbey, H.; Vera, J. H. Correlation for the Third Virial Coefficient using T_c, p_c, and ω as Parameters. *AIChE J.* **1983**, *29*, 107−113.

Osborn A. G.; Douslin, D. R. Vapor Pressure Relations of 36 Sulfur Compounds Present in Petroleum. *J. Chem. Eng. Data* **1966**, *11*, 502−509.

Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: New York, 1986.

Pitzer, K. S.; Curl, R. F., Jr. The Volumetric and Thermodynamic Properties of Fluids. III. Empirical Equation for the Second Virial Coefficient. *J. Am. Chem. Soc.* **1957**, *79*, 2369−2370.

Ralston, A. W.; Selby, W. M.; Pool, W. O.; Potts, R. H. Boiling Points of n-Alkyl Primary Amines. *Ind. Eng. Chem.* **1940**, *32*, 1093−1094.

Raltson, A. W.; Horner, C. W.; Hoffman, E. J. Studies on High Molecular Weight Aliphatic Amines and their Salts. VII. The Systems Octylamine-, Dodecylamine- and Octadecylamine-Water. *J. Am. Chem. Soc.* **1942**, *64*, 1516−1523.

Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw−Hill: New York, 1987.

Riedel, L. Liquid Density in the Saturated State. Extension of the Theorem of Corresponding States II. *Chem.-Ing.-Tech.* **1954**, *26*, 259−264.

Rogers, D. W.; McLafferty, F. J. A New Hydrogen Calorimeter. Heats of Hydrogenation of Allyl and Vinyl Unsaturation Adjacent to a Ring. *Tetrahedron* **1971**, *27*, 3765−3775.

Rogers, D. W.; Munoz-Hresko, B. A Microcomputer-Controlled Microcalorimeter Calibration Circuit. 2. Enthalpies of Hydrogenation of Cyclopentene, Cyclohexene, and Cis-3-hexene. *Mikrochim. Acta (Wien)* **1984**, *2*, 427−435.

Rogers, D. W.; Dejroongruang, K. Enthalpies of Hydrogenation of the n-Heptenes and the Methylhexenes. *J. Chem. Thermodyn.* **1988**, *20*, 675−680.

Rogers, D. W.; Dejroongruang, K. Enthalpies of Hydrogenation of the Dimethylpentenes, Ethylpentenes, Methylethylbutene, and Trimethylbutene. *J. Chem. Thermodyn.* **1989**, *21*, 1115−1120.

Rogers, D. W.; Crooks, E.; Dejroongruang, K. Enthalpies of Hydrogenation of the Hexenes. *J. Chem. Thermodyn.* **1987**, *19*, 1209−1215.

Rogers, D. W.; Dejroongruang, K.; Samuel, S. D.; Fang, W.; Zhoo, Y. Enthalpies of Hydrogenation of the Octenes and the Methylheptenes. *J. Chem. Thermodyn.* **1992**, *24*, 561−565.

Rossini, F. D. Assignment of Uncertainties to Thermochemical Data. In *Experimental Thermochemistry*; Rossini, F. D., Ed.; Interscience: New York, 1956; Chapter 14, pp 297−320.

Roth, W. R.; Lennartz, H-W. Heats of Hydrogenation. I. Determination of Heats of Hydrogenation with an Isothermal Titration Calorimeter. *Chem. Ber.* **1980**, *113*, 1806−1817.

Scott, D. W.; Finke, H. L.; Gross, M. E.; Guthrie, G. B.; Huffman, H. M. 2,3-Dithiabutane: Low Temperature Heat Capacity, Heat of Fusion, Heat of Vaporization, Vapor Pressure, Entropy, and Thermodynamic Functions. *J. Am. Chem. Soc.* **1950**, *72*, 2424−2430.

Simonson, J. M.; Oakes, C. S.; Bodnar, R. J. Densities of NaCl(aq) to the Temperature 523 K at Pressures to 40 MPa Measured with a New Vibrating-Tube Densitometer. *J. Chem. Thermodyn.* **1994**, *26*, 345−359.

Steele, W. V. Fifty Years of Thermodynamics Research at Bartlesville. The Hugh M. Huffman Legacy. *J. Chem. Thermodyn.* **1995**, *27*, 135−162.

Steele, W. V.; Chirico, R. D. Thermodynamics and the Hydrodeoxygenation of 2,3-Benzofuran. In three parts: Part I. Thermodynamic Properties of 2,3-Benzofuran and 4,5-Dihydro-2,3-benzofuran, Part II. Gibbs Energies of Reaction in the Hydrodeoxygenation of 2,3-Benzofuran, Part III. Thermodynamic Equilibria. NIPER-457; DOE Fossil Energy, Bartlesville Project Office: Bartlesville, OK, November 1989. Available from NTIS, Report No. DE90000218.

Steele, W. V.; Chirico, R. D. Thermodynamic Properties of Alkenes (Mono-Olefins Larger Than C_4). *J. Phys. Chem. Ref. Data* **1993**, *22*, 377−430.

Steele, W. V.; Archer, D. G.; Chirico, R. D.; Collier, W. B.; Hossenlopp, I. A.; Nguyen, A.; Smith, N. K.; Gammon, B. E. The Thermodynamic Properties of Quinoline and Isoquinoline. *J. Chem. Thermodyn.* **1988a**, *20*, 1233−1264.

Steele, W. V.; Chirico, R. D.; Knipmeyer, S. E.; Smith, N. K. High-Temperature Heat-Capacity Measurements and Critical Property Determinations using a Differential Scanning Calorimeter. (Development of Methodology and Application to Pure Organic Compounds). NIPER-360; DOE Fossil Energy, Bartlesville Project Office: Bartlesville, OK, December 1988b. Available from NTIS Order No. DE89000709.

Steele, W. V.; Chirico, R. D.; Hossenlopp, I. A.; Nguyen, A.; Smith, N. K. In *Experimental Results from the Design Institute for Physical Property Data: Phase Equilibria and Pure Component Properties Part II*; Shih, T. T., Jones, D. K., Eds.; AIChE Symposium Series No. 271; AIChE: New York, 1989; Vol. 85, pp 140−162.

Steele, W. V.; Chirico, R. D.; Knipmeyer, S. E.; Nguyen, A. The Thermodynamic Properties of 2-Aminobiphenyl. *J. Chem. Thermodyn.* **1991**, *23*, 957−977.

Steele, W. V.; Chirico, R. D.; Knipmeyer, S. E.; Nguyen, A. DIPPR Project 821. Vapor Pressure of Organic Compounds of Industrial Interest. The 1991 Project Results. In *Experimental Results for DIPPR 1990−91 Projects on Phase Equilibria and Pure Component Properties*; Cunningham, J. R., Jones, D. K., Eds.; DIPPR Data Series No. 2; AIChE: New York, 1994, pp 154−173.

Steele, W. V.; Chirico, R. D.; Nguyen, A.; Knipmeyer, S. E. Vapor Pressures, High-Temperature Heat Capacities, Critical Properties, Derived Thermodynamic Functions, and Barriers to Methyl-Group Rotation, for the Six Dimethylpyridines. *J. Chem. Thermodyn.* **1995**, *27*, 311−334.

Strepikheev, Yu. A.; Baranov, Yu. I.; Burmistrova, O. A. Determination of the Heats of Combustion and the Heat Capacities of Several Mono- and Di-isocyanates. *Izv. Vyssh. Uchebn. Zaved. Khim. Khim.* **1962**, *5*, 387−90.

Stull, D. R. Vapor Pressure Of Pure Substances. Organic Compounds. *Ind. Eng. Chem.* **1947**, *39*, 518−550; errata **1947**, *39*, 1684.

Swietoslawski, W. *Ebulliometric Measurements*; Reinhold: New York, 1945.

TRC. *TRC Thermodynamic Tables-Nonhydrocarbons*; Thermodynamics Research Center Texas A&M University: College Station, TX, extant 1990.

Vogel, A. I. Physical Properties and Chemical Constitution. Part XXII. Some Primary, Secondary, and Tertiary Amines. *J. Chem. Soc.* **1948**, 1825−1833.

Waddington, G.; Sunner, S.; Hubbard, W. N. Combustions in a Bomb of Organic Sulfur Compounds. In *Experimental Thermochemistry*; Rossini, F. D., Eds.; Interscience: New York, 1956; Chapter 7, pp 149−179.

Wagner, W. New Vapor Pressure Measurements for Argon and Nitrogen and a New Method for Establishing Rational Vapor Pressure Equations. *Cryogenics* **1973**, *13*, 470−482.

Wagner, W.; Pruss, A. International Equations for the Saturation Properties of Ordinary Water Substance. Revised According to the International Temperature Scale Of 1990. *J. Phys. Chem. Ref. Data* **1993**, *22*, 783−787.

Received for review March 7, 1996. Accepted July 18, 1996.[⊗] 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.

JE960093T

[⊗] Abstract published in *Advance ACS Abstracts*, November 1, 1996.