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Thermodynamic Properties and Ideal-Gas Enthalpies of Formation for Methyl Benzoate, Ethyl Benzoate, (*R*)-(+)-Limonene, *tert*-Amyl Methyl Ether, *trans*-Crotonaldehyde, and Diethylene Glycol

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Ideal-gas enthalpies of formation of methyl benzoate, ethyl benzoate, (*R*)-(+)-limonene, *tert*-amyl methyl ether, *trans*-crotonaldehyde, and diethylene glycol are reported. The standard energy of combustion and hence standard enthalpy of formation of each compound in the liquid phase has been measured using an oxygen rotating-bomb calorimeter without rotation. Vapor pressures were measured to a pressure limit of 270 kPa or the lower decomposition point for each of the six compounds using a twin ebulliometric apparatus. Liquid-phase densities along the saturation line were measured for each compound over a range of temperature (ambient to a maximum of 548 K). A differential scanning calorimeter was used to measure two-phase (liquid + vapor) heat capacities for each compound in the temperature region ambient to the critical temperature or lower decomposition point. For methyl benzoate and *tert*-amyl methyl ether, 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 each of the remaining compounds. The results of the measurements were combined to derive a series of thermophysical properties including critical temperature, critical density, critical pressure, acentric factor, enthalpies of vaporization (restricted to within ±50 K of the temperature region of the experimentally determined vapor pressures), and heat capacities along the saturation line. Wagner-type vapor-pressure equations were derived for each compound. All measured and derived values were compared with those obtained in a search of the literature. Recommended critical parameters are listed for each of the compounds studied. Group-additivity parameters, useful in the application of the Benson gas-phase 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 within the Processing and Downstream Operations section of the Advanced Oil Recovery (AOR) program and the Design Institute for Physical Property Data (DIPPR) (The Design Institute for Physical Property Data and its acronym DIPPR are registered trademarks of the American Institute of Chemical Engineers (AIChE)) of the American Institute of Chemical Engineers through some of its member industrial organizations. The work performed in the ninth 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 1994, 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 shared 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 showed that there are a number of key “small” organic compounds for which thermochemical and thermophysical properties were incomplete, in question, or just completely unknown. Data on these compounds will greatly enhance the application of group-contribution methodology[1,2] as a property-estimation tool.

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

Whereas the condensed-phase enthalpy of formation of a compound is of greatest interest in the calculation of energy balances for a given chemical process, the enthalpy of formation for the ideal-gas state is of greatest interest in the general case, where the answer can be used to derive

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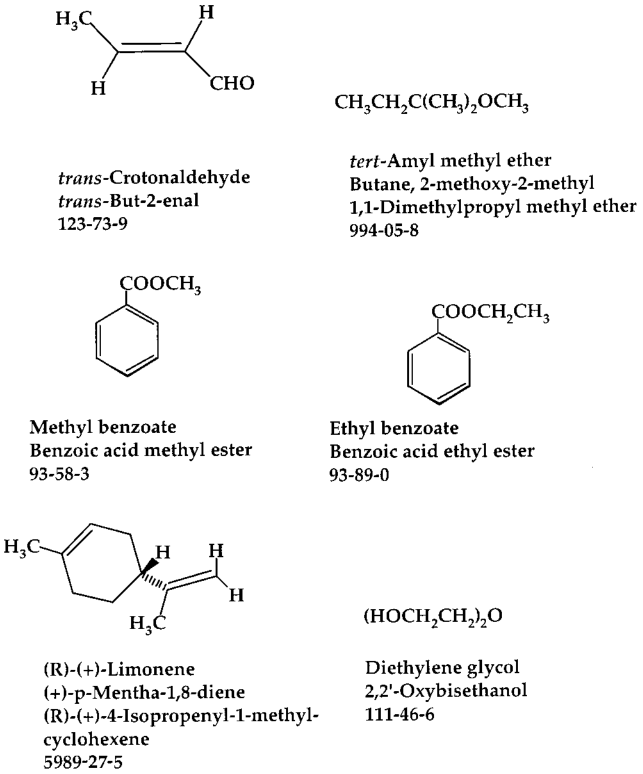

Figure 1. Structural formulas, common names, Chemical Abstracts Service names (provided by the authors), and Chemical Abstracts Service Registry Numbers (provided by the authors) for the compounds studied in this research.

a group parameter or correction factor. In the latter case, this single value can give sufficient information to enable estimations for a large group of compounds containing that molecular entity.

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

In the ninth year of the project, seven compounds were originally chosen for experimental studies. One of the compounds, 1-hydroxy-2-butanone, proved impossible to obtain in a purity greater than 99.3 mol % and, hence, was excluded from the study. The molecular structures, Chemical Abstracts Service (CAS) names (provided by the authors), commonly used trivial names, and CAS Registry Numbers (provided by the authors) of each of the remaining six 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 mol %) 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.

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

compd	$\Delta_c U^\circ_m$	vapor pressure	heat capacity	density
methyl benzoate	x	x	x	x
ethyl benzoate	x	x	x	x
(*R*)-(+)-Limonene	x	x	x	x
tert-amyl methyl ether	x	x	x	x
trans-crotonaldehyde	x	x	x	x
diethylene glycol	x	x	x	x

[a] Measurements made are denoted by x. [b] In addition, values for the critical temperature and critical density for methyl benzoate and *tert*-amyl methyl ether were determined from the DSC measurements on those compounds (critical pressures were derived using the fitting procedures). For diethylene glycol, the critical temperature obtained by Nikitin et al.[41] was used and values of the critical pressure and the critical density were derived using the fitting procedures (see text). Values for the critical temperature, critical pressure, and critical density were derived using the fitting procedures (see text) for each of the other three compounds.

Experimental Section

In this section, details are given of the apparatus and procedures used in the reported measurements. 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 mole % purity) were subjected to the calorimetric measurements. All the compounds were purchased from Aldrich Chemical Co. Gas liquid chromatography (GLC) analyses on the purchased samples gave an average purity of 99.8 mol %. All six compounds were purified by repeated spinning-band distillations. 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 and by the small differences between the boiling and condensation temperatures in the ebulliometric vapor-pressure measurements.

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. 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[3] and the gas constant, $R = 8.315\,41\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$, adopted by CODATA.[4] The platinum resistance thermometers used in these measurements were calibrated by comparison with standard thermometers whose constants were determined at the National Institute of Standards and Technology (NIST). All temperatures were measured in terms of IPTS-68 and were converted to ITS-90 using published increments.[5] 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

Table 2. Physical Properties at 298.15 K[a]

compd	ρ $kg{\cdot}m^{-3}$	$10^7(\partial V/\partial T)_p$ $m^3{\cdot}K^{-1}{\cdot}mol^{-1}$	C_p/R
methyl benzoate	1083	1.1	25.9
ethyl benzoate	1041	1.3	29.3
(*R*)-(+)-limonene	838.8	1.6	30.0
tert-amyl methyl ether	769.8	1.8	25.8
trans-crotonaldehyde	846.9	1.0	17.0
diethylene glycol	1111	0.59	27.3

[a] For each compound in the liquid phase. Values for the liquid-phase density were estimated by extrapolation of the equations listed in the footnotes tof Table 10 (see text). Values of $(\partial V/\partial T)_p$ were also estimated using the Table 10 footnote equations. The heat capacities were measured using DSC.

combustion calorimetry of organic C, H, O compounds at the National Institute for Petroleum and Energy Research have been described.[7−10] A rotating-bomb calorimeter (laboratory designation BMR II)[11] and a platinum-lined bomb (laboratory designation Pt-3b)[12] with an internal volume of 0.3934 dm^3 were used without rotation. Flexible borosilicate-glass ampules[7,13] were used to confine the samples that were liquid at 298 K. All experiments were completed within 0.01 K of $T = 298.15$ K.

NIST thermochemical benzoic acid (sample 39i) was used for calibration of the calorimeter; its specific energy of combustion is −(26434.0 ± 3.0) $J{\cdot}g^{-1}$ under certificate conditions. Conversion to standard states[14] gives −(26413.7 ± 3.0) $J{\cdot}g^{-1}$ for $\Delta_c U^\circ_m/M$, the standard specific energy of the idealized combustion reaction. The combustion measurements were performed in two separate series over a six-month time period as the purified compounds became available. Calibration experiments were interspersed with each series of measurements. Nitrogen oxides were not formed in either the calibration or compound combustion experiments because of 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 (16 776.2 ± 0.3) $J{\cdot}K^{-1}$ (mean and standard deviation of the mean) for the methyl benzoate, ethyl benzoate, *tert*-amyl methyl ether, and (*R*)-(+)-limonene measurements. In the second combustion series, ϵ(calor) was (16 776.7 ± 0.7) $J{\cdot}K^{-1}$ for the *trans*-crotonaldehyde and diethylene glycol measurements. The temperature rise in the second series was approximately 1.6 K and not the usual 2 K. This change in the “normal” procedure was made to accommodate the use of ampules of less than 1 cm^3.

The auxiliary oil (laboratory designation TKL66) had the empirical formula $CH_{1.913}$. For this material, $\Delta_c U^\circ_m/M$ was −(46042.5 ± 1.8) $J{\cdot}g^{-1}$ (mean and standard deviation). For the cotton fuse, empirical formula $CH_{1.774}O_{0.887}$, $\Delta_c U^\circ_m/M$ was −16945 $J{\cdot}g^{-1}$. Information necessary for reducing apparent mass measured in air to mass, converting the energy of the actual bomb process to that of the isothermal process, and reducing to standard states[14] is given in Table 2.

The values of density reported in Table 2 were estimated by extrapolation of the equations listed in the footnotes of Table 10. Results obtained from measurements of volumes of the ampules used in the combustion calorimetry, and their enclosed sample masses, were always within 0.2% of those listed in the table. Values of the heat capacity of each sample at 298.15 K were measured using a differential scanning calorimeter, as described later.

Carbon dioxide was recovered from the combustion products of each experiment. Anhydrous lithium hydroxide was used as adsorbent for the CO_2 recoveries.[8] The combustion products were checked for unburned carbon and other products of incomplete combustion, but none was detected. Summaries of the carbon dioxide recoveries for each calibration series and the corresponding compound energy determinations are listed in Table 3.

Table 3. Carbon Dioxide Recoveries

compd	no. of expts	% recovery[a]
benzoic acid calibration	6	99.992 ± 0.004
methyl benzoate	6	99.989 ± 0.008
ethyl benzoate	6	99.974 ± 0.006
(*R*)-(+)-limonene	6	99.972 ± 0.007
tert-amyl methyl ether	3[b]	99.982 ± 0.005
benzoic acid calibration	6	99.991 ± 0.005
trans-crotonaldehyde	5	99.957 ± 0.001
diethylene glycol	5	99.963 ± 0.008

[a] Mean and standard deviation of the mean. [b] Only three combustions out of eight were successful (see text). “Normal” statistics were used to obtain the uncertainty interval, since less than five combustions were successful (see ref 29).

Vapor-Pressure Apparatus and Procedures. The essential features of the ebulliometric equipment and procedures for vapor-pressure measurements are described in the literature.[15−17] 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.[18] In the pressure region 2 kPa to 25 kPa, decane[17] 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 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

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

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

Differential Scanning Calorimetry. The technique and methodology used in the differential scanning calorimetric measurements have been outlined.[19−24] The major difference between our measurement technique and that used by Mraw and Naas[25] is the substitution of specially designed cells (see ref 19) 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 DSC has been described.[19−24]

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

Table 4. Typical Combustion Experiments at 298.15 K for the C,H,O Compounds (p° = 101.325 KPa)[a,b]

	A	B	C	D	E	F
m'(compd)/g	1.063 849	1.031 225	0.677 826	0.769 123	0.760 708	1.060 356
m''(oil)/g	0.056 967	0.043 075	0.062 464	0.071 057	0.043 295	0. 066 859
m'''(fuse)/g	0.002 421	0.003 021	0.002 769	0.002 490	0.002 442	0.002 426
$n_i(H_2O)$/mol	0.055 35	0.055 35	0.055 35	0.055 35	0.055 35	0.055 35
m(Pt)/g	39.282	38.457	38.665	39.163	38.786	38.458
ΔT^c/K	2.001 68	2.003 36	2.001 03	1.999 12	1.600 69	1.596 79
ϵ(calor)(ΔT)/J	−33 580.5	−33 608.7	−33 569.6	−33 537.6	−26 854.4	−26 788.9
ϵ(cont)(ΔT)^d/J	−43.4	−43.1	−42.4	−43.3	−33.5	−35.5
ΔU_{ign}/J	0.8	0.8	0.8	0.8	0.8	0.8
ΔU(corr.std.states)^e/J	21.7	20.2	11.9	9.2	12.1	12.6
$-m''(\Delta_c U^\circ_m/M)$(oil)/J	2622.9	1983.3	2876.0	3271.6	1993.4	3078.4
$-m'''(\Delta_c U^\circ_m/M)$(fuse)/J	41.0	51.2	46.9	42.2	41.4	41.1
$m'(\Delta_c U^\circ_m/M)$(compd)/J	−30 937.5	−31 596.3	−30 676.4	−30 252.6	−24 840.2	−23 691.5
$(\Delta_c U^\circ_m/M)$(compd)/J·g^{-1}	−29 080.8	−30 639.7	−45 257.0	−39 339.7	−32 654.2	−22 343.0

[a] A = methyl benzoate; B = ethyl benzoate; C = (*R*)-(+)-limonene; D = *tert*-amyl methyl ether; E = *trans*-crotonaldehyde; F = diethylene glycol. [b] The symbols and abbreviations of this table are those of ref 14 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 ref 14.

Table 5. Summary of Experimental Energy of Combustion Results for T = 298.15 K and p° = 101.325 kPa[a]

compd	$\{(\Delta_c U^\circ_m/M)(\text{compd})\}/(J\cdot g^{-1})$	$\langle\{(\Delta_c U^\circ_m/M)(\text{compd})\}/(J\cdot g^{-1})\rangle$
methyl benzoate	−29 080.8, −29 086.6, −29 090.5, −29 086.4, −29 081.2, −29 086.0	−29 085.3 ± 1.5
ethyl benzoate	−30 639.7, −30 643.1, −30 636.1, −30 642.6, −30 651.1, −30 641.1	−30 642.3 ± 2.1
(*R*)-(+)-limonene	−45 257.0, −45 251.1, −45 252.4, −45 249.5, −45 255.0, −45 260.5	−45 254.2 ± 1.7
tert-amyl methyl ether[b]	−39 339.7, −39 337.0, −39 335.8	−39 337.5 ± 1.6
trans-crotonaldehyde	−32 654.2, −32 665.8, −32 661.0, −32 661.3, −32 664.3	−32 661.3 ± 2.0
diethylene glycol	−22 340.6, −22 343.3, −22 336.9, −22 336.5, −22 343.0	−22 340.1 ± 1.4

[a] The uncertainties shown are one standard deviation of the mean. [b] "Normal" statistics were used to obtain the uncertainty interval, since less than five combustions were successful (see ref 29).

Table 6. Condensed Phase Molar Thermochemical Functions at 298.15 K and p°= 101.325 kPa[a]

	$\Delta_c U^\circ_m$/kJ·mol^{-1}	$\Delta_c H^\circ_m$/kJ·mol^{-1}	$\Delta_f H^\circ_m$/kJ·mol^{-1}
methyl benzoate	−3959.98 ± 0.62	−3962.46 ± 0.62	−328.94 ± 0.74
ethyl benzoate	−4601.79 ± 0.82	−4605.51 ± 0.82	−365.23 ± 0.94
(*R*)-(+)-limonene	−6165.35 ± 0.86	−6175.26 ± 0.86	−46.48 ± 1.02
tert-amyl methyl ether	−4019.40 ± 0.54	−4026.84 ± 0.54	−335.03 ± 0.66
trans-crotonaldehyde	−2289.98 ± 0.42	−2291.76 ± 0.42	−139.77 ± 0.48
diethylene glycol	−2370.78 ± 0.46	−2373.94 ± 0.46	−629.94 ± 0.52

[a] The results listed in this table are for a stable (liquid) condensed phase at 298.15 K for each of the compounds.

at high temperatures and pressures.[26] The instrument and its operation have been described.[27] Test measurements of the density of benzene between T = 310 K and T = 523 K have been reported.[22] Results agreed with the values published by Hales and Townsend[28] 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, O compounds refer to the general reaction

$$C_aH_bO_c(\text{cr or l}) + \left(a + \frac{b}{4} - \frac{c}{2}\right)O_2(g) = aCO_2(g) + \frac{b}{2}H_2O(l) \quad (3)$$

For each compound the values of $\Delta_c U^\circ_m/M$ refer to the unit mass of sample derived from the corresponding carbon dioxide analyses of the combustion products (see Table 3). Table 6 gives derived values of the standard molar energy of combustion $\Delta_c U^\circ_m$; 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 3. The corresponding values of $\Delta_f H^\circ_m$ refer to the reaction

$$aC(\text{cr, graphite}) + \frac{b}{2}H_2(g) + \frac{c}{2}O_2(g) = C_aH_bO_c(l) \quad (4)$$

The uncertainties given in Table 6 are the "uncertainty interval."[29] 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.[30]

Vapor-Pressure Measurements. Measured vapor pressures for each of the compounds are listed in Table 7. The small differences between the boiling and condensation temperatures in the ebulliometric measurements indicated correct operation of the equipment and the high purity of the samples studied.

For five of the six compounds, the difference between the boiling and condensation temperatures (ΔT) did not increase significantly in the region above the normal boiling point. For diethylene glycol above 540 K (>170 kPa), the difference increased rapidly, reaching 0.2 K in a 15 min period. This phenomenon is normally indicative of sample decomposition. The slight increase in ΔT for *trans*-crotonaldehyde [0.011 K in the temperature region 375 K to 411 K (see Table 7)] may indicate the slow onset of decomposition for that compound.

Table 7. Summary of Vapor-Pressure Results

method[a]	T/K	p/kPa	Δp/kPa	σ/kPa	ΔT/K	method[a]	T/K	p/kPa	Δp/kPa	σ/kPa	ΔT/K
Methyl Benzoate											
decane	358.399	1.9983	−0.0001	0.0003	0.037	water	443.654	47.373	0.000	0.005	0.003
decane	373.607	4.0059	0.0003	0.0005	0.018	water	450.759	57.810	0.002	0.006	0.003
decane	380.369	5.3395	−0.0002	0.0006	0.016	water	457.913	70.110	0.002	0.007	0.002
decane	390.386	7.9948	0.0004	0.0009	0.014	water	465.105	84.503	0.000	0.008	0.001
decane	397.924	10.6555	−0.0005	0.0011	0.010	water	472.360	101.315	−0.003	0.009	0.000
decane	404.065	13.337	0.000	0.001	0.009	water	479.645	120.77	0.00	0.01	0.000
decane	410.396	16.667	0.000	0.002	0.007	water	486.979	143.23	0.00	0.01	0.000
decane	415.654	19.929	0.000	0.002	0.006	water	494.357	169.00	0.00	0.01	0.000
decane	422.598	25.028	0.000	0.002	0.006	water	501.785	198.50	0.00	0.02	−0.002
water	422.595[b]	25.026	0.000	0.003	0.005	water	509.240	232.00	0.00	0.02	−0.001
water	429.576	31.184	0.000	0.003	0.004	water	516.749	270.02	0.00	0.02	−0.001
water	436.599	38.576	0.001	0.004	0.005						
Ethyl Benzoate											
decane	369.235	2.0047	0.0000	0.0003	0.035	water	456.287	47.390	0.000	0.005	0.001
decane	384.662	3.9995	−0.0001	0.0005	0.017	water	463.557	57.833	−0.001	0.006	0.001
decane	391.572	5.3331	0.0001	0.0006	0.011	water	470.867	70.122	−0.002	0.006	0.002
decane	401.915	8.0190	−0.0001	0.0009	0.007	water	478.227	84.527	−0.002	0.008	0.001
decane	409.570	10.6694	−0.0004	0.0011	0.005	water	485.638	101.318	−0.002	0.009	0.001
decane	415.797	13.333	0.001	0.001	0.004	water	493.103	120.81	0.00	0.01	0.002
decane	422.298	16.678	0.000	0.002	0.003	water	500.601	143.25	0.00	0.01	0.003
decane	427.658	19.934	0.000	0.002	0.002	water	508.132	168.96	0.01	0.01	0.004
decane	434.751	25.029	−0.001	0.002	0.002	water	515.739	198.46	0.00	0.02	0.002
water	434.737[b]	25.020	0.001	0.003	0.002	water	523.383	232.01	0.00	0.02	0.004
water	441.892	31.194	0.000	0.003	0.001	water	531.055	269.97	0.00	0.02	0.008
water	449.066	38.581	0.001	0.004	0.002						
(*R*)-(+)−Limonene											
decane	338.514	1.9975	0.0000	0.0003	0.029	water	422.293	47.367	0.000	0.005	0.004
decane	353.309	3.9952	0.0005	0.0005	0.013	water	429.339	57.812	0.001	0.006	0.005
decane	359.988	5.3399	−0.0004	0.0007	0.012	water	436.437	70.116	0.000	0.007	0.006
decane	369.825	8.0018	−0.0003	0.0009	0.010	water	443.580	84.514	0.000	0.008	0.006
decane	377.256	10.6788	−0.0002	0.0012	0.008	water	450.784	101.308	−0.001	0.009	0.006
decane	383.196	13.319	0.000	0.001	0.007	water	458.036	120.76	0.00	0.01	0.005
decane	389.438	16.652	0.000	0.002	0.006	water	465.341	143.20	0.00	0.01	0.005
decane	394.660	19.942	0.000	0.002	0.006	water	472.693	168.95	0.00	0.01	0.006
decane	401.477	25.020	0.000	0.002	0.005	water	480.112	198.43	0.00	0.02	0.005
water	401.462[b]	25.009	0.002	0.003	0.005	water	487.573	231.95	0.00	0.02	0.006
water	408.359	31.168	0.001	0.003	0.005	water	495.083	269.93	0.01	0.02	0.007
water	415.301	38.558	0.002	0.004	0.005						
tert−Amyl Methyl Ether											
decane	309.373	16.678	−0.001	0.002	0.016	water	353.589	84.503	0.013	0.008	0.018
decane	313.604	19.951	0.000	0.002	0.017	water	359.503	101.299	0.006	0.010	0.018
decane	319.161	25.028	0.003	0.003	0.017	water	365.459	120.76	0.01	0.01	0.019
water	319.142[b]	25.012	0.006	0.003	0.017	water	371.463	143.18	−0.01	0.01	0.019
water	324.773	31.170	0.005	0.004	0.017	water	377.513	168.96	0.00	0.01	0.019
water	330.449	38.550	−0.010	0.004	0.017	water	383.607	198.39	0.00	0.02	0.020
water	336.163	47.358	−0.007	0.005	0.018	water	389.762	231.97	0.00	0.02	0.021
water	341.924	57.799	−0.001	0.006	0.018	water	395.948	269.95	0.00	0.02	0.021
water	347.735	70.096	−0.002	0.007	0.018						
trans-Crotonaldehyde											
decane	314.373	10.667	0.000	0.001	0.017	water	363.573	70.092	−0.001	0.007	0.010
decane	319.418	13.344	−0.004	0.002	0.017	water	369.468	84.506	−0.004	0.008	0.010
decane	324.602	16.665	−0.001	0.002	0.013	water	375.387	101.288	0.005	0.009	0.011
decane	328.897	19.909	0.000	0.002	0.012	water	381.347	120.76	0.00	0.01	0.012
decane	334.616	25.025	0.007	0.003	0.012	water	387.337	143.20	0.00	0.01	0.013
water	334.614[b]	25.021	0.004	0.003	0.012	water	393.365	169.00	0.00	0.01	0.015
water	340.353	31.185	0.002	0.004	0.011	water	399.414	198.43	0.00	0.02	0.017
water	346.111	38.569	0.000	0.004	0.011	water	405.498	231.94	0.00	0.02	0.020
water	351.895	47.365	−0.001	0.005	0.011	water	411.621	269.96	0.00	0.02	0.022
water	357.718	57.799	−0.002	0.006	0.010						
Diethylene Glycol											
decane	409.743[c]	2.0036	0.0017	0.0003	0.024	water	478.487	31.177	0.000	0.003	0.005
decane	424.628	4.0014	0.0002	0.0005	0.025	water	485.134	38.576	0.002	0.004	0.006
decane	431.195	5.3266	−0.0002	0.0007	0.019	water	491.776	47.365	−0.001	0.005	0.008
decane	440.941	7.9828	0.0001	0.0009	0.012	water	498.443	57.797	0.006	0.006	0.009
decane	448.241	10.6484	−0.0006	0.0012	0.010	water	505.144	70.100	0.000	0.007	0.010
decane	454.144	13.327	0.000	0.001	0.009	water	511.854	84.495	−0.003	0.008	0.011
decane	460.231	16.664	0.000	0.002	0.008	water	518.600	101.305	−0.010	0.009	0.015
decane	465.250	19.924	0.000	0.002	0.007	water	525.360	120.78	−0.01	0.01	0.020
decane	471.852	25.012	0.001	0.002	0.006	water	532.117	143.20	0.02	0.01	0.024
water	471.866[b]	25.024	0.002	0.003	0.006	water	538.908	168.94	0.00	0.01	0.031

[a] Decane or water refers to which material was used as the standard in the reference ebulliometer, T is the condensation temperature of the sample, the pressure p was calculated from the condensation temperature of the reference substance, Δp is the difference of the value of pressure, calculated with eq 6 and the parameters listed in Table 11, from the observed value of pressure, σ is the propagated error calculated from eqs 1 and 2, and 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.

Differential Scanning Calorimetry. Table 8 lists the two-phase (liquid + vapor) heat capacities $C_{x,\mathrm{m}}^{\mathrm{II}}$ determined by DSC for each compound 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. In this research, the thermal expansion of the cells was expressed as

$$V_x(T)/V_x(298.15\ \mathrm{K}) = 1 + ay + by^2 \tag{5}$$

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

For methyl benzoate and *tert*-amyl methyl ether, measurements in 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 each case, 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 5, and the measured temperatures at which conversion to a single phase was observed.

Critical temperatures and critical densities were derived graphically for methyl benzoate and *tert*-amyl methyl ether 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 by Knipmeyer et al.[21] The rapid heating method was used previously for critical temperature and critical density determinations for 2-aminobiphenyl,[31] dibenzothiophene,[32] carbazole, and benzofuran.[24]

For each of the other four compounds, extensive sample decomposition precluded attainment of heat-capacity measurements above the highest listed temperatures reported in Table 8.

Densitometry. Measured densities for each compound 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 $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ at 298.15 K is the only value necessary to obtain $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}$ (g, 298.15 K), the benefit of 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.

Fitting Procedures. For all the compounds, except diethylene glycol, the same general fitting procedures were used. The number of fitting parameters differed depending on whether a critical temperature could be determined experimentally. For *tert*-amyl methyl ether and methyl benzoate, critical temperatures were determined from the DSC measurements and, hence, only the critical pressure p_{c} was included in the variables. For ethyl benzoate, (*R*)-(+)-limonene, and *trans*-crotonaldehyde, extensive high-temperature sample decomposition precluded critical temperature measurements and, therefore, both T_{c} and p_{c} were included as variables. 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 $C_{x,\mathrm{m}}^{\mathrm{II}}$ given in Table 8. A summary of the procedure follows.

The Wagner equation[33] in the formulation given by Ambrose and Walton[34]

$$\ln(p/p_{\mathrm{c}}) = (1/T_{\mathrm{r}})[AY + BY^{1.5} + CY^{2.5} + DY^5] \tag{6}$$

where $T_{\mathrm{r}} = T/T_{\mathrm{c}}$ and $Y = (1 - T_{\mathrm{r}})$, was fitted to the measured vapor pressures (Table 7). As noted above, the critical pressure [and, for ethyl benzoate, (*R*)-(+)-limonene, and *trans*-crotonaldehyde, the critical temperature T_{c}] was (were) included in the variables. The vapor-pressure fitting procedure including the minimization equation and the relative weightings is detailed in ref 24.

For fitting the two-phase heat capacities obtained in a cell of volume V_x, the experimental $C_{x,\mathrm{m}}^{\mathrm{II}}$ values (Table 8) were converted to $C_{V.\mathrm{m}}^{\mathrm{II}}$ by means of eq 5 for the cell expansion and the vapor-pressure fit for $(\partial p/\partial T)_{\mathrm{sat}}$,

$$C_{V.\mathrm{m}}^{\mathrm{II}} = C_{x,\mathrm{m}}^{\mathrm{II}} - T/n\{(\partial V_x/\partial T)_x(\partial p/\partial T)_{\mathrm{sat}}\} \tag{7}$$

The values of $C_{V.\mathrm{m}}^{\mathrm{II}}$ 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 ref 24). The functional form chosen for variation of the second derivative of the chemical potential with temperature was

$$(\partial^2\mu/\partial T^2)_{\mathrm{sat}}/(\mathrm{J{\cdot}K^{-2}{\cdot}mol^{-1}}) = \sum_{i=0}^{n} b_i(1 - T/T_{\mathrm{c}})^i \tag{8}$$

For compounds where sufficient information was available to evaluate reliably $(\partial^2\mu/\partial T^2)_{\mathrm{sat}}$ (e.g., benzene[35] and toluene[36]), four terms (i.e., expansion to $n = 3$) were required to represent the function.[24] Thus, four terms were used in this research. Estimates of liquid-phase molar volumes V_{m}(l) for each compound were made using the equations listed in the footnotes of Table 10. In earlier work in this project, the estimates were made with the extended corresponding-states equation of Riedel[37] as formulated by Hales and Townsend:[28]

$$(\rho/\rho_{\mathrm{c}}) = 1.0 + 0.85Y + (1.6916 + 0.9846\omega)Y^{1/3} \tag{9}$$

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. However, often eq 9 was not a good representation of the measured densities. A power series of the type

$$\rho = \rho_{\mathrm{c}} + A(1 - T_{\mathrm{r}})^{1/3} + B(1 - T_{\mathrm{r}})^{2/3} + C(1 - T_{\mathrm{r}}) + ... \tag{10}$$

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[38−40] and was used in this study; see Table 10.

The above procedures were not used for diethylene glycol. Diethylene glycol decomposed well below the critical region, and the measured $C_{x,\mathrm{m}}^{\mathrm{II}}$ values (Table 8) were virtually independent of cell filling. The absence of measured critical properties precluded application of the methodology used in the previous section. Literature estimates[41] of the critical temperature and critical density were used in the fitting procedures for the Wagner vapor-pressure equation, allowing the critical pressure to be a variable.

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 results are given in Table 7 (column 4, labeled Δp). Details

Table 8. Two-Phase (Liquid + Vapor) Heat Capacities

Methyl Benzoate

	$C^{\mathrm{II}}_{\mathrm{X,m}}/R$				$C^{\mathrm{II}}_{\mathrm{X,m}}/R$		
T/K	m/g = 0.011 511 $V_c{}^a = 0.0522$	m/g = 0.016 030 $V_c{}^a = 0.0522$	m/g = 0.021 114 $V_c{}^a = 0.0522$	T/K	m/g = 0.011 511 $V_c{}^a = 0.0522$	m/g = 0.016 030 $V_c{}^a = 0.0522$	m/g = 0.021 114 $V_c{}^a = 0.0522$
315.0	27.4	27.0	26.6	515.0	38.2	36.7	36.1
335.0	27.8	27.8	27.5	535.0	39.7	38.2	37.1
355.0	28.9	28.5	28.4	555.0	41.3	39.4	38.2
375.0	29.6	29.5	29.4	575.0	43.0	40.8	39.3
395.0	31.1	30.8	30.1	595.0	43.7	42.0	40.1
415.0	32.0	31.5	31.1	615.0	46.1	43.5	41.2
435.0	33.0	32.6	32.1	635.0	48.6	44.8	42.7
455.0	34.5	33.6	33.0	655.0	50.2	47.9	44.3
475.0	35.8	34.9	34.0	675.0	53.8	51.3	46.6
495.0	36.7	36.0	35.0	695.0[b]	49.3	50.2	45.1

Ethyl Benzoate

	$C^{\mathrm{II}}_{\mathrm{X,m}}/R$				$C^{\mathrm{II}}_{\mathrm{X,m}}/R$		
T/K	m/g = 0.010 439 $V_c{}^a = 0.0522$	m/g = 0.014 109 $V_c{}^a = 0.0522$	m/g = 0.021 048 $V_c{}^a = 0.0522$	T/K	m/g = 0.010 439 $V_c{}^a = 0.0522$	m/g = 0.014 109 $V_c{}^a = 0.0522$	m/g = 0.021 048 $V_c{}^a = 0.0522$
315.0	29.6	30.1	30.0	455.0	38.0	37.5	37.3
335.0	30.8	30.8	30.8	475.0	39.3	38.7	38.5
355.0	31.8	31.9	32.0	495.0	40.7	39.7	39.8
375.0	32.6	32.9	33.0	515.0	42.2	41.3	40.8
395.0	34.0	34.0	34.1	535.0	43.9	42.7	42.0
415.0	35.0	35.1	35.1	555.0	45.8	44.1	43.0
435.0	36.7	36.0	36.2	575.0	47.7	45.5	44.1

(*R*)-(+)-Limonene

	$C^{\mathrm{II}}_{\mathrm{X,m}}/R$				$C^{\mathrm{II}}_{\mathrm{X,m}}/R$		
T/K	m/g = 0.009279 $V_c{}^a = 0.0522$	m/g = 0.015524 $V_c{}^a = 0.0522$	m/g = 0.019836 $V_c{}^a = 0.0522$	T/K	m/g = 0.009279 $V_c{}^a = 0.0522$	m/g = 0.015524 $V_c{}^a = 0.0522$	m/g = 0.019836 $V_c{}^a = 0.0522$
315.0	31.7	31.7	31.6	475.0	44.1	43.5	43.1
335.0	32.5	33.1	32.8	495.0	46.0	45.3	44.2
355.0	33.9	34.6	34.1	515.0	48.2	47.2	45.4
375.0	34.9	35.9	35.6	535.0	50.6	49.1	47.0
395.0	36.8	37.3	37.0	555.0	53.3	50.1	48.5
415.0	38.4	38.9	38.5	575.0	55.6	52.4	49.9
435.0	40.2	40.3	40.0	595.0	58.3	54.6	52.1
455.0	42.1	42.0	41.4	615.0	61.2	58.3	55.9

tert-Amyl Methyl Ether

	$C^{\mathrm{II}}_{\mathrm{X,m}}/R$				$C^{\mathrm{II}}_{\mathrm{X,m}}/R$		
T/K	m/g = 0.008268 $V_c{}^a = 0.0522$	m/g = 0.013941 $V_c{}^a = 0.0522$	m/g = 0.019041 $V_c{}^a = 0.0522$	T/K	m/g = 0.008268 $V_c{}^a = 0.0522$	m/g = 0.013941 $V_c{}^a = 0.0522$	m/g = 0.019041 $V_c{}^a = 0.0522$
315.0	26.8	26.6	26.5	435.0	37.2	34.6	33.9
335.0	28.3	27.8	27.7	455.0	39.4	36.1	35.1
355.0	30.0	28.9	28.7	475.0	41.8	37.3	36.4
375.0	31.2	30.3	29.8	495.0	44.6	39.3	38.1
395.0	33.4	31.6	31.0	515.0	48.5	42.2	40.8
415.0	35.3	33.1	32.4	535.0[b]	35.2	41.9	38.1

trans-Crotonaldehyde

	$C^{\mathrm{II}}_{\mathrm{X,m}}/R$				$C^{\mathrm{II}}_{\mathrm{X,m}}/R$		
T/K	m/g = 0.010594 $V_c{}^a = 0.0522$	m/g = 0.015687 $V_c{}^a = 0.0522$	m/g = 0.020195 $V_c{}^a = 0.0522$	T/K	m/g = 0.010594 $V_c{}^a = 0.0522$	m/g = 0.015687 $V_c{}^a = 0.0522$	m/g = 0.020195 $V_c{}^a = 0.0522$
315.0	18.0	17.5	17.7	435.0	22.9	21.7	21.4
335.0	18.6	18.2	18.1	455.0	24.1	22.6	22.2
355.0	19.2	18.8	18.7	475.0	25.8	23.5	23.1
375.0	20.0	19.2	19.4	495.0	27.3	24.4	23.9
395.0	21.0	20.1	20.0	515.0	28.9	25.8	25.0
415.0	22.0	21.0	20.7	535.0	31.3	27.1	26.6

Diethylene Glycol

	$C^{\mathrm{II}}_{\mathrm{X,m}}/R$				$C^{\mathrm{II}}_{\mathrm{X,m}}/R$		
T/K	m/g = 0.010374 $V_c{}^a = 0.0522$	m/g = 0.016698 $V_c{}^a = 0.0522$	m/g = 0.021912 $V_c{}^a = 0.0522$	T/K	m/g =0.010374 $V_c{}^a = 0.0522$	m/g = 0.016698 $V_c{}^a = 0.0522$	m/g = 0.021912 $V_c{}^a = 0.0522$
315.0	29.2	28.8	28.3	375.0	31.7	31.2	31.0
335.0	30.0	29.6	29.3	395.0	32.8	32.1	31.8
355.0	30.8	30.4	30.2	415.0	33.7	33.1	32.7

Table 8 (Continued)

Diethylene Glycol

	$C^{\mathrm{II}}_{X,\mathrm{m}}/R$				$C^{\mathrm{II}}_{X,\mathrm{m}}/R$		
T/K	m/g = 0.010374 $V_c{}^a$ = 0.0522	m/g = 0.016698 $V_c{}^a$ = 0.0522	m/g = 0.021912 $V_c{}^a$ = 0.0522	T/K	m/g =0.010374 $V_c{}^a$ = 0.0522	m/g = 0.016698 $V_c{}^a$ = 0.0522	m/g = 0.021912 $V_c{}^a$ = 0.0522
435.0	34.7	33.7	33.7	555.0[c]	40.8	38.5	37.9
455.0	35.6	34.5	34.2	575.0[c]	42.3	39.5	38.7
475.0	36.2	35.3	35.0	595.0[c]	43.7	40.4	39.4
495.0	37.3	36.2	35.8	615.0[c]	45.0	41.1	39.8
515.0	38.3	36.8	36.5	635.0[c]	47.9	42.8	41.3
535.0[c]	39.5	37.8	37.3	655.0[c]	56.1	52.6	51.0

[a] Volume of 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. [c] Values may include enthalpies of compound decomposition (see text).

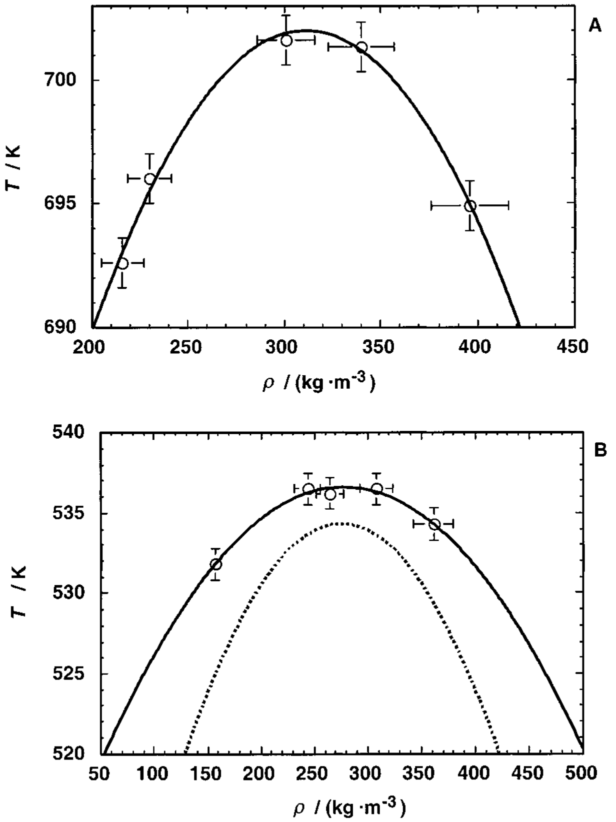

Figure 2. Vapor−liquid coexistence in the region of the critical point. In both figures the curves are drawn as an aid to the eye and do not represent any theoretically valid equation. The crosses span the range of uncertainty. (A) methyl benzoate; (B) *tert*-amyl methyl ether. In part B the dashed line represents the previous results obtained at NIPER within the DIPPR 821 Project for Project year 1991.[23]

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
Methyl Benzoate		*tert*-Amyl Methyl Ether	
216.0	692.6	156.9	531.8
229.9	696.0	243.8	536.5
300.7	701.6	264.3	536.2
339.8	701.3	307.5	536.5
396.2	694.9	361.1	534.3

of the fits of the measured liquid-phase densities to eq 10 are given in Table 10, [100(ρ − ρ_{calc})/ρ], and the listed footnotes of that table.

For each of the compounds except diethylene glycol, values of $C^{\mathrm{II}}_{V,\mathrm{m}}(\rho{=}\rho_{\mathrm{sat}})$ were derived from the parameters listed in Table 11 and corresponding $C_{\mathrm{sat,m}}$ values derived using eq 5 of ref 24. The results for $C_{\mathrm{sat,m}}/R$ are reported in Table 12. The estimated uncertainty in these values is 1%.

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

T/K	ρ/kg·m^{-3}	100(ρ − ρ_{calc})/ρ	T/K	ρ/kg·m^{-3}	100(ρ − ρ_{calc})/ρ
Methyl Benzoate[b]			Ethyl Benzoate[c]		
323.135	1058.9	0.04	323.135	1017.0	0.02
348.130	1034.9	−0.01	348.130	993.9	−0.01
373.124	1010.2	−0.05	373.124	970.1	−0.03
398.117	985.6	−0.02	398.117	945.9	−0.04
423.115	960.4	0.02	423.115	921.3	−0.01
448.112	933.5	0.00	448.112	895.8	0.02
473.109	906.2	0.04	473.109	869.1	0.01
498.110	877.1	0.03	498.110	841.4	0.04
523.109	846.1	−0.04	523.109	811.4	−0.05
(R)-(+)-Limonene[d]			*tert*-Amyl Methyl Ether[e]		
323.135	818.4	0.02	323.135	743.6	0.02
348.130	798.6	−0.02	348.130	717.8	−0.01
373.124	778.3	−0.04	373.124	691.1	−0.01
398.117	757.8	0.01	398.117	663.1	0.05
423.115	736.3	0.05	423.115	632.1	−0.01
448.112	712.8	−0.03	448.112[f]	596.6	−0.32
trans-Crotonaldehyde[g]			Diethylene Glycol[h]		
323.135	821.0	0.00	323.135	1094.2	0.03
348.130	794.4	0.00	348.130	1075.4	−0.02
373.124	767.1	0.00	373.124	1056.2	−0.05
398.117	738.8	0.00	398.117	1037.0	0.00
			423.115	1016.6	0.02
			448.112	995.2	0.05
			473.109	971.7	−0.04
			498.110[f]	946.1	−0.21

[a] ρ_{calc} values were calculated using eq 10 and the parameters listed below. [b] $\rho_{\mathrm{calc}} = 334.2 + 669.1(1 - T/702)^{1/3} + 36.0(1 - T/702)^{2/3} + 288.5(1 - T/702)$. [c] $\rho_{\mathrm{calc}} = 316.6 + 632.4(1 - T/707)^{1/3} + 36.2(1 - T/707)^{2/3} + 295.2(1 - T/707)$. [d] $\rho_{\mathrm{calc}} = 266.5 + 526.1(1 - T/655)^{1/3} + 85.7(1 - T/655)^{2/3} + 153.6(1 - T/655)$. [e] $\rho_{\mathrm{calc}} = 263.5 + 640.3(1 - T/537)^{1/3} - 264.6(1 - T/537)^{2/3} + 381.8(1 - T/537)$. [f] Values not included in fit because of probable compound decomposition. [g] $\rho_{\mathrm{calc}} = 284.3 + 779.7(1 - T/565)^{1/3} - 573.1(1 - T/565)^{2/3} + 641.3(1 - T/565)$. [h] $\rho_{\mathrm{calc}} = 319.4 + 643.9(1 - T/753)^{1/3} + 482.5(1 - T/753)^{2/3} - 160.75(1 - T/753)$.

Enthalpies of Vaporization. The enthalpies of vaporization $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ listed in Table 13 were derived from the Wagner-equation fits (Table 11) using the Clapeyron equation:

$$\mathrm{d}p/\mathrm{d}T = \Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}/(T\Delta_{\mathrm{l}}^{\mathrm{g}}V_{\mathrm{m}}) \qquad (11)$$

where $\Delta_{\mathrm{l}}^{\mathrm{g}}V_{\mathrm{m}}$ is the increase in molar volume from the liquid to the real vapor. For each of these compounds, estimates of the liquid-phase volumes were made using eq 10 and the parameters given in Table 10. Vapor-phase volumes were calculated with the virial equation of state

Table 11. Parameters for Eqs 6 and 8, Critical Constants, and Acentric Factors[a]

Methyl Benzoate				Ethyl Benzoate			
A	−8.712 34	b_0	−0.419 60	A	−8.852 24	b_0	−0.443 03
B	3.438 76	b_1	−0.705 17	B	3.425 96	b_1	−1.174 68
C	−4.216 95	b_2	1.034 06	C	−4.508 94	b_2	2.351 11
D	−3.201 47	b_3	−1.260 10	D	−3.477 50	b_3	−2.487 77
T_c	702 K	p_c	4020 kPa	T_c	707 K	p_c	3480 kPa
ρ_c	334 kg·m^{-3}	ω	0.4048	ρ_c	317 kg·m^{-3}	ω	0.4415
(*R*)-(+)-Limonene				*tert*-Amyl Methyl Ether			
A	−8.017 89	b_0	−0.660 07	A	−9.310 27	b_0	−0.395 89
B	2.159 18	b_1	0.0	B	5.516 74	b_1	−1.773 80
C	−3.208 46	b_2	−1.132 66	C	−5.520 01	b_2	5.093 13
D	−3.534 87	b_3	0.994 00	D	−1.354 83	b_3	−6.143 72
T_c	655 K	p_c	2900 kPa	T_c	537 K	p_c	3550 kPa
ρ_c	267 kg·m^{-3}	ω	0.3757	ρ_c	264 kg·m^{-3}	ω	0.3413
trans-Crotonaldehyde				Diethylene Glycol			
A	−7.245 31	b_0	−0.337 39	A	−11.905 74		
B	0.638 83	b_1	−0.016 76	B	8.280 76		
C	−1.530 55	b_2	−0.811 00	C	−10.482 05		
D	−3.123 88	b_3	0.491 64	D	−1.475 86		
T_c	565 K	p_c	3870 kPa	T_c	753 K	p_c	6250 kPa
ρ_c	284 kg·m^{-3}	ω	0.3349	ρ_c	319 kg·m^{-3}	ω	0.6946

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

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	$C_{\mathrm{sat,m}}/R$	T/K	$C_{\mathrm{sat,m}}/R$
		Methyl Benzoate			
300.0	26.0	440.0	32.2	580.0	38.2
320.0	27.0	460.0	33.1	600.0	39.2
340.0	27.9	480.0	33.9	620.0	40.2
360.0	28.7	500.0	34.8	640.0	41.6
380.0	29.6	520.0	35.6	660.0	43.9
400.0	30.5	540.0	36.5		
420.0	31.4	560.0	37.3		
		Ethyl Benzoate			
300.0	29.4	440.0	36.5	580.0	43.4
320.0	30.4	460.0	37.5	600.0	44.2
340.0	31.4	480.0	38.6	620.0	45.0
360.0	32.4	500.0	39.6	640.0	46.0
380.0	33.4	520.0	40.6	660.0	47.5
400.0	34.4	540.0	41.6	680.0	50.9
420.0	35.4	560.0	42.5		
		(*R*)-(+)-Limonene			
300.0	30.1	420.0	38.7	540.0	46.8
320.0	31.7	440.0	40.0	560.0	48.6
340.0	33.2	460.0	41.3	580.0	50.6
360.0	34.7	480.0	42.6	600.0	53.2
380.0	36.0	500.0	43.9	620.0	56.9
400.0	37.4	520.0	45.3		
		tert-Amyl Methyl Ether			
300.0	25.9	380.0	29.6	460.0	34.2
320.0	26.6	400.0	30.8	480.0	35.3
340.0	27.5	420.0	32.0	500.0	37.3
360.0	28.5	440.0	33.1		
		trans-Crotonaldehyde			
300.0	17.1	400.0	19.7	500.0	23.6
320.0	17.7	420.0	20.3	520.0	25.2
340.0	18.2	440.0	20.9	540.0	27.8
360.0	18.7	460.0	21.6		
380.0	19.2	480.0	22.5		

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

T/K	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$/kJ·mol^{-1}	T/K	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$/kJ·mol^{-1}
	Methyl Benzoate		
298.15[b]	55.49 ± 0.22	440.0	45.80 ± 0.23
300.0[b]	55.36 ± 0.22	460.0	44.42 ± 0.32
320.0[b]	53.90 ± 0.20	480.0	42.98 ± 0.42
340.0[b]	52.50 ± 0.18	500.0	41.46 ± 0.53
360.0	51.13 ± 0.17	520.0[b]	39.87 ± 0.70
380.0	49.80 ± 0.17	540.0[b]	38.2 ± 0.86
400.0	48.47 ± 0.17	560.0[b]	36.4 ± 1.1
420.0	47.15 ± 0.20		
	Ethyl Benzoate		
298.15[b]	58.66 ± 0.25	460.0	46.71 ± 0.30
320.0[b]	56.92 ± 0.22	480.0	45.19 ± 0.38
340.0[b]	55.39 ± 0.20	500.0	43.60 ± 0.52
360.0[b]	53.91 ± 0.20	520.0	41.93 ± 0.67
380.0	52.46 ± 0.18	540.0[b]	40.14 ± 0.83
400.0	51.03 ± 0.18	560.0[b]	38.3 ± 1.0
420.0	49.61 ± 0.20	580.0[b]	36.2 ± 1.3
440.0	48.18 ± 0.23		
	(*R*)-(+)-Limonene		
290.0[b]	50.16 ± 0.18	430.0	40.87 ± 0.30
298.15[b]	49.59 ± 0.18	450.0	39.42 ± 0.42
310.0[b]	48.77 ± 0.17	470.0	37.89 ± 0.55
330.0[b]	47.43 ± 0.17	490.0	36.23 ± 0.70
350.0	46.12 ± 0.15	510.0[b]	34.45 ± 0.88
370.0	44.84 ± 0.15	530.0[b]	32.5 ± 1.1
390.0	43.54 ± 0.18	550.0[b]	30.4 ± 1.3
410.0	42.23 ± 0.23		
	tert-Amyl Methyl Ether		
260.0[b]	36.54 ± 0.12	360.0	30.69 ± 0.28
280.0[b]	35.44 ± 0.12	380.0	29.37 ± 0.40
298.15[b]	34.42 ± 0.12	400.0[b]	27.97 ± 0.53
300.0[b]	34.31 ± 0.12	420.0[b]	26.50 ± 0.70
320.0	33.16 ± 0.15	440.0[b]	24.9 ± 0.9
340.0	31.95 ± 0.20		
	trans-Crotonaldehyde		
260.0[b]	39.64 ± 0.13	360.0	34.51 ± 0.22
280.0[b]	38.61 ± 0.12	380.0	33.35 ± 0.32
298.15[b]	37.70 ± 0.12	400.0	32.05 ± 0.45
300.0[b]	37.61 ± 0.12	420.0[b]	30.61 ± 0.60
320.0	36.61 ± 0.13	440.0[b]	28.98 ± 0.78
340.0	35.59 ± 0.17	460.0[b]	27.1 ± 1.0
	Diethylene Glycol		
298.15[b]	78.56 ± 0.60	480.0	61.13 ± 0.27
360.0[b]	72.60 ± 0.35	500.0	59.16 ± 0.32
380.0[b]	70.69 ± 0.32	520.0	57.15 ± 0.38
400.0[b]	68.78 ± 0.30	540.0	55.08 ± 0.50
420.0	66.88 ± 0.27	560.0[b]	52.96 ± 0.65
440.0	64.98 ± 0.25	580.0[b]	50.79 ± 0.83
460.0	63.07 ± 0.25	600.0[b]	48.5 ± 1.1

[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 equation.

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

	$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}(\mathrm{l})$	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}$	$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}(\mathrm{g})$
compd	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}
methyl benzoate	−328.94 ± 0.74	55.49 ± 0.22	−273.45 ± 0.77
ethyl benzoate	−365.23 ± 0.94	58.66 ± 0.25	−306.57 ± 0.97
(*R*)-(+)-limonene	−46.48 ± 1.02	49.61 ± 0.18	3.09 ± 1.04
tert-amyl methyl ether	−335.03 ± 0.66	34.64 ± 0.12	−300.39 ± 0.67
trans-crotonaldehyde	−139.77 ± 0.48	37.83 ± 0.12	−101.94 ± 0.49
diethylene glycol	−629.94 ± 0.52	78.56 ± 0.60	−551.38 ± 0.79

truncated at the third virial coefficient. Second virial coefficients were estimated with the corresponding-states equation of Pitzer and Curl,[42] and third virial coefficients were estimated with the corresponding-states method of Orbey and Vera.[43] This formulation for third virial coefficients was applied successfully in analyses of the thermodynamic properties of benzene and toluene.[22] 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%.

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 Table 14 the enthalpies of vaporization, $\Delta_l^g H_m$, have been converted to the corresponding values for the ideal gas, $\Delta_l^g H_m^\circ$, using the following estimates of ($H^\circ - H$) in kilojoules per mole for the real gas at its saturation vapor pressure at 298.15 K: (*R*)-(+)-limonene, 0.02; *tert*-amyl methyl ether, 0.22; *trans*-crotonaldehyde, 0.13. The corrections for the less volatile compounds were calculated to be negligibly small. These corrections were calculated using eq 20 of ref 27 and the virial coefficients derived above.

Discussion

General Comments. In the next 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.[44] Comparison of liquid-phase density measurements is restricted to those reported for a temperature range of at least 20 K.

Methyl Benzoate. A search of the literature through June 1996 revealed two previous determinations of the energy of combustion and hence enthalpy of formation of methyl benzoate. The two reports are by Stohmann et al. in 1887[45] (probably just of historic interest) and by Hall and Baldt in 1971.[46] Hall and Baldt report a value for the energy of combustion of methyl benzoate, $\Delta_c U_m^\circ = -(3945.4 \pm 2.4)\ \mathrm{kJ{\cdot}mol^{-1}}$. The result is less negative than the value, $\Delta_c H_m^\circ = -(3959.98 \pm 0.62)\ \mathrm{kJ{\cdot}mol^{-1}}$, obtained in this research (Table 6). Hall and Baldt list a purity of >99.9% for their sample, and the work would appear to be carefully done. However, in Table 16 of ref 40, it is shown that, for later work on bicyclo[2,2,1]heptane, Hall et al.[47] obtained an enthalpy of combustion also less negative (~15 kJ·mol^{-1}) than that obtained at NIPER. In addition, use of the group-additivity parameters derived in that report[40] from the measurements on butyl acrylate unveil a similar (~29 kJ·mol^{-1}) error in the derived ideal-gas enthalpy of formation for methyl acrylate obtained by Hall and Baldt.[46] An explanation of the differences obtained in the du Pont Central Research Department work is lacking at present. Among the possibilities may be an error in the calibration of the bomb calorimeter resulting in the use of a wrong ϵ(calor).

The literature search produced references to determinations of the vapor pressure,[46,48–51] heat capacity,[46,52] density,[53–64] and enthalpy of vaporization[65] of methyl benzoate.

No previous measurements of the critical properties for methyl benzoate were found in the literature search. In this research (see Table 9 and Figure 2), a value of T_c = 702 K was determined. As a result of those measurements and the fitting procedures used in this research, values of $T_c = (702 \pm 1)$ K, $p_c = (4020 \pm 200)$ kPa, and $\rho_c = (334 \pm 10)\ \mathrm{kg{\cdot}m^{-3}}$ are recommended for use in corresponding-states representations of methyl benzoate.

Figure 3 compares the vapor-pressure measurements reported in the literature[46,48–51] with values obtained using the Wagner equation and the parameters listed in Table 11. Also shown in the figure is a solid line representing the DIPPR 801 1995 version of the vapor-pressure equation[44] for methyl benzoate. The results due to Kahlbaum[48] (published in 1898!) are remarkably consistent with those obtained in this research, particularly those within the temperature range 360 K to 450 K, where the reported values lie in a ±0.3% band of those obtained in this research.

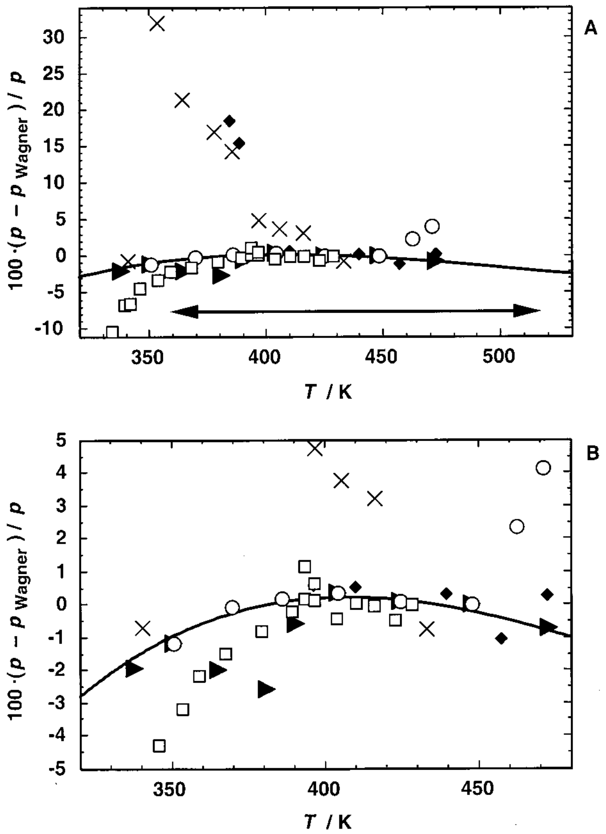

Figure 3. Comparison of literature vapor pressures for methyl benzoate with those obtained using the Wagner equation and the parameters listed in Table 11. The double-headed arrow represents the range of the measurements made in this research and reported in Table 7. The solid curves represent the DIPPR Project 801 Database 1995 version of the vapor-pressure equation (see text).[44] (○) Kahlbaum;[48] (solid triangle pointing right) Stull;[49] (◆) Dreisbach and Shrader;[50] (×) Hall and Baldt;[46] (□) Katayama.[51]

Hall and Baldt[46] measured a heat capacity $C_{sat}/R = 26.0$ at 297 K. Fuchs[52] listed a heat capacity $C_{sat}/R = (26.62 \pm 0.13)$ at 298.15 K for methyl benzoate. Extrapolation of the results obtained in this research gives $C_{sat}/R = (25.9 \pm 0.3)$ at 298.15 K (Table 12), in poor agreement with Fuchs' value.

Figure 4 compares values for the saturated liquid-phase density of methyl benzoate found in a search of the literature[53–64] with values calculated using eq 10 and the parameters listed in the footnotes of Table 10. Also shown in the figures is a solid line representing the DIPPR 801 1995 density equation for methyl benzoate.[44] The results reported by Jaeger[54] appear to have the wrong temperature dependence. The recent wide-temperature range measurements of Mustafaev et al.[64] also deviate markedly [in the opposite direction to those of Jaeger (see Figure 4)] from those obtained in this research. All other values agree with values calculated using eq 10 and the parameters listed in the footnotesof Table 10 within the combined uncertainty intervals. No obvious explanation of the abnormal results arises.

Kusano and Wadsö[65] measured the enthalpy of vaporization of methyl benzoate at 298.15 K using a vaporization calorimeter. Their result $\Delta_l^g H_m^\circ(298.15\ \mathrm{K}) = (55.57 \pm 0.04)\ \mathrm{kJ{\cdot}mol^{-1}}$ is in excellent agreement with the value obtained in this research of $(55.49 \pm 0.22)\ \mathrm{kJ{\cdot}mol^{-1}}$ (Table 14). Kusano and Wadsö derived an enthalpy of vaporization

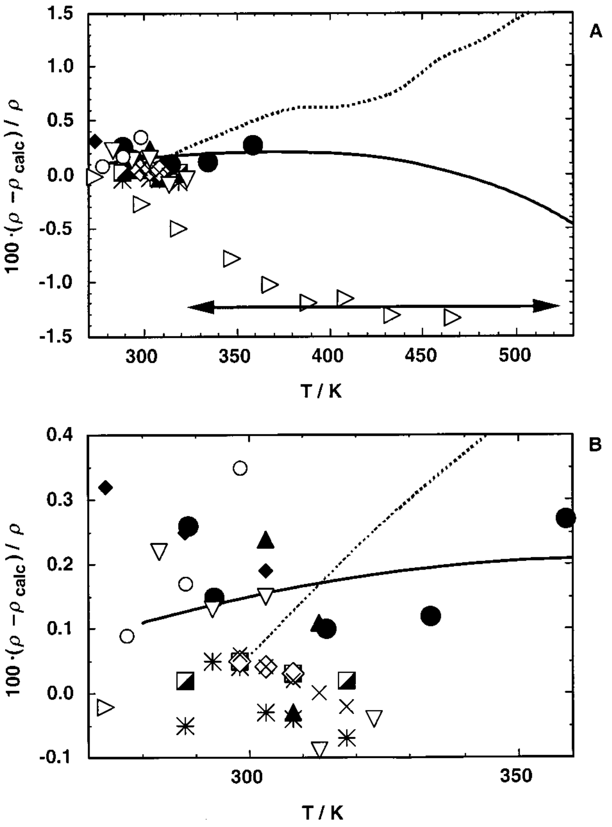

Figure 4. Comparison of literature values for the saturation liquid-phase density measurements for methyl benzoate with those obtained using eq 10 and the parameters listed in the footnotes of Table 10. In part A, the double-headed arrow represents the range of the measurements made in this research and reported in Table 10. In parts A and B, the solid curve represents the DIPPR Project 801 Database 1995 saturation liquid-phase density equation[44] and the dashed curve the results of Mustafaev et al.[64] (○) Perkin.[53] (triangle pointing right) Jaeger;[54] (◆) Timmermans and Hennaut-Roland;[55] (▲) Phadke et al;[56] (●) Vogel;[57] (▽) Garcia and Ortega;[58] (∗) Garcia et al;[59] (◇) Aminabhavi and Raikar[60] and Aminabhavi et al.;[61] (◪) Blanco et al.;[62] (×) Aminabhavi et al.[63]

of 52.5 kJ·mol^{-1} from the vapor-pressure measurements listed by Stull.[49] That result provides corroborating evidence that the vapor pressures listed by Stull have the wrong temperature dependence in the region of 298 K. Hall and Baldt[46] derived $\Delta_{\mathrm{l}}^{\mathrm{g}}H^{\circ}_{\mathrm{m}}$(298.15 K) = 43.72 kJ·mol^{-1}, which, because of the method used to derive the value, would be better assigned to the midpoint of the temperature range of their vapor-pressure measurements, 387 K. Even then, the value seems in error compared with the values obtained in this research (Table 13).

Addition of the group-additivity parameters[1,2] to estimate the enthalpy of formation of methyl benzoate follows:

5	$C_b-(C_b)_2(H)$	13.82 × 5	69.10
1	$C_b-(C_b)_2(CO)$	17.50 × 1	117.50
1	$CO-(C_b)(O)$	−137.50 × 1	−137.30
1	$O-(CO)(C)$	−179.70 × 1	−179.70
1	$C-(O)(H)_3$	−42.25 × 1	−42.25

($\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$($C_8H_8O_2$(g), 298.15 K) = −272.65 kJ·mol^{-1}

The value determined in this research is ($\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ $C_8H_8O_2$, 298.15 K) = −(273.45 ± 0.77) kJ·mol^{-1} (Table 14). The difference, 0.8 kJ·mol^{-1}, is well within the "normal spread", ±4 kJ·mol^{-1}, and signifies that [especially when combined with the results for ethyl benzoate (see below)] the earlier energy of combustion measurements by Hall and Baldt[46] were flawed.

Since this research was finished, a paper by Maksimuk et al.[132] has been published on the standard enthalpies of formation of some methyl esters of benzene carboxylic acids which includes measurements of the thermochemical properties of methyl benzoate. Maksimuk et al.[132] report an energy of combustion for methyl benzoate, $\Delta_{\mathrm{c}}U^{\circ}_{\mathrm{m}}$(l) = −(3954.53 ± 0.60) kJ·mol^{-1}, which should be compared to a value of $\Delta_{\mathrm{c}}U^{\circ}_{\mathrm{m}}$ = −(3959.98 ± 0.62) kJ·mol^{-1} obtained at NIPER. The corresponding enthalpies of formation are $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$($C_8H_8O_2$(l), 298.15 K) = −(334.42 ± 1.21) kJ·mol^{-1} (ref 132) and $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$($C_8H_8O_2$(l), 298.15 K) = −(328.94 ± 0.74) kJ·mol^{-1} (NIPER). Maksimuk et al.[132] also measured an enthalpy of evaporation at 303 K: $\Delta_{\mathrm{l}}^{\mathrm{g}}H^{\circ}_{\mathrm{m}}$($C_8H_8O_2$, 298.15 K) = (57.30 ± 0.24) kJ·mol^{-1}, compared to an interpolated value (Table 13) of $\Delta_{\mathrm{l}}^{\mathrm{g}}H^{\circ}_{\mathrm{m}}$($C_8H_8O_2$, 298.15 K) = (55.14 ± 0.22) kJ·mol^{-1} (NIPER). These differences are larger than they should be for modern accurate and precise measurements on pure components. In support of the NIPER enthalpy of vaporization is the calorimetric measurement of Kusano and Wadsö,[65] $\Delta_{\mathrm{l}}^{\mathrm{g}}H^{\circ}_{\mathrm{m}}$($C_8H_8O_2$, 298.15 K) = (55.57 ± 0.04) kJ·mol^{-1}. Also, the small difference between the boiling and condensation temperatures in the ebulliometric measurements (see Table 7) points to a pure sample of methyl benzoate. Further corroboration of the NIPER sample purity is the percentage CO_2 recoveries (99.989 ± 0.008) (see Table 3) obtained during the measurements. A lower energy of combustion usually indicates the presence of moisture (water) in that sample. 0.14 mol % water in the Minsk methyl benzoate sample would account for the energy of combustion difference noted above.

Ethyl Benzoate. A search of the literature through June 1996 revealed only one previous determination of the energy of combustion and hence enthalpy of formation of ethyl benzoate. The report by Stohmann et al.[45] in 1887 is probably just of historic interest. However, the 1887 work has been abstracted by several authors over the intervening years,[66−68] leading to greater significance being attached to the results than is warranted.

The literature search produced references to determinations of the vapor pressure,[49,51,69,70] heat capacity,[52,71] and density[53−63,72−75] of ethyl benzoate.

Stein[70] in her M.S. thesis reported measurements of the critical properties for ethyl benzoate. Rapid sample decomposition was evident, and extrapolations to "zero time" were made to estimate the critical properties. Values of T_{c} = 668.65 K and p_{c} = 2590 kPa were reported by Stein. As a result of the measurements made and fitting procedures used in this research, values of T_{c} = (707 ± 10) K, p_{c} = (3480 ± 500) kPa, and ρ_{c} = (317 ± 20) kg·m^{-3} are recommended for use in corresponding-states representations of ethyl benzoate. Both the critical temperature and critical pressure values are in stark contrast to those of Stein. The recommended values are "in line" with those recommended for methyl benzoate (loc. cit.). For example, the critical temperature difference between methyl and ethyl compounds is "in line" with such differences for other methyl/ethyl compound pairs.

Figure 5 compares the vapor-pressure measurements reported in the literature[49,51,69,70] for ethyl benzoate with values obtained using the Wagner equation and the parameters listed in Table 11. Also shown in the figures is a solid line representing the DIPPR 801 1995 version of the vapor-pressure equation[44] for ethyl benzoate. For results reported by Stein[70] above 600 K, it would appear that sample decomposition precluded accurate measurement of the vapor pressure. Below that temperature,

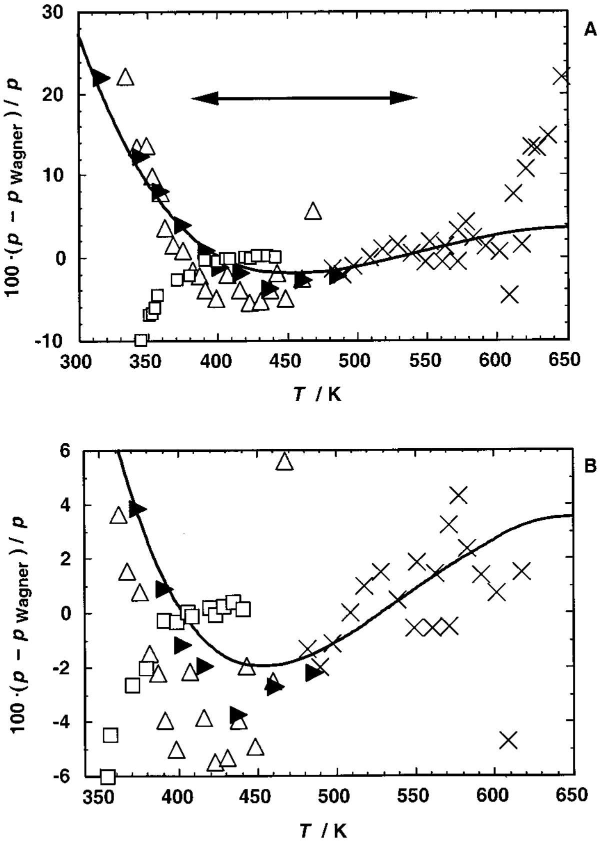

Figure 5. Comparison of literature vapor pressures for ethyl benzoate with those obtained using the Wagner equation and the parameters listed in Table 11. The double-headed arrow represents the range of the measurements made in this research and reported in Table 7. The solid curves represent the DIPPR Project 801 Database 1995 version of the vapor-pressure equation (see text).[44] (△) Hieber and Reindl;[69] (solid triangle pointing right) Stull;[49] (×) Stein;[70] (□) Katayama.[51]

Steins' measurements agree within her experimental scatter with those obtained in this research and reported in Table 7 or derived using the Wagner equation and the parameters listed in Table 11.

Kolossowsky and Udowenko[71] measured the heat capacity $C_{sat}/R = (29.12 \pm 0.30)$ at 292.75 K. Fuchs[52] listed the heat capacity $C_{sat}/R = (29.59 \pm 0.04)$ at 298.15 K for ethyl benzoate. Extrapolation of the results obtained in this research (Table 12) gives $C_{sat}/R = (28.7 \pm 0.3)$ and (29.0 ± 0.3) at 292.75 K and 298.15 K, respectively. As was the case for methyl benzoate (loc. cit.), the value listed by Fuchs has an overoptimistic uncertainty interval attached.

Figure 6 compares values for the saturated liquid-phase density of ethyl benzoate found in a search of the literature[53-63,72-75] with values calculated using eq 10 and the parameters listed in the footnotes of Table 10. Also shown in the figure is a solid line representing the DIPPR 801 1995 density equation for ethyl benzoate (see ref 44). The results reported by Jaeger[54] appear to have the wrong temperature dependence [opposite to that for methyl benzoate (see Figure 4)]. The recent 50 K temperature range measurements of Andorian[73] also deviate markedly (in the opposite direction to those of Jaeger (see Figure 6A)] from those obtained in this research. All other densities agree within the combined uncertainty intervals with values calculated using eq 10 and the parameters listed in the footnotes of Table 10. No obvious explanation of the abnormal results arises.

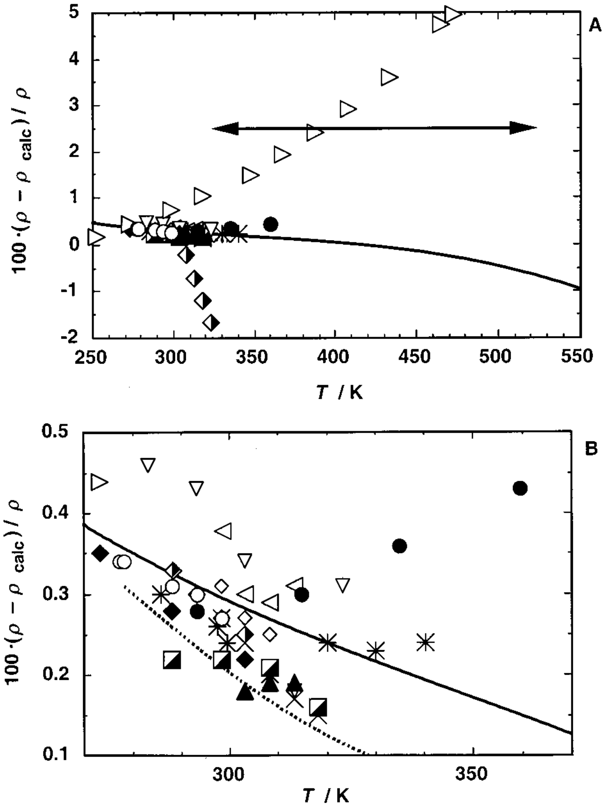

Figure 6. Comparison of literature values for the saturation liquid-phase density measurements for ethyl benzoate with those obtained using eq 10 and the parameters listed in the footnotes of Table 10. In part A, the double-headed arrow represents the range of the measurements made in this research and reported in Table 10. In parts A and B, the solid curve represents the DIPPR Project 801 Database 1995 saturation liquid-phase density equation[44] and the dashed curve the results of Karpushina et al.[74] (○) Perkin;[53] (∗) Kremann and Meingast;[72] (triangle pointing right) Jaeger;[54] (◆) Timmermans and Hennaut-Roland;[55] (▲) Phadke et al.;[56] (●) Vogel;[57] (diamond with solid right side) Andorian;[73] (▽) Garcia and Ortega;[58] (∗) Garcia et al.;[59] (triangle pointing left) Joshi et al.;[75] (◇) Aminabhavi and Raikar[60] and Aminabhavi et al.;[61] (◪) Blanco et al.;[62] (×) Aminabhavi et al.[63]

Addition of the group-additivity parameters[1,2] to estimate the enthalpy of formation of ethyl benzoate follows:

5	$C_b-(C_b)_2(H)$	13.82 × 5	69.10
1	$C_b-(C_b)_2(CO)$	17.50 × 1	17.50
1	$CO-(C_b)(O)$	−137.50 × 1	−137.30
1	$O-(CO)(C)$	−179.70 × 1	−179.70
1	$C-(O)(C)(H)_2$	−33.94 × 1	−33.91
1	$C-(O)(H)_3$	−42.25 × 1	−42.25

$(\Delta_f H^\circ_m(C_9H_{10}O_2(g), 298.15\ K) = -306.56$ kJ·mol^{-1}

The value determined in this research is $\Delta_f H^\circ_m(C_9H_{10}O_2(g), 298.15\ K) = -(306.57 \pm 0.97)$ kJ·mol^{-1} (Table 14).

(R)-(+)-Limonene. The literature search revealed three previous determinations of the energy of combustion and hence enthalpy of formation of (*R*)-(+)-limonene and the optical inactive isomer dipentene. Two of the reports are just of historic interest: those of Auwers et al.[76,77] and Swietoslawski.[78] Hawkins and Eriksen[79] reported measurements on both (*R*)-(+)-limonene and the optical inactive isomer, dipentene, obtaining values of $\Delta_c U^\circ_m/M = -(45\ 225.2 \pm 3.6)$ J·g^{-1} and $\Delta_c U^\circ_m/M = -(45\ 247.8 \pm 4.1)$ J·g^{-1}, respectively. The purity of the limonene sample used by Hawkins and Eriksen was low, only 98%. The dipentene sample had a purity of 99.3 mol %. The dipentene result is in excellent agreement with the value obtained in this

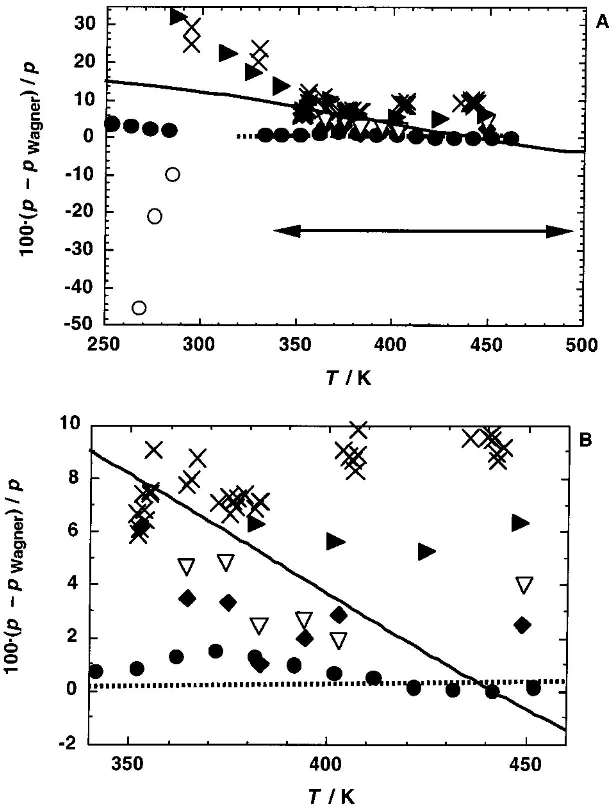

Figure 7. Comparison of literature vapor pressures for (R)-(+)-limonene with those obtained using the Wagner equation and the parameters listed in Table 11. The double-headed arrow represents the range of the measurements made in this research and reported in Table 7. The solid curves represent the DIPPR Project 801 Database 1995 version of the vapor-pressure equation (see text)[44] and the dotted lines the Antoine equation reported in Table 1 of the paper by Nadais and Bernardo-Gil.[84] (×) Pickett and Peterson;[81] (○) Linder;[82] (◆) Rudakov and Korotov;[83] (▽) Rudakov and Korotov[83] (dipentene); (solid triangle pointing right) Stull;[49] (●) Espinosa Díaz et al.[85]

research for (R)-(+)-limonene, $\Delta_c U^\circ_m/M = -(45\,254.2 \pm 1.7)$ J·g^{-1} (see Table 5). Gur′yan et al.,[80] in a study of the thermodynamics of isomerization of monocyclic terpene hydrocarbons, list enthalpies of formation for (R)-(+)-limonene and dipentene. Both values used in the study were derived using a Benson-type group-additivity scheme.

The literature search produced references to determinations of the vapor pressure,[49,81−85] heat capacity,[71,86] density,[87−91] and enthalpy of vaporization[92] of (R)-(+)-limonene.

Rapid decomposition in the region of the critical point prevented measurement of the critical temperature and density using the DSC method. Smith et al.[93] report measurements of the critical properties of several terpenes including (R)-(+)-limonene using a rapid heating method and extrapolations to "zero time". Smith et al. lists values of $T_c = (652 \pm 2)$ K and $\rho_c = (290 \pm 10)$ kg·m^{-3}. As a result of the measurements made and fitting procedures used in this research, values of $T_c = (655 \pm 5)$ K, $p_c = (2900 \pm 500)$ kPa, and $\rho_c = (267 \pm 15)$ kg·m^{-3} are recommended for use in corresponding-states representations of (R)-(+)-limonene.

Figure 7 compares the vapor-pressure measurements reported in the literature[49,81−85] for (R)-(+)-limonene with values obtained using the Wagner equation and the parameters listed in Table 11. Also shown in the figure is a solid line representing the DIPPR 801 1995 version of the vapor-pressure equation for (R)-(+)-limonene.[44] For the reported vapor-pressure measurements, the experimental scatter is large (typically ±2%). Each of the early sets of vapor pressures,[49,81−83] except one,[82] is higher than the corresponding values obtained in this research and reported in Table 7 or derived using the Wagner equation and the parameters listed in Table 11. The three low pressure points reported by Linder in 1931 are the only pressures listed in the literature prior to 1993 that are lower than values obtained in this research (see Figure 7A). Agreement between the measurements reported in this research and the recent results of Nadais and Bernardo-Gil[84] and Espinosa Díaz et al.[85] is good, well within the uncertainty intervals assigned in ref 85.

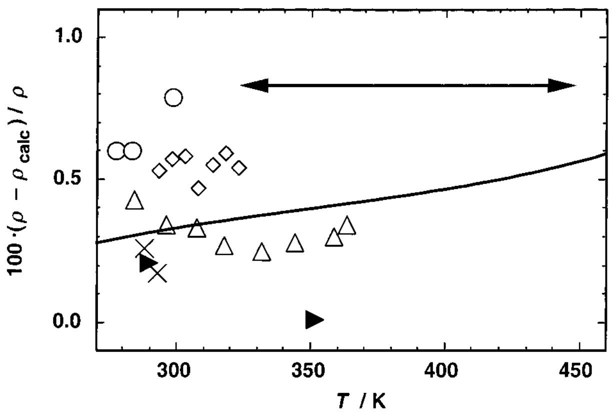

Figure 8. Comparison of literature values for the saturation liquid-phase density measurements for (R)-(+)-limonene with those obtained using eq 10 and the parameters listed in the footnotes of Table 10. The double-headed arrow represents the range of the measurements made in this research and reported in Table 10. The solid curve represents the DIPPR Project 801 Database 1995 saturation liquid-phase density equation.[44] (○) Perkin;[87] (solid triangle pointing right) Eijkman;[88] (×) Auwers et al.;[89] (△) Mitchell and Smith;[90] (◇) Ribeiro and Bernado-Gil.[91]

Kolossowsky and Udowenko[71] measured a heat capacity $C_{\mathrm{sat}}/R = (30.03 \pm 0.21)$ at 293.4 K. Extrapolation of the results obtained in this research (Table 12) gives $C_{\mathrm{sat}}/R = (30.7 \pm 0.3)$ at 293.4 K. Gallis et al.[86] studied (R)-(+)-limonene by DSC and adiabatic calorimetry in the temperature region 5 K to 250 K. The narrow liquid-phase temperature region of their measurements, and the relatively long extrapolation to join the C_{sat} results reported in this research (Table 12), could lead to various interpretations of the agreement between the values. However, the agreement is, at best, 1%.

Figure 8 compares values for the saturated liquid-phase density of (R)-(+)-limonene found in a search of the literature[87−91] with values calculated using eq 10 and the parameters listed in the footnotes of Table 10. Also shown in the figures is a solid line representing the DIPPR 801 1995 density equation for (R)-(+)-limonene.[44] All the measured densities listed are higher [0.3% to 0.6% (see Figure 8)] than the corresponding values calculated using eq 10 and the parameters listed in the footnotes of Table 10. Only the value at 351.45 K by Eijkman[88] is in good agreement with this research.

Atik et al.,[92] using samples of 99.95 mol % purity, measured the enthalpy of vaporization of both (+)-limonene and (−)-limonene at 298.15 K using microconduction and carrier-gas flow-type calorimetry. Their results, $\Delta_l^g H^\circ_m$[(+)-limonene, 298.15 K] = (48.92 ± 0.08) kJ·mol^{-1} and $\Delta_l^g H^\circ_m$[(−)-limonene, 298.15 K] = (49.00 ± 0.08), respectively, can be compared with the value

$\Delta_l^g H_m^\circ$[(*R*)-(+)-limonene, 298.15 K] = (49.61 ± 0.18) kJ·mol^{-1} (Table 14) obtained in this research.

Addition of the group-additivity parameters (see refs 1, 2, and 39) to estimate the enthalpy of formation of (*R*)-(+)-limonene follows:

2	C−(C)$_2$(H)$_2$	−20.21 × 2	−40.42
2	C−(C$_d$)(H)$_3$	−42.25 × 2	−84.50
2	C$_d$−(C$_d$)(C)$_2$	43.29 × 2	86.58
1	C$_d$−(C$_d$)(C)(H)	35.96 × 1	35.96
1	C−(C$_d$)(C)(H)$_2$	−19.93 × 1	−19.93
1	C−(C$_d$)(C)$_2$(H)	−6.20 × 1	−6.20
1	C$_d$−(C$_d$)(H)$_2$	26.21 × 2	26.21
1	ring strain (cyclohexene)	5.10 × 1	5.10

($\Delta_f H_m^\circ$($C_{10}H_{16}$(g), 298.15 K) = 2.80 kJ·mol^{-1}

The value determined in this research is $\Delta_f H_m^\circ$($C_{10}H_{16}$(g), 298.15 K) = (3.09 ± 1.04) kJ·mol^{-1} (Table 14), in excellent agreement with the group-additivity value.

tert-Amyl Methyl Ether. Thermophysical property measurements on this compound were made by our group in the DIPPR 821 Project for 1991.[94] However, at that time, the energy of combustion was not a slated property measurement and, as noted in ref 94, there were unexplained problems with the ebulliometric measurements in that research with the difference between the boiling and condensation temperatures (ΔT) increasing significantly above 389 K. An attempt was made to make a measurement at 270 kPa (395.6 K), but ΔT started at approximately 0.07 K and rapidly increased by several tenths of a degree. This phenomenon is normally indicative of sample decomposition, but measurements in the critical region were possible by DSC. Because of these problems, a new sample was obtained for the measurements reported in this research.

The critical properties of *tert*-amyl methyl ether were previously measured in this laboratory[94] using the sample discussed in the previous paragraph. In the previous research, values of T_c = 534 K and ρ_c = (275 ± 13) kg·m^{-3} were determined in those DSC measurements with a corresponding critical pressure of 3200 kPa derived in the fitting procedures. In this research (see Table 9 and Figure 2), values of T_c = 537 K and ρ_c = 264 kg·m^{-3} were determined in the DSC measurements. The corresponding critical pressure derived using the fitting procedures was 3550 kPa. As a result of the measurements made and fitting procedures used in the present research, values of T_c = (537 ± 2) K, p_c = (3550 ± 300) kPa, and ρ_c = (264 ± 10) kg·m^{-3} were recommended to DIPPR 821 Committee members for use in corresponding-states representations of *tert*-amyl methyl ether.

After the completion of the research, Wilson et al.[95] published the results of studies on critical property measurements using both a "traditional static method" and a "new flow method" for measurements on reactive compounds. Wilson et al. noted that "*tert*-amyl methyl ether showed a slow but significant change in the observed critical pressure and temperature as a function of time." Figures 3 and 4 in ref 95 depict the results for the ether. They state, "the critical properties of this compound changed quite linearly with time, and the critical properties at zero residence time can be extrapolated reliably." Wilson et al. reported T_c = (536.20 ± 0.2) K, p_c = (3191 ± 40) kPa, and a critical volume which translates to the critical density ρ_c = (271 ± 1) kg·m.$^{-3}$ Agreement between their results and the above recommended values is good and within the combined uncertainty intervals.

As noted above (Tables 3 and 5), just three energy of combustion measurements were successful during the present study. Initially, a dozen ampules were filled, but because of overnight problems with the air conditioning system, seven were lost, as the temperature rose by several Kelvin in the laboratory, accompanying a temperature inversion outside. (Oklahoma weather is sometimes difficult to predict, and occasionally, the temperature can rise during the night.) During the next day, two more broke, probably because of the fragility of the glass ampules after the temperature shock.

Rozhnov et al.[96] measured the energy of combustion and hence the standard enthalpy of formation of *tert*-amyl methyl ether during a study of the thermodynamics of the gas-phase synthesis reaction of this important gasoline oxygen additive. Because the unresolved problems with the earlier sample noted above pointed to difficulty in obtaining a pure sample and the measurements of Rozhnov et al.[96] were not based on CO_2 analyses, a repeat of the measurement of the energy of combustion was thought necessary. The energy of combustion obtained by Rozhnov et al., $\Delta_c U_m^\circ/M$ = −(39 273 ± 14) J·g^{-1}, compares with the value of $\Delta_c U_m^\circ/M$ = −(39 337.5 ± 1.2) J·g^{-1} obtained here (Table 5). The corresponding standard enthalpies of formation are $\Delta_f H_m^\circ$($C_6H_{14}O$(l)) = −(341.79 ± 0.79) kJ·mol^{-1} and $\Delta_f H_m^\circ$($C_6H_{14}O$(l)) = −(335.03 ± 0.66) kJ·mol^{-1}, respectively. The difference in the energies of combustion would amount to 0.16 mol % water in the Russian sample.

When the results of the present research were presented to the DIPPR 871 Committee members, two published studies of the liquid-phase equilibria involving methanol, 2-methylbut-1-ene or 2-methylbut-2-ene, and *tert*-amyl methyl ether[97,98] were discussed within the text of the report. Both research groups derived enthalpies of reaction for the formation of the ether via both butene isomers. For the reaction

$$\text{methanol(l)} + \text{2-methylbut-1-ene(l)} = \text{methyl } \textit{tert}\text{-amyl ether(l)} \quad (12)$$

Serda et al.[97] gave $\Delta_r H_m^\circ$ = −35.8 kJ·mol^{-1} and Rihko et al.[98] gave $\Delta_r H_m^\circ$ = −(33.6 ± 5.1) kJ·mol^{-1}.

For the reaction

$$\text{methanol(l)} + \text{2-methylbut-2-ene(l)} = \text{methyl } \textit{tert}\text{-amyl ether(l)} \quad (13)$$

Serda et al.[97] gave $\Delta_r H_m^\circ$ = −32.8 kJ·mol^{-1} and Rihko et al.[98] gave $\Delta_r H_m^\circ$ = −(26.8 ± 2.3) kJ·mol^{-1}. Since then, several other papers on the thermodynamics of the reaction between the butenes and methanol to produce *tert*-amyl methyl ether have appeared in the literature.[99−103] Table 15 lists the enthalpies of reactions 12 and 13 obtained during those studies and the corresponding values derived for the enthalpy of formation of *tert*-amyl methyl ether in the liquid phase at the denoted temperature. In deriving the enthalpy of formation of *tert*-amyl methyl ether, the recommended values for the liquid-phase enthalpies of formation of methanol, 2-methylbut-1-ene, and 2-methylbut-2-ene listed by Pedley[104] were used. Results listed in Table 15 point to a value of $\Delta_r H_m^\circ$ = −(35 ± 1) kJ·mol^{-1} for reaction 12; $\Delta_r H_m^\circ$ = −(27 ± 1) kJ·mol^{-1} for reaction 13, and a standard enthalpy of formation for *tert*-amyl methyl ether of $\Delta_f H_m^\circ$($C_6H_{14}O$(l)) = −(335 ± 1) kJ·mol^{-1}, all in excellent agreement with the results obtained in this research. Using the Rozhnov et al.[96] enthalpy of formation $\Delta_f H_m^\circ$($C_6H_{14}O$(l)) = −(341.79 ± 0.79) kJ·mol^{-1} gives values for reactions 12 and 13 which are approximately 7 kJ·mol^{-1} more negative, outside the boundaries set by the equilibria studies.

Table 15. Literature Values for the Enthalpies of Reactions 12 and 13 and the Corresponding Derived Enthalpies of Formation for *tert*-Amyl Methyl Ether in the Liquid Phase

	$\Delta_r H$/kJ·mol^{-1}		$\Delta_f H_m$/kJ·mol^{-1}
ref	reaction 12	reaction 13	TAME[a]
98	−33.6 ± 5.1	−26.8 ± 2.3	−333.7 −334.5
97	−35.8	−32.8	−335.9 −340.5
99	−36.4 ± 2.5	−28.4 ± 2.5	−333.1 −331.2
100	−32.8	−25.6	−332.9 −333.3
101	−34.9 ± 2.5	−27.1 ± 2.5	−335.1 −334.8
102	−33.6	−26.8	−333.7 −334.5
103	−32.96	−23.50	−333.1 −331.2
this research[b]	−34.9 ± 1.0	−27.3 ± 1.4	−335.03[c] −335.03[c]

[a] The values for the enthalpy of formation of TAME were derived using the reported enthalpies for reactions 12 and 13, respectively, and the recommended values for the enthalpies of formation for methanol, 2-methylbut-1-ene, and 2-methylbut-2-ene listed in ref 104. [b] The values listed for the enthalpies of reactions 12 and 13, respectively, were calculated using the enthalpies of formation for methanol, 2-methylbut-1-ene, and 2-methylbut-2-ene listed in ref 104 and the enthalpy of formation for TAME determined here (Table 6). [c] See Table 6.

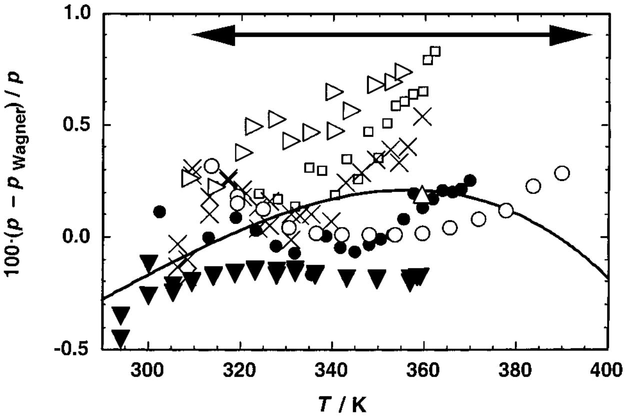

Figure 9. Comparison of literature vapor pressures for *tert*-amyl methyl ether with those obtained using the Wagner equation and the parameters listed in Table 11. The double-headed arrow represents the range of the measurements made in this research and reported in Table 7. The solid curve represents the DIPPR Project 801 Database 1995 version of the vapor-pressure equation (see text).[44] (△) Evans and Edlung;[105] (▼) Cervenkova and Boublik;[107] (triangle pointing right) Palazewska-Tulinska et al.;[106] (∗) Krähenbühl and Gmehling;[108] (○) Steele et al.;[94] (●) Toghiani et al.;[109] (□) Aucejo et al.[110] The second point for Evans and Edlung (at 298.15 K) is not shown on the figure (the deviation is 0.7%).

In 1936 Evans and Edlung[105] reported a value of the vapor pressure at 298.15 K and a normal boiling point. As noted in the Figure 9 caption, the 298 K value is 0.7% lower than that obtained using the Wagner equation and the parameters listed in Table 11. The 101.325 kPa value is 0.2% higher than the corresponding pressure obtained in this research. Vapor-pressure measurements (twin ebulliometric with water and tetradecane as standards) were reported by Palazewska-Tulinska et al.[106] Their results are compared with those reported in this research in Figure 9. As can be seen in Figure 9, the results of Palazewska-Tulinska et al. deviate approximately linearly from values calculated using the Wagner parameters listed in Table 11 (0.3% lower at 309 K to 1.0% higher at 358 K). Palazewska-Tulinska et al. list a purity of 99.94% for their sample (similar to that of the sample used here), so it is difficult to elucidate a reason for the differences. Vapor-pressure measurements were also reported in 1984 by Cervenkova and Boublik[107] and are compared in Figure 9. Their results are not consistent with either those of Palazewska-Tulinska et al.[106] or those of this research. Cervenkova and Boublik[107] also used twin ebulliometers with water as the standard and list a sample purity of 99% by GLC analysis. As noted above, thermophysical property measurements on this compound were made by our group in the DIPPR 821 Project for 1991.[94] The unexplained problems with the ebulliometric measurements in the earlier research[94] were not reproduced in the present measurements. Across the ebulliometric vapor-pressure measurements (see Table 7), from 16 kPa to 270 kPa, ΔT rose only 0.005 K from 0.016 K to 0.021 K. Across the temperature region 330 K to 370 K, the 1994 results are less than 0.1% higher than those obtained in the present research. However, at the extremes (313 K and 390 K), the difference rises to 0.3%.

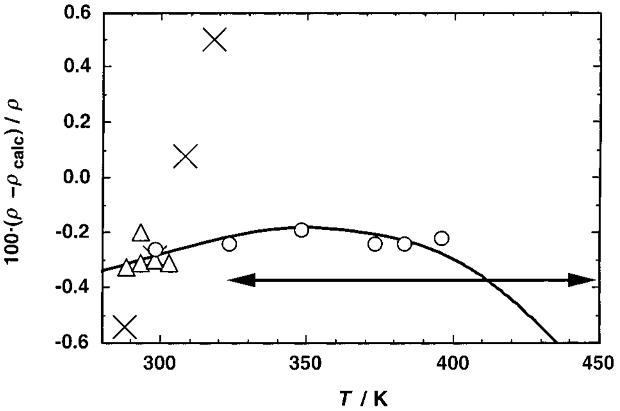

Figure 10. Comparison of literature values for the saturation liquid-phase density measurements for *tert*-amyl methyl ether with those obtained using eq 10 and the parameters listed in the footnotes of Table 10. The double-headed arrow represents the range of the measurements made in this research and reported in Table 10. The solid curve represents the DIPPR Project 801 Database saturation liquid-phase density equation.[44] (△) Evans and Edlung;[105] (○) Steele et al.;[94] (∗) Govender et al.[111] The point at 328.15 K for Govender et al.[111] is not shown (the deviation is 1.1%).

Three more recent sets of vapor-pressure measurements on *tert*-amyl methyl ether were found in the literature search: Krähenbühl et al.,[108] Toghiani et al.,[109] and Aucejo et al.[110]. All three are compared with the present results in Figure 9. The Krähenbühl et al.[108] measurements have an internal scatter of $\pm 0.002p$. Below 342 K, agreement with the present measurements is excellent. Similarly, the agreement of the Toghiani et al.[109] measurements with those reported here is excellent below, in this case, 355 K. The results reported by Aucejo et al.[110] resemble those of Palazewska-Tulinska et al.,[106] deviating approximately linearly from values calculated using the Wagner parameters listed in Table 11 (0.2% higher at 314 K to 0.8% higher at 360 K).

Figure 10 compares the density measurements reported in the earlier DIPPR Project 821 work,[94] some values listed by Evans and Edlung,[105] and recent measurements by Govender et al.[111] with values obtained using eq 10 and the parameters listed in the footnotes of Table 10. The present saturated liquid-phase densities are higher than any previously measured values with substantial deviations when compared with the Anton Paar vibrating-tube measurements of Govender et al.[111] No explanation for the differences can be found at present.

Evans and Edlung[105] report an enthalpy of vaporization at 298.15 K of 33.3 kJ·mol^{-1}. Rozhnov et al.[96] list four different values for the enthalpy of vaporization of methyl *tert*-amyl ether at 298.15 K: 35.8 kJ·mol^{-1} from unpublished calorimetric measurements, 34.8 kJ·mol^{-1} derived from the vapor-pressure results of Cervenkova and Boublik,[107] an evaluated value of (34.8 ± 1.5) kJ·mol^{-1} derived from group additivity, and an "assessed" value of (35.3 ± 1.5) kJ·mol^{-1}. Values of $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}(\mathrm{C_6H_{14}O}, 298.15\ \mathrm{K}) = (34.42 \pm 0.12)\ \mathrm{kJ{\cdot}mol^{-1}}$ and $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(\mathrm{C_6H_{14}O}, 298.15\ \mathrm{K}) = (34.64 \pm 0.12)\ \mathrm{kJ{\cdot}mol^{-1}}$ are obtained in this research for the enthalpies of vaporization of *tert*-amyl methyl ether to the real and ideal gases, respectively, at 298.15 K.

Addition of the group-additivity parameters[1,2,40] to estimate the enthalpy of formation of *tert*-amyl methyl ether follows:

3	$\mathrm{C-(C)(H)_3}$	−42.25 × 3	−126.75
1	$\mathrm{C-(C)_2(H)_2}$	−20.21 × 1	−20.21
1	$\mathrm{C-(C)_3(O)}$	−27.63 × 1	−27.63
1	$\mathrm{O-(C)_2}$	−99.50 × 1	−99.50
1	$\mathrm{C-(O)(H)_3}$	−42.25 × 1	−42.25
4	1,4-gauche interactions	4.00 × 4	16.00
	$(\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}(\mathrm{C_6H_{14}O(g)}, 298.15\ \mathrm{K}) = -300.34\ \mathrm{kJ{\cdot}mol^{-1}}$		

The value determined in this research is $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}(\mathrm{C_6H_{14}O(g)}, 298.15\ \mathrm{K}) = -(300.39 \pm 0.67)\ \mathrm{kJ{\cdot}mol^{-1}}$ (Table 14), in perfect agreement with the group-additivity value.

***trans*-Crotonaldehyde.** Tjebbes[112] reported results of a combustion calorimetric study on butanal and some related compounds. Included in those compounds was butenal (*trans*-crotonaldehyde). Tjebbes noted problems in obtaining the aldehydes in a "very pure state", noting in particular how unstable the compounds were during distillations at temperatures higher than 50 °C and how sensitive the compounds were to oxidation. The water content of the aldehydes was determined via GLC analyses. Tjebbes reported an energy of combustion of $\Delta_{\mathrm{c}}U_{\mathrm{m}}^{\circ}/M = -(32\,599 \pm 2)\ \mathrm{J{\cdot}g^{-1}}$, for *trans*-crotonaldehyde after correcting for a 0.02% water content. The corresponding standard enthalpy of formation of liquid-phase *trans*-crotonaldehyde is $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}(\mathrm{C_4H_6O(l)}, 298.15\ \mathrm{K}) = -(144.1 \pm 0.8)\ \mathrm{kJ{\cdot}mol^{-1}}$ (see ref 113). Cox and Pilcher,[113] listing the ideal-gas enthalpy of vaporization $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(\mathrm{C_4H_6O}, 298.15\ \mathrm{K}) = (38.1 \pm 0.8)\ \mathrm{kJ{\cdot}mol,^{-1}}$ derived the ideal-gas standard enthalpy of formation of *trans*-crotonaldehyde $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}(\mathrm{C_4H_6O(g)}, 298.15\ \mathrm{K}) = -(106.0 \pm 1.1)\ \mathrm{kJ{\cdot}mol^{-1}}$. Earlier in 1938, Dolliver et al.,[114] as part of a program measuring the enthalpies of hydrogenation of oxygen-containing compounds, studied the catalytic hydrogenation of crotonaldehyde. Their results when combined with modern values for the enthalpies of formation of the reactants and products give the ideal-gas standard enthalpy of formation $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}(\mathrm{C_4H_6O(g)}, 298.15\ \mathrm{K}) = -(100.6 \pm 1.4)\ \mathrm{kJ{\cdot}mol^{-1}}$ (see ref 113), in poor agreement with the energy of combustion study. Because of the importance of *trans*-crotonaldehyde in the derivation of group-additivity parameters for $\alpha\beta$-unsaturated aldehydes, conformation of either the Tjebbes[112] or the Dolliver et al.[114] result would be desirable.

A literature search produced references to determinations of the vapor pressure,[115−117] heat capacity,[117] density,[89,112,117] and enthalpy of vaporization[118] of *trans*-crotonaldehyde.

Rapid decomposition in the region of the critical point prevented measurement of the critical temperature and density using the DSC method. As a result of the measurements made and fitting procedures used in this research, values of $T_{\mathrm{c}} = (565 \pm 5)$ K, $p_{\mathrm{c}} = (3870 \pm 500)$ kPa, and $\rho_{\mathrm{c}} = (284 \pm 15)\ \mathrm{kg{\cdot}m^{-3}}$ are recommended for use in corresponding-states representations of *trans*-crotonaldehyde.

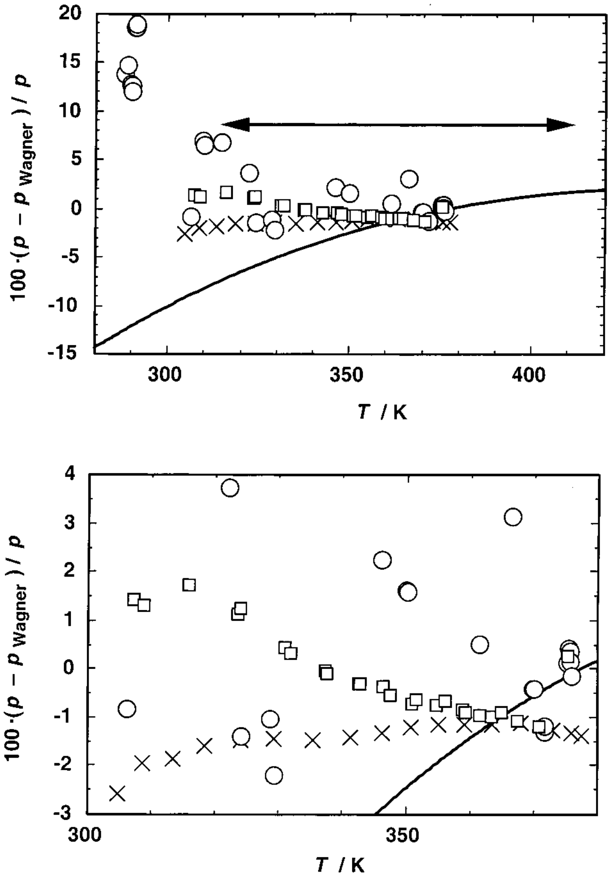

Figure 11. Comparison of literature vapor pressures for *trans*-crotonaldehyde with those obtained using the Wagner equation and the parameters listed in Table 11. The double-headed arrow represents the range of the measurements made in this research and reported in Table 7. The solid curve represents the DIPPR Project 801 Database 1995 version of the vapor-pressure equation (see text).[44] (□) Waradzin and Skubla;[115] (×) Markovnik et al.;[116] (○) Baglay et al.[117]

Figure 11 compares literature values of the vapor pressure of -crotonaldehyde with those derived using the Wagner equation and the parameters listed in Table 11. Also shown in the figure is a solid line representing the DIPPR 801 1995 version of the vapor-pressure equation[44] for *trans*-crotonaldehyde. The agreement with the measurements of Waradzin and Skubla[115] is good (±1%) across most of the overlap temperature region. Similarly, the agreement with the measurements of Markovnik et al.[116] is good (−1.5%) across most of the overlap temperature region. There is a 5% scatter in the results reported by Baglay et al.[117]

Figure 12 compares literature values for the saturation density of *trans*-crotonaldehyde with values obtained using eq 10 and the parameters listed in the footnotes of Table 10. The present saturated liquid-phase densities are lower than any previously measured values. Values obtained using the DIPPR 801 1995 density equation[44] are in excellent agreement with those measured in this research.

Wiberg et al.[118] report measuring vapor pressures and deriving three values of the enthalpy of vaporization for *trans*-crotonaldehyde: 38.83 kJ·mol^{-1} using an Antoine equation and so forth and 37.2 kJ·mol^{-1} applying a

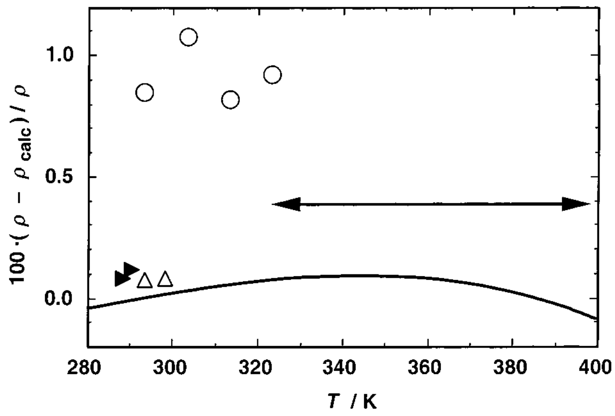

Figure 12. Comparison of literature values for the saturation liquid-phase density measurements for *trans*-crotonaldehyde with those obtained using eq 10 and the parameters listed in the footnotes of Table 10. The double-headed arrow represents the range of the measurements made in this research and reported in Table 10. The solid curve represents the DIPPR Project 801 Database 1995 saturation liquid-phase density equation.[44] (solid triangle pointing right) Auwers and Eisenlohr;[89] (△) Tjebbes;[112] (○) Baglay et al.[117]

"Clausius−Clapeyron method", both at 325.2 K, and a "heat capacity corrected" value of (38.9 ± 1.3) kJ·mol^{-1} at 298.15 K. There are no actual vapor pressures listed in the paper, and what little can be garnered comes from their Table 6. In that table, the temperature range of the ebulliometric measurements (using only 1 cm^3 of sample) is 300 K to 350 K with corresponding pressures of 5.426 kPa to 46.52 kPa. Using the Wagner equation and the parameters listed in Table 11, values of 5.364 kPa and 44.32 kPa are derived for 300 K and 350 K, respectively. Values of $\Delta_l^g H_m(C_4H_6O$, 298.15 K) = (37.70 ± 0.12) kJ·mol^{-1} and $\Delta_l^g H_m^\circ(C_4H_6O$, 298.15 K) = (37.83 ± 0.12) kJ·mol^{-1} are obtained in this research for the enthalpies of vaporization of *trans*-crotonaldehyde to the real and ideal gases, respectively, at 298.15 K. At 325.2 K, the real-gas enthalpy of vaporization interpolated using the results listed in Table 13 is $\Delta_l^g H_m(C_4H_6O$, 325.2 K) = (36.35 ± 0.15) kJ·mol^{-1}. As noted above, Cox and Pilcher[113] list the ideal-gas enthalpy of vaporization $\Delta_l^g H_m^\circ(C_4H_6O$, 298.15 K) = (38.1 ± 0.8) kJ·mol^{-1}, in good agreement with the value obtained in this research.

Addition of the group-additivity parameters[1,2,40] to estimate the enthalpy of formation of *trans*-crotonaldehyde follows (see note on group-additivity values in the Conclusions section below):

1	$C-(C_d)(H)_3$	−42.25 × 1	−42.25
1	$C_d-(C_d)(C)(H)$	35.96 × 1	35.96
1	$C_d-(C_d)(CO)(H)$	25.90 × 1	25.90
1	$CO-(C_d)(H)$	−121.84 × 1	−121.84

($\Delta_f H_m^\circ(C_4H_6O(g)$, 298.15 K) = −102.23 kJ·mol^{-1}

The value determined in this research is $\Delta_f H_m^\circ(C_4H_6O(g)$, 298.15 K) = −(101.94 ± 0.49) kJ·mol^{-1} (Table 14), in excellent agreement with the group-additivity value. The ideal-gas enthalpy of formation confirms the hydrogenation study of Dolliver et al.,[114] $\Delta_f H_m^\circ(C_4H_6O(g)$, 298.15 K) = −(100.6 ± 1.4) kJ·mol^{-1} (see ref 113), over the Tjebbes[112] energy of combustion study.

Diethylene Glycol. Moureu and Dodé[119] reported results of a combustion calorimetric study on several glycols, diols, and oxides. Included in those compounds was diethylene glycol. Moureu and Dodé obtained $\Delta_c U_m^\circ/M$ = −(22 400 ± 22) J·g^{-1}, from duplicate combustions of diethylene glycol. The corresponding standard enthalpy of formation of liquid-phase diethylene glycol is $\Delta_f H_m^\circ(C_4H_{10}O_3(l)$, 298.15 K) = −(628.5 ± 2.4) kJ·mol^{-1} (see ref 120). Pedley et al.[120] list the ideal-gas enthalpy of vaporization $\Delta_l^g H_m^\circ(C_4H_{10}O_3$, 298.15 K) = (57.3 ± 5.9) kJ·mol^{-1}, obtained from the vapor-pressure measurements of Gallaugher and Hibbert,[121] hence deriving the ideal-gas standard enthalpy of formation of diethylene glycol $\Delta_f H_m^\circ(C_4H_{10}O_3(g)$, 298.15 K) = −(571.2 ± 6.3) kJ·mol^{-1}. This value is ~20 kJ·mol^{-1} more negative than the summation of the group-additivity parameters for this molecule (see below). Because of this large discrepancy and the fact that only two combustions were made during the French study, the energy of combustion of diethylene glycol was redetermined under modern conditions on a pure sample.

In the present study, the energy of combustion obtained was $\Delta_c U_m^\circ/M$ = −(22 340 ± 1.4) J·g^{-1}. The corresponding standard enthalpy of formation of liquid-phase diethylene glycol is $\Delta_f H_m^\circ(C_4H_{10}O_3$, l 298.15 K) = −(629.94 ± 0.52) kJ·mol^{-1}. The difference between the two combustion studies (1.4 kJ·mol^{-1}) is less than the uncertainty interval assigned to the Moureu and Dodé result.[119] Hence, the large discrepancy was not resolved by the combustion study.

A literature search produced references to determinations of the vapor pressure,[49,122−127] heat capacity,[128] and density.[121,122,129,130]

Rapid decomposition in the region of the critical point prevented measurement of the critical temperature and density using the DSC method. Anselme and Teja[131] also were unable to obtain measurement of either a critical temperature or a critical density in their study of the critical properties of "rapidly reacting substances." They note that the critical temperature of diethylene glycol is greater than 723.5 K, and their partially filled ampules exploded when heated to that temperature. Recently, Nikitin et al.[41] have studied the critical temperatures and pressures of several poly(ethylene glycol)s using a pulse-heating method. Nikitin et al.[41] list a critical temperature of 753 K for diethylene glycol with a corresponding critical pressure of 4770 kPa. The critical temperature has been accepted in this research with a corresponding critical pressure of 6250 kPa derived using the fitting procedures (see above). Values of T_c = (753 ± 5) K, p_c = (6250 ± 500) kPa, and ρ_c = (319 ± 15) kg·m^{-3} are recommended for use in corresponding-states representations of diethylene glycol.

Figure 13 compares the values of the vapor pressure of diethylene glycol obtained in the literature search with those obtained in this research (Table 7) or derived using the Wagner equation and the parameters listed in Table 11. Shown in the figure are solid and dashed lines representing the DIPPR 801 1995 version of the vapor-pressure equation[44] for diethylene glycol and the Gallaugher and Hibbert[123] linear representation. Gallaugher and Hibbert[123] note that their sample decomposed above 438 K. The onset for decomposition for the sample used in the present research was above 540 K (>170 kPa). The values reported by Stull[49] in his review differ by ~30% from those obtained here. Across the overlap region (424 K to 516 K), agreement with the values reported in 1927 by Rinkenbach[122] is good (see Figure 13). The measurements of Daubert et al.[127] are approximately 4% higher than those obtained in this research across the region of overlap. The Daubert et al. results fall into three mutually incompatible groups: 444 K to 496 K, 540 K to 569 K, and 579 K to 634 K. Sample decomposition could account for the incompatibilities. The ebulliometric measurements of Ambrose and

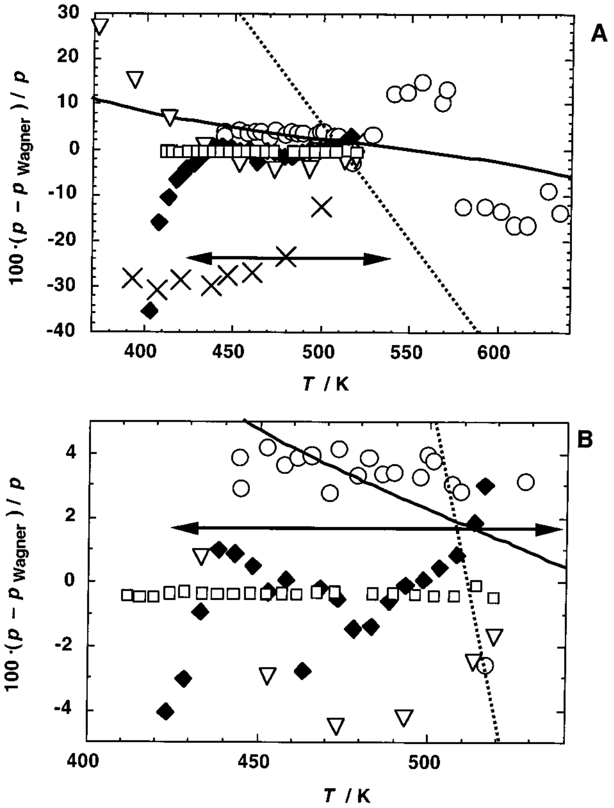

Figure 13. Comparison of literature vapor pressures for diethylene glycol with those obtained using the Wagner equation and the parameters listed in Table 11. The double-headed arrow represents the range of the measurements made in this research and reported in Table 7. The solid and dashed curves represent the DIPPR Project 801 Database 1995 version of the vapor-pressure equation (see text)[44] and the equation of Gallaugher and Hibbert,[123] respectively. (◆) Rinkenbach;[122] (×) Stull;[49] (▽) Klyucheva and Yarym-Agaev;[125] (○) Ambrose and Hall;[126] (∗) Daubert et al.[127] Not shown on the graph is the low temperature (298 K to 373 K, three points) measurements of Brunner[124] (see text).

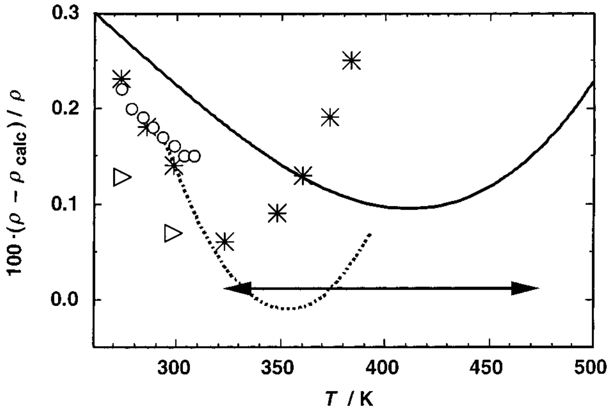

Figure 14. Comparison of literature values for the saturation liquid-phase density measurements for diethylene glycol with those obtained using eq 10 and the parameters listed in the footnotes of Table 10. The double-headed arrow represents the range of the measurements made in this research and reported in Table 10. The solid and dashed curves represent the DIPPR Project 801 Database 1995[44] and the Gallaugher and Hibbert[121] saturation liquid-phase density equations, respectively. (triangle pointing right) Bridgman;[129] (○) Rinkenbach;[122] (∗) Eichis and Zhitomirskii.[130]

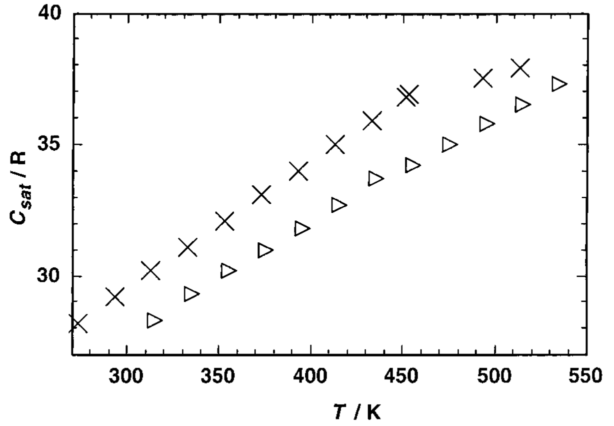

Figure 15. Comparison of the liquid-phase heat capacities for diethylene glycol obtained by Stephens and Tamplin (1979) with those for the 0.021 912 g sample in a cell of volume 0.0522 cm^3 given in Table 8. (×) Stephens and Tamplin;[128] (triangle pointing right) the 0.021 912 g sample.

Hall[126] are in the best agreement with the present results. However, the difference (~ −0.004p across the overlap region) is larger than what would be estimated from the uncertainties normally assigned to such measurements. Ambrose and Hall do note that there was a temperature gradient of 0.02 K across the thermometer pocket of the ebulliometer. That unusual occurrence may be related to the larger than normal difference between the National Physical Laboratory measurements and those reported here. Not shown in Figure 13 are the three measurements of Brunner.[124] The reported measurements at 298 K, 323 K, and 373 K differ from values derived using the Wagner equation and the parameters listed in Table 11 by −250%, −483%, and −171%, respectively.

Figure 14 compares literature values for the saturation density of diethylene glycol with values obtained using eq 10 and the parameters listed in the footnotes of Table 10. The present saturated liquid-phase densities are lower than any previously measured values.

Figure 15 compares the liquid-phase heat capacities for diethylene glycol obtained by Stephens and Tamplin[128] with those for the 0.021 912 g sample in a cell of volume 0.0522 cm^3 given in Table 8. Agreement between both sets of values is poor and cannot be explained at present. Stephens and Tamplin assign the change in slope of the plot at 451 K to decomposition that can be compared to the case of Gallaugher and Hibbert.[123] Note that their sample decomposed above 438 K. The onset for decomposition for the sample used in the present research was 540 K.

Pedley et al.[120] list the ideal-gas enthalpy of vaporization $\Delta_l^g H_m^\circ(C_4H_{10}O_3$, 298.15 K) = (57.3 ± 5.9) kJ·mol^{-1}, obtained from the vapor-pressure measurements of Gallaugher and Hibbert.[121] The vapor-pressure measurements of Gallaugher and Hibbert are very different from those obtained in this research (see Figure 13). The real/ideal-gas enthalpy of vaporization $\Delta_l^g H_m^\circ(C_4H_{10}O_3$, 298.15 K) = (78.56 ± 0.60) kJ·mol^{-1} obtained in this research accounts for the 20 kJ·mol^{-1} difference in the ideal-gas enthalpies of formation noted in the first paragraph of this section.

Addition of the group-additivity parameters[1,2,40] to estimate the enthalpy of formation of diethylene glycol follows:

4	C−(C)(O)(H)$_2$	−33.91 × 4	−135.64
1	O−(C)$_2$	−99.50 × 1	−99.50
2	O−(C)(H)	−158.68 × 2	−317.36

$(\Delta_f H_m^\circ(C_4H_{10}O_3(g), 298.15\ K) = -552.50\ kJ{\cdot}mol^{-1}$

The value determined in this research is $\Delta_f H_m^\circ(C_4H_{10}O_3(g)$,

Table 16. "Recommended" Critical Properties[a]

compd	T_c/K	p_c/kPa	ρ_c/kg·m^{-3}
methyl benzoate	702 ± 1	4020 ± 200	334 ± 10
ethyl benzoate	707 ± 10	3480 ± 500	317 ± 20
(*R*)-(+)-limonene	655 ± 5	2900 ± 500	267 ± 15
tert-amyl methyl ether	537 ± 2	3550 ± 300	264 ± 10
trans-crotonaldehyde	565 ± 5	3870 ± 500	284 ± 15
diethylene glycol	753 ± 5	6250 ± 500	319 ± 15

[a] For methyl benzoate and *tert*-amyl methyl ether the reported critical temperatures and critical densities and their uncertainty intervals were obtained from the DSC measurements. For diethylene glycol, the critical temperature is that obtained by Nikitin et al.[41] For the remaining compounds, the critical temperatures are estimates. The critical pressures listed were determined using the fitting procedures detailed in the text.

298.15 K) = −(551.38 ± 0.79) kJ·mol^{-1} (Table 14), in excellent agreement with the group-additivity value.

Conclusions. Ideal-gas standard enthalpies of formation were derived for methyl benzoate, ethyl benzoate, (*R*)-(+)-limonene, *tert*-amyl methyl ether, *trans*-crotonaldehyde, and diethylene glycol. In each case, agreement between the values derived from the experimental measurements and summation of the relevant group-additivity parameters is excellent, resolving some apparent large discrepancies in the literature. Table 16 lists "recommended" values for the critical properties for each of the compounds studied.

Note on Use of Groups. Three different values for the $C_d-(CO)(C_d)(H)$ group-additivity parameter exist: Eigenmann et al.[68] list the value 20.9 kJ·mol^{-1}, Reid et al.[2] list the value 35.59 kJ·mol^{-1}, and a third value of 25.9 kJ·mol^{-1} was used internally by the NIPER Group. The 25.9 kJ·mol^{-1} value is derived from a "complete" analysis of all oxygen-containing compounds for which "reliable" standard ideal-gas enthalpies of formation exist in the literature. That value is recommended in conjunction with the following values:

$CO-(C_d)(C)$	−120.9 kJ·mol^{-1}
$CO-(C_d)(O)$	−129.9 kJ·mol^{-1}
$CO-(C_d)(H)$	−121.6 kJ·mol^{-1}

If either the Eigenmann et al.[68] or the Reid et al.[2] values for the $C_d-(CO)(C_d)(H)$ group-additivity parameter are used, then the following entities should hold (from the 1992 Project 871 results,[94] the 1994 Project 871 results,[40] and this research, respectively):

$$(CO)-(C_d)(O) + C_d-(CO)(C_d)(H) = -104.0\ \mathrm{kJ\cdot mol^{-1}}$$

$$(CO)-(C_d)(C) + C_d-(CO)(C_d)(H) = -95.0\ \mathrm{kJ\cdot mol^{-1}}$$

and

$$(CO)-(C_d)(H) + C_d-(CO)(C_d)(H) = -95.7\ \mathrm{kJ\cdot mol^{-1}}$$

All calculations using these group-additivity parameters should be undertaken with care.

Acknowledgment

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