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DETERMINATION OF SOME PURE COMPOUND IDEAL-GAS ENTHALPIES OF FORMATION

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Topical Report

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EXECUTIVE SUMMARY

This paper describes a new approach to the improvement of group-additivity methodology for estimation of thermodynamic data.

It has long been recognized that it is impractical to carry out experimental measurements of the thermodynamic properties of all the multitude of organic substances existing that are of importance in such areas as the processing of alternate fuel sources. Experimental measurements on a restricted number of carefully selected molecules can be used to relate thermodynamic properties to molecular structure followed by estimation of properties for great numbers of related molecules without experimental measurements. Many people have worked on these correlation methods. The correlations have been used by many workers to estimate properties where no experimental values exist even for the parent molecules. Unavoidably, sometimes the methodolgy went astray. In many instances inexperienced people correlated data that had already been derived by correlation.

In spite of the weaknesses resulting from excessive extrapolations, good correlational methods have evolved, and they serve a very useful purpose not only in extending the existing data, but also in pointing out places where experimental data are needed. It was from weaknesses exposed by these correlations that this project was founded.

Representatives of the Department of Energy (Bartlesville Project Office), the Design Institute for Physical Data (DIPPR), and the National Institute for Petroleum and Energy Research (NIPER) agreed on a list of compounds for which the determination of the enthalpy of formation in the ideal-gas state would be of benefit to all the participants. Nine compounds were agreed upon for study in the first year's effort, and the ideal-gas state enthalpies of formation of acrylamide, succinimide, γ-butyrolactone, 2-pyrrolidone, 2,3-dihydrofuran, 3,4-dihydro-2H-pyran, 1,3-cyclohexadiene, 1,4-cyclohexadiene, and 1-methyl-1-phenylhydrazine are reported here.

Data on these compounds will enhance the application of group-additivity methodology. It is hoped that this effort will be continued during the coming years to fill other data gaps already noted.

The nine compounds studied will permit an expansion of the data base for the ideal-gas standard enthalpy of formation of organic compounds, necessitating a great deal of revision of earlier estimated values. This task is an essential part of any good estimation scheme. As incorrect or imprecise data are revised, the corresponding group parameters also need revision, and such revision often has far-reaching ramifications

and cannot be done in isolation. For example, any changes of the values for the groups derived from the alkanes will necessitate changes to most other group's values. This revision is a task not to be taken lightly. Such a revision is in progress at NIPER as part of a research program funded by the Department of Energy's Office of Energy Research.

ABSTRACT

The results of a study aimed at improvement of group-additivity methodolgy for estimation of thermodynamic properties of organic substances are reported. Specific weaknesses where ring corrections were unknown or next-nearest-neighbor interactions were only estimated because of lack of experimental data are addressed by experimental studies of enthalpies of combustion in the condensed-phase and vapor pressure measurements. Ideal-gas enthalpies of formation are reported for acrylamide, succinimide, γ-butyrolactone, 2-pyrrolidone, 2,3-dihydrofuran, 3,4-dihydro-2H-pyran, 1,3-cyclohexadiene, 1,4-cyclohexadiene, and 1-methyl-1-phenylhydrazine. Ring corrections, group terms, and next-nearest-neighbor interaction terms useful in the application of group-additivity correlations are derived.

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1. INTRODUCTION

This research was funded jointly by the U. S. Department of Energy (DOE) through Fossil Energy's Advanced Process Technology Research program and the Design Institute for Physical Property Data (DIPPR)* of the American Institute of Chemical Engineers through some of its member industrial organizations. Work performed in this project (DIPPR Research Project 871: Determination of Pure Compound Ideal–Gas Enthalpies of Formation) represents the outcome of a series of meetings in late 1986 in which representatives of the DOE Bartlesville Project Office, the Design Institute for Physical Property Data (DIPPR), and the National Institute for Petroleum and Energy Research (NIPER) agreed on a list of compounds for which the determination of the enthalpy of formation in the ideal–gas state would be of benefit to all the participants.

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

DIPPR's goal is to develop, organize, maintain, and make available reliable physical property data for industrially important chemical compounds. Initially, work is in progress compiling data on 1,000 compounds important to industry. Where no data exist, prediction is attempted using estimation methods. These estimations require a strong base of accurate and precise data on basic molecular structures.

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

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

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

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

Whereas condensed–phase enthalpy of formation of a compound is of greatest interest in the calculation of energy balances for a given chemical process, the enthalpy of formation for the ideal–gas state is of greatest interest in the general case, where the answer can be used to derive a given group 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 first year of the project, nine compounds were chosen for study. These compounds are listed in table 1. The derivation of ideal–gas standard enthalpies of formation for each of the compounds required data in addition to the standard enthalpy of combustion determination. A listing of the required auxiliary data for each of the nine compounds is given in table 1. In the two cases where the sample under study was a solid, (acrylamide and succinimide) no attempt was made to measure the enthalpy of sublimation or the vapor pressure of the solid. The reason for that decision was a prior knowledge of the problems associated with the accurate and precise determination of such data. The chemical literature contains a wealth of data on the vapor pressure of solids and enthalpies of sublimation, but most of it is in serious disagreement. For example, in another project we have had reason to collect the available literature data on the enthalpy of sublimation of naphthalene and its vapor pressure in the solid phase over a range of temperature. The 17 data sets (3) show a vapor pressure for naphthalene at 298.15 K with a range of 50 per cent and a corresponding range of 40 per cent in the enthalpy of sublimation at the same temperature.

The purity of the sample employed in a measurement of a thermodynamic property can significantly affect the overall accuracy of the measurement. The degree of inaccuracy introduced by the presence of impurities in the sample under study will

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

Compound	$\Delta_c U^o_m$	Vapor pressure	Heat capacity
acrylamide	....	....	....
succinimide	....	....	....
γ–butyrolactone	....	....	
2–pyrrolidone	....	....	
2,3–dihydrofuran	....	....	
3,4–dihydro–2H–pyran	....	....	
1,3–cyclohexadiene	....	....	
1,4–cyclohexadiene	....	....	
1–methyl–1–phenyl–hydrazine	....	....	

a Measurements made are denoted by ····

depend on a number of factors. In the case of the measurement of enthalpies of combustion the presence of small amounts (less than 0.1 per cent) of isomeric impurities will usually not have a significant effect on the overall 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. A common impurity in organic compounds is water. This impurity contributes no heat on combustion of the sample. Thus, a 0.1 mass per cent of water would cause a 0.1 per cent error in an energy of combustion value, based on the mass of sample taken and its assumed molecular weight. Such an error would have a serious effect on the derived enthalpy of formation, since the enthalpy of formation is a relatively small number derived by the use of a Hess cycle, which includes the enthalpies of combustion of each of the elements present in the compound. The error can be avoided in two ways: either the proportion of water in the sample can be determined by accurate analysis and an allowance for it made, or the energy of combustion can be calculated from the number of moles of a product, e.g. by determination of the number of moles of carbon dioxide formed. This is the reason for the determination of the percentage carbon dioxide recovered in all the combustions reported in this project.

To minimize errors due to impurities all the samples used in this research were purified either by recrystallization followed by solvent removal in vacuo or by spinning–band distillation. The samples were purified until the purity was greater than 99.9 per cent as determined by gas–liquid chromatographic analysis before subsequent thermodynamic property measurements

2. EXPERIMENTAL

In this section of the report, details are given of the apparatus and procedures used in obtaining the experimental data. These have been previously described in the literature and in various DOE reports. Therefore, details have been kept to a minimum here and the literature referenced for further consultation.

Energy of Combustion Apparatus and Procedures

The basic apparatus and procedures used at NIPER for the combustion calorimetry of CHON compounds have been described (4–6). A rotating bomb calorimeter (laboratory designation BMR II) (7) and platinum–lined bombs (laboratory designations Pt–5 and B57I) (8) with internal volumes of 0.3954 dm^3 and 0.3945 dm^3, respectively, were used without rotation. For each experiment, 1.0 cm^3 of water was added to the bomb, and the bomb was flushed and charged to 3.04 MPa with pure oxygen. Except in the case of the 2–pyrrolidone combustion series, each experiment was

started at 296.15 K and by judicious choice of sample and auxiliary masses completed very close to 298.15 K. For 2–pyrrolidone the temperature range used in the determinations was 298.65 K to 300.65 K to ensure that the sample was in the liquid phase at the start of each combustion. Flexible borosilicate glass ampoules (6,9) were used to confine the liquid samples.

Temperatures were measured by quartz crystal thermometry (10,11). A computer was used to control the combustion experiments and record the results. The quartz thermometer was calibrated with a platinum resistance thermometer. Counts of the crystal oscillation were taken over periods of 100 seconds throughout the experiments; integration of the time–temperature curve is inherent in the quartz thermometer readings (12).

National Bureau of Standards 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 (13) gives -26413.7 ± 3.0 $J \cdot g^{-1}$ for $\Delta_c U^o_m$, the specific energy of the idealized combustion reaction.

A set of calibration experiments interspersed within the acrylamide and succinimide experiments (using bomb Pt–5) gave $\varepsilon = 16784.61 \pm 0.24$ $J \cdot K^{-1}$ (mean and standard deviation for six experiments), (ε is the energy equivalent of the calorimeter less its contents). Within the combustion series on γ–butyrolactone the calibration series (Pt–5) gave $\varepsilon = 16785.71 \pm 0.53$ $J \cdot K^{-1}$ (mean and standard deviation for six experiments). For 2–pyrrolidone (in the temperature range 298.65 to 300.65 K and using bomb B57I), the calibration series gave $\varepsilon = 16644.74 \pm 0.72$ $J \cdot K^{-1}$ (mean and standard deviation for six experiments). For the remaining compounds the calibration series (B57I) gave $\varepsilon = 16641.27 \pm 0.21$ $J \cdot K^{-1}$ (mean and standard deviation for six experiments).

The auxiliary oil (laboratory designation TKL66) had the empirical formula $CH_{1.913}$. For this material $\Delta_c U^o_m = -46042.5 \pm 1.8$ $J \cdot g^{-1}$ (mean and standard deviation). For the cotton fuse, empirical formula $CH_{1.774}O_{0.887}$, $\Delta_c U^o_m$ was -16945 $J \cdot g^{-1}$.

Data necessary for reducing weights measured in air to masses, converting the energy of the actual bomb process to that of the isothermal process, and reducing to standard states (13) are listed in table 2. All the listed data were measured in this laboratory except where designated as estimated.

Nitric acid formed during the combustion of nitrogen–containing compounds was determined by titration with standard sodium hydroxide (14). Combustions on those

TABLE 2. Physical properties at 298.15 K except as noted[a]

Compound	molar mass $g \cdot mol^{-1}$	ρ $kg \cdot m^{-3}$	C_p/R	$10^7(\delta V/\delta T)_P$ $m^3 \cdot K^{-1}$
acrylamide	71.0791	1127	13.3	(0.29)
succinimide	99.0895	1418 (1250)[b]	14.9	(0.41)
γ–butyrolactone	86.0908	1125	33.8	0.68
2–pyrrolidone	85.1061	1107	20.4[c]	0.58
2,3–dihydrofuran	70.0914	927	14.7	0.65
3,4–dihydro–2H–pyran	84.1184	922	(21)	0.79
1,3–cyclohexadiene	80.130	837.7	17.0	1.21
1,4–cyclohexadiene	80.130	849.7	17.1	1.08
1–methyl–1–phenyl–hydrazine	122.1704	1038	(31)	(1.2)

[a] Values in parentheses are estimates.

[b] At 405 K

[c] At 300 K

compounds which contained no nitrogen gave no nitric acid because of the high purity of the oxygen used and the bomb flushing procedure prior to each combustion.

Carbon dioxide was also recovered from the combustion products of each experiment. Anhydrous lithium hydroxide was used as absorbant (5). The combustion products were checked for unburned carbon and other products of incomplete combustion, but none was detected. Details of the percentage recoveries in the carbon dioxide analyses for each compound studied are given in the "Results" section of this report.

Vapor Pressure Apparatus and Procedures

The essential features of the ebulliometric equipment and procedures are extensively described in the literature by Swietoslawski (15), Osborn and Douslin (16), and Chirico et al. (17). The ebulliometers were used to reflux the substance under study with a standard of known vapor pressure under a common helium atmosphere. The boiling and condensation temperatures of the two substances were determined, and the vapor pressure was derived using the condensation temperature of the standard, water or n–decane. Reference 17 details the procedures used by our group to establish n–decane as a secondary standard for ebulliometric vapor pressure measurements. Previously, at NIPER, the low–pressure standard for ebulliometric measurements was benzene, which has a lower operational pressure limit of 9.6 kPa due to its high vapor pressure at its triple point. The use of n–decane lowers the pressure limit for measurements to 2.0 kPa.

The imprecision in the temperature measurements in the ebulliometric vapor pressure measurements was 0.001 K. This gives a variance of

$$\sigma_i^2 = (0.001)^2 \left[(dP_{ref}/dT)^2 + (dP_{samp}/dT)^2 \right] \qquad (2.1)$$

where P_{ref} is the vapor pressure of the reference substance (n–decane for pressures less than 19 kPa, and water for pressures greater than 19 kPa), and P_{samp} is the vapor pressure of the sample under study. The imprecisions in the reference substances are adequately described by the following expressions:

$$\sigma(P)/P = 5.56 / T^2 \text{ and } \sigma(P)/P = 5.00 / T^2 \qquad (2.2)$$

for n–decane and water, respectively.

The vapor pressure measurements for each compound are tabulated in the "Results" section of this report. Following standard practice (16) the results obtained

in the ebulliometric measurements were adjusted to common pressures. The common pressures, the condensation temperature for the sample, and the difference between that condensation temperature and the corresponding boiling temperature are reported. A relatively small difference between the boiling and condensation temperatures indicates (a) correct operation of the equipment, and (b) a high–purity sample. For each of the samples both criteria are fulfilled.

Cox Equation Fits to the Vapor Pressure Results

Previous studies in this laboratory (18) have shown that the Cox equation (19) can adequately represent measured vapor pressure data from the triple point pressure to three bars. Scott and Osborn (18) also showed the Antoine equation, the most commonly used to represent vapor pressure data, does not extrapolate well outside the experimental range. In contrast, the Cox equation extrapolates with reasonable precision over at least a 50 K range.

The Cox equation in the form:

$$\ln(P/P_{ref}) = [\,1 - (T_{ref}/T)]\,\exp(A + BT + CT^2) \qquad (2.3)$$

was fit to the experimental vapor pressure data. P_{ref} was chosen to be 101.325 kPa so that T_{ref} was "the normal boiling point." In those fits, the sums of the weighted squares in the following function were minimized:

$$\Delta = \ln[\ln(P/P_{ref})/(1 - T_{ref}/T)] - A - BT - CT^2 \qquad (2.4).$$

The weighting factors, Wt, were the reciprocals of the variance in Δ derived from the propagation of errors in the temperature and pressure determinations. Wt is defined as

$$1/Wt = (\delta\Delta/\delta T)^2\,\sigma^2(T) + (\delta\Delta/\delta P)^2\,\sigma^2(P) \qquad (2.5).$$

Parameters derived from the fits are given in tables in the "Results" section of this report.

Enthalpies of Vaporization

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

$$dP/dT = \Delta_l^g H / (T\,\Delta_l^g V) \qquad (2.6)$$

where, $\Delta_l^g V$, is the increase in volume from the liquid to the real vapor. In the calculation of $\Delta_l^g V$, estimates of the second virial coefficients were made using the correlation of Scott et al. (20), and liquid densities were taken from the literature or measured in this laboratory (see table 2). Derived enthalpies of vaporization are reported in the "Results" section.

Heat Capacity and Enthalpy of Fusion Determinations

The technique of differential scanning calorimetry (DSC) has been developed by Mraw (21–23) to a stage where thermodynamic data accurate to near 1 per cent can be obtained provided that a standard procedure is followed. In these measurements of heat capacity and enthalpy of fusion on acrylamide and succinimide, we have applied the methodology of Mraw as outlined in reference 23. The only major difference in our measurement technique has been the substitution of the aluminum "volatile sample" cells available from Perkin Elmer and used by Mraw with specially designed cells. These cells, designed and manufactured in–house, are made out of 174 stainless steel and are internally gold plated to diminish the catalytic effect of metals on the rate of decomposition of the compound under study at high temperature. The cells can withstand both high pressures (to 7.6 MPa) and high temperatures (to 800 K). In "normal" operation, correction is made for the enthalpy involved in vaporizing small amounts of the sample under study into the vapor space of the sealed pans. However, in this work, such corrections were negligible because of the low vapor pressures in the region where the heat capacity determinations were made.

3. RESULTS

In this section the experimental results obtained for each compound are discussed. To enable easy extraction of the data for a single compound, details are repeated in full for each compound individually.

Acrylamide

Acrylamide, CH_2=CHCONH$_2$, was obtained from Fluka Chemical Corporation with an advertised purity of 99.99 per cent. This purity level was confirmed by high pressure liquid chromatographic (HPLC) analysis. Therefore, no further purification of the commercial sample was required.

Combustion Bomb Calorimetric Results

Six determinations of the energy of combustion of acrylamide were made. The percentage carbon dioxide recovery was 99.98 ± 0.02 (mean and standard deviation). A typical combustion experiment is summarized in table 3. It is impractical to list summaries for each combustion, but values of $\Delta_c U^o_m/M$ for all the experiments are reported in table 4. All values of $\Delta_c U^o_m/M$ in tables 3 and 4 refer to the reaction:

$$C_3H_5ON\ (c) + 15/4\ O_2\ (g) = 3\ CO_2\ (g) + 5/2\ H_2O\ (l) + 1/2\ N_2\ (g) \qquad (3.1).$$

Table 5 gives derived molar values of $\Delta_c U^o_m$, the standard energy of combustion; $\Delta_c H^o_m$, the standard enthalpy of combustion; and $\Delta_f H^o_m$, the standard enthalpy of formation. Values of $\Delta_c U^o_m$ and $\Delta_c H^o_m$ refer to reaction **3.1**. The value of $\Delta_f H^o_m$ refers to the reaction:

$$3\ C\ (c,\ graphite) + 5/2\ H_2\ (g) + 1/2\ O_2\ (g) + 1/2\ N_2\ (g) = C_3H_5ON\ (c) \qquad (3.2).$$

Uncertainties given in table 5 are the uncertainty interval (24). The enthalpies of formation of gaseous CO_2 and liquid H_2O were taken to be −393.51 ± 0.13 and −285.830 ± 0.040 kJ mol^{-1}, respectively, as assigned by CODATA (25).

Enthalpy of Fusion and Heat Capacity

Results from the heat capacity and enthalpy of fusion determination for acrylamide are given in table 6. The tabulated results are the mean of two determinations using 12 and 20 mg samples. The uncertainties assigned to the measured heat capacities and enthalpy of fusion are 1 per cent in each case. The heat capacity in the liquid phase was linear to 415 K, where a large exothermic peak denoted the onset of polymerization. Figure 1 is a plot of the measured condensed–phase heat capacity for acrylamide.

TABLE 3. Typical combustion experiment for acrylamide at 298.15 K (p° = 101.325 kPa)[a]

m'(compound)/g	1.360343
m''(auxiliary oil)/g	0.0
m'''(fuse)/g	0.001154
$n_i(H_2O)$/mol	0.05335
m(Pt)/g	20.21
$\Delta T=(t_i - t_f + \Delta t_{corr})$/K	1.923521
ε(calor)(ΔT)/J	−32285.55
ε(cont)(ΔT)/J [b]	−37.31
ΔU_{ign}/J	0.75
$\Delta U_{dec}(HNO_3)$/J	81.44
ΔU(corr. to std. states)/J [c]	19.34
$-m''(\Delta_c U^\circ_m/M)$(oil)/J	0.0
$-m'''(\Delta_c U^\circ_m/M)$(fuse)/J	19.55
$m'(\Delta_c U^\circ_m/M)$(compound)/J	−32201.78
$(\Delta_c U^\circ_m/M)$(compound)/J·g^{-1}	−23671.81

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

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

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

TABLE 4. Summary of experimental enthalpy of combustion results for acrylamide. Values of $(\Delta_c U^\circ_m/M)(\text{compound})/J\cdot g^{-1}$ at 298.15 K and p° =101.325 kPa

	$(\Delta_c U^\circ_m/M)(\text{compound})$
	$J\cdot g^{-1}$
	−23671.8
	−23671.6
	−23670.2
	−23669.7
	−23668.4
	−23664.5
mean	−23669.4
standard deviation	1.1

TABLE 5. Molar thermochemical functions for acrylamide at 298.15 K and p° = 101.325 kPa

	$\Delta_c U^\circ_m$ / $kJ\cdot mol^{-1}$	$\Delta_c H^\circ_m$ / $kJ\cdot mol^{-1}$	$\Delta_f H^\circ_m$ / $kJ\cdot mol^{-1}$
Acrylamide	−1682.40 ± 0.26	−1683.02 ± 0.26	−212.08 ± 0.30

TABLE 6. Condensed phase heat capacity and enthalpy of fusion for acrylamide

T/K	C_{sat} /R	State
305	13.71	c
315	14.37	c
325	15.16	c
335	15.70	c
345	16.31	c
365	22.58	l
375	22.80	l
385	23.02	l
395	23.30	l
405	23.61	l
415	23.82	l

Solid $C_{sat}/R = 0.0653\ T - 6.17$

Liquid $C_{sat}/R = 0.02546\ T + 13.26$

$\Delta_c^l H_m^o(358\ K) = 15.33\ kJ\ mol^{-1}$

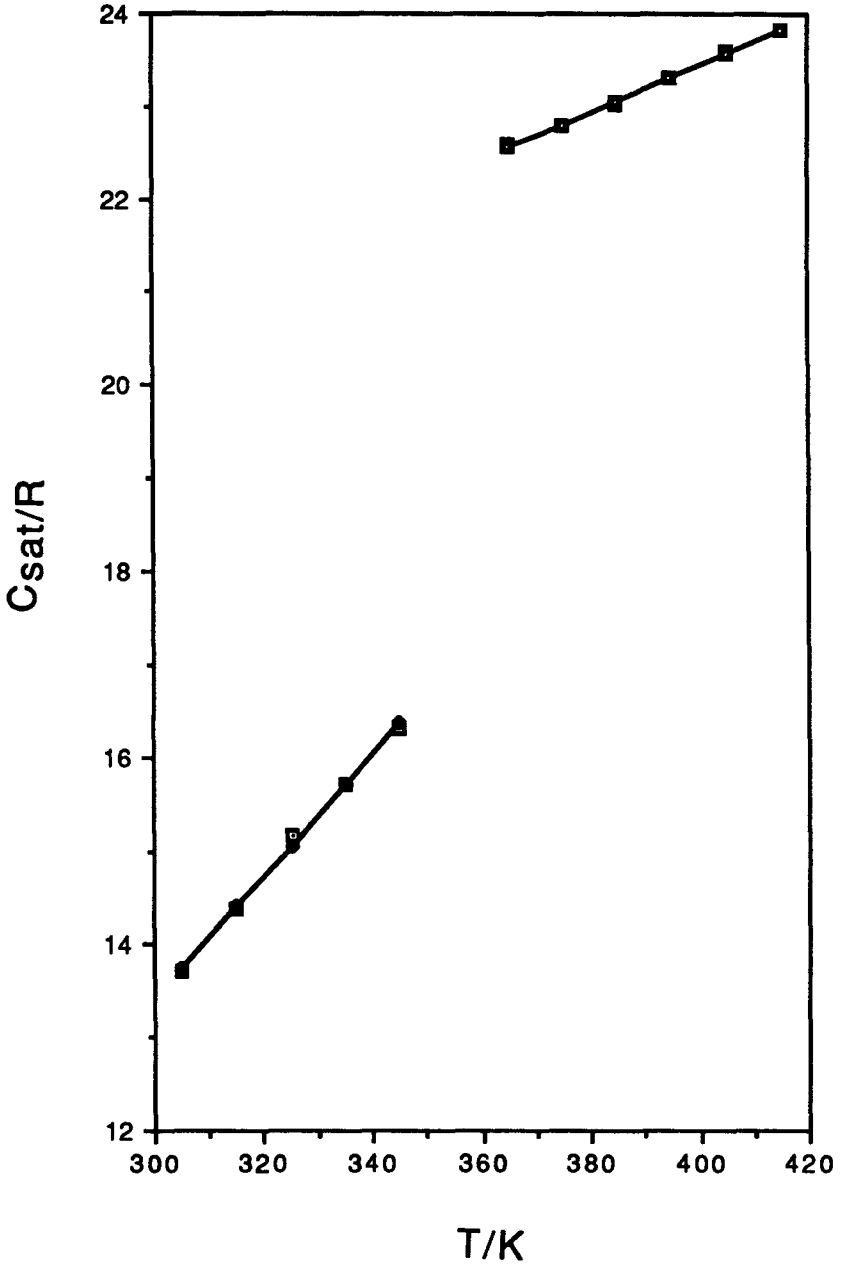

Figure 1. Heat capacity against temperature for acrylamide.

Vapor Pressure Determinations

Attempts to obtain vapor pressure measurements for acrylamide using the twin ebulliometric apparatus were unsuccessful. The samples polymerized on heating approximately 30 K above the melting point in agreement with the results of Carpenter and Davis (26). (See also the section on enthalpy of fusion and heat capacity above.)

Carpenter and Davis give a plot of vapor pressure data for acrylamide obtained using a gas saturation technique for the solid phase and measurements made on a liquid sample "admixed with 3–5 per cent solid cupric chloride," which "slowed" polymerization. In the absence of other measurements, the data of Carpenter and Davis were combined with the above measured enthalpy of fusion to obtain thermodynamically consistent vapor pressures for acrylamide.

Using an enlargement of the plot given by Carpenter and Davis (26), the vapor pressure data given in table 7 was interpolated. The solid–phase data can be represented by an Antoine equation of the form:

$$\ln(p/p^\circ) = 21.445 - 9839 / T \qquad (3.3)$$

where p° is 101.325 kPa. Hence, in the temperature range 303 to 358 K, the mean enthalpy of sublimation of acrylamide is 81.81 kJ mol^{-1}. At the melting point, 358 K, equation (**3.3**) gives a vapor pressure of 0.242 kPa. Using the enthalpy of fusion derived above, $\Delta_c^l H_m^o$(358 K), of 15.33 kJ mol^{-1} the enthalpy of vaporization is 81.81 – 15.33 = 66.48 kJ mol^{-1}. Assuming a constant enthalpy of vaporization over a short temperature range (50 K), the liquid–phase vapor pressure can be represented by the equation:

$$\ln(p/p^\circ) = 16.302 - 7996 / T \qquad (3.4).$$

The vapor pressures calculated using equation (**3.4**) are listed in table 7 column 3. As is shown in table 7, there is good agreement with the experimental data of Carpenter and Davis (26) in the range 358 K to 405 K. Above that temperature, the experimental pressures are lower than the calculated values as expected with the presence of a significant degree of polymerization.

TABLE 7. Interpolated vapor pressures for acrylamide[a]

T/K	P_{obs}/Pa	P_{calc}/Pa	Δ/Pa
298.15	1.0	0.98	0.02
313.0	4.4	4.7	−0.3
328.0	20.0	19.6	0.4
358.0	242.6	241.1	1.5
375	617	669	−52
383	1033	1044	−11
388	1300	1366	−66
395	2060	1969	91
405	3146	3246	−100
411	3813	4330	−517
415	4280	5223	−943
420	5053	6570	−1517

[a] Data interpolated from a plot in reference 23.

Succinimide

Succinimide, $C_4H_5O_2N$, was obtained from Aldrich Chemicals with an advertised purity of greater than 99 per cent. HPLC analysis confirmed this purity level, with succinamide and ammonium succinate being the major impurities. The sample was recrystallized three times from isopropanol followed by drying under vacuum overnight at 320 K to remove excess solvent. The sample was then ground to facilitate further solvent removal and dried under vacuum at 320 K for one week. Analysis of this sample by HPLC showed a purity level of greater than 99.95 per cent.

Combustion Bomb Calorimetric Results

Six determinations of the energy of combustion of succinimide were made. The percentage carbon dioxide recovery was 99.99 ± 0.01 (mean and standard deviation). A typical combustion experiment is summarized in table 8. It is impractical to list summaries for each combustion, but values of $\Delta_c U^o_m/M$ for all the experiments are reported in table 9. All values of $\Delta_c U^o_m/M$ in tables 8 and 9 refer to the reaction:

$$C_4H_5O_2N\ (c) + 17/4\ O_2\ (g) = 4\ CO_2\ (g) + 5/2\ H_2O\ (l) + 1/2\ N_2\ (g) \qquad (3.5).$$

Table 10 gives derived molar values of $\Delta_c U^o_m$, the standard energy of combustion; $\Delta_c H^o_m$, the standard enthalpy of combustion; and $\Delta_f H^o_m$, the standard enthalpy of formation. Values of $\Delta_c U^o_m$ and $\Delta_c H^o_m$ refer to reaction **3.5**. The value of $\Delta_f H^o_m$ refers to the reaction:

$$4\ C\ (c,\ graphite) + 5/2\ H_2\ (g) + O_2\ (g) + 1/2\ N_2\ (g) = C_4H_5O_2N\ (c) \qquad (3.6).$$

Uncertainties given in table 10 are the uncertainty interval (24). The enthalpies of formation of gaseous CO_2 and liquid H_2O were taken to be −393.51 ± 0.13 and −285.830 ± 0.040 kJ mol^{-1}, respectively, as assigned by CODATA (25).

Enthalpy of Fusion and Heat Capacity

Results from the heat capacity and enthalpy of fusion determination for succinimide are given in table 11. The results are the mean of two determinations using 15 and 20 mg samples, respectively. The uncertainties assigned to the measured heat capacities and enthalpy of fusion are 1 per cent. Figure 2 is a plot of the measured condensed–phase heat capacity for succinimide.

Vapor Pressure Determinations

The experimentally determined ebulliometric vapor–pressure measurements obtained for succinimide are reported in table 12. The least–squares evaluated Cox equation parameters are given in table 13. Details of the Cox equation fits are given in table 12.

Enthalpies of Vaporization

Derived enthalpies of vaporization for succinimide from the Cox equation fit using the Clapeyron equation and the data reported in table 2 are listed in table 14.

TABLE 8. Typical combustion experiment for succinimide at 298.15 K (p° = 101.325 kPa)[a]

m'(compound)/g	1.832798
m''(auxiliary oil)/g	0.0
m'''(fuse)/g	0.001668
$n_i(H_2O)$/mol	0.05335
m(Pt)/g	20.81
$\Delta T=(t_i - t_f + \Delta t_{corr})$/K	2.021652
ε(calor)(ΔT)/J	−33932.64
ε(cont)(ΔT)/J [b]	−40.07
ΔU_{ign}/J	0.75
$\Delta U_{dec}(HNO_3)$/J	82.17
ΔU(corr. to std. states)/J [c]	30.27
$-m''(\Delta_c U^\circ_m/M)(oil)$/J	0.0
$-m'''(\Delta_c U^\circ_m/M)(fuse)$/J	28.26
$m'(\Delta_c U^\circ_m/M)(compound)$/J	−33831.26
$(\Delta_c U^\circ_m/M)(compound)/J\cdot g^{-1}$	−18458.8

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

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

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

TABLE 9. Summary of experimental enthalpy of combustion results for succinimide. Values of $(\Delta_c U^\circ_m/M)(\text{compound})/J\cdot g^{-1}$ at 298.15 K and p° =101.325 kPa

	$(\Delta_c U^\circ_m/M)(\text{compound})$
	$J\cdot g^{-1}$
	−18458.8
	−18458.7
	−18456.7
	−18458.0
	−18456.3
	−18458.1
mean	−18457.8
standard deviation	0.42

TABLE 10. Molar thermochemical functions for succinimide at 298.15 K and p° = 101.325 kPa

	$\Delta_c U^\circ_m$	$\Delta_c H^\circ_m$	$\Delta_f H^\circ_m$
	$kJ\cdot mol^{-1}$	$kJ\cdot mol^{-1}$	$kJ\cdot mol^{-1}$
Succinimide	−1828.98 ± 0.24	−1828.36 ± 0.24	−460.25 ± 0.30

TABLE 11. Condensed–phase heat capacity and enthalpy of fusion for succinimide

T/K	C_{sat} /R	State
305	15.24	c
315	15.65	c
325	16.10	c
335	16.54	c
345	17.03	c
355	17.39	c
405	24.09	l
415	24.35	l
425	24.63	l
435	24.91	l
445	25.16	l
455	25.42	l
465	25.68	l
475	25.94	l
485	26.20	l
495	26.49	l

Solid $C_{sat}/R = 0.0438\ T + 1.871$

Liquid $C_{sat}/R = 0.0265\ T + 13.38$

$\Delta_c^l H_m^o(400\ K) = 17.00\ kJ\ mol^{-1}$

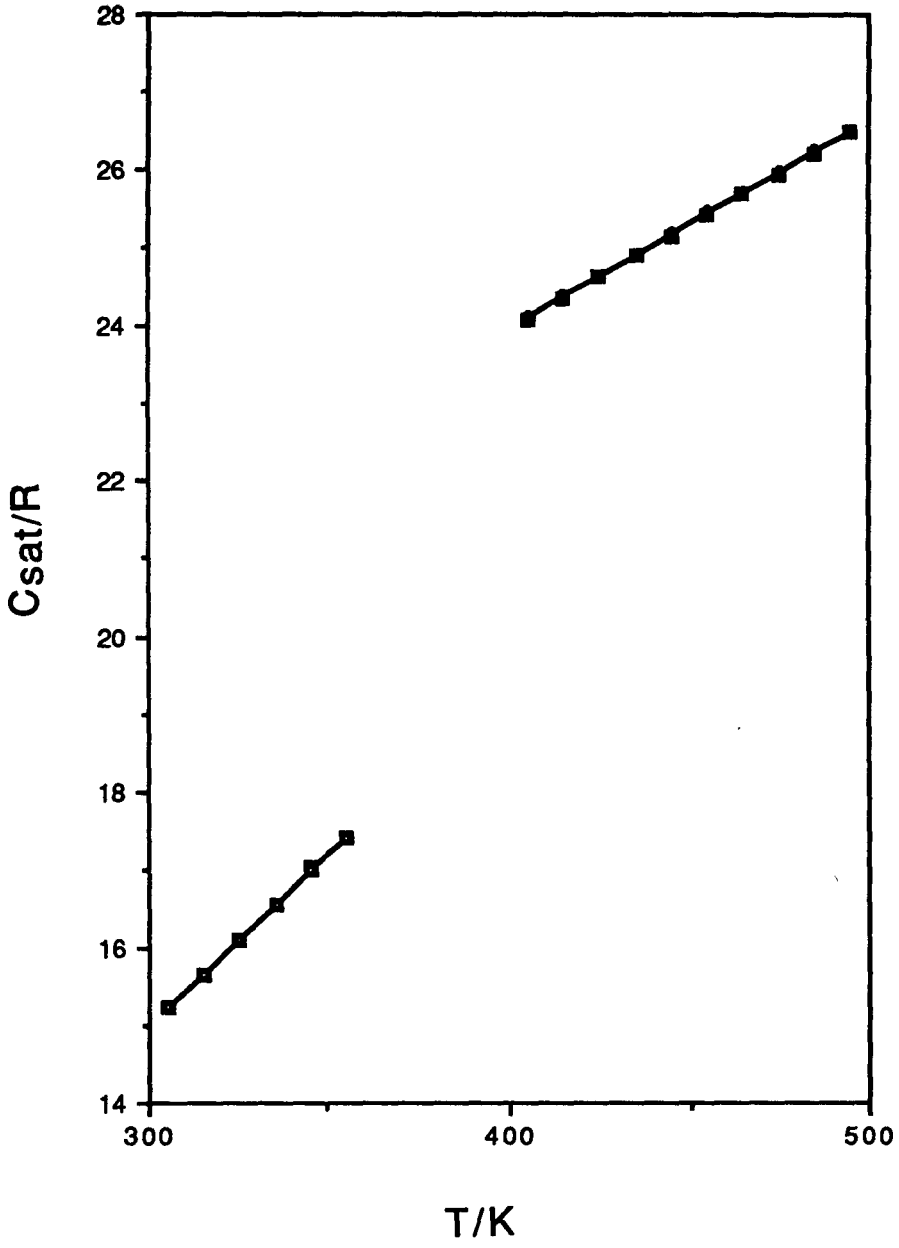

Figure 2. Heat capacity against temperature for succinimide.

TABLE 12. Summary of vapor pressure results for succinimide; decane or water refers to which material was used as the standard in the reference ebulliometer, the pressure P for ebulliometric measurements was calculated from the condensation temperature of the reference substance, in the ebulliometric measurements T is the condensation temperature of the sample, $T_{boil} - T_{cond}$ is the difference between the boiling and condensation temperatures for the sample in the ebulliometer, ΔP is the difference of the calculated value of pressure from the observed value of pressure, σ_i is the propagated error calculated from equations **2.1** and **2.2.**

Material	$\frac{P}{kPa}$	$\frac{T}{K}$	$\frac{T_{boil} - T_{cond}}{K}$	$\frac{\Delta P}{kPa}$	$\frac{\sigma_i}{kPa}$
		succinimide			
decane	1.9998	444.305	0.136	−0.0003	0.0001
decane	2.6664	451.254	0.091	0.0005	0.0001
decane	3.9997	461.513	0.051	−0.0001	0.0002
decane	5.3329	480.453	0.039	0.0005	0.0003
decane	7.9993	488.884	0.040	0.0002	0.0005
decane	10.6658	495.665	0.048	−0.0016	0.0006
decane	13.3322	495.665	0.048	−0.0018	0.0007
decane	16.6653	502.672	0.061	−0.0032	0.0008
decane	19.9330	508.435	0.100	0.0120	0.0011
water	25.0233	516.039	0.120	−0.0061	0.0013
water	31.1774[a]	523.759	0.155	−0.1411	0.0016
water	47.3748[a]	538.686	0.315	0.0177	0.0023
water	70.1209[a]	553.920	0.485	−0.3666	0.0032
water	101.325[a]	569.471	0.705	−2.146	0.004

[a] Sample decomposition, point given zero weight in Cox equation fit.

TABLE 13. Cox equation constants and fitting parameters for succinimide

T_{ref} / K	568.6 ± 0.3
A	3.2709 ± 0.0206
10^3B/K	−2.3758 ± 0.0865
10^6C/K^2	2.1574 ± 0.0908
Data Range/K	444 − 517
Normalized Covariance Terms [a]	
AB	−0.99980
AC	0.99919
BC	−0.99979

[a] Cross terms of the normalized variance–covariance matrix.

TABLE 14. Enthalpies of vaporization of succinimide obtained from the Cox and Clapeyron equations

T/K	$\Delta_l^g H$ / kJ·mol^{-1}
290.00	86.93 ± 5.41
298.15	85.75 ± 4.53
300.00	85.49 ± 3.47
320.00	82.71 ± 2.74
340.00	80.08 ± 1.65
360.00	77.78 ± 0.95
380.00	75.32 ± 0.50
400.00	73.20 ± 0.23
420.00	71.28 ± 0.10
440.00	69.55 ± 0.04
460.00	68.03 ± 0.03
480.00	66.72 ± 0.04
500.00	65.63 ± 0.07
520.00	64.74 ± 0.10
540.00	64.08 ± 0.14
560.00	63.64 ± 0.20
580.00	63.40 ± 0.29
600.00	63.35 ± 0.44

γ-Butyrolactone

γ-Butyrolactone, $C_4H_6O_2$, was obtained from Fluka Chemical Corporation with an advertised purity of greater than 99 per cent. Gas–liquid–chromatographic (GLC) analysis of the sample registered a purity level of greater than 99.98 per cent. Hence, no further purification was needed.

Combustion Bomb Calorimetric Results

Six determinations of the energy of combustion of γ-butyrolactone were made. The percentage carbon dioxide recovery was 100.00 ± 0.01 (mean and standard deviation for five experiments). A typical combustion experiment is summarized in table 15. It is impractical to list summaries for each combustion, but values of $\Delta_c U^o_m/M$ for all the experiments are reported in table 16. All values of $\Delta_c U^o_m/M$ in tables 15 and 16 refer to the reaction:

$$C_4H_6O_2\ (c) + 9/2\ O_2\ (g) = 4\ CO_2\ (g) + 3\ H_2O\ (l) \qquad (3.7).$$

Table 17 gives derived molar values of $\Delta_c U^o_m$, the standard energy of combustion; $\Delta_c H^o_m$, the standard enthalpy of combustion; and $\Delta_f H^o_m$, the standard enthalpy of formation. Values of $\Delta_c U^o_m$ and $\Delta_c H^o_m$ refer to reaction **3.7**. The value of $\Delta_f H^o_m$ refers to the reaction:

$$4\ C\ (c, \text{graphite}) + 3\ H_2\ (g) + O_2\ (g) = C_4H_6O_2\ (c) \qquad (3.8).$$

Uncertainties given in table 17 are the uncertainty interval (24). The enthalpies of formation of gaseous CO_2 and liquid H_2O were taken to be –393.51 ± 0.13 and –285.830 ± 0.040 kJ mol^{-1}, respectively, as assigned by CODATA (25).

Vapor Pressure Determinations

The experimentally determined ebulliometric vapor–pressure measurements obtained for γ-butyrolactone are reported in table 18. The least-squares evaluated Cox equation parameters are given in table 19. Details of the Cox equation fits are given in table 18.

Enthalpies of Vaporization

Derived enthalpies of vaporization for γ-butyrolactone from the Cox equation fit using the Clapeyron equation and the data reported in table 2 are listed in table 20.

TABLE 15. Typical combustion experiment for γ-butyrolactone at 298.15 K (p° = 101.325 kPa)[a]

m'(compound)/g	1.072856
m''(auxiliary oil)/g	0.038536
m'''(fuse)/g	0.001020
$n_i(H_2O)$/mol	0.05335
m(Pt)/g	33.32
$\Delta T=(t_i - t_f + \Delta t_{corr})$/K	1.599104
$\varepsilon(calor)(\Delta T)$/J	−26842.10
$\varepsilon(cont)(\Delta T)$/J [b]	−31.95
ΔU_{ign}/J	0.75
$\Delta U_{dec}(HNO_3)$/J	0.0
ΔU(corr. to std. states)/J [c]	17.42
$-m''(\Delta_c U^\circ_m/M)(oil)$/J	1774.28
$-m'''(\Delta_c U^\circ_m/M)(fuse)$/J	17.28
$m'(\Delta_c U^\circ_m/M)(compound)$/J	−25064.32
$(\Delta_c U^\circ_m/M)(compound)/J\cdot g^{-1}$	−23362.24

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

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

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

TABLE 16. Summary of experimental enthalpy of combustion results for γ–butyrolactone. Values of $(\Delta_c U^o_m/M)(\text{compound})/J\cdot g^{-1}$ at 298.15 K and p° =101.325 kPa.

	$(\Delta_c U^o_m/M)(\text{compound})$
	$J\cdot g^{-1}$
	−23362.2
	−23340.6[a]
	−23360.8
	−23361.9
	−23362.6
	−23360.1
mean	−23361.5
standard deviation	0.5

[a] Value discarded due to soot formation.

TABLE 17. Molar thermochemical functions for γ–butyrolactone at 298.15 K and p° = 101.325 kPa

	$\Delta_c U^o_m$	$\Delta_c H^o_m$	$\Delta_f H^o_m$
	$kJ\cdot mol^{-1}$	$kJ\cdot mol^{-1}$	$kJ\cdot mol^{-1}$
γ–butyrolactone	−2011.22 ± 0.28	−2012.46 ± 0.28	−419.07 ± 0.36

TABLE 18. Summary of vapor pressure results for γ–butyrolactone; decane or water refers to which material was used as the standard in the reference ebulliometer, the pressure P for ebulliometric measurements was calculated from the condensation temperature of the reference substance, in the ebulliometric measurements T is the condensation temperature of the sample, $T_{boil} - T_{cond}$ is the difference between the boiling and condensation temperatures for the sample in the ebulliometer, ΔP is the difference of the calculated value of pressure from the observed value of pressure, σ_i is the propagated error calculated from equations **2.1** and **2.2.**

Material	P / kPa	T / K	$T_{boil} - T_{cond}$ / K	ΔP / kPa	σ_i / kPa
			γ–butyrolactone		
decane	1.9998	361.087	0.069	−0.0005	0.0001
decane	2.6664	367.393	0.055	0.0000	0.0002
decane	5.3329	383.716	0.032	0.0005	0.0003
decane	7.9993	394.084	0.030	−0.0003	0.0005
decane	10.6658	401.836	0.028	0.0033	0.0005
decane	13.3322	408.109	0.029	0.0033	0.0007
decane	16.6653	414.616	0.027	0.0030	0.0008
decane	19.9330	420.021	0.024	−0.0010	0.0010
water	25.0233	427.121	0.023	−0.0024	0.0011
water	31.1774	434.288	0.024	0.0236	0.0015
water	38.5648	441.431	0.023	−0.0088	0.0019
water	47.3748	448.637	0.022	−0.0113	0.0023
water	57.8179	455.878	0.023	−0.0118	0.0028
water	70.1209	463.155	0.021	−0.0141	0.0032
water	84.5330	470.465	0.021	−0.0130	0.0038
water	101.325	477.810	0.020	−0.012	0.004
water	120.793	485.188	0.020	−0.004	0.005
water	143.246	492.586	0.020	0.048	0.006
water	169.019	500.032	0.020	0.056	0.007
water	198.488	507.517	0.019	0.048	0.008
water	232.017	515.037	0.016	0.011	0.009
water	270.022	522.601	0.013	−0.107	0.009

TABLE 19. Cox equation constants and fitting parameters for γ–butyrolactone

T_{ref} / K	477.805 ± 0.002
A	2.79557 ± 0.00310
10^3B/K	−1.14428 ± 0.01445
10^6C/K^2	8.76968 ± 0.01664
Data Range/K	361 – 523
Normalized Covariance Terms[a]	
AB	−0.99849
AC	0.99329
BC	−0.99810

[a] Cross terms of the normalized variance–covariance matrix.

TABLE 20. Enthalpies of vaporization of γ–butyrolactone obtained from the Cox and Clapeyron equations

T/K	$\Delta_l^g H$ / kJ·mol^{-1}
290.00	53.89 ± 0.17
298.15	53.46 ± 0.13
300.00	53.37 ± 0.12
320.00	52.36 ± 0.07
340.00	51.37 ± 0.03
360.00	50.39 ± 0.02
380.00	49.44 ± 0.02
400.00	48.51 ± 0.04
420.00	47.58 ± 0.07
440.00	46.66 ± 0.10
460.00	45.75 ± 0.14
480.00	44.82 ± 0.20
500.00	43.89 ± 0.27
520.00	42.94 ± 0.37
540.00	41.95 ± 0.47
560.00	40.93 ± 0.60
580.00	39.86 ± 0.76
600.00	38.72 ± 0.94

2–Pyrrolidone

2–Pyrrolidone, C_4H_7ON, was obtained from Aldrich Chemicals with an advertised purity of greater than 99 per cent. Gas–liquid–chromatographic (GLC) analysis of the sample registered a purity level of greater than 99.6 per cent. The calorimetric sample was twice distilled using a spinning–band still. GLC analysis of the product of the second distillation gave a sample purity of greater than 99.99 per cent.

Combustion Bomb Calorimetric Results

2–Pyrrolidone has a triple point of 298.08 K. Measurements of the energy of combustion were made with an initial temperature of 298.65 K: hence, the results refer to the liquid phase. Six determinations of the energy of combustion of 2–pyrrolidone were made. The percentage carbon dioxide recovery was 100.02 ± 0.01 (mean and standard deviation). A typical combustion experiment is summarized in table 21. It is impractical to list summaries for each combustion, but values of $\Delta_c U^o_m/M$ for all the experiments are reported in table 22.

All values of $\Delta_c U^o_m/M$ in tables 21 and 22 refer to the reaction:

$$C_4H_7ON\ (l) + 21/4\ O_2\ (g) = 4\ CO_2\ (g) + 7/2\ H_2O\ (l) + 1/2\ N_2\ (g) \qquad (3.9).$$

Table 23 gives derived molar values of $\Delta_c U^o_m$, the standard energy of combustion; $\Delta_c H^o_m$, the standard enthalpy of combustion; and $\Delta_f H^o_m$, the standard enthalpy of formation. Values of $\Delta_c U^o_m$ and $\Delta_c H^o_m$ refer to reaction **3.9**. The value of $\Delta_f H^o_m$ refers to the reaction:

$$4\ C\ (c,\ graphite) + 7/2\ H_2\ (g) + 1/2\ O_2\ (g) + 1/2\ N_2\ (g) = C_4H_7ON\ (l) \qquad (3.10).$$

Uncertainties given in table 23 are the uncertainty interval (24). The enthalpies of formation of gaseous CO_2 and liquid H_2O were taken to be –393.51 ± 0.13 and –285.830 ± 0.040 kJ mol^{-1}, respectively, as assigned by CODATA (25).

Vapor Pressure Determinations

The experimentally determined ebulliometric vapor–pressure measurements obtained for 2–pyrrolidone are reported in table 24. The least–squares evaluated Cox equation parameters are given in table 25. Details of the Cox equation fits are given in table 24.

Enthalpies of Vaporization

Derived enthalpies of vaporization for 2–pyrrolidone from the Cox equation fit using the Clapeyron equation and the data reported in table 2 are listed in table 26.

TABLE 21. Typical combustion experiment for 2–pyrrolidone at 298.15 K (p° = 101.325 kPa)[a]

m'(compound)/g	1.109743
m''(auxiliary oil)/g	0.071034
m'''(fuse)/g	0.000968
$n_i(H_2O)$/mol	0.05335
m(Pt)/g	20.21
$\Delta T=(t_i - t_f + \Delta t_{corr})$/K	2.006466
ε(calor)(ΔT)/J	−33397.10
ε(cont)(ΔT)/J [b]	−38.46
ΔU_{ign}/J	0.75
$\Delta U_{dec}(HNO_3)$/J	58.80
ΔU(corr. to std. states)/J [c]	17.34
$-m''(\Delta_c U^\circ_m/M)$(oil)/J	3270.57
$-m'''(\Delta_c U^\circ_m/M)$(fuse)/J	16.40
$m'(\Delta_c U^\circ_m/M)$(compound)/J	30071.7
$(\Delta_c U^\circ_m/M)$(compound)/J·g^{-1}	27097.9

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

[b] ε_i(cont)(t_i − 298.15 K) + ε_f(cont)(298.15 K − $t_f + \Delta t_{corr}$).

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

TABLE 22. Summary of experimental enthalpy of combustion results for 2–pyrrolidone. Values of $(\Delta_c U^o_m/M)$(compound)/J·g^{-1} at 298.15 K and p° =101.325 kPa.

	$(\Delta_c U^o_m/M)$(compound)
	J·g^{-1}
	−27097.7
	−27100.2
	−27097.9
	−27096.8
	−27100.9
	−27098.5
mean	−27098.6
standard deviation	0.7

TABLE 23. Molar thermochemical functions for 2–pyrrolidone at p° = 101.325 kPa.

	$\Delta_c U^o_m$ / kJ·mol^{-1}	$\Delta_c H^o_m$ / kJ·mol^{-1}	$\Delta_f H^o_m$ / kJ·mol^{-1}
2–pyrrolidone.	−2306.52 ± 0.34[a]	−2308.40 ± 0.34[b]	−266.04 ± 0.42[b]

[a] Value at 300.65 K.

[b] Value at 298.15 K.

TABLE 24. Summary of vapor pressure results for 2–pyrrolidone; decane or water refers to which material was used as the standard in the reference ebulliometer, the pressure P for ebulliometric measurements was calculated from the condensation temperature of the reference substance, in the ebulliometric measurements T is the condensation temperature of the sample, $T_{boil} - T_{cond}$ is the difference between the boiling and condensation temperatures for the sample in the ebulliometer, ΔP is the difference of the calculated value of pressure from the observed value of pressure, σ_i is the propagated error calculated from equations **2.1** and **2.2.**

Material	P / kPa	T / K	$T_{boil} - T_{cond}$ / K	ΔP / kPa	σ_i / kPa
			2–pyrrolidone		
decane	1.9998	405.682	0.094	−0.0011	0.0001
decane	2.6664	412.152	0.073	0.0029	0.0001
decane	3.9997	421.802	0.056	−0.0020	0.0002
decane	5.3329	428.950	0.031	0.0006	0.0003
decane	7.9993	439.551	0.026	0.0001	0.0005
decane	10.6658	447.481	0.018	−0.0036	0.0006
decane	13.3322	453.850	0.025	0.0041	0.0007
decane	16.6653	460.472	0.023	0.0007	0.0008
decane	19.9330	465.949	0.024	0.0027	0.0010
water	25.0233	473.148	0.025	0.0004	0.0011
water	31.1774	480.374	0.027	−0.0049	0.0015
water	47.3748	494.883	0.035	−0.0016	0.0021
water	57.8179	502.196	0.033	−0.0289	0.0025
water	70.1209	509.499	0.038	−0.0009	0.0029
water	84.5330	516.845	0.044	0.0019	0.0034
water	101.325	524.315	0.037	−0.233	0.004

TABLE 25. Cox equation constants and fitting parameters for 2–pyrrolidone

T_{ref} / K	524.220 ± 0.005
A	2.94459 ± 0.01558
10^3B/K	−1.13067 ± 0.07085
10^6C/K^2	6.78896 ± 0.08038
Data Range/K	405 – 524
Normalized Covariance Terms[a]	
AB	−0.99961
AC	0.99842
BC	−0.99960

[a] Cross terms of the normalized variance–covariance matrix.

TABLE 26. Enthalpies of vaporization of 2–pyrrolidone obtained from the Cox and Clapeyron equations

T/K	$\Delta_l^g H$ / kJ·mol^{-1}
290.00	69.21 ± 1.85
298.15	68.66 ± 1.51
300.00	68.54 ± 1.45
320.00	67.20 ± 0.84
340.00	65.87 ± 0.46
360.00	64.54 ± 0.22
380.00	63.24 ± 0.09
400.00	61.94 ± 0.04
420.00	60.66 ± 0.03
440.00	59.40 ± 0.04
460.00	58.13 ± 0.07
480.00	56.85 ± 0.10
500.00	55.57 ± 0.14
520.00	54.25 ± 0.21
540.00	52.91 ± 0.29
560.00	51.52 ± 0.40
580.00	50.09 ± 0.55
600.00	48.59 ± 0.74

2,3–Dihydrofuran

2,3–Dihydrofuran, C_4H_6O, was obtained from Aldrich Chemicals with an advertised purity of greater than 99 per cent. Gas–liquid–chromatographic (GLC) analysis of the sample registered a purity level of greater than 99.7 per cent. The calorimetric sample was twice distilled using the spinning–band still. GLC analysis of the product of the second distillation gave a sample purity of greater than 99.95 per cent.

Combustion Bomb Calorimetric Results

Six determinations of the energy of combustion of 2,3–dihydrofuran were made. A typical combustion experiment is summarized in table 27. The percentage carbon dioxide recovery was 100.11 ± 0.04 (mean and standard deviation). It is impractical to list summaries for each combustion, but values of $\Delta_c U^o_m/M$ for all the experiments are reported in table 28. All values of $\Delta_c U^o_m/M$ in tables 27 and 28 refer to the reaction:

$$C_4H_6O\ (l) + 5\ O_2\ (g) = 4\ CO_2\ (g) + 3\ H_2O\ (l) \qquad (3.11).$$

Table 29 gives derived molar values of $\Delta_c U^o_m$, the standard energy of combustion, $\Delta_c H^o_m$; the standard enthalpy of combustion; and $\Delta_f H^o_m$, the standard enthalpy of formation. Values of $\Delta_c U^o_m$ and $\Delta_c H^o_m$ refer to reaction **3.11**. The value of $\Delta_f H^o_m$ refers to the reaction:

$$4\ C\ (c,\ graphite) + 3\ H_2\ (g) + 1/2\ O_2\ (g) = C_4H_6O\ (l) \qquad (3.12).$$

Uncertainties given in table 29 are the uncertainty interval (24). The enthalpies of formation of gaseous CO_2 and liquid H_2O were taken to be −393.51 ± 0.13 and −285.830 ± 0.040 kJ mol^{-1}, respectively, as assigned by CODATA (25).

Vapor Pressure Determinations

The experimentally determined ebulliometric vapor–pressure measurements obtained for 2,3–dihydrofuran are reported in table 30. The least–squares evaluated Cox equation parameters are given in table 31. Details of the Cox equation fits are given in table 30.

Enthalpies of Vaporization

Derived enthalpies of vaporization for 2,3–dihydrofuran from the Cox equation fit using the Clapeyron equation and the data reported in table 2 are listed in table 32.

TABLE 27. Typical combustion experiment for 2,3–dihydrofuran at 298.15 K (p° = 101.325 kPa)[a]

m'(compound)/g	0.985802
m''(auxiliary oil)/g	0.025550
m'''(fuse)/g	0.001119
$n_i(H_2O)$/mol	0.05335
m(Pt)/g	39.92
$\Delta T=(t_i - t_f + \Delta t_{corr})$/K	2.036329
$\varepsilon(calor)(\Delta T)$/J	−33887.10
$\varepsilon(cont)(\Delta T)$/J [b]	−43.07
ΔU_{ign}/J	0.75
$\Delta U_{dec}(HNO_3)$/J	0.0
ΔU(corr. to std. states)/J [c]	16.59
$-m''(\Delta_c U^\circ_m/M)(oil)$/J	1176.37
$-m'''(\Delta_c U^\circ_m/M)(fuse)$/J	18.96
$m'(\Delta_c U^\circ_m/M)(compound)$/J	32717.5
$(\Delta_c U^\circ_m/M)(compound)/J\cdot g^{-1}$	−33188.7

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

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

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

TABLE 28. Summary of experimental enthalpy of combustion results for 2,3–dihydrofuran. Values of $(\Delta_c U^\circ_m/M)$(compound)/J·g^{-1} at 298.15 K and p° =101.325 kPa.

	$(\Delta_c U^\circ_m/M)$(compound)
	J·g^{-1}
	−33188.7
	−33187.1
	−33185.7
	−33183.1
	−33186.3
	−33181.7
mean	−33185.4
standard deviation	1.1

TABLE 29. Molar thermochemical functions for 2,3–dihydrofuran at 298.15 K and p° = 101.325 kPa

	$\Delta_c U^\circ_m$	$\Delta_c H^\circ_m$	$\Delta_f H^\circ_m$
	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}
2,3–dihydrofuran	−2326.03 ± 0.30	−2328.51 ± 0.30	−103.02 ± 0.38

TABLE 30. Summary of vapor pressure results for 2,3–dihydrofuran; decane or water refers to which material was used as the standard in the reference ebulliometer, the pressure P for ebulliometric measurements was calculated from the condensation temperature of the reference substance, in the ebulliometric measurements T is the condensation temperature of the sample, $T_{boil} - T_{cond}$ is the difference between the boiling and condensation temperatures for the sample in the ebulliometer, ΔP is the difference of the calculated value of pressure from the observed value of pressure, σ_i is the propagated error calculated from equations **2.1** and **2.2.**

Material	$\frac{P}{kPa}$	$\frac{T}{K}$	$\frac{T_{boil} - T_{cond}}{K}$	$\frac{\Delta P}{kPa}$	$\frac{\sigma_i}{kPa}$
		2,3–dihydrofuran			
water	70.1209	317.178	0.013	−0.0008	0.0038
water	84.5330	322.380	0.015	0.0042	0.0043
water	101.325	327.616	0.017	0.006	0.005
water	120.793	332.885	0.018	0.008	0.006
water	143.246	338.191	0.019	0.003	0.007
water	169.019	343.532	0.019	−0.009	0.008
water	232.017	354.329	0.024	0.007	0.010
water	270.022	359.792	0.029	−0.003	0.011

TABLE 31. Cox equation constants and fitting parameters for 2,3–dihydrofuran

T_{ref} / K	327.6 ± 0.1
A	2.61881 ± 0.02711
10^3B/K	–0.79117 ± 0.15865
10^6C/K^2	0.46689 ± 0.23180
Data Range/K	317 – 360
Normalized Covariance Terms[a]	
AB	–0.99978
AC	0.99918
BC	–0.99981

[a] Cross terms of the normalized variance–covariance matrix.

TABLE 32. Enthalpies of vaporization of 2,3–dihydrofuran obtained from the Cox and Clapeyron equations

T/K	$\Delta_l^g H$ / kJ·mol^{-1}
290.00	31.10 ± 0.07
298.15	30.77 ± 0.08
300.00	30.69 ± 0.08
320.00	29.79 ± 0.13
340.00	28.76 ± 0.22
360.00	27.60 ± 0.32
380.00	26.30 ± 0.44
400.00	24.86 ± 0.59
420.00	23.28 ± 0.78
440.00	21.57 ± 1.00

3,4-Dihydro-2H-pyran

3,4-Dihydro-2H-pyran, C_5H_8O, was obtained from Aldrich Chemicals with an advertised purity of greater than 99 per cent. Gas-liquid-chromatographic (GLC) analysis of the sample registered a purity level of greater than 97.5 per cent. The calorimetric sample was twice distilled using the spinning-band still. GLC analysis of the product of the second distillation gave a sample purity of greater than 99.95 per cent. Due to an accident on the vacuum transfer line, the combustion sample was exposed to air for a short period. 3,4-Dihydro-2H-pyran is highly hygroscopic and is difficult to dry (27). It was obviously contaminated with a little water during the mishap, hence the subsequent measurements are based on the percentage carbon dioxide recovery and not mass of sample burned.

Combustion Bomb Calorimetric Results

Six determinations of the energy of combustion of 3,4-dihydro-2H-pyran were made. A typical combustion experiment is summarized in table 33. The percentage carbon dioxide recovery was 99.82 ± 0.04 (mean and standard deviation). It is impractical to list summaries for each combustion, but values of $\Delta_c U^o_m/M$ for all the experiments are reported in table 34. All values of $\Delta_c U^o_m/M$ in tables 33 and 34 refer to the reaction:

$$C_5H_8O\ (l) + 13/2\ O_2\ (g) = 5\ CO_2\ (g) + 4\ H_2O\ (l) \qquad (3.13).$$

Table 35 gives derived molar values of $\Delta_c U^o_m$, the standard energy of combustion, $\Delta_c H^o_m$; the standard enthalpy of combustion, and $\Delta_f H^o_m$; the standard enthalpy of formation. Values of $\Delta_c U^o_m$ and $\Delta_c H^o_m$ refer to reaction **3.13**. The value of $\Delta_f H^o_m$ refers to the reaction:

$$5\ C\ (c, graphite) + 4\ H_2\ (g) + 1/2\ O_2\ (g) = C_5H_8O\ (l) \qquad (3.14).$$

Uncertainties given in table 35 are the uncertainty interval (24). The enthalpies of formation of gaseous CO_2 and liquid H_2O were taken to be −393.51 ± 0.13 and −285.830 ± 0.040 kJ mol^{-1}, respectively, as assigned by CODATA (25).

Vapor Pressure Determinations

The experimentally determined ebulliometric vapor-pressure measurements obtained for 3,4-dihydro-2H-pyran are reported in table 36. The least-squares evaluated Cox equation parameters are given in table 37. Details of the Cox equation fits are given in table 36.

Enthalpies of Vaporization

Derived enthalpies of vaporization for 3,4–dihydro–2H–pyran from the Cox equation fit using the Clapeyron equation and the data reported in table 2 are listed in table 38.

TABLE 33. Typical combustion experiment for 3,4–dihydro–2H–pyran at 298.15 K (p° = 101.325 kPa)[a]

m'(compound)/g	0.921653
percentage carbon dioxide recovery	99.842
m''(auxiliary oil)/g	0.026001
m'''(fuse)/g	0.001214
$n_i(H_2O)$/mol	0.05335
m(Pt)/g	39.31
$\Delta T=(t_i - t_f + \Delta t_{corr})$/K	2.016553
ε(calor)(ΔT)/J	−33558.00
ε(cont)(ΔT)/J [b]	−42.56
ΔU_{ign}/J	0.75
$\Delta U_{dec}(HNO_3)$/J	0.0
ΔU(corr. to std. states)/J [c]	15.15
$-m''(\Delta_c U^\circ_m/M)$(oil)/J	1197.14
$-m'''(\Delta_c U^\circ_m/M)$(fuse)/J	20.57
$m'(\Delta_c U^\circ_m/M)$(compound)/J	−32366.95
$(\Delta_c U^\circ_m/M)$(compound)/J·g^{-1}	−35173.9[d]

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

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

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

[d] Based on carbon dioxide analysis.

TABLE 34. Summary of experimental enthalpy of combustion results for 3,4–dihydro–2H–pyran. Values of $(\Delta_c U^\circ_m/M)$(compound)/$J \cdot g^{-1}$ at 298.15 K and p° =101.325 kPa.

	$(\Delta_c U^\circ_m/M)$(compound)
	$J \cdot g^{-1}$
	−35198.5
	−35176.6
	−35183.6
	−35181.4
	−35175.6
	−35173.9
mean	−35181.6
standard deviation	3.7

TABLE 35. Molar thermochemical functions for 3,4–dihydro–2H–pyran at 298.15 K and p° = 101.325 kPa

	$\Delta_c U^\circ_m$ / $kJ \cdot mol^{-1}$	$\Delta_c H^\circ_m$ / $kJ \cdot mol^{-1}$	$\Delta_f H^\circ_m$ / $kJ \cdot mol^{-1}$
3,4–dihydro–2H–pyran	−2959.42 ± 0.80	−2963.14 ± 0.80	−147.73 ± 0.86

TABLE 36. Summary of vapor pressure results for 3,4–dihydro–2H–pyran; decane or water refers to which material was used as the standard in the reference ebulliometer, the pressure P for ebulliometric measurements was calculated from the condensation temperature of the reference substance, in the ebulliometric measurements T is the condensation temperature of the sample, $T_{boil} - T_{cond}$ is the difference between the boiling and condensation temperatures for the sample in the ebulliometer, ΔP is the difference of the calculated value of pressure from the observed value of pressure, σ_i is the propagated error calculated from equations **2.1** and **2.2**.

Material	P / kPa	T / K	$T_{boil} - T_{cond}$ / K	ΔP / kPa	σ_i / kPa
		3,4–dihydro–2H–pyran			
decane	10.6658	299.424	0.034	0.0005	0.0007
decane	13.3322	304.256	0.036	0.0013	0.0008
decane	16.6653	309.280	0.036	0.0013	0.0010
decane	19.9330	313.463	0.037	−0.0028	0.0011
water	25.0233	318.971	0.038	−0.0061	0.0013
water	31.1774	324.523	0.038	−0.0111	0.0016
water	38.5648	330.095	0.064	0.0150	0.0022
water	47.3748	335.733	0.018	0.0088	0.0026
water	57.8179	341.414	0.020	0.0064	0.0030
water	70.1209	347.138	0.020	0.0009	0.0034
water	84.5330	352.905	0.019	−0.0034	0.0041
water	101.325	358.718	0.017	−0.011	0.005
water	120.793	364.572	0.019	−0.008	0.006
water	143.246	370.470	0.022	−0.004	0.006
water	169.019	376.413	0.022	−0.007	0.007
water	198.488	382.402	0.025	−0.004	0.008
water	232.017	388.431	0.036	0.009	0.009
water	270.022	394.507	0.051	0.005	0.010

TABLE 37. Cox equation constants and fitting parameters for 3,4–dihydro–2H–pyran

T_{ref} / K	358.714 ± 0.002
A	2.79381 ± 0.00752
10^3B/K	−1.72379 ± 0.04461
10^6C/K^2	1.70968 ± 0.06540
Data Range/K	299 – 395
Normalized Covariance Terms[a]	
AB	−0.99931
AC	0.99726
BC	−0.99931

[a] Cross terms of the normalized variance–covariance matrix.

TABLE 38. Enthalpies of vaporization of 3,4–dihydro–2H–pyran obtained from the Cox and Clapeyron equations

T/K	$\Delta_l^g H$ / kJ·mol^{-1}
290.00	35.35 ± 0.03
298.15	34.92 ± 0.04
300.00	34.82 ± 0.05
320.00	33.74 ± 0.08
340.00	32.65 ± 0.13
360.00	31.54 ± 0.21
380.00	30.41 ± 0.30
400.00	29.25 ± 0.41
420.00	28.04 ± 0.57
440.00	26.76 ± 0.74
460.00	25.39 ± 0.96

1,3–Cyclohexadiene

1,3–Cyclohexadiene, C_6H_8, was obtained from Fluka Chemical Corporation with an advertised purity of greater than 97 per cent. Gas–liquid–chromatographic (GLC) analysis of the sample registered a purity level of greater than 98 per cent. The calorimetric sample was twice distilled using the spinning–band still. GLC analysis of the product of the second distillation gave a sample purity of greater than 99.95 per cent.

Combustion Bomb Calorimetric Results

Six determinations of the energy of combustion of 1,3–cyclohexadiene were made. A typical combustion experiment is summarized in table 39. The percentage carbon dioxide recovery was 99.98 ± 0.01 (mean and standard deviation). It is impractical to list summaries for each combustion, but values of $\Delta_c U^o_m/M$ for all the experiments are reported in table 40. All values of $\Delta_c U^o_m/M$ in tables 39 and 40 refer to the reaction:

$$C_6H_8\ (l) + 8\ O_2\ (g) = 6\ CO_2\ (g) + 4\ H_2O\ (l) \qquad \textbf{(3.15)}.$$

Table 41 gives derived molar values of $\Delta_c U^o_m$, the standard energy of combustion; $\Delta_c H^o_m$, the standard enthalpy of combustion; and $\Delta_f H^o_m$, the standard enthalpy of formation. Values of $\Delta_c U^o_m$ and $\Delta_c H^o_m$ refer to reaction **3.15**. The value of $\Delta_f H^o_m$ refers to the reaction:

$$6\ C\ (c, \text{graphite}) + 4H_2\ (g) = C_6H_8\ (l) \qquad \textbf{(3.16)}.$$

Uncertainties given in table 41 are the uncertainty interval (24). The enthalpies of formation of gaseous CO_2 and liquid H_2O were taken to be –393.51 ± 0.13 and –285.830 ± 0.040 kJ mol^{-1}, respectively, as assigned by CODATA (25).

Vapor Pressure Determinations

The experimentally determined ebulliometric vapor–pressure measurements obtained for 1,3–cyclohexadiene are reported in table 42. The least–squares evaluated Cox equation parameters are given in table 43. Details of the Cox equation fits are given in table 42.

Enthalpies of Vaporization

Derived enthalpies of vaporization for 1,3–cyclohexadiene from the Cox equation fit using the Clapeyron equation and the data reported in table 2 are listed in table 44.

TABLE 39. Typical combustion experiment for 1,3–cyclohexadiene at 298.15 K (p° = 101.325 kPa)[a]

m'(compound)/g	0.692036
m''(auxiliary oil)/g	0.053480
m'''(fuse)/g	0.001205
$n_i(H_2O)$/mol	0.05335
m(Pt)/g	32.72
$\Delta T=(t_i - t_f + \Delta t_{corr})$/K	2.000822
ε(calor)(ΔT)/J	−33296.22
ε(cont)(ΔT)/J [b]	−39.22
ΔU_{ign}/J	0.75
$\Delta U_{dec}(HNO_3)$/J	0.0
ΔU(corr. to std. states)/J [c]	13.82
$-m''(\Delta_c U^\circ_m/M)$(oil)/J	2462.37
$-m'''(\Delta_c U^\circ_m/M)$(fuse)/J	20.41
$m'(\Delta_c U^\circ_m/M)$(compound)/J	−30838.09
$(\Delta_c U^\circ_m/M)$(compound)/J·g^{-1}	−44561.4

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

[b] ε_i(cont)(t_i − 298.15 K) + ε_f(cont)(298.15 K − $t_f + \Delta t_{corr}$).

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

TABLE 40. Summary of experimental enthalpy of combustion results for 1,3–cyclohexadiene. Values of $(\Delta_c U^\circ_m/M)$(compound)/J·g^{-1} at 298.15 K and p° =101.325 kPa.

	$(\Delta_c U^\circ_m/M)$(compound)
	J·g^{-1}
	−44561.4
	−44563.5
	−44571.6
	−44563.2
	−44560.8
	−44555.2
mean	−44562.6
standard deviation	2.2

TABLE 41. Molar thermochemical functions for 1,3–cyclohexadiene at 298.15 K and p° = 101.325 kPa

	$\Delta_c U^\circ_m$	$\Delta_c H^\circ_m$	$\Delta_f H^\circ_m$
	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}
1,3–cyclohexadiene	−3570.83 ± 0.54	−3575.79 ± 0.54	71.41 ± 0.62

TABLE 42. Summary of vapor pressure results for 1,3–cyclohexadiene; decane or water refers to which material was used as the standard in the reference ebulliometer, the pressure P for ebulliometric measurements was calculated from the condensation temperature of the reference substance, in the ebulliometric measurements T is the condensation temperature of the sample, $T_{boil} - T_{cond}$ is the difference between the boiling and condensation temperatures for the sample in the ebulliometer, ΔP is the difference of the calculated value of pressure from the observed value of pressure, σ_i is the propagated error calculated from equations **2.1** and **2.2**.

Material	$\frac{P}{kPa}$	$\frac{T}{K}$	$\frac{T_{boil} - T_{cond}}{K}$	$\frac{\Delta P}{kPa}$	$\frac{\sigma_i}{kPa}$
		1,3–cyclohexadiene			
decane	13.3322	298.646	0.006	−0.0008	0.0008
decane	16.6653	303.693	0.004	0.0003	0.0009
decane	19.9330	307.893	0.005	0.0001	0.0011
water	25.0233	313.430	0.004	−0.0002	0.0013
water	31.1774	319.011	0.004	0.0022	0.0017
water	38.5648	324.640	0.004	0.0015	0.0022
water	47.3748	330.315	0.004	0.0003	0.0025
water	57.8179	336.037	0.004	−0.0011	0.0030
water	70.1209	341.806	0.004	−0.0037	0.0035
water	84.5330	347.622	0.005	−0.0043	0.0041
water	101.325	353.484	0.005	−0.004	0.005
water	120.793	359.393	0.009	0.006	0.005
water	143.246	365.355	0.012	−0.004	0.006
water	169.019	371.361	0.016	0.000	0.007
water	198.488	377.416	0.022	0.009	0.008
water	232.017	383.517	0.031	0.012	0.009
water	270.022	389.672	0.044	−0.015	0.010

TABLE 43. Cox equation constants and fitting parameters for 1,3–cyclohexadiene

T_{ref} / K	353.483 ± 0.001
A	2.73996 ± 0.00261
10^3B/K	−1.61657 ± 0.01554
10^6C/K^2	1.62374 ± 0.02289
Data Range/K	298 – 390
Normalized Covariance Terms[a]	
AB	−0.99935
AC	0.99744
BC	−0.99936

[a] Cross terms of the normalized variance–covariance matrix.

TABLE 44. Enthalpies of vaporization of 1,3–cyclohexadiene obtained from the Cox and Clapeyron equations

T/K	$\Delta_l^g H$ / kJ·mol^{-1}
290.00	33.58 ± 0.04
298.15	33.17 ± 0.05
300.00	33.08 ± 0.06
320.00	32.08 ± 0.10
340.00	31.05 ± 0.16
360.00	29.97 ± 0.24
380.00	28.85 ± 0.34
400.00	27.66 ± 0.52
420.00	26.39 ± 0.64
440.00	25.00 ± 0.85
460.00	23.46 ± 1.10

1,4–Cyclohexadiene

1,4–Cyclohexadiene, C_6H_8, was obtained from Fluka Chemical Corporation with an advertised purity of greater than 99 per cent. Gas–liquid–chromatographic (GLC) analysis of the sample registered a purity level of 98 per cent. The calorimetric sample was twice distilled using the spinning–band still. GLC analysis of the product of the second distillation gave a sample purity of greater than 99.9 per cent.

Combustion Bomb Calorimetric Results

Six determinations of the energy of combustion of 1,4–cyclohexadiene were made. A typical combustion experiment is summarized in table 45. The percentage carbon dioxide recovery was 99.97 ± 0.02 (mean and standard deviation). It is impractical to list summaries for each combustion, but values of $\Delta_c U^o_m/M$ for all the experiments are reported in table 46. All values of $\Delta_c U^o_m/M$ in tables 45 and 46 refer to the reaction:

$$C_6H_8\ (l) + 8\ O_2\ (g) = 6\ CO_2\ (g) + 4\ H_2O\ (l) \qquad (3.17).$$

Table 47 gives derived molar values of $\Delta_c U^o_m$, the standard energy of combustion; $\Delta_c H^o_m$, the standard enthalpy of combustion; and $\Delta_f H^o_m$, the standard enthalpy of formation. Values of $\Delta_c U^o_m$ and $\Delta_c H^o_m$ refer to reaction **3.17**. The value of $\Delta_f H^o_m$ refers to the reaction:

$$6\ C\ (c,\ graphite) + 4H_2\ (g) = C_6H_8\ (l) \qquad (3.18).$$

Uncertainties given in table 47 are the uncertainty interval (24). The enthalpies of formation of gaseous CO_2 and liquid H_2O; were taken to be –393.51 ± 0.13 and –285.830 ± 0.040 kJ mol^{-1}, respectively, as assigned by CODATA (25).

Vapor Pressure Determinations

The experimentally determined ebulliometric vapor–pressure measurements obtained for 1,4–cyclohexadiene are reported in table 48. The least–squares evaluated Cox equation parameters are given in table 49. Details of the Cox equation fits are given in table 48.

Enthalpies of Vaporization

Derived enthalpies of vaporization for 1,4–cyclohexadiene from the Cox equation fit using the Clapeyron equation and the data reported in table 2 are listed in table 50.

TABLE 45. Typical combustion experiment for 1,4–cyclohexadiene at 298.15 K (p° = 101.325 kPa)[a]

m'(compound)/g	0.700633
m''(auxiliary oil)/g	0.043693
m'''(fuse)/g	0.001092
$n_i(H_2O)$/mol	0.05335
m(Pt)/g	39.92
$\Delta T=(t_i - t_f + \Delta t_{corr})$/K	1.995762
ε(calor)(ΔT)/J	−33212.01
ε(cont)(ΔT)/J [b]	−41.11
ΔU_{ign}/J	0.75
$\Delta U_{dec}(HNO_3)$/J	0.0
ΔU(corr. to std. states)/J [c]	13.84
$-m''(\Delta_c U^\circ_m/M)$(oil)/J	2011.73
$-m'''(\Delta_c U^\circ_m/M)$(fuse)/J	18.50
$m'(\Delta_c U^\circ_m/M)$(compound)/J	−31208.3
$(\Delta_c U^\circ_m/M)$(compound)/J·g^{-1}	−44543.0

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

[b] ε_i(cont)$(t_i - 298.15\ K) + \varepsilon_f$(cont)$(298.15\ K - t_f + \Delta t_{corr})$.

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

TABLE 46. Summary of experimental enthalpy of combustion results for 1,4–cyclohexadiene. Values of $(\Delta_c U^\circ_m/M)$(compound)/$J \cdot g^{-1}$ at 298.15 K and p° =101.325 kPa.

	$(\Delta_c U^\circ_m/M)$(compound)
	$J \cdot g^{-1}$
	−44543.0
	−44542.7
	−44536.3
	−44544.7
	−44544.1
	−44536.8
mean	−44541.3
standard deviation	1.5

TABLE 47. Molar thermochemical functions for 1,4–cyclohexadiene at 298.15 K and p° = 101.325 kPa

	$\Delta_c U^\circ_m$	$\Delta_c H^\circ_m$	$\Delta_f H^\circ_m$
	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$
1,4–cyclohexadiene	−3569.12 ± 0.48	−3574.08 ± 0.48	69.70 ± 0.58

TABLE 48. Summary of vapor pressure results for 1,4–cyclohexadiene; decane or water refers to which material was used as the standard in the reference ebulliometer, the pressure P for ebulliometric measurements was calculated from the condensation temperature of the reference substance, in the ebulliometric measurements T is the condensation temperature of the sample, $T_{boil} - T_{cond}$ is the difference between the boiling and condensation temperatures for the sample in the ebulliometer, ΔP is the difference of the calculated value of pressure from the observed value of pressure, σ_i is the propagated error calculated from equations **2.1** and **2.2**.

Material	$\frac{P}{kPa}$	$\frac{T}{K}$	$\frac{T_{boil} - T_{cond}}{K}$	$\frac{\Delta P}{kPa}$	$\frac{\sigma_i}{kPa}$
		1,4–cyclohexadiene			
decane	7.9993	296.173	0.011	0.0005	0.0005
decane	10.6658	302.255	0.008	−0.0004	0.0006
decane	13.3322	307.179	0.008	−0.0001	0.0008
decane	16.6653	312.299	0.007	−0.0003	0.0009
decane	19.9330	316.558	0.006	−0.0016	0.0011
water	25.0233	322.170	0.006	−0.0026	0.0013
water	31.1774	327.818	0.009	0.0055	0.0017
water	38.5648	333.518	0.008	0.0039	0.0022
water	47.3748	339.261	0.008	0.0023	0.0025
water	57.8179	345.050	0.007	−0.0010	0.0030
water	70.1209	350.882	0.007	−0.0030	0.0035
water	84.5330	356.757	0.007	−0.0014	0.0041
water	101.325	362.679	0.006	−0.006	0.005
water	120.793	368.644	0.006	−0.002	0.005
water	143.246	374.654	0.006	−0.001	0.006
water	169.019	380.707	0.005	0.004	0.007
water	198.488	386.807	0.005	0.006	0.008
water	232.017	392.950	0.004	0.003	0.009
water	270.022	399.137	0.004	−0.006	0.010

TABLE 49. Cox equation constants and fitting parameters for 1,4–cyclohexadiene

T_{ref} / K	362.677 ± 0.001
A	2.77051 ± 0.00188
10^3B/K	−1.65194 ± 0.00110
10^6C/K^2	1.64408 ± 0.00159
Data Range/K	296 – 400
Normalized Covariance Terms[a]	
AB	−0.99945
AC	0.99760
BC	−0.99933

[a] Cross terms of the normalized variance–covariance matrix.

TABLRE 50. Enthalpies of vaporization of 1,4–cyclohexadiene obtained from the Cox and Clapeyron equations

T/K	$\Delta_l^g H$ / kJ·mol^{-1}
290.00	35.47 ± 0.03
298.15	35.05 ± 0.04
300.00	34.95 ± 0.05
320.00	33.92 ± 0.07
340.00	32.88 ± 0.12
360.00	31.81 ± 0.20
380.00	30.71 ± 0.29
400.00	29.54 ± 0.42
420.00	28.31 ± 0.56
440.00	27.00 ± 0.75
460.00	25.53 ± 0.98

1-Methyl-1-phenylhydrazine

1-Methyl-1-phenylhydrazine, $C_7H_{10}N_2$, was obtained from Aldrich Chemicals with an advertised purity of greater than 95 per cent. Gas-liquid-chromatographic (GLC) analysis of the sample registered a purity level of greater than 95.8 per cent. The calorimetric sample was twice distilled using the spinning-band still. GLC analysis of the product of the second distillation gave a sample purity of greater than 99.95 per cent.

Combustion Bomb Calorimetric Results

Six determinations of the energy of combustion of 1-methyl-1-phenylhydrazine were made. A typical combustion experiment is summarized in table 51. The percentage carbon dioxide recovery was 99.96 ± 0.02 (mean and standard deviation). It is impractical to list summaries for each combustion, but values of $\Delta_c U^o_m/M$ for all the experiments are reported in table 52. All values of $\Delta_c U^o_m/M$ in tables 51 and 52 refer to the reaction:

$$C_7H_{10}N_2\ (l) + 19/2\ O_2\ (g) = 7\ CO_2\ (g) + 5\ H_2O\ (l) + N_2\ (g) \qquad (3.19).$$

Table 53 gives derived molar values of $\Delta_c U^o_m$, the standard energy of combustion; $\Delta_c H^o_m$, the standard enthalpy of combustion; and $\Delta_f H^o_m$, the standard enthalpy of formation. Values of $\Delta_c U^o_m$ and $\Delta_c H^o_m$ refer to reaction **3.19**. The value of $\Delta_f H^o_m$ refers to the reaction:

$$7\ C\ (c, \text{graphite}) + 5\ H_2\ (g) + N_2\ (g) = C_7H_{10}N_2\ (l) \qquad (3.20).$$

Uncertainties given in table 53 are the uncertainty interval (24). The enthalpies of formation of gaseous CO_2 and liquid H_2O were taken to be −393.51 ± 0.13 and −285.830 ± 0.040 kJ mol^{-1}, respectively, as assigned by CODATA (25).

Vapor Pressure Determinations

The experimentally determined ebulliometric vapor-pressure measurements obtained for 1-methyl-1-phenylhydrazine are reported in table 54. The least-squares evaluated Cox equation parameters are given in table 55. Details of the Cox equation fits are given in table 54.

Enthalpies of Vaporization

Derived enthalpies of vaporization for 1-methyl-1-phenylhydrazine from the Cox equation fit using the Clapeyron equation and the data reported in table 2 are listed in table 56.

TABLE 51. Typical combustion experiment for 1–methyl–1–phenylhydrazine at 298.15 K (p° = 101.325 kPa)[a]

m'(compound)/g	0.894520
m''(auxiliary oil)/g	0.038042
m'''(fuse)/g	0.001234
$n_i(H_2O)$/mol	0.05335
m(Pt)/g	20.21
$\Delta T=(t_i - t_f + \Delta t_{corr})$/K	2.012211
$\varepsilon(calor)(\Delta T)$/J	−33485.75
$\varepsilon(cont)(\Delta T)$/J [b]	−37.62
ΔU_{ign}/J	0.75
$\Delta U_{dec}(HNO_3)$/J	48.29
ΔU(corr. to std. states)/J [c]	15.40
$-m''(\Delta_c U^\circ_m/M)(oil)$/J	1751.53
$-m'''(\Delta_c U^\circ_m/M)(fuse)$/J	20.91
$m'(\Delta_c U^\circ_m/M)(compound)$/J	−31686.5
$(\Delta_c U^\circ_m/M)(compound)/J\cdot g^{-1}$	−35422.9

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

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

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

TABLE 52. Summary of experimental enthalpy of combustion results for 1–methyl–1–phenylhydrazine. Values of $(\Delta_c U^\circ_m/M)$(compound)/$J \cdot g^{-1}$ at 298.15 K and p° =101.325 kPa.

	$(\Delta_c U^\circ_m/M)$(compound)
	$J \cdot g^{-1}$
	−35422.9
	−35421.3
	−35412.8
	−35439.0
	−35426.7
	−35411.3
mean	−35422.3
standard deviation	4.1

TABLE 53. Molar thermochemical functions for 1–methyl–1–phenylhydrazine at 298.15 K and p° = 101.325 kPa

	$\Delta_c U^\circ_m$ / $kJ \cdot mol^{-1}$	$\Delta_c H^\circ_m$ / $kJ \cdot mol^{-1}$	$\Delta_f H^\circ_m$ / $kJ \cdot mol^{-1}$
1–methyl–1–phenyl–hydrazine	−4327.59 ± 1.12	−4331.31 ± 1.12	147.59 ± 1.18

TABLE 54. Summary of vapor pressure results for 1–methyl–1–phenylhydrazine; decane or water refers to which material was used as the standard in the reference ebulliometer, the pressure P for ebulliometric measurements was calculated from the condensation temperature of the reference substance, in the ebulliometric measurements T is the condensation temperature of the sample, $T_{boil} - T_{cond}$ is the difference between the boiling and condensation temperatures for the sample in the ebulliometer, ΔP is the difference of the calculated value of pressure from the observed value of pressure, σ_i is the propagated error calculated from equations **2.1** and **2.2**.

Material	$\frac{P}{kPa}$	$\frac{T}{K}$	$\frac{T_{boil} - T_{cond}}{K}$	$\frac{\Delta P}{kPa}$	$\frac{\sigma_i}{kPa}$
		1–methyl–1–phenylhydrazine			
decane	1.9998	384.780	0.082	−0.0005	0.0001
decane	2.6664	391.124	0.048	0.0010	0.0002
decane	5.3329	407.570	0.033	−0.0004	0.0003
decane	7.9993	418.004	0.031	−0.0007	0.0004
decane	10.6658	425.820	0.028	−0.0018	0.0006
decane	13.3322	432.126	0.027	0.0010	0.0007
decane	16.6653	438.672	0.032	0.0025	0.0008
decane	19.9330	444.108	0.033	0.0020	0.0010
water	25.0233	451.262	0.028	−0.0033	0.0011
water	31.1774[a]	458.371	0.027	0.0653	0.0015
water	38.5648[a]	465.584	0.028	0.0847	0.0019
water	47.3748[a]	472.849	0.028	0.0885	0.0023
water	57.8179[a]	480.146	0.024	0.0978	0.0028
water	70.1209[a]	487.470	0.008	0.1235	0.0033

[a] Sample decomposition suspected.

TABLE 55. Cox equation constants and fitting parameters for 1–methyl–1–phenyl–hydrazine

T_{ref} / K	502.3 ± 0.1
A	2.97179 ± 0.01234
10^3B/K	−1.51860 ± 0.00597
10^6C/K^2	1.12106 ± 0.07213
Data Range/K	384 – 488
Normalized Covariance Terms[a]	
AB	−0.99977
AC	0.99910
BC	−0.99977

[a] Cross terms of the normalized variance–covariance matrix.

TABLE 56. Enthalpies of vaporization of 1–methyl–1–phenylhydrazine obtained from the Cox and Clapeyron equations

T/K	$\Delta_l^g H$ / kJ·mol^{-1}
298.15	63.19 ± 0.68
300.00	63.03 ± 0.64
320.00	61.49 ± 0.33
340.00	59.98 ± 0.15
360.00	58.50 ± 0.06
380.00	57.06 ± 0.03
400.00	55.66 ± 0.04
420.00	54.28 ± 0.06
440.00	52.93 ± 0.12
460.00	51.58 ± 0.18
480.00	50.22 ± 0.22
500.00	48.86 ± 0.31
520.00	47.45 ± 0.42
540.00	46.00 ± 0.58

Derived Ideal–Gas Standard Enthalpies of Formation

The derivation of the standard enthalpy of formation of an ideal–gas from the corresponding value in the condensed state (solid or liquid) requires knowledge of the standard enthalpy of sublimation or vaporization. For each of the compounds except acrylamide, the standard enthalpy of vaporization has been derived from the vapor–pressure measurements via the Cox equation constants, the Clapeyron equation, and an estimation of the second virial coefficient using the equation of Scott et al. (18). The derived values are listed in the respective tables and summarized in table 57. For acrylamide, a value of 81.60 kJ mol^{-1} was derived for the enthalpy of sublimation at 330 K (see above) from the data of Carpenter and Davis (26). In the absence of any values for the heat capacity of acrylamide in the gas phase, this value cannot be corrected to 298.15 K. Therefore, we have assumed 81.60 kJ mol^{-1} as the standard enthalpy of sublimation of acrylamide at 298.15 K and arbitrarily assigned it an uncertainty interval of 1.7 kJ mol^{-1}. Combination of that value with the standard enthalpy of formation of crystalline acrylamide (table 5) of -212.08 ± 0.30 kJ mol^{-1} gave

$$\Delta_f H^o_m (C_3H_5ON, g, 298.15\ K) = -130.5 \pm 1.7\ kJ\ mol^{-1}.$$

The standard enthalpy of combustion of succinimide was also determined in the crystalline state. Therefore, for that compound in addition to the derived standard enthalpy of vaporization (table 14), the standard enthalpy of fusion, $\Delta^l_c H^o_m$, was required. The value, 12.32 kJ mol^{-1}, was calculated using the equation:

$$\Delta^l_c H^o_m(298.15\ K) = \Delta^l_c H^o_m\ (400\ K) + \int_{400}^{298.15} \{C^o_p(c) - C^o_p(l)\}dT \quad (3.21)$$

and the data given in table 11. Combination of that value, the standard enthalpy of vaporization 85.75 ± 9.06 kJ mol^{-1}, and the standard enthalpy of formation in the crystalline state, -460.25 ± 0.30 kJ mol,$^{-1}$ gave a standard enthalpy of formation in the ideal–gas state:

$$\Delta_f H^o_m (C_4H_5O_2N, g, 298.15\ K) = -362.2 \pm 9.3\ kJ\ mol^{-1}.$$

For the remaining seven compounds, the standard enthalpies of combustion were determined for the liquid phase; hence, the corresponding ideal–gas standard enthalpies of formation were derived by combination of the liquid–phase standard enthalpy of formation with the standard enthalpy of vaporization. A summary of the derived standard enthalpies of formation in the ideal–gas state is given in table 57.

TABLE 57. Derived standard enthalpies of formation for the ideal–gas at 298.15 K and p° = 101.325 kPa. All values in $kJ \cdot mol^{-1}$.

Compound	$\Delta_f H^\circ_m$(c or l, 298.15 K)	$\Delta^l_c H^\circ_m$(298.15 K)	$\Delta^g_l H^\circ_m$(298.15 K)	$\Delta_f H^\circ_m$(g, 298.15 K)
Acrylamide	–212.08 ± 0.30		81.60 ± 1.7[a]	–130.5 ± 1.7
Succinimide	–460.25 ± 0.30	12.32 ± 1.20	85.75 ± 9.06	–362.2 ± 9.3
γ–butyrolactone	–419.07 ± 0.36		53.46 ± 0.26	–365.61 ± 0.44
2–pyrrolidone	–266.04 ± 0.42		68.66 ± 3.03	–197.38 ± 3.06
2,3–dihydrofuran	–103.02 ± 0.38		30.77 ± 0.17	–72.25 ± 0.41
3,4–dihydro–2H–pyran	–147.73 ± 0.86		34.92 ± 0.08	–112.81 ± 0.90
1,3–cyclohexadiene	71.41 ± 0.62		33.17 ± 0.10	104.58 ± 0.63
1,4–cyclohexadiene	69.70 ± 0.58		35.05 ± 0.08	104.75 ± 0.59
1–methyl–1–phenyl–hydrazine	147.59 ± 1.18		63.19 ± 1.36	210.78 ± 1.66

[a] See text.

Derived Group–Additivity Values.

The continued expansion of the data base for the ideal–gas standard enthalpy of formation of organic compounds necessitates the upgrading and revision of the values assigned to each individual group. This task is an essential part of building any good estimation scheme. As incorrect or imprecise data are revised, the corresponding group parameters also need revision, but such a revision normally has far–reaching ramifications and cannot be done in isolation. For example, any change in the values assigned to the groups derived from the alkanes will necessitate changes to most other groups values. Therefore, the revision task is a major project and cannot be undertaken lightly. Such a revision is in progress at NIPER at present as a part of a research program funded by the Department of Energy's Office of Energy Research. In addition, revision of the parameters is a goal of the ASTM E–27.07 Committee within their CHETAH program revisions.

Each of the compounds reported here contains a group or ring correction term which was either not available to Benson when he wrote his monograph (1) in 1976 or is a revision of his assigned value. Details of the calculation of each group or ring correction are given below. All assigned group values have been taken from Professor Benson's monograph (1).

Acrylamide

Benson does not list a value for the group CO $-(C_d)(N)$.
Calculation of the group contribution:

Group or Correction Term	Number	Value $kJ \cdot mol^{-1}$	Contribution $kJ \cdot mol^{-1}$
$C_d-(C_d)(H)_2$	1	26.19	26.19
$C_d-(C_d)(H)(CO)$	1	20.92	20.92
$CO-(C_d)(N)$	1	?	?
$N-(H)_2(CO)$	1	−62.34	−62.34
		Σ	−15.23 + ?
		$\Delta_f H^o_m$	−130.5 ± 1.6

and

$CO-(C_d)(N)$ is assigned a value of -115.3 kJ mol^{-1}.

Succinimide

Benson lists a value of 35.6 kJ·mol^{-1} for the ring correction term derived using an estimated standard enthalpy of sublimation.

Calculation of the ring correction term:

Group or Correction Term	Number	Value kJ·mol^{-1}	Contribution kJ·mol^{-1}
C–(CO)(C)(H)$_2$	2	–21.75	–43.5
CO–(N)(C)	2	–137.25	–274.4
N–(CO)$_2$(H)	1	–77.8	–77.8
Ring correction	1	?	?
		Σ	–395.7 + ?
		$\Delta_f H^o_m$	–362.2 ± 9.3

and

the ring correction is assigned a value of 33.5 kJ mol^{-1}.

γ–Butyrolactone

Benson does not list a value for the ring correction term for a lactone ring.

Calculation of the ring correction term:

Group or Correction Term	Number	Value kJ·mol^{-1}	Contribution kJ·mol^{-1}
C–(C)$_2$(H)$_2$	1	–20.63	–20.63
C–(O)(C)(H)$_2$	1	–27.20	–27.20
O–(CO)(C)	1	–180.33	–180.33
CO–(O)(C)	1	–146.86	–146.86
C–(CO)(C)(H)$_2$	1	–21.76	–21.76
Ring correction	1	?	?
		Σ	–396.78 + ?
		$\Delta_f H^o_m$	–365.61 ± 0.44

and

the ring correction is assigned a value of 31.2 kJ·mol^{-1}.

2-Pyrrolidone

Benson does not list a value for the ring correction term for a lactam ring.

Calculation of the ring correction term:

Group or Correction Term	Number	Value kJ·mol^{-1}	Contribution kJ·mol^{-1}
C-(C)$_2$(H)$_2$	1	-20.63	-20.63
C-(N)(C)(H)$_2$	1	-27.61	-27.61
N-(H)(CO)(C)	1	-18.41	-18.41
CO-(N)(C)	1	-137.24	-137.24
C-(CO)(C)(H)$_2$	1	-21.76	-21.76
Ring correction	1	?	?
		Σ	-225.65 + ?
		$\Delta_f H^o_m$	-197.38 ± 3.06

and

the ring correction is assigned a value of 28.3 kJ mol^{-1}.

2,3-Dihydrofuran

Benson lists a value for the ring correction term of 19.7 kJ·mol^{-1} derived using estimated data.

Calculation of the ring correction term:

Group or Correction Term	Number	Value kJ·mol^{-1}	Contribution kJ·mol^{-1}
C$_d$-(C$_d$)(C)(H)	1	35.94	35.94
C$_d$-(C$_d$)(O)(H)	1	35.98	35.98
O-(C$_d$)(C)	1	-127.61	-127.61
C-(O)(C)(H)$_2$	1	-33.89	-33.89
C-(C)(C$_d$)(H)$_2$	1	-19.92	-19.92
Ring correction	1	?	?
		Σ	-109.5 + ?
		$\Delta_f H^o_m$	-72.25 ± 0.41

and

the ring correction is assigned a value of 37.3 kJ mol^{-1}.

3,4-Dihydro-2H-pyran

Benson lists a value for the ring correction term of 5.0 $kJ \cdot mol^{-1}$ derived using an estimated standard enthalpy of vaporization value.

Calculation of the ring correction term:

Group or Correction Term	Number	Value $kJ \cdot mol^{-1}$	Contribution $kJ \cdot mol^{-1}$
$C_d-(C_d)(C)(H)$	1	35.94	35.94
$C_d-(C_d)(O)(H)$	1	35.98	35.98
$O-(C_d)(C)$	1	−127.61	−127.61
$C-(O)(C)(H)_2$	1	−33.89	−33.89
$C-(C)(C_d)(H)_2$	1	−19.92	−19.92
$C-(C)(H)_2$	1	−20.63	−20.63
Ring correction	1	?	?
		Σ	−130.13 + ?
		$\Delta_f H^o_m$	−112.81 ± 0.90

and

the ring correction is assigned a value of 17.3 $kJ\ mol^{-1}$.

1,3–Cyclohexadiene

Benson lists a value for the ring correction term of 20.0 kJ·mol^{-1} but the value has remained uncertain (28).

Calculation of the ring correction term:

Group or Correction Term	Number	Value kJ·mol^{-1}	Contribution kJ·mol^{-1}
C_d–(C_d)(C)(H)	2	35.94	71.88
C_d–(C_d)$_2$(H)	2	28.37	56.74
C–(C)(C_d)(H)$_2$	2	–19.92	–39.84
Ring correction	1	?	?
		Σ	88.78 + ?
		$\Delta_f H^o_m$	104.58 ± 0.63

and

the ring correction is assigned a value of 15.8 kJ mol^{-1}.

1,4–Cyclohexadiene

Benson lists a value for the ring correction term of 2.1 kJ·mol^{-1} but the value has remained uncertain (28).

Calculation of the ring correction term:

Group or Correction Term	Number	Value kJ·mol^{-1}	Contribution kJ·mol^{-1}
C_d–(C_d)(C)(H)	4	35.94	143.76
C–(C_d)$_2$(H)$_2$	2	–17.95	–35.90
Ring correction	1	?	?
		Σ	107.86 + ?
		$\Delta_f H^o_m$	104.75 ± 0.59

and

the ring correction is assigned a value of –3.1 kJ mol^{-1}.

1-methyl-1-phenylhydrazine

Benson does not list a value for the group N-(N)(C_b)(C).

Calculation of the group contribution:

Group or Correction Term	Number	Value kJ·mol^{-1}	Contribution kJ·mol^{-1}
C_b-(C_b)$_2$(H)	5	13.81	69.05
C_b-(C_b)$_2$(N)	1	-2.09	-2.09
N-(C_b)(C)(N)	1	?	?
C-(H)$_3$(N)	1	-42.17	-42.17
N-(H)$_2$ (N)	1	47.70	47.70
		Σ	72.49 + ?
		$\Delta_f H^o_m$	210.78 ± 1.66

and

the N-(N)(C_b)(C) group is assigned a value of 138.3 kJ mol^{-1}.

4. DISCUSSION

A search of Chemical Abstracts (to June 1987) failed to find any data for comparison purposes on the thermodynamic properties measured here for acrylamide. The group-additivity method was used to estimate the enthalpy of polymerization of acrylamide in the hypothetical ideal-gas state. Application of the procedure using the data obtained here gave an enthalpy of polymerization of -97 kJ mol^{-1}, which can be compared to a measured value of -83 ± 3 kJ mol^{-1}, obtained by Dainton et al. (29) from measurements in aqueous solution.

Coleman and Skinner (30) measured the standard enthalpy of combustion of succinimide. They report a value (three combustions) of -1829.6 ± 0.2 kJ mol^{-1} a difference of 1.2 kJ mol^{-1} from the value reported here -1828.36 ± 0.14 kJ mol^{-1}. The difference is outside the combined uncertainty interval (0.34 kJ mol^{-1}) and in the absence of any further information, we are unable to reconcile the difference. Coleman and Skinner estimated an standard enthalpy of sublimation of 92 kJ mol^{-1} which is in good agreement with the value 98.1 ± 9.2 kJ mol^{-1} obtained in this research.

Vapor-pressure measurements on γ-butyrolactone have been reported by three groups (32-34). McKinley and Copes (32) reported vapor pressure measurements in the range 392 to 477 K. Yarym-Agev et al. (33) give an equation:

$$\log (P/mm\ Hg) = 16.6772 - 3018.8/T - 2.7935 \log(T) \qquad 4.1$$

to represent the data in the range 273 to 478 K. Yarym–Agev et al. (33) also report an equation:

$$(\Delta_l^g H/\ kJ \cdot mol^{-1}) = 56.5 - 2.30 \cdot 10^{-2}\ T \qquad 4.2$$

to represent the enthalpy of vaporization in that temperature region. (Equation **4.2** is wrongly abstracted in Chemical Abstracts: the exponential term is missing.) Evstropov et al. (34) have measured the vapor pressure of γ–butyrolactone in the temperature region 338 to 360 K as a part of a study which also included measurement of the standard enthalpy of combustion and adiabatic heat capacity determinations between 14 and 330 K. Each vapor–pressure data set is incompatible with the others and with that reported in table 18. The only details given by McKinley and Copes (32) are: measurements were made using an isoteniscope; they used a 'highly purified' sample and they report their data in integer K. The difference between their reported vapor pressures and those given here range from –10 per cent at 392 K to +1.7 per cent at 474 K. At 361 K, our lowest temperature measurement, the agreement between the value calculated using the equation of Yarym–Agev et al. (33) and our measured value is good; 1.9998 kPa (our value), 1.974 kPa (from equation **4.1**). The percentage deviation between our measurements and that calculated from equation **4.1** remains constant as the temperature increases (1.4 per cent) and at our normal boiling point (101.325 kPa) application of equation **4.1** gives 99.9 kPa . In contrast, at 360 K, Evstropov et al. (34) report a vapor pressure of 2.53 kPa which is 33 per cent greater than that found here or calculated using equation **4.1**. Evstropov et al. (34) gave a sample purity of 99.83 per cent (obtained both from carbon dioxide analysis during enthalpy of combustion measurements and an adiabatic calorimetric melting study). If we assume that the sample impurity was water (a reasonable assumption, since both analyses gave the same percentage purity), we calculate an energy of combustion from the data given, $-23367 \pm 10\ J\,g^{-1}$, in excellent agreement with the value $-23361.5 \pm 0.5\ J\,g^{-1}$ measured here. Hence, the large difference between the vapor pressures at 360 K is a function of the 0.13 per cent water impurity in the sample of Evstropov et al. (34).

Kudchadker and Kudchadker (35) have made a complete vibrational assignment for γ–butyrolactone and calculated the ideal–gas thermodynamic properties over the temperature range 100 to 1500 K. They assigned 10 of the frequencies by comparison

with similar compounds. Table 58 compares the standard entropies for the ideal–gas state calculated using our Cox equation fit of the vapor pressures of γ–butyrolactone and the condensed phase entropy data of Evstropov et al. (34) with those given by Kudchadker and Kudchadker (35) at 298.15 K and 350 K. The difference of one unit of R suggests problems with the low–frequency vibrational assignments.

Strepikheev et al. (36) have measured the standard enthalpy of combustion of 2–pyrrolidone. They report a value of -2288.2 ± 0.4 kJ mol^{-1} which is considerably lower than that found here, -2308.40 ± 0.34 kJ mol^{-1}. Strepikheev et al. (36) give insufficient details of sample purity, etc., to facilitate further comparison. Kolesov et al. (37) report standard entropies at 298.15 K and 350 K of 22.06R and 25.52R, respectively. Kudchadker and Kudchadker (35) have made a complete vibrational assignment for 2∠pyrrolidone and calculated the ideal–gas thermodynamic properties over the temperature range 100 to 1500 K. They assigned ten of the frequencies, including the two lowest, by comparison with similar compounds. Table 59 compares the standard entropies for the ideal–gas state calculated using our Cox equation fit of the vapor pressures of 2–pyrrolidone and the condensed–phase entropy data of Kolesov et al. (37) with those given by Kudchadker and Kudchadker (35) at 298.15 K and 350 K. As in the case of γ–butyrolactone the difference, here greater than 2 units of R at 300 K, suggests problems with the low–frequency vibrational assignments. However, the heat capacity data of Kolesov et al. (37) from which the condensed–phase entropies are calculated only extends to 60 K, necessitating a very long extrapolation to $T \rightarrow 0$ with a large associated uncertainty.

Allinger et al. (38) have measured the enthalpy of hydrogenation of 2,3–dihydrofuran in n–hexane solution at 298.15 K. They report $\Delta_r H^o_m$ values of -107.07 ± 1.50 kJ mol^{-1} and -105.86 ± 1.00 kJ mol^{-1} for two series of determinations. Combination of our standard enthalpies of formation for the condensed and ideal–gas states at 298.15 K for 2,3–dihydrofuran (table 57) with the standard enthalpies of formation for tetrahydrofuran (39) gave $\Delta_r H^o_m$ values of -111.93 ± 0.82 kJ mol^{-1} and -113.17 ± 0.72 kJ mol^{-1} in the gas and liquid phases, respectively, for the hydrogenation reaction. The difference between the values reported by Allinger et al. and those calculated here for the ideal–gas phase might be reflective of the different enthalpies of solution of 2,3–dihydrofuran and tetrahydrofuran in n–hexane.

Allinger et al. (38) have also measured the enthalpy of hydrogenation of

TABLE 58. Comparison of the ideal–gas entropies for γ–butyrolactone (298.15 K and 350 K) calculated by Kudchadker and Kudchadker (35) with those obtained from the measurements reported here

	298.15 K	350.0 K
$(\Delta_0^T S_m^\circ/R)(l)$	23.754	26.640
$\ln(p/p^\circ)$	−7.582	−4.460
$\Delta_l^g S/R$	21.568	17.484
$(\Delta_0^T S_m^\circ/R)$ (g)	37.740	39.664
Reference (35)	36.7	38.5

TABLE 59. Comparison of the ideal–gas entropies for 2–pyrrolidone (300 K and 350 K) calculated by Kudchadker and Kudchadker (35) with those obtained from the measurements reported here

	300.0 K	350.0 K
$(\Delta_0^T S_m^\circ/R)(l)$	22.06	25.52
$\ln(p/p^\circ)$	−10.755	−6.920
$\Delta_l^g S/R$	27.478	22.406
$(\Delta_0^T S_m^\circ/R)$ (g)	38.78	41.01
Reference (35)	36.29	39.87

3,4–dihydro–2H–pyran in n–hexane solution at 298.15 K. They report $\Delta_r H^o_m$ values of −104.06 ± 1.17 kJ mol^{-1} and −102.59 ± 0.88 kJ mol^{-1} for two series of determinations. Combination of our standard enthalpies of formation for the condensed and ideal–gas states at 298.15 K for 3,4–dihydro–2H–pyran (table 57) with the standard enthalpies of formation for tetrahydropyran (39) gave $\Delta_r H^o_m$ values of −110.6 ± 1.5 kJ mol^{-1}and −110.6 ± 0.9 kJ mol^{-1} in the gas and liquid phases, respectively, for the hydrogenation reaction. Again, the difference between the values reported by Allinger et al. and those calculated here for the ideal–gas phase might be reflective of the different enthalpies of solution of 3,4–dihydro–2H–pyran and tetrahydropyran in n–hexane. The standard enthalpy of combustion of 3,4–dihydro–2H–pyran has been measured previously by Cass et al. (27) who obtained a $\Delta_c H^o_m$ value of −2953.4 ± 1.26 kJ mol^{-1} ehich is in poor agreement with that obtained here, −2962.85 ± 0.80 kJ mol^{-1}. Also, the data of Cass et al. (27) for both tetrahydrofuran and tetrahydropyran, reported in the same paper, do not agree with the presently accepted values (39). The standard enthalpy of vaporization given by Cass et al. for tetrahydropyran, 34.9 kJ mol^{-1} is the same as that found here for 3,4–dihydro–2H–pyran (table 38).

There have been no previous determinations of the standard enthalpies of combustion of either 1,3– or 1,4–cyclohexadiene. In 1936, Kistiakowsky et al. (40) reported an enthalpy of hydrogenation of 1,3–cyclohexadiene to cyclohexane in the gas phase of −229.6 ± 0.4 kJ mol^{-1}. Turner et al. (41) subsequently determined the enthalpies of hydrogenation of both dienes in acetic acid solution at 298.15 K, obtaining values of −224.4 ± 1.2 kJ mol^{-1} and −225.5 ± 1.4 kJ mol^{-1} for the 1,3–diene and the 1,4–diene, respectively. Using the data reported in table 57 and the standard enthalpies of formation in the liquid and ideal–gas states for cyclohexane (31), we calculated the following enthalpies of hydrogenation at 298.15 K:

1,3–cyclohexadiene

$\Delta_r H^o_m$ −227.89 ± 0.88 kJ mol^{-1} in the liquid phase

$\Delta_r H^o_m$ −228.01 ± 0.88 kJ mol^{-1} in the ideal–gas phase

1,4–cyclohexadiene

$\Delta_r H^o_m$ −226.18 ± 0.86 kJ mol^{-1} in the liquid phase

$\Delta_r H^o_m$ −228.18 ± 0.86 kJ mol^{-1} in the ideal–gas phase.

Again, the differences observed between the values calculated here and those obtained by Turner et al. (41) might be reflective of the different enthalpies of solution of the dienes and cyclohexane in the solvent, acetic acid. The difference between the enthalpy of hydrogenation observed by Kistiakowsky et al. (40) and that reported here is of the

same order of magnitude to that between their enthalpy of hydrogenation of benzene in the gas phase and that calculated using modern thermochemical data (31).

The standard enthalpies of formation in the ideal–gas phase for both dienes obtained here are the same within the combined experimental uncertainties in agreement with the calculated free energy of equilibration at 368 K of 2434 J mol^{-1} from the equilibrium data of Bates et al. (42). The statistical factor in the equilibration accounts for 2121 J mol^{-1} of the observed free energy difference and the remainder is probably the difference in the absolute entropies of the dienes.

Meyer and Hotz (43) have reported "high precision vapor pressure data" obtained via comparative ebulliometry for 1,3–cyclohexadiene. In the pressure range of overlap with the measurements reported here (tables 42 and 43) the deviation between their pressures and those obtained by NIPER is constant at –25 Pa, which is within the uncertainty limits in the pressure measurements. Letcher and Marsicano (44) report vapor–pressure measurements on both dienes in the temperature range 303 to 322 K. For 1,3–cyclohexadiene the difference, {p (reference 44) – p (NIPER data)} ranges from –60 Pa to –220 Pa between 303 K and 322 K. For 1,4–cyclohexadiene the difference, {p (reference 44) – p (NIPER data)} averages +160 Pa. In both cases, the small differences are within the combined uncertainites in the pressure measurements.

A search of the literature through June 1987 failed to find any thermochemical or thermophysical data for 1–methyl–1–phenylhydrazine.

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