J. Chem. Eng. Data **1997,** *42,* 1037−1052

Thermodynamic Properties and Ideal-Gas Enthalpies of Formation for Dicyclohexyl Sulfide, Diethylenetriamine, Di-*n*-octyl Sulfide, Dimethyl Carbonate, Piperazine, Hexachloroprop-1-ene, Tetrakis(dimethylamino)ethylene, *N*,*N*′-Bis-(2-hydroxyethyl)ethylenediamine, and 1,2,4-Triazolo[1,5-*a*]pyrimidine

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This paper reports measurements made for DIPPR Research Project 871 in the 1993 Project Year. The results of the study are aimed at improvement of group-contribution methodology for estimation of thermodynamic properties of organic substances. 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 hexachloroprop-1-ene, *N*,*N*′-bis(2-hydroxyethyl)ethylenediamine, dimethyl carbonate, di-*n*-octyl sulfide, dicyclohexyl sulfide, diethylenetriamine, tetrakis(dimethylamino)ethylene, piperazine, and 1,2,4-triazolo[1,5-*a*]pyrimidine are reported. Enthalpies of fusion were determined for *N*,*N*′-bis(2-hydroxyethyl)ethylenediamine, piperazine and 1,2,4-triazolo[1,5-*a*]pyrimidine. Two-phase (solid + vapor) or (liquid + vapor) heat capacities were determined from 300 K to the critical region or earlier decomposition temperature for each compound studied. Liquid-phase densities along the saturation line were measured for *N*,*N*′-bis-(2-hydroxyethyl)ethylenediamine, dimethyl carbonate, and dicyclohexyl sulfide. For dimethyl carbonate and piperazine, critical temperatures and critical densities were determined from the DSC results and corresponding critical pressures derived from the fitting procedures. Fitting procedures were used to derive critical temperatures, critical pressures, and critical densities for hexachloroprop-1-ene, di-*n*-octyl sulfide, dicyclohexyl sulfide, and diethylenetriamine. Group-additivity parameters and 1,4-interaction terms useful in the application of group-contribution correlations were 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 seventh 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 1992 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. The enthalpy of formation is the thermodynamic property most needed for evaluation of the energy hazard potential of an organic compound. 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. A second-order group-contribution methodology for the calculation of ideal-gas thermodynamic properties has been outlined in detail by Benson (1976). However, this text lacks parameters for a number of important groups and correction terms for several important ring structures. Parameters for some structural groups were derived from data that have since been shown

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S0021-9568(97)00098-8 CCC: $14.00

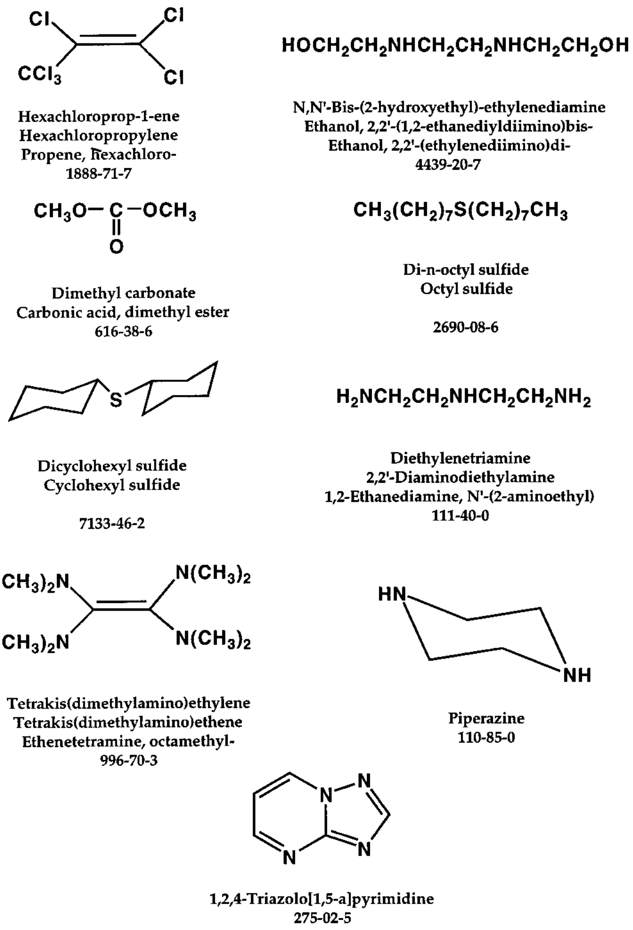


Figure 1. Structural formulas, common names, Chemical Abstract Service names (provided by the authors), and Chemical Abstract Services Registry Numbers (provided by the authors) for the compounds studied in this research.

to be incorrect. In the absence of data, application of the methodology for the estimation of thermochemical properties for some important organic compound types is impossible.

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

In the seventh year of the project, nine compounds were chosen for experimental studies. The molecular structures, Chemical Abstract Service (CAS) names, commonly used trivial names, and CAS Registry Numbers of the compounds studied are listed in Figure 1. The derivation of ideal-gas standard energies 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 auxilliary 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 energies of combustion, with CO_2 analyses determining the amount of reaction, nonisomeric impurities are highlighted. The presence of a small amount of water (say 0.05 mol %) in the sample will often not be detected in the gas−liquid chromatographic analysis of the sample but is readily detected by the CO_2 analysis. Then the determination of the energy of combustion should be based on the CO_2 analysis and not the mass of sample used in the calorimetric measurement. 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

Since the combustion calorimetric techniques used differ from compound to compound, details of the combustion calorimetric methodology are given below. The apparatus and procedures used in obtaining the auxilliary experimental data (see Table 1) necessary to derive the ideal-gas enthalpies of formation have been previously described in the literature and in various DOE reports. In addition, the earlier papers published in this journal under the DIPPR auspices (Steele et al., 1996a−c) give detailed references to the experimental techniques and fitting procedures. Therefore, in this paper no details are given, and the reader is referred to Steele et al. (1996a−c) and the earlier publications referenced therein.

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 thermophysical property measurements. All compounds were purchased from Aldrich Chemical Co. Gas−liquid chromatographic (GLC) analyses on the purchased samples gave an average purity of 98 mol % in agreement with Aldrich specifications. The compounds were purified at NIPER by repeated distillations using a spinning-band column. GLC analyses of the samples used in the measurements gave purities of at least 99.95 mol % for each compound. The high purity of each sample was confirmed subsequently by the percentage CO_2 recoveries in the combustion calorimetric measurements (Table 3) and/or by the small differences between the boiling and condensation temperatures in the ebulliometric vapor-pressure measurements listed in column 6 of Table 7.

All transfers of the purified samples were done 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. GLC analysis of the decane sample failed to show any impurity peaks.

Physical Constants. Molar values are reported in terms of the 1991 relative atomic masses (IUPAC, 1993) and the gas constant, $R = 8.314\ 51\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$, adopted by CODATA (Cohen and Taylor, 1988). The platinum resistance thermometers and the quartz crystal thermometer used in these measurements were calibrated by comparison with standard platinum resistance thermometers whose constants were determined at the National Institute for Standards and Technology (NIST) in the 1950s or early 1970s. All temperatures are reported in terms of ITS-90 (Goldberg and Weir, 1990; Mangum and Furukawa, 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 previously in Good (1969, 1972), Good and Smith (1969), Steele et al.

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

compound (state)	$\Delta_c U_m^\circ$	vapor pressure	heat capacity	density	T_c, ρ_c
diethylenetriamine (l)	x	x	x		
N,*N*′-bis(2-hydroxyethyl)ethylenediamine (cr)	x	x	x	x	
dimethyl carbonate (l)	x	x	x	x	x
1,2,4-triazolo[1,5-*a*]pyrimidine (cr)	x	x	x		
dicyclohexyl sulfide (l)	x	x	x	x	
di-*n*-octyl sulfide (l)	x	x	x		
tetrakis(dimethylamino)ethylene (l)	x	x	x		
piperazine (cr)	x	x	x		x
hexachloroprop-1-ene (l)	x	x	x		

[a] Measurements made are denoted by x. [b] State denotes whether crystalline (cr) or liquid (l) at ambient temperature.

Table 2. Physical Properties at 298.15 K[a]

compound	ρ/kg·m^{-3}	$10^7(\partial V/\partial T)_p$/m^3·K^{-1}·mol^{-1}	C_p/R
diethylenetriamine (l)	956	1.2	33.2
N,*N*′-bis(2-hydroxyethyl)ethylenediamine (cr)	1180	(0.3)	25.2
dimethyl carbonate (l)	1062	1.3	19.7
1,2,4-triazolo[1,5-*a*]pyrimidine (cr)	1560	(0.3)	14.8
di-*n*-octyl sulfide (l)	839	2.2	62.5
tetrakis(dimethylamino)ethylene (l)	862	1.8	44.7
dicyclohexyl sulfide (l)	968	1.5	39.2
piperazine (cr)	1260	(0.3)	14.4
hexachloroprop-1-ene (l)	1757	1.2	25.4

[a] Values in parentheses are estimates.

(1988), and Hubbard et al. (1954) and Waddington et al. (1956), respectively. These procedures were followed for eight of the nine compounds studied in this reported research. Details of the combustion calorimetric techniques and procedures for the chlorine-containing compound, hexachloroprop-1-ene, follow in the next section.

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 combustions of the sulfur-containing compounds and without rotation for the remaining compounds. Flexible borosilicate-glass ampules (Guthrie et al., 1952; Good, 1972) were used to confine the samples that were liquid at 298 K [dimethyl carbonate, di-*n*-octyl sulfide, dicyclohexyl sulfide, diethylenetriamine, and tetrakis(dimethylamino)ethylene]. Piperazine was burned in pellet form enclosed in two polyester-film bags (Good et al., 1956). All experiments were completed within 0.01 K of $T = 298.15$ K.

The auxilliary 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}. The value for $\Delta_c U_m^\circ$/M obtained for the polyester film, empirical formula $C_{10}H_8O_4$, was a function of the relative humidity (RH) in the laboratory during the weighing (Good et al., 1956). 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, either from measurements of volumes of the ampules used in the combustion calorimetry, and their enclosed sample masses, for the liquid samples, or from the dimensions of a pellet of known mass for the compounds that were solid at 298.15 K {*N*,*N*′-bis(2-hydroxyethyl)ethylenediamine, piperazine, and 1,2,4-triazolo[1,5-*a*]pyrimidine}. Values of the heat capacity of each sample at 298.15 K were measured using a DSC.

NIST thermochemical benzoic acid (sample 39i) was used for calibration of the calorimeter; its specific energy of combustion is −(26 434.0 ± 3.0) J·g^{-1} under certificate conditions. Conversion to standard states (Hubbard et al., 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 eight 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. The energy equivalent of the calorimeter, ϵ(calor), obtained during each calibration series is listed in Table 3. The small changes in the energy equivalent between the various combustion series were due to small repairs to the bomb to cure leaking gaskets that develop with age and continual usage.

In the combustion of the sulfur-containing compounds, di-*n*-octyl sulfide and dicyclohexyl sulfide, the bomb initially contained 10 cm^3 of water. One atmosphere of air was left in the bomb, which was subsequently charged with pure oxygen to a total pressure of 3.04 MPa. In addition, rotation of the bomb was started at the “midtime of the combustion” (Waddington et al., 1956) and continued to the finish of the combustion experiments. This ensured a homogeneous solution of aqueous sulfuric acid in the bomb at the conclusion of the measurements. In the benzoic acid calibration measurements for the fifth and seventh series of combustions, rotation was also instituted to ensure exact consistency between the measurements.

In the di-*n*-octyl sulfide and dicyclohexyl sulfide combustions, the final bomb solutions were analyzed for nitric acid, nitrous acid, and total acids (Hubbard et al., 1954; Waddington et al., 1956). The amount of sulfuric acid was obtained by difference. No evidence of thermally significant amounts of SO_2, or of sulfuric acid attack on the borosilicate glass ampule or bomb, was found. {Leaving the atmosphere of air in the platinum-lined bomb before charging to a total pressure of 3.04 MPa with pure oxygen ensured that all the sulfur was converted to SO_3 by the Contact Process, [i.e., the industrial method of preparation of sulfuric acid (Harrer, 1969)].} No nitrous acid was observed in the combustions of the sulfur-containing compounds.

Table 3. Carbon Dioxide Recoveries and Calorimeter Energy Equivalents

compound	no. of expts	% recovery[a]	energy equivalent[a]/J·g^{-1}
benzoic acid calibration	9	100.001 ± 0.003	
diethylenetriamine	9	100.000 ± 0.005	
ϵ(calor)			16 773.5 ± 0.4
benzoic acid calibration	6	100.012 ± 0.005	
N,*N*′-bis(2-hydroxyethyl)ethylenediamine	6	99.916 ± 0.022[b]	
ϵ(calor)			16 772.7 ± 0.5
benzoic acid calibration	6	100.009 ± 0.009	
dimethyl carbonate	6	99.838 ± 0.033[b]	
ϵ(calor)			16 776.2 ± 0.9
benzoic acid calibration	6	99.991 ± 0.007	
1,2,4-triazolo[1,5-*a*]pyrimidine	6	99.999 ± 0.005	
ϵ(calor)			16 774.1 ± 0.4
benzoic acid calibration	6	99.997 ± 0.007	
di-*n*-octyl sulfide	6	99.990 ± 0.009[c]	
ϵ(calor)			16 779.1 ± 0.5
benzoic acid calibration	6	99.990 ± 0.004	
tetrakis(dimethylamino)ethylene	5	99.998 ± 0.005	
ϵ(calor)			16 776.2 ± 0.6
benzoic acid calibration	6	99.992 ± 0.005	
dicyclohexyl sulfide	6	99.993 ± 0.006[c]	
ϵ(calor)			16 777.1 ± 0.3
benzoic acid calibration	6	100.001 ± 0.005	
piperazine	6	99.706 ± 0.007[b]	
ϵ(calor)			16 775.0 ± 0.6

[a] Mean and standard deviation of the mean. [b] Results of combustion study based on percentage CO_2 recovery (see text). [c] Sulfuric acid recovery (see text).

Nitric acid, formed during combustions of the nitrogen-containing compounds, diethylenetriamine, *N*,*N*′-bis(2-hydroxyethyl)ethylenediamine, 1,2,4-triazolo[1,5-*a*]pyrimidine, tetrakis(dimethylamino)ethylene, and piperazine, was determined by titration with standard sodium hydroxide (Good and Moore, 1970). Carbon dioxide was also recovered from the combustion products of each experiment. (Due to the relatively large amount of water used to ensure a homogeneous solution of sulfuric acid in the di-*n*-octyl sulfide and dicyclohexyl sulfide combustions, no CO_2 recoveries were made for those two compounds.) 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.

Energy of Combustion Procedures for Hexachloroprop-1-ene. The apparatus and experimental procedures used in the combustion calorimetry of organic C,H,N,O,Cl compounds at NIPER have been described previously (Smith et al., 1964). The corrosive nature of the products of combustion, HCl and Cl_2, are circumvented by the use of a tantalum-lined bomb and fittings in conjunction with thin-walled Vycor crucibles. In the earlier work at NIPER both arsenious oxide and hydrazine dihydrochloride were used as reducing agents to convert Cl_2 to HCl. Other researchers (Hu and Sinke, 1969; Hu et al., 1972, 1974) have developed detailed corrections to standard states for the combustion of chlorine-containing compounds removing the necessity for the specially designed comparison experiments used in the earlier NIPER work. In the series of combustions on hexachloroprop-1-ene, the computational method detailed by Hu et al. (1974) for determination of the standard energy of combustion of organochlorine compounds using arsenious oxide as the reducing agent was followed. In the combustions reported here a rotating-bomb calorimeter (laboratory designation BMR II) (Good et al., 1956) and a tantalum-lined bomb (laboratory designation Ta-1) (Smith et al., 1964) with an internal volume of 0.341 dm^3 were used with rotation and a platinum crucible. Flexible borosilicate-glass ampules (Guthrie et al., 1952; Good, 1972) were used to confine the hexachloroprop-1-ene sample. Sufficient sample was burnt to ensure a temperature rise of 1 K. A 50 cm^3 aliquot of 0.0902 M As_2O_3 was added to the bomb. The bomb was flushed and charged with oxygen to a pressure of 3.04 MPa. All experiments were completed within 0.01 K of T = 298.15 K.

Calibration experiments, using NIST thermochemical benzoic acid (sample 39i), were interspersed with the hexachloroprop-1-ene measurements. Nitrogen oxides were not formed in the combustion experiments due to the high purity of the oxygen used and preliminary bomb flushing. The energy equivalent of the calorimeter, ϵ(calor), obtained was (16 721.4 ± 0.8) J·K^{-1} (mean and standard deviation of the mean).

After each hexachloroprop-1-ene combustion, the bomb was slowly discharged and carefully opened, and the crucible and all interior surfaces were rinsed off with hot deionized water. The washings were analyzed for As_2O_3 by iodometry and for platinum or gold by colorimetric methods. No Pt or Au was ever detected in the colorimetric experiments. Due to the relatively large amount of water used to ensure a homogeneous solution at the completion of the combustion, no CO_2 recoveries were attempted. The combustion products were checked for unburned carbon and other products of incomplete combustion, but none was detected.

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; $\Delta_c U^\circ_m/M$ for all the combustion calorimetric measurements made on each of these compounds are reported in Table 5. Values of $\Delta_c U^\circ_m/M$ in Tables 4 and 5 for the C,H,O,N compounds refer to the general reaction

$$C_aH_bO_cN_d(\mathrm{cr\ or\ l}) + \left(a + \frac{b}{4} - \frac{c}{2}\right)O_2(g) = aCO_2(g) + \frac{b}{2}H_2O(l) + \frac{d}{2}N_2(g) \quad (1)$$

Values of $\Delta_c U^\circ_m/M$ in Tables 4 and 5 for the C,H,S

Table 4. Typical Combustion Experiments at 298.15 K for the Compounds Studied (p° = 101.325 kPa)[a,b]

	A	B	C	D	E	F
m'(compound)/g	0.940 131	1.165 566	1.168 662	1.151 656	0.837 753	0.906 737
m''(oil)/g	0.064 149	0.068 140	0.143 509	0.143 281	0.051 918	0.0
m''(fuse)/g	0.001 031	0.001 544	0.000 847	0.000 896	0.001 447	0.002 237
m'''‘(bag)/g	0.0	0.0	0.0	0.0	0.0	0.102 026
$n_i(H_2O)$/mol	0.055 35	0.055 35	0.055 35	0.055 35	0.055 35	0.055 35
m(Pt)/g	19.969	19.969	19.969	19.969	19.969	32.204
ΔT/K[c]	2.003 89	2.029 66	1.499 07	2.002 02	2.000 57	2.001 82
ϵ(calor)(ΔT)/J	−33 612.2	−34 042.9	−25 148.7	−33 582.1	−33 561.9	−33 580.5
ϵ(cont)(ΔT)/J[d]	−37.2	−37.8	−28.6	−37.6	−43.3	−40.3
ΔU_{ign}/J	0.8	0.8	0.8	0.8	0.8	0.8
ΔU(corr std states)/J[e]	8.1	13.6	17.4	23.2	10.1	12.0
$\Delta U_{dec}(HNO_3)$/J	133.9	86.9	0.0	155.1	87.6	94.5
$-m''(\Delta_c U^\circ_m/M)$(oil)/J	2 953.6	1 556.0	6 607.5	6 597.0	2 390.4	0.0
$-m'''(\Delta_c U^\circ_m/M)$(fuse)/J	17.5	26.2	14.3	15.2	24.5	37.9
$-m''''(\Delta_c U^\circ_m/M)$(bag)/J	0.0	0.0	0.0	0.0	0.0	2 331.9
m$'(\Delta_c U^\circ_m/M)$(compound)/J	−30 535.5	−32 397.2	−18 537.3	−26 828.4	−31 091.8	−31 143.7
$(\Delta_c U^\circ_m/M)$(compound)/J·g^{-1}	−32 480.0	−27 795.3	−15 862.0	−23 295.5	−37 113.2	−34 347.0

	G	H	I
m'(compound)/g	0.708 069	0.859 949	0.604 595
m''(oil)/g	0.057 089	0.067 944	0.273 000
m'''(fuse)/g	0.001 005	0.001 561	0.001 215
$n_i(H_2O)$/mol	0.553 5	0.553 5	0.0
$n_i(As_2O_3)$/mol	0.0	0.0	0.004 510
m(Pt)/g	32.473	39.299	38.665
ΔT/K[c]	2.000 78	2.302 50	0.994 480
ϵ(calor)(ΔT)/J	−33 571.2	−38 629.3	−16 629.1
ϵ(cont)(ΔT)/J[d]	−114.3	−135.8	−216.6
ΔU_{ign}/J	0.8	0.8	0.8
ΔU(corr std states)/J[e]	19.7	23.8	49.8
$\Delta U_{dec}(HNO_3)$/J	48.5	45.8	0.0
$\Delta U_{dil}(H_2SO_4)$/J	2.7	1.2	0.0
$\Delta U_{dec}(As_2O_5)$/J	0.0	0.0	1 166.5
ΔU_{dil}(HCl)/J	0.0	0.0	−5.4
$-m''(\Delta_c U^\circ_m/M)$(oil)/J	2 628.5	3 128.3	12 569.6
$-m'''(\Delta_c U^\circ_m/M)$(fuse)/J	17.0	26.5	20.6
$m'(\Delta_c U^\circ_m/M)$(compound)/J	−30 968.3	−35 538.7	−3 043.9
$(\Delta_c U^\circ_m/M)$(compound)/J·g^{-1}	−43 736.3	−41 326.5	−5 034.7

[a] A = Diethylenetriamine; B = *N*,*N'*-bis(2-hydroxyethyl)ethylene; C = dimethyl carbonate; D = 1,2,4-triazolo[1,5-*a*]pyrimidine; E = piperazine; F = tetrakis(dimethylamino)ethylene; G = di-*n*-octyl sulfide; H = dicyclohexyl sulfide; I = hexachloroprop-1-ene. [b] The symbols and abbreviations of this table are those of Hubbard et al. (1956) or, for hexachloroprop-1-ene, Hu et al. (1974), except as noted. [c] $\Delta T/K = (T_i - T_f + \Delta T_{corr})/K$. [d] $\epsilon_i(\text{cont})(T_i - 298.15\ K) + \epsilon_f(\text{cont})(298.15\ K - T_f + \Delta T_{corr})$. [e] Items 81 to 85, 87 to 90, 93, and 94 of the computational form of Hubbard et al. (1956) or, for hexachloroprop-1-ene, Hu et al. (1974).

compounds refer to the general reaction

$$C_aH_bS(l) + \left(\frac{4a+b+6}{4}\right)O_2(g) + \left(\frac{232-b}{2}\right)H_2O(l) = aCO_2(g) + H_2SO_4\cdot 115H_2O(aq) \quad (1a)$$

Values of $\Delta_c U^\circ_m/M$ in Tables 4 and 5 for hexachloroprop-1-ene refer to the reaction

$$C_3Cl_6(l) + 1.5O_2(g) + 3603H_2O(l) = 3CO_2(g) + 6[HCl\cdot 600H_2O](aq) \quad (1b)$$

For *N*,*N'*-bis(2-hydroxyethyl)ethylenediamine, dimethyl carbonate, and piperazine, the values of $\Delta_c U^\circ_m/M$ refer to unit mass of sample derived from the corresponding carbon dioxide analyses of the combustion products (see Table 3). Corrections for the small amounts of nitric acid, formed during the combustions of the nitrogen-containing compounds, were made during the conversion to standard states (Hubbard et al., 1956) on the basis of a value of −59.7 kJ·mol^{-1} for the energy of formation of 0.1 mol·dm^{-3} HNO_3(aq) from N_2, O_2, and H_2O(l).

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,O compounds refer to eq 1. The corresponding values of $\Delta_f H^\circ_m$ refer to the reaction

$$a\text{C(cr, graphite)} + \frac{b}{2}H_2(g) + \frac{c}{2}O_2(g) + \frac{d}{2}N_2(g) = C_aH_bO_cN_d(\text{cr or l}) \quad (2)$$

Values of $\Delta_c U^\circ_m$ and $\Delta_c H^\circ_m$ for the C,H,S compounds refer to eq 1a. The corresponding values of $\Delta_f H^\circ_m$ refer to the reaction

$$a\text{C(cr, graphite)} + \frac{b}{2}H_2(g) + \text{S(cr, rhombic)} = C_aH_bS(l) \quad (2a)$$

For hexachloroprop-1-ene, values of $\Delta_c U^\circ_m$ and $\Delta_c H^\circ_m$ for the C,H,S compounds refer to eq 1b. The corresponding values of $\Delta_f H^\circ_m$ refer to the reaction

$$3\text{C(cr, graphite)} + 3Cl_2(g) = C_3Cl_6(l) \quad (2b)$$

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) kJ·mol^{-1} and −(285.830 ± 0.042) kJ·mol^{-1}, respectively, as assigned by CODATA (Cox et al., 1989). Since solutions of the exact concentration ($H_2SO_4\cdot 115H_2O$ or $HCl\cdot 600H_2O$) were not formed in each combustion measurement for the sulfur- or chlorine-containing compounds, enthalpies of

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

Diethylenetriamine
$\{(\Delta_c U^\circ_m/M)(\text{compound})\}/(\text{J}\cdot\text{g}^{-1})$
−32 480.4, −32 543.3, −32 483.2, −32 523.3
−32 514.8, −32 511.8, −32 510.3, −32 507.3
−32, 509.0
$\langle\{(\Delta_c U^\circ_m/M)(\text{compound})\}/(\text{J}\cdot\text{g}^{-1})\rangle$ −32 509.3 ± 6.4
N,*N*′-Bis(2-hydroxyethyl)ethylenediamine
$\{(\Delta_c U^\circ_m/M)(\text{compound})\}/(\text{J}\cdot\text{g}^{-1})$
−27 795.3, −27 791.2, −27 793.5
−27 791.3, −27 786.0, −27 794.2
$\langle\{(\Delta_c U^\circ_m/M)(\text{compound})\}/(\text{J}\cdot\text{g}^{-1})\rangle$ −27 791.9 ± 1.4
Dimethyl Carbonate
$\{(\Delta_c U^\circ_m/M)(\text{compound})\}/(\text{J}\cdot\text{g}^{-1})$
−15 862.0, −15 866.8, −15 869.9
−15 865.8, −15 868.4, −15 868.6
$\langle\{(\Delta_c U^\circ_m/M)(\text{compound})\}/(\text{J}\cdot\text{g}^{-1})\rangle$ −15 866.9 ± 1.2
1,2,4-Triazolo[1,5-*a*]pyrimidine
$\{(\Delta_c U^\circ_m/M)(\text{compound})\}/(\text{J}\cdot\text{g}^{-1})$
−23 295.5, −23 289.8, −23 288.7
−23 298.5, −23 286.8, −23 274.9
$\langle\{(\Delta_c U^\circ_m/M)(\text{compound})\}/(\text{J}\cdot\text{g}^{-1})\rangle$ −23 289.0 ± 3.4
Di-*n*-octyl Sulfide
$\{(\Delta_c U^\circ_m/M)(\text{compound})\}/(\text{J}\cdot\text{g}^{-1})$
−43 736.3, −43 725.3, −43 727.0
−43 736.1, −43 724.7, −43 722.6
$\langle\{(\Delta_c U^\circ_m/M)(\text{compound})\}/(\text{J}\cdot\text{g}^{-1})\rangle$ −43 728.7 ± 2.5
Tetrakis(dimethylamino)ethylene
$\{(\Delta_c U^\circ_m/M)(\text{compound})\}/(\text{J}\cdot\text{g}^{-1})$
−37 113.2, −37 116.9, −37 105.4
−37 117.6, −37 096.6
$\langle\{(\Delta_c U^\circ_m/M)(\text{compound})\}/(\text{J}\cdot\text{g}^{-1})\rangle$ −37 109.9 ± 4.0
Dicyclohexyl Sulfide
$\{(\Delta_c U^\circ_m/M)(\text{compound})\}/(\text{J}\cdot\text{g}^{-1})$
−41 326.6, −41 331.7, −41 333.3
−41 332.8, −41 334.6, −41 345.7
$\langle\{(\Delta_c U^\circ_m/M)(\text{compound})\}/(\text{J}\cdot\text{g}^{-1})\rangle$ −41 334.1 ± 2.6
Piperazine
$\{(\Delta_c U^\circ_m/M)(\text{compound})\}/(\text{J}\cdot\text{g}^{-1})$
−34 347.0, −34 342.9, −34 340.9
−34 342.2, −34 351.9, −34 352.7
$\langle\{(\Delta_c U^\circ_m/M)(\text{compound})\}/(\text{J}\cdot\text{g}^{-1})\rangle$ −34 346.3 ± 2.1
Hexachloroprop-1-ene
$\{(\Delta_c U^\circ_m/M)(\text{compound})\}/(\text{J}\cdot\text{g}^{-1})$
−5034.7, −5034.2, −5030.6
−5038.2, −5035.2, −5033.8
$\langle\{(\Delta_c U^\circ_m/M)(\text{compound})\}/(\text{J}\cdot\text{g}^{-1})\rangle$ −5034.5 ± 2.0

[a] The uncertainties shown are 1 standard deviation of the mean.

dilution to the standard state were estimated by interpolation (see Table 4). The values of the enthalpy of formation of $H_2SO_4\cdot nH_2O$ and $HCl\cdot nH_2O$ were interpolated from the tables in Wagman et al. (1982) adjusted to the CODATA (Cox et al., 1989) assigned values for $SO^{2-}{}_4$(aq) and Cl^-(aq). An uncertainty interval of ±0.2 $kJ\cdot mol^{-1}$ was assigned to each of the sulfuric and hydrochloric acid enthalpies of formation.

Vapor-Pressure Measurements. Measured vapor pressures for each of the compounds are listed in Table 7. In the table the vapor pressure, the condensation temperature, and the difference between the condensation and boiling temperatures are reported. The small differences between the boiling and condensation temperatures in the ebulliometric measurements (particularly in the middle of the vapor-pressure range) indicated correct operation of the equipment and the high purity of the samples studied. Five of the compounds studied decomposed during the vapor-pressure measurements.

Inclined-piston vapor-pressure measurements for both *N*,*N*′-bis(2-hydroxyethyl)ethylenediamine and 1,2,4-triazolo[1,5-*a*]pyrimidine are also listed in Table 7 along with ebulliometric measurements. For the latter compound two of the measured inclined-piston vapor pressures are sublimation pressures (see Table 7). Sample decomposition curtailed the ebulliometric vapor pressure measurements for both compounds.

The difference between the boiling and condensation temperatures (ΔT) for tetrakis(dimethylamino)ethylene increased significantly above 490 K. An attempt was made to make a measurement at 143.2 kPa (493 K), but ΔT started at 0.1 K and rose rapidly to greater than 0.3 K. For both sulfur-containing compounds sample decomposition became extensive above the temperatures listed in Table 7. The difference between the boiling and condensation temperatures (ΔT) for hexachloroprop-1-ene increased significantly above 515 K. An attempt was made to make a measurement at 198.5 kPa (519 K), but ΔT started at 0.06 K and rapidly increased by a factor of 10.

During measurements on piperazine (m.p. 384.6 K), a silicone heat transfer fluid heated to 390 K was rapidly circulated through the condenser of the sample ebulliometer. Care was taken to ensure no piperazine was allowed to escape from the top of the condenser, as that would ensure contamination of the rest of the apparatus. In the past such contamination problems have curtailed ebulliometric vapor-pressure measurements at NIPER on other high-melting solids such as anthracene.

Differential Scanning Calorimetry. Using a DSC, heat-capacities were determined at 20 K intervals with a heating rate of 0.083 $K\cdot s^{-1}$ and a 120 s equilibration period between additions of energy. Table 8 lists results derived from the heat capacity measurements determined by DSC for all of the compounds. The estimated uncertainty in the heat capacity values determined using the NIPER DSC procedures is 1%. For dimethyl carbonate and piperazine, measurements into the critical region were possible. For both compounds an abrupt decrease in the heat capacity associated with the conversion from two phases to one phase was observed (see Table 8). In both cases sample decomposition was greatly reduced by employing a single continuous stream of energy at a heating rate of 0.333 $K\cdot s^{-1}$. Temperatures at which conversion to the single phase occurred were measured for both compounds. Table 9 reports the density, obtained from the mass of sample and the cell volume, V_x, calculated with eq 3

$$V_x(T)/V_x(298.15\ \text{K}) = 1 + ay + by^2 \qquad (3)$$

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

Table 6. Condensed Phase Molar Thermochemical Functions at 298.15 K and p^o = 101.325 kPa

	$\Delta_c U^\circ_m/kJ\cdot mol^{-1}$	$\Delta_c H^\circ_m/kJ\cdot mol^{-1}$	$\Delta_f H^\circ_m/kJ\cdot mol^{-1}$
diethylenetriamine (l)	−3353.92 ± 1.38	−3358.26 ± 1.38	−73.68 ± 1.42
N,*N*′-bis(2-hydroxyethyl)ethylene (cr)	−4118.93 ± 0.68	−4123.89 ± 0.68	−523.81 ± 0.80
dimethyl carbonate (l)	−1429.28 ± 0.30	−1429.28 ± 0.30	−608.74 ± 0.36
1,2,4-triazolo[1,5-*a*]pyrimidine (cr)	−2797.34 ± 1.00	−2794.86 ± 1.00	255.65 ± 1.02
di-*n*-octyl sulfide (l)	−11304.65 ± 1.94	−11329.44 ± 1.94	−427.81 ± 2.20
tetrakis(dimethylamino)ethylene (l)	−7434.19 ± 1.88	−7444.11 ± 1.88	79.05 ± 2.00
dicyclohexyl sulfide (l)	−8199.48 ± 1.20	−8216.83 ± 1.20	−251.40 ± 1.40
piperazine (l)	−2958.50 ± 0.54	−2962.22 ± 0.54	−40.97 ± 0.60
hexachloroprop-1-ene (l)	−1252.3 ± 0.50	−1248.6 ± 0.50	−74.2 ± 0.7

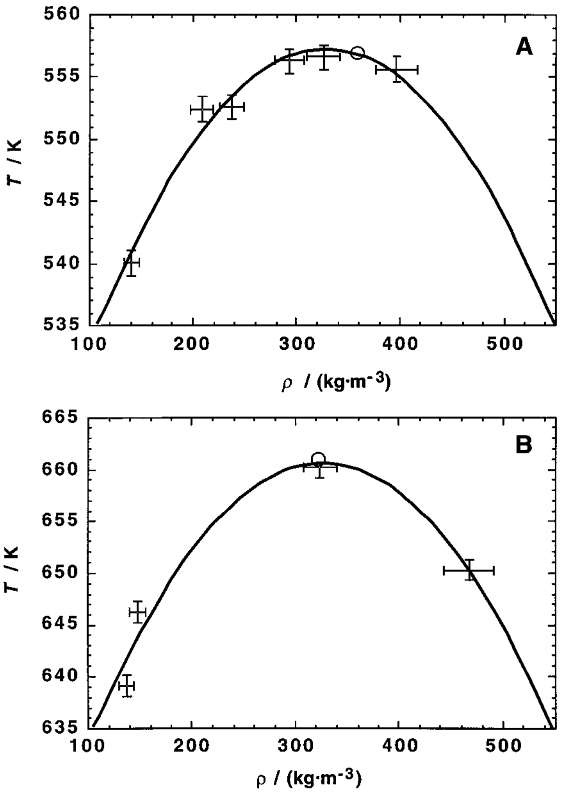


Figure 2. Vapor−liquid coexistence in the region of the critical point: (A) dimethyl carbonate; (B) piperazine. ○ denotes the critical temperatures and critical densities derived in the fitting procedures. The curves are drawn as an aid to the eye and do not represent any theoretically valid equation. The crosses span the range of uncertainty.

10^{-8} K^{-2}, and the measured temperature at which conversion to a single phase was observed.

Critical temperatures and critical densities were derived graphically for dimethyl carbonate and piperazine 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 (Chirico and Steele, 1994). The rapid heating method was used previously for critical temperature and critical density determinations for 2-aminobiphenyl (Steele et al., 1991a), dibenzothiophene (Chirico et al., 1991), and carbazole, phenanthrene, and benzofuran (Steele, 1995).

For all the other compounds (diethylenetriamine, di-*n*-octyl sulfide, dicyclohexyl sulfide, hexachloroprop-1-ene, *N*,*N*′-bis(2-hydroxyethyl)ethylenediamine, 1,2,4-triazolo[1,5-*a*]pyrimidine, and tetrakis(dimethylamino)ethylene), the upper temperature bound of the DSC heat capacity measurements was set by sample decomposition. Decomposition occurred before the difference between $C^{\mathrm{II}}_{\mathrm{x,m}}$ and $C_{\mathrm{sat,m}}$ became significant. Table 8 lists equations representing the variation of saturated heat capacity, $C_{\mathrm{sat,m}}$, with temperature for each of those compounds.

For the compounds that were solid at ambient temperature, *N*,*N*′-bis(2-hydroxyethyl)ethylenediamine, piperazine, and 1,2,4-triazolo[1,5-*a*]pyrimidine, by judicious choice of starting temperature, the melting endotherms during the DSC enthalpy measurements occurred in the center of a heating cycle. The measured enthalpies during those particular heating cycles contained the enthalpy of fusion plus enthalpies for raising the solid from the initial temperature to the melting point and for raising the liquid from the melting point to the final temperature. Details of the derived enthalpies of fusion for *N*,*N*′-bis(2-hydroxyethyl)ethylenediamine, piperazine, and 1,2,4-triazolo[1,5-*a*]pyrimidine at their melting points and the corresponding values at 298.15 K are reported in Table 8. Equations, representing the heat capacities for the liquid and solid phases for each compound, which were used in the "adjustment" to 298.15 K are also reported in Table 8. [Note: the heat capacity equations should only be used to derive values within the temperature ranges specified in Table 8; extrapolation outside the temperature range will produce erroneous values.]

Densitometry. Measured densities for dimethyl carbonate, *N*,*N*′-bis(2-hydroxyethyl)ethylenediamine, and dicyclohexyl sulfide in the liquid phase along the saturation line are listed in Table 10. The temperatures are precise to ±0.005 K. As derived (Chirico and Steele, 1994), the expected accuracy of the densities is ±0.1 kg·m^{-3}.

Fitting Procedures. 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 $\Delta^{\mathrm{l}}_{\mathrm{g}}H_m$ at 298.15 K is the only value necessary to obtain $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$(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.

For dimethyl carbonate, 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. A summary of the procedure was outlined in Steele (1995) and Steele et al. (1996b). The Wagner equation (Wagner, 1973) in the formulation given by Ambrose (Ambrose and Walton, 1989)

$$\ln(p/p_{\mathrm{c}}) = (1/T_{\mathrm{r}})[AY + BY^{1.5} + CY^{2.5} + DY^{5}] \qquad (4)$$

where $T_{\mathrm{r}} = T/T_{\mathrm{c}}$ and $Y = (1 \text{ to } T_{\mathrm{r}})$, was fitted to the measured vapor pressures (Table 7). The vapor-pressure fitting procedure including the minimization equation and the relative weightings is detailed in Steele (1995). For dimethyl carbonate, a critical temperature was determined from the DSC measurements and, hence, only the critical pressure p_{c} was included in the variables.

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 8) were converted to $C^{\mathrm{II}}_{\mathrm{x,m}}$ by means of eq 3 for the cell expansion and the vapor-pressure fit for $(\partial p/\partial T)_{\mathrm{sat}}$

$$C^{\mathrm{II}}_{\mathrm{x,m}} = C^{\mathrm{II}}_{\mathrm{x,m}} - T/n\{(\partial V_x/\partial T)_x(\partial p/\partial T)_{\mathrm{sat}}\} \qquad (5)$$

The values of $C^{\mathrm{II}}_{\mathrm{x,m}}$ 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

$$(\partial^2\mu/\partial T^2)_{\mathrm{sat}}/(\mathrm{J{\cdot}K^{-2}{\cdot}mol^{-1}}) = \sum_{i=0}^{3} b_i\,(1 - T/T_{\mathrm{c}})^i \qquad (6)$$

Details of the weighting procedures, etc., are given by Steele (1995).

For piperazine, the derived critical temperature (T_{c} = 661 K) and critical density (ρ_{c} = 322 kg·m^{-3}) were used as fitting parameters. The two-phase heat capacities $C^{\mathrm{II}}_{\mathrm{x,m}}$ measured using the DSC were not sufficient to enable simultaneous nonlinear least-squares fit of the vapor pressures and the $C^{\mathrm{II}}_{\mathrm{x,m}}$values. The parameters listed in Table 11 were derived from a least-squares fit of the vapor pressures alone.

Exceptions to the above procedures were made for each of the remaining compounds. Diethylenetriamine, di-*n*-octyl sulfide, tetrakis(dimethylamino)ethylene, dicyclohexyl

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
Diethylenetriamine											
d	370.500	1.9998	0.0012	0.0001	0.082	w	445.531	38.568	−0.001	0.002	0.032
d	385.132	3.9946	−0.0052	0.0003	0.049	w	452.260	47.361	−0.001	0.002	0.032
d	391.620	5.3310	0.0032	0.0003	0.044	w	459.039	57.795	−0.006	0.003	0.029
d	401.296	7.9904	−0.0028	0.0005	0.036	w	465.857	70.099	−0.002	0.003	0.032
d	408.557	10.6665	0.0011	0.0006	0.036	w	472.716	84.514	−0.001	0.004	0.033
d	414.362	13.309	0.001	0.001	0.034	w	479.619	101.313	−0.008	0.005	0.032
d	420.458	16.651	0.002	0.001	0.034	w	486.550	120.77	0.00	0.01	0.037
d	425.524	19.937	0.005	0.001	0.033	w	493.520	143.19	−0.01	0.01	0.037
d	432.156	25.034	0.011	0.001	0.032	w	500.542	168.99	0.00	0.01	0.041
d	432.154[b]	25.033	0.011	0.001	0.032	w	507.606	198.48	0.00	0.01	0.041
w	432.181	25.044	0.000	0.001	0.033	w	514.699	231.98	−0.01	0.01	0.040
w	438.820	31.174	0.001	0.002	0.034	w	521.828	269.97	0.03	0.01	0.048
Dimethyl Carbonate											
d	310.560	13.322	0.001	0.001	0.027	w	352.093	70.099	0.006	0.004	0.014
d	315.460	16.663	0.005	0.001	0.023	w	357.646	84.527	0.010	0.004	0.014
d	319.548	19.945	−0.002	0.001	0.020	w	363.240	101.348	0.004	0.005	0.013
d	324.866	25.009	−0.002	0.001	0.018	w	368.847	120.77	0.00	0.01	0.014
w	324.874[b]	25.018	−0.001	0.002	0.017	w	374.498	143.20	−0.01	0.01	0.012
w	330.257	31.177	0.000	0.002	0.016	w	380.197	169.01	−0.02	0.01	0.012
w	335.666	38.561	0.000	0.002	0.014	w	385.926	198.49	−0.01	0.01	0.012
w	341.113	47.374	−0.001	0.003	0.013	w	391.683	232.00	0.00	0.01	0.013
w	346.588	57.813	0.002	0.003	0.013	w	397.479	270.01	0.03	0.01	0.013
Di-*n*-octyl Sulfide											
d	464.501	1.9984	0.0002	0.0001	0.079	d	519.365	13.321	0.001	0.001	0.026
d	482.688	3.9910	−0.0010	0.0002	0.061	d	526.997	16.655	−0.003	0.001	0.023
d	490.872	5.3320	−0.0001	0.0003	0.046	d	533.294	19.904	−0.005	0.001	0.027
d	502.905	7.9816	0.0015	0.0004	0.028	d	541.688	25.047	0.004	0.001	0.039
d	512.041	10.6627	0.0014	0.0005	0.031	w	549.981[c]	31.184	0.043	0.002	0.050
Tetrakis(dimethylamino)ethylene											
d	357.701	2.0000	−0.0007	0.0001	0.089	w	431.927	31.173	0.000	0.002	0.045
d	373.345	3.9990	0.0024	0.0002	0.075	w	439.355	38.582	0.015	0.002	0.061
d	380.354	5.3297	0.0027	0.0003	0.060	w	446.818	47.362	0.014	0.002	0.062
d	390.859	8.0033	0.0014	0.0004	0.046	w	454.371	57.797	0.008	0.003	0.063
d	398.742	10.6710	−0.0016	0.0006	0.041	w	461.994	70.094	−0.003	0.003	0.061
d	405.136	13.338	−0.007	0.001	0.035	w	469.690	84.522	−0.010	0.004	0.063
d	411.765	16.666	−0.006	0.001	0.035	w	477.435	101.306	−0.010	0.004	0.073
d	417.278	19.925	−0.007	0.001	0.044	w	485.248	120.77	0.00	0.01	0.085
d	424.580	25.035	0.007	0.001	0.045						
Dicyclohexyl Sulfide											
d	421.249	2.0005	0.0001	0.0001	0.070	d	483.327	16.659	0.000	0.001	0.018
d	428.545	2.6704	−0.0002	0.0002	0.043	d	489.655	19.925	−0.001	0.001	0.017
d	439.278	3.9985	0.0001	0.0002	0.034	d	498.003	25.021	0.000	0.001	0.019
d	447.377	5.3368	0.0002	0.0003	0.026	w	506.404	31.173	0.001	0.002	0.020
d	459.399	8.0039	−0.0001	0.0004	0.023	w	514.882	38.570	−0.001	0.002	0.023
d	468.423	10.6686	0.0000	0.0005	0.021	w	523.379[c]	47.378	0.032	0.002	0.034
d	475.710	13.323	0.000	0.001	0.018						
Piperazine											
w	417.997	90.976	0.005	0.004	0.053	w	440.928	169.04	0.00	0.01	0.064
w	421.772	101.321	−0.009	0.005	0.053	w	447.397	198.48	0.00	0.01	0.065
w	428.104	120.77	0.00	0.01	0.058	w	453.916	232.00	0.00	0.01	0.067
w	434.490	143.24	0.01	0.01	0.062	w	460.477	269.97	0.00	0.01	0.068
Hexachloroprop-1-ene											
d	366.413	2.0010	0.0000	0.0001	0.040	w	441.709	31.182	0.000	0.002	0.013
d	382.381	3.9983	0.0000	0.0002	0.033	w	449.173	38.562	−0.001	0.002	0.014
d	389.501	5.3265	0.0002	0.0003	0.028	w	456.702	47.376	−0.001	0.002	0.013
d	400.177	8.0012	−0.0005	0.0004	0.025	w	464.266	57.792	−0.002	0.003	0.014
d	408.148	10.6634	−0.0001	0.0006	0.019	w	471.913	70.115	0.003	0.003	0.015
d	414.567	13.309	0.000	0.001	0.016	w	479.590	84.499	0.004	0.004	0.016
d	421.345	16.669	0.001	0.001	0.015	w	487.344	101.300	−0.004	0.004	0.016
d	426.921	19.930	0.000	0.001	0.014	w	495.145	120.77	−0.01	0.01	0.019
d	434.298	25.031	0.000	0.001	0.015	w	502.993	143.23	0.01	0.01	0.026
w	434.289[b]	25.027	0.003	0.001	0.013	w	510.882[c]	169.05	0.07	0.01	0.050
N,*N*′-Bis(2-hydroxyethyl)ethylenediamine[d]											
ip	399.473	0.0270	0.0000	0.0001		ip	460.150	0.9155	0.0000	0.0002	
ip	410.150	0.0550	0.0000	0.0001		ip	470.150	1.4763	0.0000	0.0003	
ip	420.142	0.1029	0.0000	0.0001		ip	475.149	1.8581	0.0000	0.0004	
ip	430.151	0.1861	0.0000	0.0001		d	476.838	2.0057	0.0000	0.0001	0.074
ip	440.154	0.3258	0.0000	0.0001		d	492.718	3.9934	0.0001	0.0002	0.090
ip	450.151	0.5536	0.0000	0.0002		d	499.733	5.3258	−0.0001	0.0003	0.100

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
					1,2,4-Triazolo[1,5-*a*]pyrimidine[d]						
ip	370.110[e]	0.0214	−0.0225	0.0002		d	472.933	5.339	−0.0042	0.0003	0.015
ip	390.008[e]	0.0919	−0.0506	0.0002		d	484.951	7.9897	0.0002	0.0004	0.010
ip	420.001	0.6521	0.0042	0.0002		d	493.987	10.6514	0.0041	0.0005	0.010
ip	430.007	1.0158	0.0020	0.0003		d	501.307	13.321	0.006	0.001	0.015
ip	440.002	1.5454	−0.0010	0.0003		d	508.938	16.679	0.005	0.001	0.019
ip	450.006	2.3024	−0.0046	0.0005		d	515.195	19.935	0.000	0.001	0.023
ip	454.997	2.7898	−0.0043	0.0005		d	523.459	25.032	−0.012	0.001	0.036

[a] Water (w) or decane (d) refers to which material was used 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 4 or 7 and the parameters listed in Table 5, from the observed value of pressure ($\Delta p = p - p_{\mathrm{Wagner}}$) or ($\Delta p = p - p_{\mathrm{Antoine}}$), respectively. σ is the propagated error calculated using $\sigma(p) = 1.5 \times 10^{-4}p + 0.2$ Pa (inclined piston) or $\sigma(p) = (0.001)\{(\mathrm{d}p_{\mathrm{ref}}/\mathrm{d}T)^2 + (\mathrm{d}p_x/\mathrm{d}T)^2\}^{1/2}$ (ebulliometer). ΔT is the difference between the boiling and condensation temperatures ($T_{\mathrm{boil}} - T_{\mathrm{cond}}$) for the sample. [b] Values at this temperature were not included in the fit of the Wagner equation. The measurement was an overlap point between the use of decane and water as the pressure measurement standards. [c] Values at this temperature were not included in the fit of the Wagner equation due to sample decomposition (see text). [d] Due to the short temperature range of the measurements and the lack of reliable critical properties, the results were fit to the Antoine vapor-pressure equation (see text). [e] Point excluded from the Antoine-equation fit, sublimation pressure (see text).

Table 8. Two-Phase (Liquid + Vapor) Heat Capacities or $C_{\mathrm{sat,m}}$ Equations and Enthalpies of Fusion (R = 8.314 51 J·K^{-1}·mol^{-1})

T/K	$C^{\mathrm{II}}_{x,\mathrm{m}}/R$	$C^{\mathrm{II}}_{x,\mathrm{m}}/R$	$C^{\mathrm{II}}_{x,\mathrm{m}}/R$
	Dimethyl Carbonate		
mass/g	0.011 118	0.015 826	0.021 424
vol/cell/(cm^3)[a]	0.052 72	0.053 39	0.053 39
315.0	20.9	20.3	20.1
335.0	21.2	20.9	20.7
355.0	22.1	21.7	21.3
375.0	23.8	22.5	22.1
395.0	24.9	23.5	22.9
415.0	25.9	24.5	23.6
435.0	27.2	25.7	24.5
455.0	28.9	26.5	25.3
475.0	30.8	27.6	26.3
495.0	33.2	29.6	27.5
515.0	35.5	31.1	28.9
535.0	39.1	33.8	30.8
555.0[b]	25.3	33.1	29.6

Diethylenetriamine (Liquid)

$C_{\mathrm{sat,m}}/R = 38.72 - 0.0454\cdot T + 9.266 \times 10^{-5}\cdot T^2$ (in temperature range 290 K to 550 K)

Di-*n*-octyl Sulfide (Liquid)

$C_{\mathrm{sat,m}}/R = 46.55 - 0.0279\cdot T + 9.300 \times 10^{-5}\cdot T^2$ (in temperature range 290 K to 550 K)

Dicyclohexyl Sulfide (Liquid)

$C_{\mathrm{sat,m}}/R = 13.72 - 0.0788\cdot T + 1.836 \times 10^{-5}\cdot T^2$ (in temperature range 290 K to 520 K)

Hexachloroprop-1-ene (Liquid)

$C_{\mathrm{sat,m}}/R = 26.71 - 0.0106\cdot T + 3.220 \times 10^{-5}\cdot T^2$ (in temperature range 290 K to 500 K)

Tetrakis(dimethylamino)ethylene

$C_{\mathrm{sat,m}}/R = 26.831 - 0.0507\cdot T + 3.06 \times 10^{-5}\cdot T^2$ (in temperature range 290 K to 480 K)

N,*N*′-Bis(2-hydroxyethyl)ethylenediamine

crystalline $C_{\mathrm{sat,m}}/\mathrm{R} = 0.100\cdot T - 4.60$ (in temperature range 290 to 373.2 K)
liquid $C_{\mathrm{sat,m}}/\mathrm{R} = 0.071\cdot T + 22.70$ (in temperature range 373.2 to 485 K)
$\Delta_{\mathrm{c}}^{\mathrm{l}}H^\circ_{\mathrm{m}}$ (373.2 K) = (49.7 ± 0.5) kJmol^{-1}
$\Delta_{\mathrm{c}}^{\mathrm{l}}H^\circ_{\mathrm{m}}$ (298.15 K) = (38.7 ± 0.8) kJmol^{-1}

1,2,4-Triazolo[1,5-*a*]pyrimidine

crystalline $C_{\mathrm{sat,m}}/\mathrm{R} = 0.0509\cdot T - 0.395$ (in temperature range 290 to 419.5 K)
liquid $C_{\mathrm{sat,m}}/\mathrm{R} = 0.0262\cdot T + 14.106$ (in temperature range 419.5 to 525 K)
$\Delta_{\mathrm{c}}^{\mathrm{l}}H^\circ_{\mathrm{m}}$ (419.5 K) = (19.4 ± 0.4) kJmol^{-1}
$\Delta_{\mathrm{c}}^{\mathrm{l}}H^\circ_{\mathrm{m}}$ (298.15 K) = (13.7 ± 0.7) kJmol^{-1}

Piperazine

crystalline $C_{\mathrm{sat,m}}/\mathrm{R} = 0.0651\cdot T - 5.62$ (in temperature range 295 to 384.6 K)
liquid $C_{\mathrm{sat,m}}/\mathrm{R} = 0.06084\cdot T + 2.14$ (in temperature range 384.6 to 505 K)
$\Delta_{\mathrm{c}}^{\mathrm{l}}H^\circ_{\mathrm{m}}$ (384.6 K) = (26.7 ± 0.3) kJmol^{-1}
$\Delta_{\mathrm{c}}^{\mathrm{l}}H^\circ_{\mathrm{m}}$ (298.15 K) = (22.2 ± 0.6) kJmol^{-1}

[a] Volume of cell is given for 298.15 K. [b] Values not used in fitting procedures since above the critical temperature.

sulfide, and hexachloroprop-1-ene decomposed well removed from the critical region, and the measured heat capacity values were independent of cell filling. Hence, estimates were made for the critical temperatures of those compounds. The critical pressures were selected with Waring's criterion for $T_{\mathrm{r}} = 0.85$ (Waring, 1954). Application of this criterion was discussed recently by Steele (1995).

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
Dimethyl Carbonate			
140.4	540.1	292.9	556.3
208.4	552.4	325.7	556.6
236.9	552.6	396.6	555.6
Piperazine			
136.5	639.1	323.7	660.2
147.2	646.3	467.3	650.3

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

T/K	ρ/kg·m^{-3}	100($\rho - \rho_{calc}$)/ρ
Dimethyl Carbonate[b]		
308.141	1049.6	0.00
323.137	1029.6	0.01
348.130	995.1	0.01
373.123	959.3	−0.02
393.119	930.2	0.01
Dicyclohexyl Sulfide[c]		
323.137	950.5	0.00
348.130	932.3	0.01
373.123	913.6	−0.02
398.119	895.7	0.03
423.115	876.5	−0.03
448.112	858.1	0.01
N,*N*′-Bis(2-hydroxyethyl)ethylenediamine[d]		
398.120	1014.6	
413.115	994.7	
448.115	947.2	

[a] ρ_{calc} values were calculated using eq 10 and the parameters listed below. [b] $\rho_{calc} = 358.0 + 975.8(1 - T/557)^{1/3} - 715.1(1 - T/557)^{2/3} + 813.9(1 - T/557)$. [c] $\rho_{calc} = 283.5 + 1130.0(1 - T/770)^{1/3} - 1240.5(1 - T/770)^{2/3} + 1012.4(1 - T/770)$. [d] Due to short temperature range no fit was attempted.

Both *N*,*N*′-(2-hydroxyethyl)ethylenediamine and 1,2,4-triazolo[1,5-*a*]pyrimidine decomposed well removed from the critical region, measured vapor pressures covered a relatively narrow range of temperature (Table 7), and the measured heat capacities were independent of cell filling. Also, for both compounds all estimating procedures gave unrealistic values for the critical parameters. Hence, for those compounds, the Antoine equation in the form

$$\log(p/p_{ref}) = A + B/\{(T/\mathrm{K}) + C\} \qquad (7)$$

with $p_{ref} = 1$ kPa, was fit to the available vapor pressure data (Table 7).

Derived Results. Table 11 listed the parameters derived using the procedures outlined above and in Steele et al. (1996b). Details of the fits using to the vapor-pressure results are given in Table 7 (column 4 labeled $\Delta p = p - p_{Wagner}$ with p_{Wagner} calculated using the parameters listed in Table 11).

Values of $C^{II}_{x,m}(\rho = \rho_{sat})$ for dimethyl carbonate were derived from the parameters listed in Table 11 and corresponding $C_{sat,m}$ values were obtained using eq 6 of Steele et al. (1995). The results for $C_{sat,m}/R$ are reported in Table 13. The estimated uncertainty in these values is 1%.

Enthalpies of vaporization $\Delta_l^g H_m$ were derived from the Wagner- or Antoine-equation fits (Tables 11 and 12) using the Clapeyron equation

$$\mathrm{d}p/\mathrm{d}T = \Delta_l^g H_m/(T\,\Delta_l^g V_m) \qquad (8)$$

where $\Delta_l^g V_m$ is the increase in molar volume from the liquid to the real vapor. In earlier work in this project, the liquid-phase density estimates were made with the extended corresponding-states equation (Riedel, 1954) as formulated by Hales and Townsend (1972)

$$(\rho/\rho_c) = 1.0 + 0.85Y + (1.6916 + 0.9846\omega)Y^{1/3} \qquad (9)$$

with $Y = (1 - T/T_c)$, ρ_c = critical density, and ω = acentric factor. The acentric factor, ω, is defined as $[-\log(p/p_c) - 1]$, where p is the vapor pressure at $T/T_c = 0.7$ and p_c is the critical pressure. However, often eq 9 was not a good

Table 11. Parameters for Eq 4 and Eq 6, Critical Constants, and Acentric Factors[a]

Diethylenetriamine			
A	−8.704 71		
B	2.234 61		
C	−5.098 54		
D	−4.288 48		
T_c = 677 K		p_c = 3050 kPa	
ρ_c = 287 kg·m^{-3}		ω = 0.5437	

Dimethyl Carbonate			
A	−8.242 79	b_0	−0.303 23
B	3.255 66	b_1	−0.811 19
C	−4.282 49	b_2	1.711 16
D	−2.119 40	b_3	−2.372 67
T_c = 557 K		p_c = 4800 kPa	
ρ_c = 358 kg·m^{-3}		ω = 0.3365	

Di-*n*-octyl Sulfide			
A	−11.382 45		
B	5.132 35		
C	−6.503 42		
D	−8.404 72		
T_c = 780 K		p_c = 1800 kPa	
ρ_c = 231 kg·m^{-3}		ω = 0.8069	

Tetrakis(dimethylamino)ethylene			
A	−8.337 25		
B	2.874 47		
C	−4.080 37		
D	−3.542 04		
T_c = 680 K		p_c = 2400 kPa	
ρ_c = 310 kg·m^{-3}		ω = 0.3389	

Dicyclohexyl Sulfide			
A	−10.738 45		
B	6.626 14		
C	−7.126 38		
D	−2.309 80		
T_c = 770 K		p_c = 2370 kPa	
ρ_c = 283.5 kg·m^{-3}		ω = 0.5446	

Piperazine			
A	−8.106 64		
B	3.362 81		
C	−4.529 62		
D	−3.827 80		
T_c = 661 K		p_c = 5800 kPa	
ρ_c = 322 kg·m^{-3}		ω = 0.3103	

Hexachloroprop-1-ene			
A	−10.63678		
B	6.87228		
C	−7.48169		
D	−0.41208		
T_c = 680 K		p_c = 2500 kPa	
ρ_c = 485 kg·m^{-3}		ω = 0.5086	

[a] The parameters listed in this table are those derived from the fitting procedures.

Table 12. Antoine Equation Parameters[a,b]

	A	B
p_{ref}/kPa	1.0	1.0
A	8.2392	6.62545
B	−3218.9	−2321.46
C	−71.2795	−79.308
range/K[c]	400−500	420−523

[a] The parameters listed in this table are those derived from the fitting procedures. [b] A = *N*,*N*′-bis(2-hydroxyethyl)ethylenediamine; B = 1,2,4-triazolo[1,5-*a*]pyrimidine. [c] Temperature range of the vapor pressures used in the fit.

Table 13. Values of $C_{sat,m}/R$ (R = 8.314 51 J·K^{-1}·mol^{-1})[a]

T/K	$C_{sat,m}$/R	T/K	$C_{sat,m}/R$
	Dimethyl Carbonate		
300.0	19.8	440.0	23.6
320.0	20.2	460.0	24.4
340.0	20.6	480.0	25.1
360.0	21.2	500.0	26.1
380.0	21.7	520.0	27.8
400.0	22.3	540.0	32.6
420.0	23.0		

representation of the measured densities. A power series of the type

$$\rho = \rho_c + A(1 - T_r)^{1/3} + B(1 - T_r)^{2/3} + C(1 - T_r) + ... \tag{10}$$

has proved to be a better representation of the measured densities for a wide range of compound types from alkanes through compounds containing highly polar groups (Steele, 1996). For both dimethyl carbonate and dicyclohexyl sulfide, estimates of the liquid-phase volumes were made using eq 10 and the parameters given in the footnotes to Table 10. For hexachloroprop-1-ene, di-*n*-octyl sulfide, diethylenetriamine, tetrakis(dimethylamino)ethylene, and piperazine, the absence of measured densities prevented use of the power series equation. For those compounds, eq 9, in combination with the parameters listed in Table 11, was used to derive estimates of the liquid-phase volumes. For all the compounds except *N*,*N*′-(2-hydroxyethyl)ethylenediamine and 1,2,4-triazolo[1,5-*a*]pyrimidine, 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 (Pitzer and Curl, 1957), and third virial coefficients were estimated with the corresponding-states method (Orbey and Vera, 1983). This formulation for third virial coefficients was applied successfully in analyses of the thermodynamic properties of benzene and toluene (Chirico and Steele, 1994). Third virial coefficients are required for accurate calculation of the gas volume for pressures greater than 1 bar. Uncertainties in the virial coefficients are assumed to be 10% of the respective numerical values.

The absence of critical properties precluded using the methodology outlined above for *N*,*N*′-(2-hydroxyethyl)ethylenediamine and 1,2,4-triazolo[1,5-*a*]pyrimidine. For 1,2,4-triazolo[1,5-*a*]pyrimidine liquid-phase volumes were derived using a density of 1720 kg·m^{-3} at 430 K and a coefficient of expansion of 1.5 × 10^{-7} m^{3}·K^{-1}. For, *N*,*N*′-(2-hydroxyethyl)ethylenediamine, liquid-phase volumes were derived using the densities listed in Table 10 and an average coefficient of cubic expansion obtained from the measurements. 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% of the respective numerical values.

Table 14. 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}
	Diethylenetriamine		
298.15[b]	63.44 ± 0.65	440.0	50.54 ± 0.40
300.0[b]	63.26 ± 0.63	460.0	48.68 ± 0.45
320.0[b]	61.31 ± 0.55	480.0	46.72 ± 0.55
340.0[b]	59.44 ± 0.50	500.0	44.65 ± 0.68
360.0[b]	57.63 ± 0.47	520.0	42.43 ± 0.86
380.0	55.85 ± 0.43	540.0[b]	40.1 ± 1.1
400.0	54.10 ± 0.40	560.0[b]	37.5 ± 1.3
420.0	52.34 ± 0.38	580.0[b]	34.8 ± 1.6
	Dimethyl Carbonate		
280.0[b]	38.77 ± 0.25	380.0	32.41 ± 0.37
298.15[b]	37.70 ± 0.23	400.0	30.91 ± 0.50
300.0[b]	37.59 ± 0.23	420.0[b]	29.28 ± 0.65
320.0	36.38 ± 0.23	440.0[b]	27.54 ± 0.81
340.0	35.13 ± 0.25	460.0[b]	25.7 ± 1.0
360.0	33.82 ± 0.28		
	N,*N*′-Bis(2-hydroxyethyl)ethylenediamine		
298.15[c,d]	106.4 ± 6.4	440.0	87.71 ± 0.22
300.0[c,d]	106.0 ± 6.4	460.0	86.20 ± 0.20
360.0[c,d]	95.81 ± 0.25	480.0	84.81 ± 0.22
380.0[c]	93.36 ± 0.25	500.0	83.47 ± 0.23
400.0	91.24 ± 0.23	520.0[c]	82.15 ± 0.30
420.0	89.37 ± 0.22		
	1,2,4-Triazolo[1,5-*a*]pyrimidine		
298.15[c,d]	82.5 ± 13.1	500.0	62.4 ± 2.1
420.0[c]	67.5 ± 2.9	520.0	61.2 ± 2.0
440.0[c]	66.0 ± 2.5	540.0[c]	60.1 ± 2.0
460.0[c]	64.7 ± 2.3	560.0[c]	59.0 ± 2.1
480.0	63.5 ± 2.2	580.0[c]	57.8 ± 2.1
	Di-*n*-octyl Sulfide		
298.15[b]	95.0 ± 10.7	500.0	67.76 ± 0.53
400.0[b]	79.34 ± 0.84	520.0	65.73 ± 0.53
420.0[b]	76.76 ± 0.71	540.0	63.73 ± 0.56
440.0[b]	74.33 ± 0.64	560.0[b]	61.73 ± 0.62
460.0	72.03 ± 0.60	580.0[b]	59.68 ± 0.76
480.0	69.85 ± 0.56	600.0[b]	57.55 ± 0.95
	Tetrakis(dimethylamino)ethylene		
298.15[b]	53.85 ± 0.46	420.0	45.02 ± 0.31
300.0[b]	53.71 ± 0.45	440.0	43.56 ± 0.36
320.0[b]	52.18 ± 0.39	460.0	42.04 ± 0.43
340.0[b]	50.71 ± 0.36	480.0	40.44 ± 0.54
360.0	49.27 ± 0.33	500.0[b]	38.76 ± 0.68
380.0	47.86 ± 0.31	520.0[b]	36.97 ± 0.85
400.0	46.45 ± 0.31	540.0[b]	35.1 ± 1.0
	Dicyclohexyl Sulfide		
298.15[b]	69.02 ± 0.68	480.0	55.15 ± 0.38
360.0[b]	64.10 ± 0.51	500.0	53.66 ± 0.41
380.0[b]	62.57 ± 0.47	520.0	52.14 ± 0.46
400.0[b]	61.06 ± 0.45	540.0[b]	50.59 ± 0.54
420.0	59.57 ± 0.42	560.0[b]	49.01 ± 0.65
440.0	58.10 ± 0.40	580.0[b]	47.37 ± 0.80
460.0	56.63 ± 0.38		
	Piperazine		
298.15[b,e]	50.1 ± 1.9	440.0	38.90 ± 0.40
360.0[b,e]	45.14 ± 0.31	460.0	37.26 ± 0.50
380.0[b,e]	43.60 ± 0.28	480.0[b]	35.57 ± 0.63
400.0[b]	42.06 ± 0.29	500.0[b]	33.81 ± 0.79
420.0	40.50 ± 0.33	520.0[b]	32.0 ± 1.0
	Hexachloroprop-1-ene		
298.15[b]	54.77 ± 0.43	440.0	46.01 ± 0.34
300.0[b]	54.67 ± 0.42	460.0	44.60 ± 0.41
320.0[b]	53.51 ± 0.40	480.0	43.13 ± 0.49
340.0[b]	52.34 ± 0.37	500.0	41.60 ± 0.62
360.0	51.14 ± 0.35	520.0[b]	40.01 ± 0.78
380.0	49.92 ± 0.33	540.0[b]	38.36 ± 0.96
400.0	48.66 ± 0.32	560.0[b]	36.6 ± 1.2
420.0	47.36 ± 0.32		

[a] Uncertainty intervals are twice the standard deviation. [b] The value at this temperature was calculated with extrapolated vapor pressures derived from the fitted Wagner equation. [c] The value at this temperature was calculated with extrapolated vapor pressures derived from the fitted Antoine equation. [d] The value at this temperature was calculated with extrapolated vapor pressures derived from the fitted Antoine equation and represents the supercooled liquid below the triple point. [e] The value at this temperature was calculated with extrapolated vapor pressures derived from the fitted Wagner equation and represents the supercooled liquid below the triple point.

Table 15. Thermochemical Properties at 298.15 K (R = 8.31451 J·K^{-1}·mol^{-1} and p° = 101.325 kPa)

compound	$\Delta_f H^\circ_m$(c)/ kJ·mol^{-1}	$\Delta_c^l H^\circ_m$/ kJ·mol^{-1}	$\Delta_f H^\circ_m$(l)/ kJ·mol^{-1}	$\Delta_g^l H^\circ_m$/ kJ·mol^{-1}	$\Delta_f H^\circ_m$(g)/ kJ·mol^{-1}
diethylenetriamine			−73.68 ± 1.42	63.44 ± 0.65	−10.2 ± 1.6
N,*N*′-bis(2-hydroxyethyl)ethylenediamine	−523.81 ± 0.80	38.7 ± 0.8	−485.11 ± 1.13	106.4 ± 6.4	−378.7 ± 6.5
dimethyl carbonate			−608.74 ± 0.36	37.70 ± 0.23	−571.0 ± 0.4
1,2,4-triazolo[1,5-*a*]pyrimidine	255.65 ± 1.02	13.7 ± 0.7	269.3 ± 1.3	82.5 ± 13.1	351.8 ± 13.2
di-*n*-octyl sulfide			−427.81 ± 2.20	95.0 ± 10.7	−332.8 ± 11.0
tetrakis(dimethylamino)ethylene			79.05 ± 2.00	53.85 ± 0.46	132.9 ± 2.0
dicyclohexyl sulfide			−251.40 ± 1.40	69.02 ± 0.68	−182.4 ± 1.6
piperazine	−40.97 ± 0.60	22.2 ± 0.6	−18.5 ± 0.8	50.1 ± 1.9	31.6 ± 2.0
hexachloroprop-1-ene			−74.2 ± 0.7	54.77 ± 0.43	−19.4 ± 0.8

Derived enthalpies of vaporization are reported in Table 14. 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 15 summarizes the thermochemical property measurements and derived ideal-gas standard enthalpies of formation for all the compounds of this study. The enthalpy of vaporization, $\Delta_g^l H_m$, for dimethyl carbonate was converted to the corresponding value for the ideal gas, $\Delta_l^g H^\circ_m$, using an estimate; $(H^\circ - H) = 0.06$ kJ·mol^{-1}, for the real gas at its saturation vapor pressure at 298.15 K. The estimate was calculated using eq 20 of Chirico et al. (1993) and the virial coefficients derived above. The corresponding corrections for the remaining compounds that are less volatile were calculated to be negligibly small.

Discussion

General Comments. In this section of the paper, the results obtained for each compound are discussed and compared with available literature values and relevant group-contribution parameters are derived. Emphasis is given to comparison of the measured properties of this research with experimentally determined values reported in the literature. Only passing references are made to correlated values available in the literature, mostly those abstracted in DIPPR Project 801 (Daubert and Danner, 1993). Comparison of liquid-phase density measurements is restricted to those reported for a temperature range of at least 20 K.

Diethylenetriamine. A critical temperature of (677 ± 5) K, a critical pressure of (3050 ± 200 kPa), and a critical density of (287 ± 15) kg·m^{-3} were obtained from the fitting procedures used in this research for diethylenetriamine. No other experimentally determined values for these properties were obtained in a search of the literature.

Vapor pressures for diethylenetriamine have been reported in the literature by Wilson (1935), Sivokova et al. (1967), and Daubert and Hutchison (1990). Figure 3 compares the various literature vapor pressures with values calculated with the Wagner-equation parameters listed in Table 11. The results shown for Wilson (1935) were obtained by interpolation from a large-scale "blowup" of the graph given in the review article.

Figure 4 compares values for the heat capacity of diethylenetriamine found in a search of the literature with the results derived in this research (Table 13). The results ascribed to Domalski and Hearing (1990) were calculated using the group-additivity parameters given in the review article. The results question the applicability of the Domalski and Hearing (1990) listed group parameters in the estimation of heat capacities for polyfunctional amines.

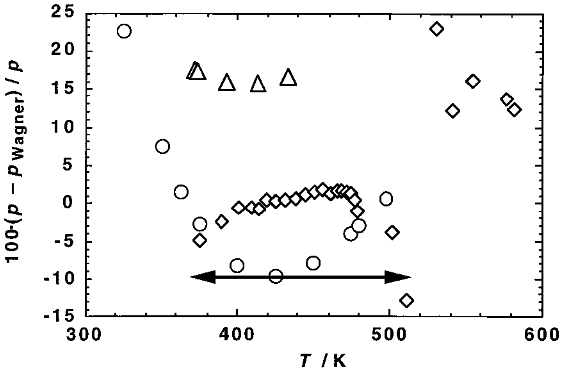


Figure 3. Comparison of literature vapor pressures for diethylenetriamine with values obtained using the Wagner equation and the parameters listed in Table 11. The double-headed arrow represents the range of the measurements of this research and reported in Table 7. Key: (△) Wilson (1960); (○) Sivokova et al. (1967); (◇) Daubert and Hutchison (1990).

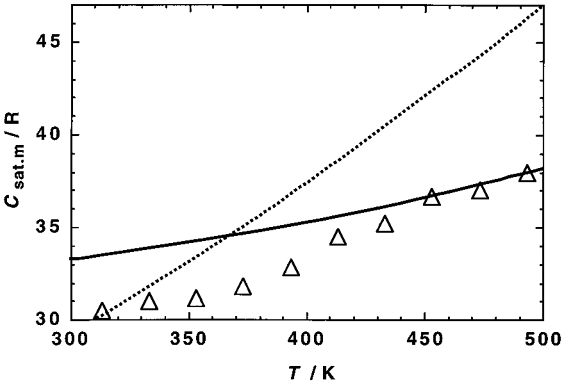


Figure 4. Comparison of literature heat capacity values for diethylenetriamine with those obtained in this research, Table 13. The solid line represents the measurements of this research and reported in Table 13. The dashed line denotes values obtained using the correlation of Domalski and Hearing (1990). Key: (△) Bobylev et al. (1988).

Good and Moore (1970) measured energies of combustion and derived ideal-gas enthalpies of formation for a series of diamines. Compounds studied included ethylenediamine, 1,2-propanediamine, 1,2-butanediamine, and 2-methyl-1,2-propanediamine. Using the group-additivity parameters (Benson, 1976; Reid et al., 1987), small but significant discrepancies existed between the estimated and experimentally derived ideal-gas enthalpies of formation for the diamines.

compound	$\Delta_f H^\circ_m$(g)/kJ·mol^{-1}	Σ groups
ethylenediamine	−(17.6 ± 0.6)	−15.0
1,2-propanediamine	−(53.6 ± 0.5)	−51.4
1,2-butanediamine	−(74.0 ± 0.8)	−72.1
2-methyl-1,2-propanediamine	−(90.2 ± 0.7)	−85.2

A 1,4-nitrogen−nitrogen interaction enthalpy of −2.2

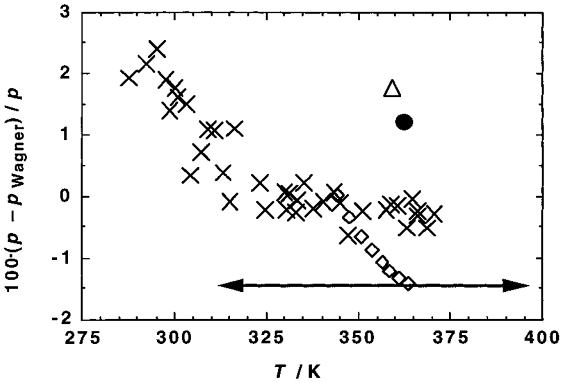


Figure 5. Comparison of literature vapor pressures for dimethyl carbonate with values obtained using the Wagner equation and the parameters listed in Table 11. The double-headed arrow represents the range of the measurements of this research and reported in Table 7. Key: (●) Vogel (1948); (◇) Wright (1960); (△) Cross et al. (1976); (×) Jiang and Zhang (1987).

kJ·mol^{-1} would correct for the discrepancies in all cases except for 2-methyl-1,2-propanediamine.

Addition of the group-additivity parameters (Benson, 1976; Reid et al., 1987) and the 1,4-N−N interaction enthalpy gives

2	N−(C)(H)$_2$	20.1 × 2	40.2
1	N−(C)(H)$_2$	64.5 × 1	64.5
4	C−(N)(C)(H)$_2$	−27.6 × 4	−110.4
2	1,4-N,N interaction energy	−2.2 × 2	−4.4

$$\Delta_f H^\circ_m(C_4H_{13}N_3, g, 298.15\ K) = -10.1\ kJ\cdot mol^{-1}$$

The value determined in this research is: $\Delta_f H^\circ_m(C_4H_{13}N_3$, g, 298.15 K)−(10.2 ± 1.6) kJ·mol^{-1} (Table 15), in excellent agreement with the group-additivity estimation.

N,N′-Bis(2-hydroxyethyl)ethylenediamine. No thermophysical property measurements on *N,N′*-bis(2-hydroxyethyl)ethylenediamine were found in a search of the literature from 1930 through January 1997. Realization of the necessity for a 1,4-nitrogen−nitrogen interaction enthalpy for 1,2-diamines led to the introduction of a 1,4-nitrogen−oxygen interaction energy in compounds such as *N,N′*-bis(2-hydroxyethyl)ethylenediamine. Using the group parameters given in Benson (1976) and in Reid et al. (1987) in combination with the 1,4-N−N interaction enthalpy gives

2	O−(C)(H)	−158.68 × 2	−317.4
2	C−(C)(O)(H)$_2$	−33.91 × 2	−67.8
4	C−(N)(C)(H)$_2$	−27.6 × 4	−110.4
2	N−(C)$_2$(H)	64.5 × 2	129.0
1	1,4-N,N interaction energy	−2.2 × 1	−2.2
2	1,4-N,O interaction energy	−?.? × 1	?.?

$$\Delta_f H^\circ_m(C_6H_{16}N_2O_2, g, 298.15\ K) = ?.?\ kJ\cdot mol^{-1}$$

The value determined in this research is $\Delta_f H^\circ_m(C_6H_{16}N_2O_2$, g, 298.15 K)−(378.7 ± 6.5) kJ·mol^{-1} (Table 15). Therefore a −5.0 kJ·mol^{-1} 1,4-N,O interaction energy is derived.

Dimethyl Carbonate. A critical temperature of (557 ± 1) K and a critical density of (358 ± 10) kg·m^{-3} were obtained from the fitting procedures used in this research for dimethyl carbonate. No other experimentally determined values for these properties were obtained in a search of the literature.

Figure 5 compares values for the vapor pressure of dimethyl carbonate found in a literature search (Vogel, 1948; Wright, 1960; Jiang and Zang, 1967; Cross et al., 1976; Thiebaut et al., 1976) with values calculated using the Wagner equation and the parameters listed in Table 11.

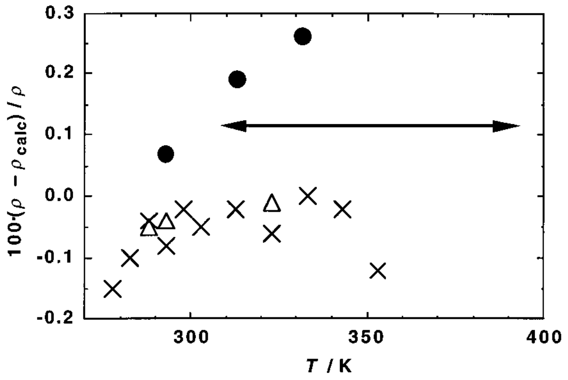


Figure 6. Comparison of literature values for the saturation liquid-phase density measurements for dimethyl carbonate with those obtained using eq 10 and the parameters listed in the footnotes to Table 10. The double-headed arrow represents the range of the measurements of this research and reported in Table 10. Key: (△) Kogerman and Kranig (1927); (●) Vogel (1948); (×) Thiebaut et al. (1976).

Figure 6 compares values for the density of dimethyl carbonate found in a literature search (Kogerman and Kranig, 1927; Vogel, 1948; Thiebaut et al., 1976) with values calculated using eq 10 and the parameters listed in the footnotes to Table 10. [Only densities over a range of temperature were abstracted from the literature. Numerous single-point values (usually at 293 K) were also found in the search but excluded from consideration.] Agreement between the densities measured in this research and by both Kogerman and Kranig (1927) and Thiebaut et al. (1976) is excellent.

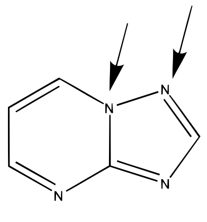
Using the group parameters given by Benson (1976) and in Reid et al. (1987) and the O−(CO)(C) group parameter derived in earlier work (Steele et al., 1991b)

2	C−(O)(H)$_3$	−42.4 × 2	−84.8
2	O−(CO)(C)	−179.71 × 2	−359.4
1	CO−(O)$_2$	?.? × 1	?.?

$$\Delta_f H^\circ_m(C_3H_6O_3, g, 298.15\ K)\ ?.? = kJ\cdot mol^{-1}$$

The value determined in this research is ($\Delta_f H^\circ_m(C_3H_6O_3$, g, 298.15 K)−(571.0 ± 0.4) kJ·mol^{-1} (Table 15). Therefore −126.8 kJ·mol^{-1} is derived for the CO−(O)$_2$ group-additivity parameter. Summation of the group-additivity parameters for diethyl carbonate gives a value of −638.5 kJ·mol^{-1} for the ideal-gas enthalpy of formation, in excellent agreement with the value of −(637.9 ± 0.8) kJ·mol^{-1} listed by Pedley et al. (1986). For diphenyl carbonate Pedley et al. (1986) assessed the ideal-gas enthalpy of formation as −(311.2 ± 8.6) kJ·mol^{-1}, which compares well with a value of −307.6 kJ·mol^{-1} calculated using the group-additivity parameters.

1,2,4-Triazolo[1,5-a]pyrimidine. No thermochemical or thermophysical property measurements on 1,2,4-triazolo[1,5-*a*]pyrimidine were found in a search of the literature from 1930 through January 1997. At this time it is not possible to determine each of the group-additivity terms and ring correction parameters in 1,2,4-triazolo[1,5-*a*]pyrimidine. There are no individual group-additivity terms derived in the literature for either of the nitrogen atoms in the molecular environments shown by the arrows:



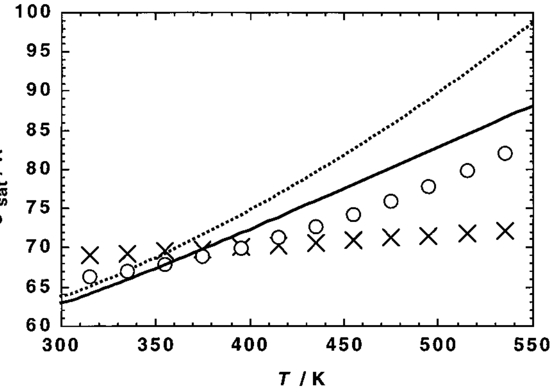


Figure 7. Comparison of literature heat capacity values for di-*n*-octyl sulfide with those obtained in this research, Table 8. The solid line represents the measurements of this research and reported in Table 8 (20.5 mg set). The dashed line denotes values obtained using the correlation of Domalski and Hearing (1990). Key: (×) Tutubalina et al. (1982); (○) Yaws et al. (1988) correlation.

Di-n-octyl Sulfide. Figure 7 compares values for the heat capacity of di-*n*-octyl sulfide found in a search of the literature with the results obtained in this research (Table 8). As would be expected, below 400 K the correlations of Yaws et al. (1988) and Domalski and Hearing (1990) are in excellent agreement with the measured values. However, above 400 K the correlations diverge to either side of the DSC measurements.

Using the group parameters (Benson, 1976; Reid et al., 1987) gives

2	$C-(C)(H)_2$	−42.2 × 2	−84.4
12	$C-(C)_2(H)_2$	−20.72 × 12	−248.6
2	$C-(S)(C)(H)_2$	−23.66 × 2	−47.3
1	$S-(C)_2$	48.19 × 1	48.2

$\Delta_f H^\circ_m(C_{16}H_{34}S, g, 298.15\ K) = -332.1\ kJ\cdot mol^{-1}$

The value determined in this research is $\Delta_f H^\circ_m(C_{16}H_{34}S, g, 298.15\ K) = -(332.8 \pm 11.0)\ kJ\cdot mol^{-1}$ (Table 15). Agreement is excellent showing than none of the group-additivity parameters used in the estimation require revision.

Tetrakis(dimethylamino)ethylene. Tetrakis(dimethylamino)ethylene has been used for many years to detect the scintillation light from gas scintillation proportional counters (Anderson, 1988). Hence values for the vapor pressure in the vicinity of ambient temperature have been measured on several occasions (Anderson, 1981, 1988; Holroyd et al., 1987). Figure 8 compares three such sets of measurements with values obtained using the Wagner equation and the parameters listed in Table 11. Note that the measurements made in this research started at 358 K, and hence the comparison is made to extrapolated values. The later measurements of Anderson (1988) appear to be an improvement over both his earlier values and those due to Holroyd et al. (1987).

A listing of the group-additivity parameters required to estimate an ideal-gas enthalpy of formation for tetrakis(dimethylamino)ethylene follows

2	$C_d-(C_d)(N)_2$	?.? × 2	?.?
4	$N-(C_d)(C)_2$	?.? × 4	?.?
8	$C-(N)(H)_3$	−42.2 × 8	−337.6
2	*cis* interactions	?.? × 2	?.?

$\Delta_f H^\circ_m(C_{10}H_{24}N_4, g, 298.15\ K) = -?.?\ kJ\cdot mol^{-1}$

The value determined in this research is $\Delta_f H^\circ_m(C_{10}H_{24}N_4, g, 298.15\ K) = (132.9 \pm 2.0)\ kJ\cdot mol^{-1}$ (Table 15). Further measurements on compounds containing one, but not all three, unknown group-additivity parameters are required to separate out each parameter. All that can be stated at present is

$$C_d-(C_d)(N)_2 + 2[N-(C_d)(C)_2] + \text{a } cis \text{ interaction} = 235.3\ kJ\cdot mol^{-1}$$

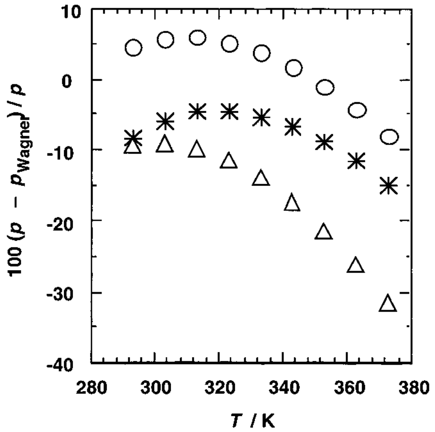


Figure 8. Comparison of literature vapor pressures for tetrakis(dimethylamino)ethylene with values obtained using the Wagner equation and the parameters listed in Table 11. The temperature range of the ebulliometric vapor pressure measurements made in this research (Table 7) was higher, 357.7 K to 485.2 K, than the literature values depicted. Key: (△) Anderson (1981); (*) Holroyd et al. (1987); (○) Anderson (1988).

Dicyclohexyl Sulfide. A search of the literature from 1930 through January 1997 failed to find any significant thermochemical or thermophysical property measurements on dicyclohexyl sulfide. Only references to measurement of the boiling point at reduced pressure obtained during synthesis and purification of the compound were obtained.

Using the group parameters (Benson, 1976; Reid et al., 1987) gives

10	$C-(C)_2(H)_2$	−20.72 × 10	−207.2
2	$C-(S)(C)_2(H)$	−11.05 × 2	−22.1
1	$S-(C)_2$	48.19 × 1	48.2

$\Delta_f H^\circ_m(C_{12}H_{22}S, g, 298.15\ K) = -181.1\ kJ\cdot mol^{-1}$

The value determined in this research is $\Delta_f H^\circ_m(C_{12}H_{22}S, g, 298.15\ K) = -(182.4 \pm 1.6)\ kJ\cdot mol^{-1}$ (Table 15). Agreement is excellent showing than none of the group-additivity parameters used in the estimation require revision.

Piperazine. Walton (1978) in his compilation lists a critical temperature of 657 K and a critical pressure of 4650 kPa for piperazine with no definition of whether they are estimates or experimentally determined values. In the research reported here a critical temperature of (661 ± 1) K was measured for piperazine by the DSC methodology and a critical pressure of 5800 kPa derived by the fitting procedures.

An enthalpy of fusion of $(26.7 \pm 0.3)\ kJ\cdot mol^{-1}$ at a melting point of 384.6 K was determined in this research (Table 8). Witschonke (1954) reported corresponding values of $22.1\ kJ\cdot mol^{-1}$ (derived at NIPER from the cryoscopic constant of 1.8 mol % per °C listed in Table 1 of Witschonke's paper) and 384.55 K, respectively.

Bedford et al. (1963) measured the energy of combustion of piperazine and derived a standard enthalpy of formation $\Delta_f H^\circ_m(C_4H_{10}N_2, cr, 298.15\ K) = -(45.6 \pm 1.6)\ kJ\cdot mol^{-1}$. The corresponding value obtained in this research is $-(40.97 \pm 0.60)\ kJ\cdot mol^{-1}$ (Table 6). In both cases, the calorimetric samples were burnt in Mylar bags and the CO_2 recoveries averaged 99.7 mol %. The probable cause for the low CO_2 recoveries was the hydroscopic nature of piperazine. At NIPER, during database compilations, it

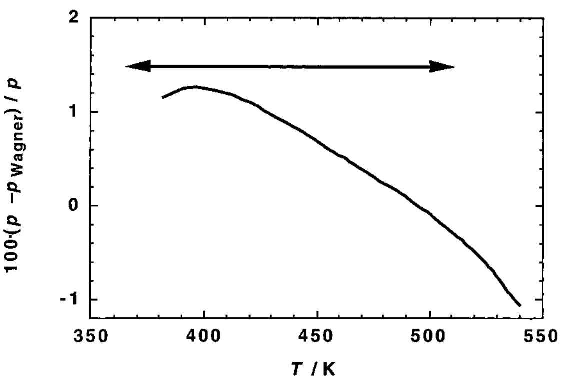


Figure 9. Comparison of Dreisbach (1959) vapor pressures (using the 109 °C to 267 °C listed Antoine constants) for hexachloroprop-1-ene with values obtained using the Wagner equation and the parameters listed in Table 11. The double-headed arrow represents the range of the measurements of this research and reported in Table 7.

has been noted that other results from Mortimer's laboratory in the early 1960s differ by upward of 6 kJ·mol^{-1} from results obtained in other reputable laboratories. This difference has been tentatively ascribed to a possible error in calibration of the bomb calorimeter.

Using the group parameters (Benson, 1976; Reid et al., 1987) gives

2	N−(C)$_2$(H)	64.5 × 2	129.0
4	C−(N)(C)(H)$_2$	−27.6 × 4	−110.4
1	ring strain	?.? × 1	?.?

$$\Delta_f H^\circ_m(C_4H_{10}N_2, g, 298.15\ K) = ?.?\ kJ \cdot mol^{-1}$$

The value determined in this research is $\Delta_f H^\circ_m$($C_4H_{10}N_2$, g, 298.15 K) = (31.6 ± 2.0) kJ·mol^{-1} (Table 15). Therefore, a ring-strain enthalpy (energy) of 13.0 kJ·mol^{-1} in piperazine is derived.

Hexachloroprop-1-ene. Dreisbach (1959) in his monograph presenting the physical properties of 476 organic straight-chain compounds lists vapor pressures, densities etc., for hexachloroprop-1-ene, all measured or estimated at Dow Chemical Company. Figure 9 compares vapor pressures derived using the listed Antoine equation with those derived using the Wagner equation and the constants listed in Table 11.

Dreisbach (1959) lists an enthalpy of vaporization of 55.6 kJ·mol^{-1} at 298.15 K for hexachloroprop-1-ene, in good agreement with the derived value of (54.77 ± 0.43) kJ·mol^{-1} obtained in this research (Table 14).

Dreisbach lists critical properties of T_c = 720 K, p_c = 3195 kPa, and ρ_c = 580 kg·m^{-3}. The corresponding derived properties from this research are T_c = 680 K, p_c = 2500 kPa, and ρ_c = 485 kg·m^{-3} (Table 11).

Using the group parameters (Benson, 1976; Reid et al., 1987) gives

1	C−(Cl)$_3$(C$_d$)	?.? × 1	?.?
1	C$_d$−(C$_d$)(C)(Cl)	−8.8 × 1	−8.8
1	C$_d$−(C$_d$)(Cl)$_2$	−7.5 × 1	−7.5
1	*cis* Cl,Cl interaction	1.3 × 1	1.3

$$\Delta_f H^\circ_m(C_3Cl_6, g, 298.15\ K) = ?.?\ kJ \cdot mol^{-1}$$

The value determined in this research is $\Delta_f H^\circ_m$(C_3Cl_6, g, 298.15 K), −(19.4 ± 0.8) kJ·mol^{-1} (Table 15). Hence, a value of −4.4 kJ·mol^{-1} is derived for the C−(Cl)$_3$(C$_d$) group-additivity parameter.

Conclusions

Revised or New Groups, Ring-Strain Energies, and Interaction Terms. From the measured ideal-gas enthalpies of formation of diethylenetriamine and *N*,*N*′-bis-(2-hydroxyethyl)ethylenediamine, respectively, a 1,4-*N*,*N* interaction term of −2.2 kJ·mol^{-1} and 1,4-N,O interaction term of −5.0 kJ·mol^{-1} were derived. A value of −126.8 kJ·mol^{-1} was derived for the CO−(O)$_2$ group-additivity parameter. A standard ideal-gas enthalpy of formation for tetrakis(dimethylamino)ethylene was derived. In the absence of other enthalpies of formation it was impossible to separate the three terms: C$_d$ −(C$_d$)(N)$_2$ + 2N−(C$_d$)(C)$_2$ + *cis* interaction = 235.3 kJ·mol^{-1}. A standard ideal-gas enthalpy of formation for 1,2,4-triazolo[1,5-*a*]pyrimidine was determined, but lack of individual group-additivity terms and ring-strain energies prevented the assignment of individual values. A strain energy term for the piperazine ring system of 13.0 kJ·mol^{-1} was derived. For the two sulfur-containing compounds (dicyclohexyl sulfide and di-*n*-octyl sulfide), agreement between the derived ideal-gas enthalpies of formation and values obtained by summation of the relevant group-additivity parameters was excellent, showing that no revision of the parameters was required. A value of −4.4 kJ·mol^{-1} was derived for the C−(Cl)$_3$(C$_d$) group-additivity parameter.

Acknowledgment

This is contribution number 367 from the Bartlesville Thermodynamics Research Laboratory. The research was accomplished when the Laboratory was part of the entity known as the National Institute for Petroleum and Energy Research (NIPER). At the time of publication of this paper, the corresponding entity is BDM Petroleum Technologies. The authors acknowledge Jim Reynolds of the NIPER Characterization Group for purification of samples. The authors also acknowledge the helpful discussions with members of the DIPPR Research Project 871 Committee, especially the Chairman, Al L. Coignet, and the then DIPPR Technical Director, T. B. Selover, Jr.

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Received for review April 22, 1997. Accepted September 4, 1997.⊗ We gratefully acknowledge the financial support of the participating companies in Design Institute for Physical Property Data (DIPPR) Project 871. This research was accomplished within the Work for Others Program at NIPER as part of the cooperative agreement with the U.S. Department of Energy DE-FC22-83FE60149.

JE9700986

⊗ Abstract published in *Advance ACS Abstracts,* October 15, 1997.