4464 *J. Phys. Chem. A* **2007,** *111,* 4464−4477

Calculation of Entropy and Heat Capacity of Organic Compounds in the Gas Phase. Evaluation of a Consistent Method without Adjustable Parameters. Applications to Hydrocarbons

DeLos F. DeTar*

Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida 32306-4390

Received: September 26, 2006; In Final Form: February 8, 2007

The purpose of this study has been to determine how well a consistent ab initio thermostatistical method reproduces experimental values of heat capacity and entropy. The method has been applied to calculation of heat capacity and entropy of a representative set of hydrocarbons that includes compounds consisting of multiple conformers. All C_p and S values are for the gaseous state at 1 atm; units are cal K^{-1} mol^{-1}. A detailed sensitivity (error) analysis has been performed to determine the root mean square (rms) values of errors expected of the *calculated values*: these are 0.27 cal for C_p and 0.36 cal for entropy. In comparing calculated values with experimental values, it is necessary to consider also the uncertainties of the experimental data. When these are included, the expected rms values of C_p(experimental) − C_p(calculated) values at 298.15 K range from 0.21 to 0.73. For S(experimental) − S(calculated), they range from 0.36 to 0.72. Calculations with frequencies derived with the 6-31G(d,p) basis set and scaled by 0.91 yielded rms values for C_p(experimental) − C_p(calculated) of *individual* compounds from 0.14 to 0.84 cal and rms values for S(experimental) − S(calculated) of *individual* compounds from 0.07 to 1.11 cal. Calculated C_p values for 7 out of 16 compounds agree with experimental values within the rms uncertainty estimated for the compound, and 11 fall within twice that estimate. For entropy, the calculated values for 13 of 18 compounds agree with the very limited available experimental data within the rms estimated uncertainty for the compound, and 16 of 18 fall within twice the uncertainty.

Introduction

There are relatively few experimentally determined values of entropy; measurement of entropy to high accuracy is a demanding task. For most compounds there is *just one single measurement* of the value of the absolute gas-phase entropy by the third law procedure. All other values for a given compound that appear in the numerous published tables of entropy over a range of more than 1000 K are actually derived from this single experimental value, which is usually reported at the temperature of the boiling point of the compound. Error limits of entropy values reported by the experimentalist seem generally to have been made by an approximate "sensitivity" analysis consisting of a consideration of errors attributable to the several steps of the measurement. There are very few values of entropy measured in more than one laboratory; seldom is it possible to derive an independent error estimate of accuracy.

Experimental estimation of the entropy at other temperatures is done by use of eq 1. This in turn requires values of the heat capacity in the gaseous state, the measurement of which likewise requires great skill. If the temperatures of the measurements of the heat capacity include the temperature of the boiling point, then several "experimental" values of the entropy are available by applying eq 1. But many reports of measurements of gaseous heat capacities are spotty and do not include the temperature of the boiling point. While interpolations of heat capacity data within the published temperature range are usually reliable, extrapolations are questionable.

$$S_T = S_{T_{bp}} + \int_{T_{bp}}^{T} (C_p)\, dT/T \qquad (1)$$

Reports of measurements of entropy and of heat capacity are often accompanied by thermostatistical calculations of heat capacity and of entropy. These calculated values often match the experimental values to within remarkable precision, often 0.1 cal K^{-1} mol^{-1}. The results were seemingly intended to validate the accuracy of the experimental data. What had actually been done, however, was to use the thermostatistical formalism with adjustable parameters as a framework for curve fitting. As an aside, it is often possible to fit heat capacity data with equal precision by an empirical parabolic expression of temperature having no theoretical significance. Thus the capability to match experimental data with calculated values does not constitute a validation of the accuracy of the experimental data.

A limitation of the early thermostatistical calculations is that they require the availability of experimental data for calibration. In these early studies, there was seldom any attempt at a sensitivity analysis to place an estimate for the uncertainty of the calculated values.

The importance of having general and reliable methods of calculating entropy and heat capacity is obvious. The goal of the present study has been to evaluate the reliability of a de novo method that does not make use of adjustable parameters. This study extends and expands on well-known methods; these are described in the following sections.

In the present study, all calculations are for the compound as an ideal gas at one atmosphere pressure. Units are cal K^{-1} mol^{-1}.

---

* E-mail: detar@chem.fsu.edu.

10.1021/jp066312r CCC: $37.00

Empirical Methods

Before proceeding with a discussion of theoretical calculations, mention should be made of useful empirical methods that have been developed for extending the estimates of entropy and of heat capacity to new compounds. Examples include direct extrapolation of data for related compounds[1−3] or, more generally, use of group increment methods.[1,4−12] Several extensive applications of group increment calculations have been published; illustrative examples are those of Chao et al.,[13] of Wilhoit and Zwolinski,[14] and of Scott[5] (using a different approach). Rabitz and his group have been pursuing interesting new ways for extending the group increment formalism.[15]

Estimation of suitable parameters for use in the group increment methods, that is, values for group increments of structural elements, requires availability of thermodynamic data for compounds having the requisite structural elements. Experimental data must often be augmented by data obtained by thermostatistical methods using geometries, energies, and frequencies obtained by ab initio calculations performed on as large molecules as practical.

Theoretical Methods: General Considerations. In outline, theoretical calculation of thermodynamic properties of molecules requires calculation of values of the partition function. The usual first approximation is the rigid rotor−harmonic oscillator model (rrho). This treats the molecule as a rigid body having translation, overall rotation, and vibration, with all vibrations, including torsions, treated as harmonic oscillators. For hydrocarbons at temperatures up to 1000 K, electronic contributions may be neglected. The model can be improved by incorporating corrections for hindered rotation.

The necessary theoretical and practical mathematical expressions for the thermostatistical computations of entropy and of heat capacity are described in many references such as the introductory chapters of the monograph by Stull et al.,[16] the monograph by Pitzer and Pimental,[17] that of Herzberg[18] (p 511), and of Frankiss and Green.[19]

Many organic compounds of interest exist as mixtures of conformers. Two approaches have been used to get values of entropy and of heat capacity for conformer mixtures: (1) Use a model that simultaneously includes all rotational possibilities of the molecule; examples are the studies by Vansteenkiste et al.[20−23] (2) Alternatively compute the energies and partition functions for all significant conformers individually; conformers are treated as individual molecules. Values of entropy and of heat capacity are computed as the sum of fractional values based on the Boltzmann fractions. This is a method I have used previously in calculating *SM* (see below for definition).[24] It has also been used by others in a few calculations of S and C_p: Beckett et al.[25] and Aston et al.[26] It is a theoretical approach described by Grunwald in the monograph *Thermodynamics of Molecular Species*.[27]

Corrections to this estimate of entropy must include the entropy of mixing term. Corrections to the heat capacity of a mixture of conformers must include a $\mathrm{d}XE_\mathrm{g}/\mathrm{d}T$ term. $\mathrm{d}XE_\mathrm{g}/\mathrm{d}T$ is the change of energy that accompanies the change in the conformer population with temperature. The requirement for this correction has not generally been recognized. Moreover, previous attempts to make the $\mathrm{d}XE_\mathrm{g}/\mathrm{d}T$ correction have not used the correct formalism; prior applications will be mentioned in the sections describing calculations for 1,3-butadiene and cyclohexane.

It is recognized that approximations are involved in calculating the components of the partition function. Many workers have voiced concern about errors of neglecting anharmonicity of vibrations. The problem is that there are no general methods for calculating the anharmonicity component for large molecules. I follow the usual practice of neglecting anharmonicity.

Approximations are also involved in all hindered rotor estimates except for ethane. For molecules that have several rotors, the librations are coupled with each other and often coupled with vibrations. The contributions of the hindered rotors is often difficult to treat with a rigorous theory, and the usual approximation is to use the same correction for each methyl rotor. For librations of C−C−C−C sequences, a specific calculation is sometimes computed for hindered rotation about the carbon−carbon bond. Results attainable with more detailed treatment of hindered rotation will be summarized in connection with applications to individual molecules.

The Present Study. The present study applies a consistent and predefined procedure without adjustable parameters to calculate entropies and heat capacities of members of a representative set of hydrocarbons in the gaseous phase at one atmosphere in units of cal K^{-1} mol^{-1}. It extends an earlier study that examined results obtained using the rigid rotor−harmonic oscillator (rrho) approximation.[28] The present study treats a larger variety of alkanes and makes use of the Pitzer−Gwinn treatment of contributions to the entropy and the heat capacity of hindered methyl rotors.[17,29−31]

The compounds investigated in this study are gaseous hydrocarbons. They fall into five representative classes: (1) compounds having no internal rotations other than rotations of methyl groups (ethane, propane, isobutane, and neopentane), (2) compounds with freely rotating methyl groups (2-butyne, toluene), (3) compounds existing as multiple conformers (butane, pentane, 2-methylbutane, 2,3-dimethylbutane, 1,3-butadiene, cyclohexane, methylcyclohexane), (4) compounds with no methyl groups (cyclopropane, cyclobutane, cyclohexane), and (5) compounds existing as a single conformer but with rotation about a carbon−carbon bond (2,2-dimethylbutane, trimethylbutane, tetramethylbutane).

East and Radom[32] developed several ab initio recipes for calculating the entropy and the heat capacity of gaseous molecules and have applied them to a comprehensive set of small molecules. Their study provides a valuable starting point for extension to larger organic molecules. The method used in the present study is related to their method designated E2,[32] but differs in several respects as described below.

Questions I have addressed are how closely do calculated values of C_p and of entropy agree with *experimental* values if all calculations are based on the same ab initio data. Four sets of calculations are reported that differ only in the sources of the frequency data. All compounds were treated identically within the defined protocols. I have developed a sensitivity analysis that provides estimates of the uncertainties of the calculated values and of the differences between calculated and experimental values.

The Computational Method Used in This Study. The steps in the computational method used in this study are described in this section. The first step was to calculate the heat capacity and the entropy at a suitable set of temperatures in the rigid rotor−harmonic oscillator approximation. For compounds that exist as mixtures of conformers, the calculations were performed for all significant conformers. Boltzmann fractions of each conformer were calculated from the *free energies* of the conformers, and appropriate summations were made of fractional C_p and S values. If multiple conformers are present, the entropy of mixing and the $\mathrm{d}XE_\mathrm{g}/\mathrm{d}T$ were computed for each temperature. These several values were combined to obtain the entropy and the heat capacity in the rrho approximation for the compound, that is, for the mixture of conformers. And, finally, a correction was applied for hindered methyl rotors.

Calculated values were then compared with representative experimental values, and the rms value of the differences were compared with the expected range of uncertainty as estimated by a sensitivity analysis. An average of the differences of experimental minus calculated values was also calculated to indicate the bias of the calculated values. These results are summarized in Tables 1a,b and 2a,b; further information about these tables is presented below.

(1) Four sets of frequencies were investigated. Two were derived from 6-31G(d,p) frequencies, one based on a scaling factor of 0.90 and one based on a scaling factor of 0.91. The third set was derived with MP2/6-31G(d,p)//MP2/6-31G(d,p); raw frequencies less than or equal to 2000 cm^{-1} were scaled by 0.95, and frequencies greater than 2000 were scaled by 0.923. All ab initio calculations have been performed by use of the Gaussian suite of programs[33] A fourth set of frequencies is the experimental set compiled by Shimanouchi;[34−36]

The rationale for these choices is as follows: The basis set 6-31G(d) has been widely used. For hydrocarbons, 6-31G(d,p) performs identically; this set was used in the present study because proposed future calculations will need the extra flexibility for hydrogens. The scale factor 0.90 is effectively the same as the 0.8992 factor recommended by Scott and Radom,[37] and 0.91 was chosen as a compromise because auxiliary studies indicated that 0.90 might be too small to give good C_p values. The MP2 frequencies and geometries were investigated to determine whether the correlated geometries and frequencies provide an improvement; the scaling was chosen so as to reproduce selected experimental C_p data.

As can be seen from the subsequent discussion and the summary tables, the 6-31G(d,p) frequencies scaled by 0.91 were as good as the experimental frequencies and somewhat better than those scaled by 0.90. MP2 frequencies turn out to give equivalent results and offer no advantage.

(2) The geometry of a given molecule was optimized with the 6-31G(d,p) basis set for use with the experimental frequencies and with the 6-31G(d,p) frequencies. MP2/6-31G(d,p)//MP2/6-31G(d,p) geometries were used with the MP2 frequencies.

All energies of conformers and of rotational barriers are based on MP2/6-311+G(2df,2p)//6-31G(d,p) energies.

(3) For calculation of C_p, the vibrational component C(vib) is computed for each frequency for a suitable set of temperatures. The translational and rotational component of C_p for all molecules in this study is $3R$ (molar gas constant), and the conversion from C_v to C_p requires a further R. In the rrho approximation, the value of C_p(rrho) for a single conformer at a given temperature is the sum of the C(vib) terms plus $4R$.

(4) For calculation of entropy, the translational entropy and the overall rotational entropy are calculated by standard equations given in the references cited above. The vibrational component of entropy is calculated for each frequency and each temperature. $S(\text{rrho}) = S(\text{tran}) + S(\text{rot}) + S(\text{vib})$. In the present study, skeletal librations are treated as vibrations. Actually, the results of a complete quantum evaluation of the entropies of butane and of pentane yielded the same values of entropy, as obtained in this work, within less than 0.2 cal K^{-1} mol^{-1}, and both types of entropy estimates are too high. See Table 23b.

(5) The conformer of lowest energy is conveniently taken as the reference conformer. The energies and entropies of the other conformers are calculated, and Boltzmann fractions *fg* are calculated for each conformer for each temperature. As an example, for butane with $E(\text{gauche}) - E(\text{anti}) = 0.63$ kcal mol^{-1}, the *fg* of the gauche conformer is 0.405 at 298.15 K and 0.508 at 500 K.

(6) Using the *fg* data, the C_p derived from the reference conformer is modified by adding a proportionate correction for the contributions of the other conformers. This correction is usually small.

(7) A mixture of conformers has a different energy (enthalpy) than does the hypothetical pure reference conformer. For a given conformer, the difference is $fg(E(\text{conformer}) - E(\text{reference}))$. The sum of this term over all conformers is designated as XE_g in this study (extra energy of the conformer mixture based on conformer fractions calculated from free energies of conformers), eq 2. XE_g is related to *SM* used in previous references[24] except that *SM* is based on fractions calculated from energies rather than free energies. (*XE* and *SM* will differ appreciably if the conformer mixture includes conformers having different symmetry numbers.)

$d(XE_g)/dT$ can be estimated by numeric differentiation of a table of values of XE_g vs T. For a compound with conformers of just two energies, such as butane, there is a simple analytical expression derived in eqs 3. The numerical and the analytical values are, of course, the same.

$$XE_g = \sum fg_i(e_i - e_1) \tag{2}$$

$$x = \exp(\Delta s/R)\exp(-\Delta e/RT) \tag{3}$$

$$\Delta e = e_i - e_1$$

$$\Delta s = s_i - s_1$$

$$dx/dT = x\Delta eR^{-1}T^{-2}$$

$$fg = x/(1 + x)$$

$$XE_g = \Delta efg$$

$$dXE_g/dT = \Delta e(dx/dT)(1 + x)^{-2} = (\Delta e)^2(RT)^{-2}x(1 + x)^{-2}$$

$$= (\Delta e)^2R^{-1}T^{-2}[fg - fg^2]$$

As a specific example, butane consists of three conformers, t (trans or anti) and g+ and g−, two gauche conformers; all have a symmetry number of 2. Using 6-31G(d,p) frequencies with SF 0.91 and taking $E(\text{gauche}) - E(\text{trans})$ as 0.63 kcal/mol, the relative populations at 298.15 K based on free energies are 0.405 gauche and 0.595 trans. At 298.15 K, dXE_g/dT is 0.54 cal K^{-1} mol^{-1}, and this is the correction to be added to the C_p value 21.99 cal K^{-1} mol^{-1}, which in turn is the Boltzmann average of 22.02 for the trans conformer (the global minimum) and 21.94 for the gauche conformers. (Incidentally, for butane $XE = SM$.)

(8) Using the *fg* values, the *S* value based on *S* of the reference conformer is modified by adding a correction *S*(corrn). For pentane the correction *S*(corrn) to *S* of the C_{2v} reference conformer is 0.78 cal at all temperatures from 298.15 to 1000 K. For butane, on the other hand, *S*(corrn) is negligible. (Both the anti and the gauche conformers of butane have C_2 symmetry, and their vibrational entropies are nearly the same.)

(9) An entropy of mixing term is calculated based on the number of distinct conformers.[26,38−42] For example, pentane has nine nominal conformers; there are four different energies represented by tt, tg, gg, and g+g−. However, there are seven distinct conformers because all but the tt conformer exist as enantiomers. *S*(mix) is based on these seven conformers (with

the fractional amounts of g+t and of g−t doubled because g+t and tg+ are identical and both occur in the mixture and similarly for g−t).

(10) Calculation of corrections for hindered rotation of methyl groups are based on methods developed by Pitzer.[17,29,30,43,44] In the present study, values for the contributions of hindered methyl rotors to the entropy and the heat capacity have been taken from the Pitzer and Gwinn tables[17,31] by double linear interpolation using entries for $1/Q$(fr) and V/RT. The contributions have been treated as additive. A single value of S(hind rotor) (S(hr)) and of C(hind rotor) (C(hr)) is used for all methyl groups in the molecule. As an example, 2,2-dimethylbutane has four methyl groups; these hindered rotors are treated as having an average value, which is summed four times (Kilpatrick et al.[45]). The frequencies to be replaced are those for librations of methyl groups, and these are not always the lowest frequencies.

Equations for calculating Q(fr) (free rotor) are given in Herzberg,[18] in Lewis and Randall (Pitzer, Brewer),[17] and in Benson.[1] Calculation of Q(fr) requires I(red) for the methyl group. The required value of I(red) is calculated by the Herzberg eq 4 (see page 511 of Herzberg).[18] First, I(Me), the moment of inertia of a methyl group in the molecule, is calculated from the 6-31G(d,p)//6-31G(d,p) geometry. Second, the angle φ between the axis of rotation of the methyl rotor and the principal axis of rotation of the molecule, which is most nearly parallel to that axis, is obtained from a graphical representation of the molecule. The moment Ix, about that axis, may be found among the values of the three principal moments of inertia listed in Gaussian output. V, the energy of the barrier, is calculated as the difference in energy of the eclipsed conformer of the methyl group (transition state for internal rotation) and the energy of the staggered form, using MP2/6-311+G(2df,2p)//6-31G(d,p) energies.

$$I(\mathrm{red}) = I(\mathrm{Me})(1 - (\cos^2\varphi)(I(\mathrm{Me})/Ix)) \qquad (4)$$

The hr (hindered rotation) correction for the methyl groups is treated by calculating a correction term to S(rrho) or to C_p(rrho) of the conformer mixture. For entropy, the correction is the sum of the differences S(hind rotor) − S(vib) at x cm^{-1}, where S(hind rotor) is the value of the entropy of a hindered rotor at the given temperature and S(vib) at x cm^{-1} is the value of S for the torsional frequency x of a methyl group at the same temperature. The hr correction for C is similarly calculated from C(hind rotor) and C(vib) at x cm^{-1}. I have chosen this method of treating the hindered rotor components as *corrections to the rrho value* so as to exhibit directly the size of the correction. Note that the rrho values are shown for the SF 0.90 calculations. The customary treatment in earlier work was to substitute directly the several torsional libration terms with the S(hind rotor) and C(hind rotor) values. This approach was necessary at the time because the frequencies of torsional librations were seldom available.

This method of evaluating the contributions of hindered rotors involves approximations. For most alkanes, the methyl rotations are coupled with each other, and sometimes methyl librations are coupled with vibrations as well. If more than two methyl groups are present, the couplings can have complicated patterns. Nevertheless, treating methyl groups as simple rotors is an approximation that seems to work quite well for most molecules; it is the method used in the earlier studies. The corrections are somewhat dependent on the conformer; they are, for example, slightly different for (tt)-pentane and (gt)-pentane. For butane and pentane, hr corrections were computed for all conformers and the correction calculated by the sum of fg_ihrcorrn$_i$. The difference between the correction based on the average and the correction based on just the global minimum is less than 0.15 cal. Differences of hindered rotor corrections among conformers are negligible for heat capacity corrections.

Sensitivity Analysis. A sensitivity analysis treats sources of uncertainties both in experimental data and in the calculated values. Uncertainty of calculated values is based on estimation of the uncertainties of the several components of the calculation and by combining them as the square root of the sum of the respective variances. In comparing calculated values with experimental values, it is necessary to include also the uncertainty (the error estimate) of the experimental value. In Table 2a,b, the rms expectation of the calculated values and the rms of differences between calculated values and experimental values are both given.

Sensitivity Analysis Details: Uncertainties Arising from Frequencies. S(vib) and C(vib) are obtained from frequencies. Because calculated frequencies are larger than those derived from infrared and Raman spectra, they are traditionally adjusted by applying a constant scaling factor. Pople et al.[46] have reviewed earlier work and recommend 0.8929 for scaling HF/6-31G(d) frequencies and 0.9427 for MP2/6-31G(d) frequencies. Scott and Radom[37] carried out an extensive survey and recommend 0.8992 for HF 6-31G(d,p) and 0.9370 for MP2-(frozen core)//6-31G(d,p). These investigations also included compounds having an extensive series of elements. Scott and Radom also provide recommended scaling factors for many additional basis sets,[37] and there have been other investigations of scaling of frequencies applicable to further basis sets.[47,48]

Uncertainties of vibrational frequencies are a major source of uncertainties in estimation of S(vib) and C(vib). Experimental frequencies are available for a few compounds. Some of the most accurate values are those collected by Shimanouchi;[34−36] Shimanouchi lists five ranges of uncertainties and assigns an uncertainty level to each frequency. The five levels with the respective uncertainties in cm^{-1} are A(0−1), B(1−3), C(3−6), D(6−15), and E(15−30). An estimate of the effect of these uncertainties on S(vib) and on C(vib) for the Shimanouchi compounds can be made by making two calculations, one with the reported frequencies and another with all frequencies increased or decreased. Parts a and b of Table 22 (see Supporting Information) show the differences for C(vib) and S(vib) calculated with the published frequencies and those calculated with the published frequencies, each increased by half of the published uncertainties. For the augmented frequencies, C_p(vib) values are decreased by 0.04−0.12 cal at 298.15 K and by 0.06−0.13 cal at 500 K; S(vib) values are decreased from 0.01 to 0.17 cal at 298.15 K and by 0.04−0.19 cal at 500 K.

Actually, a plot of scaled calculated frequencies against Shimanouchi[34−36] frequencies is “dished.” The nonlinearity is partially compensated in the reported studies by using higher factors 0.9135 and 0.9646 for calculating zero-point vibrational energies. An important consequence of nonlinearity is that a linear scaling factor that best reproduces frequencies may not best reproduce C_p or S values because these include only a subset of the total set of experimental frequencies.

Another way to estimate the uncertainty that arises from frequencies is to compare the sums of C(vib) and S(vib) values calculated with the several basis sets with the Shimanouchi sums. The comparison for C_p is shown in Table 21a,b (Supporting Information) and for S is shown in Table 21c,d (Supporting Information). The values C(vib) shown are the sum of all values except those that pertain to methyl or skeletal librations. The figure −0.119 in column 3 of Table 21a, for example, indicates that the sum of *C*(vib) values obtained with 6-31G(d,p) frequencies with SF 0.90 is larger than the corresponding sum obtained with the Shimanouchi frequencies. At 298.15 K, the cyclohexane data are out of line, but at 500 K, the cyclohexane SF 0.91 values are in general agreement with the other SF 0.91 values; MP2/6-31G(d,p) frequencies also show deviations between cyclohexane and the other compounds. *S*(vib) results are similar, but all cyclohexane values of *S*(vib) are out of line. This result implies that there are problems with some Gaussian frequencies or else with the Shimanouchi frequencies. The rms estimates omit the data for cyclohexane. The differences are about the same at both 298.15 and 500 K. If values for cyclohexane are included, the rms of the differences of the sums increases from 0.2 to 0.3 for SF 0.90 and from 0.13 to 0.17 for SF 0.91.

These results indicate that, in making a sensitivity analysis, the uncertainty in the *C*(vib) and the *S*(vib) values is larger than might have been anticipated from previous publications; an uncertainty of 0.20 for *C*(vib) and of 0.30 for *S*(vib) has been adopted.

Sensitivity Analysis Details: Uncertainties in Estimating Contributions of Translation and Overall Rotation. *S*(tran) may be considered exact. *S*(rot) depends on ln(*I*), where *I* is the overall moment of inertia; *S*(rot) is rather insensitive to small differences in assigned values of *I*. A 10% difference in *I* causes a 0.1 cal difference in *S*(rot); for most studies, the small differences in moments of inertia will have less than 0.05 cal effect on the entropy.

Sensitivity Analysis Details: Uncertainties for Compounds that are Conformer Mixtures. For calculations of C_p, the primary source of error is in the dXE_g/dT estimates. The dXE_g/dT values are sensitive to the relative energies assumed for the conformers. If the differences in energies among conformers are small, as in butane, pentane, and 2,3-dimethylbutane, the dXE_g/dT values are well defined. However, if one conformer has a relatively high energy as in 1,3-butadiene and cyclohexane a small change in the value assigned to the relative energies of the conformers can cause a relatively large change in the dXE_g/dT values. The uncertainty in dXE_g/dT arising from uncertainties in conformer energies is 0.05 to 0.2 for most sets of alkane conformers, but it is larger for 1,3-butadiene and for cyclohexane. dXE_g/dT is estimated by numerical differentiation; if conformers have only two energy levels, an analytical differentiation has also been used (eqs 2 and 3). The two methods agree within 0.02 cal K^{-1} mol^{-1} or better.

For entropy, the value for the global minimum is taken as the reference, and a correction *S*(corrn) is applied to account for the entropy of other conformers. If all conformers have the same symmetry number, *S*(corrn) will be small and the error contributed by this term will be negligible. If some conformers differ in symmetry number, then uncertainties will arise from uncertainties of the calculated relative energies of the conformers. These uncertainties will also give rise to uncertainties in *S*(mix), the entropy of mixing term. The uncertainty in *S*(mix) is estimated to be 0.05 to 0.2 and varies with the compound.

Sensitivity Analysis Details: Uncertainties of Contributions of Hindered Methyl Group Rotors. The method used in the present study follows the traditional way of calculating the entropy and the heat capacity due to hindered methyl group rotation (libration). All methyl groups are treated as equal, and an average value is calculated for the *S*(hind rotor) and *C*(hind rotor) terms.

Many authors have discussed the calculation of *S*(hind rotor) and *C*(hind rotor) of methyl groups of alkanes, but it is a curious fact that almost without exception authors have neglected to publish the actual values that were used. Chao et al.,[43] for example, provide an extensive discussion of treatments of the hindered rotor component of the entropy and the heat capacity for propane but provide no numbers for the actual values used. It is therefore not possible to judge how large are the corrections that have been applied.

Values of the reduced moments of inertia of methyl groups and of the barriers to rotation used in calculating *S*(hind rotor) and *C*(hind rotor) are usually provided in the earlier studies. Using literature values along with independent estimates of *I*(red) based on geometries derived with the 6-31G(d,p) basis set and barriers calculated with MP2/6-311+G(2df,2p)//6-31G-(d,p) energies, it is possible to compile a set of *S*(hind rotor) and *C*(hind rotor) at a series of temperatures. It turns out that the values (apart from those of ethane) are reasonably constant. For a set of 33 values for methyl groups, the average *S*(298.15 K) for a hindered methyl rotor is 1.95 cal K^{-1} mol^{-1} and *S*(500 K) is 3.01, both with a standard deviation of 0.13; the average value of *C*(298.15 K) is 2.07 with a standard deviation of 0.05 and *C*(500 K) is 2.15 with a standard deviation of 0.07.

In the sensitivity analysis, the uncertainty in *C*(hind rotor) or in *S*(hind rotor) for one methyl group is estimated to be 0.07 cal. The variance corresponding to this error is additive because the Me hr corrections are additive. For trimethylbutane, the literature values of *I*(red) and of *V* give *C*(hind rotor) values that differ by from +0.5 at 298.15 K to −0.9 at 1000 K from the Scott and Waddington values; see Table 17a (Supporting Information).

Results

Table 1a provides an overall summary of the average rms values of differences between calculated and experimental C_p values for all compounds treated in this study, and Table 1b summarizes the rms differences of experimental minus calculated entropy. The last column in Table 1b shows the number of values of experimental entropy that are available. Somewhat lower rms values are obtained with HF 6-31G(d,p) frequencies scaled by 0.91 and by the MP2 frequencies than with frequencies scaled by 0.90; however, MP2 geometry minimizations and derived frequencies involve more expensive computation and offer no advantage over the HF geometries and frequencies. The experimental (Shimanouchi) frequencies perform less well for 1,3-butadiene and for cyclohexane; this correlates with the relatively poor correspondence between experimental and calculated frequencies for cyclohexane.

To show the improvement that comes from including hindered rotor corrections for methyl groups, there is a column in Table 1a for SF 0.91 that shows rms values for *rrho estimates* of C_p. Moreover, Tables 3 through 20 (Tables 3, 4, 7, 8, 9b,d,e, 10−13, 15−20 are in the Supporting Information) show for SF 0.90 both the rrho value for C_p and for *S* and the value corrected for hindered rotation of methyl groups.

An rms value represents the standard deviation of an observed value minus the calculated value with reference to an expected value of zero for the difference. The metric, standard deviation from the average is a measure of precision neglecting bias. The value of the average of the C_p differences provides a direct measure of the bias; the values of the averages for C_p values are shown in Table 1a. It is not generally possible to compute an average for *S*(calcd) − *S*(exptl) because there is usually only one experimental value of *S*.

Parts a and b of Table 2 summarize the results of the sensitivity analysis in terms of the estimated uncertainty of

TABLE 1: Summary of rms Values of Differences between Calculated and Experimental (a) Heat Capacities and Averages of the Same[a] and (b) Experimental Entropies[b]

(a) Values of differences between Calculated and Experimental Heat Capacities and Averages of the Same

	source of frequencies for calculating C_p(vib)								
						Shimanouchi[d]			
	SF 0.90[c] rms	SF 0.90 av	SF 0.91[c] rms	SF 0.91 av	SF 0.91 rms rrho	rms	av	MP2[e] rms	MP2 av
ethane	0.12^{f}	−0.01	0.20	0.14	0.26	0.16	0.11	0.22	0.17
cyclopropane	0.08	0.07	0.22	0.15		0.08	−0.02	0.15	0.13
propane	0.29^{i}	−0.25	0.14	−0.07	0.46	0.15	−0.04	0.12	−0.04
1,3-butadiene	0.52^{i}	−0.52	0.36	−0.35		0.76^{i}	−0.73	0.76^{i}	−0.78
2-butyne	0.11	0.09	0.25^{i}	0.25	0.75				
cyclobutane				no experimental data					
butane	0.23	0.18	0.50^{i}	0.48	0.82	0.43^{i}	0.40	0.48^{i}	0.41
isobutane	0.57^{j}	-0.55	0.30^{i}	−0.29	0.45			0.32^{i}	−0.31
pentane	0.14	−0.03	0.33^{i}	0.31	0.86				
2-methylbutane	0.47^{i}	−0.47	0.23	−0.22	0.69			0.27	−0.26
neopentane	0.74^{j}	−0.72	0.42^{i}	−0.39	0.88			0.50^{i}	−0.48
cyclohexane	$1.10^{g,i}$	−0.98	0.71	−0.52		1.70^{j}	−1.33	1.23^{i}	−1.03
2,2-dimethylbutane	0.99^{j}	−0.95	0.63^{i}	−0.59	0.75			0.74^{j}	−0.71
2,3-dimethylbutane	0.66^{j}	−0.62	0.34^{i}	−0.23	0.76			0.41^{i}	−0.34
toluene	0.11^{h}	0.01	$0.50^{h,i}$	0.41	0.60				
methylcyclohexane	0.21	0.18	0.72^{i}	0.71	0.93				
trimethylbutane	1.29^{j}	−1.28	0.84^{j}	−0.66	0.70			1.11^{j}	−0.99
tetramethylbutane				no experimental data					

(b) Summary of rms Values of Differences between Calculated and Experimental Entropies

	source of freqs for calculating S(vib)				
	SF 0.90[k]	SF 0.91[k]	Shimanouchi[l]	MP2[m]	no. S(lit) values[n]
ethane	0.12	0.15	0.08	0.16	3
cyclopropane	0.04	0.07	0.06	0.05	1
propane	0.13	0.11	0.10	0.10	3
1,3-butadiene	0.39	0.26	0.26	0.59^{q}	9^{p}
2-butyne	0.51^{q}	0.55^{q}			1
cyclobutane[o]	0.20	0.29	0.17	0.54^{q}	1
butane	0.51^{q}	0.43	0.43	0.23	2
isobutane	0.44^{q}	0.25		0.22	2
pentane	0.86^{r}	1.06^{r}			1
2-methylbutane	0.41	0.27		0.16	3
neopentane	0.71	0.59		0.58	2
cyclohexane	0.27	0.08	0.48	0.02	1
2,2-dimethylbutane	0.65^{q}	0.45		0.54^{q}	1
2,3-dimethylbutane	0.97^{r}	0.76^{q}		0.51^{q}	3
toluene	0.07	0.30			5
methylcyclohexane	0.55^{q}	0.32			1
trimethylbutane	1.39^{r}	1.11^{r}		0.94^{r}	3
tetramethylbutane	0.33	0.61^{q}		0.99^{q}	1

[a] Data are from Tables 3a through 20a (units are cal K^{-1} mol^{-1}). [b] Data are from Tables 3c through 20c (units are cal K^{-1} mol^{-1}). [c] 6-31G(d,p) frequencies. [d] Shimanouchi frequencies. [e] MP2/6-31G(d,p) frequencies. [f] See Table 2a for estimates of uncertainties of all data in this table. [g] Value of dXE_g/dT for cyclohexane is especially sensitive to assigned $E(\mathrm{tb}) - E(\mathrm{chair})$ value. [h] Based on using smoothed experimental toluene data; values using raw experimental values reflect the experimental errors and are 0.34 and 0.50. [i] This rms value is within 2 std deviations of the estimated uncertainty of the differences: experimental minus calculated. [j] This rms value is outside of 2 std deviation. All values except those flagged *i* and *j* are within 1 std deviations. See Table 2a for the estimates of the uncertainties of the data in this table. [k] 6-31G(d,p) frequencies. [l] Shimanouchi frequencies. [m] MP2/6-31G(d,p) frequencies. [n] Number of available experimental S values including those derived at temperatures other than the bp by the authors (using experimental C_p data). [o] Ring pucker treated as vibration. [p] Only smoothed values are reported. [q] This rms value is within 2 std deviations of the estimated uncertainty of the differences: experimental minus calculated. [r] This rms value is outside of 2 std deviations. All values except those flagged *p* and *q* are within 1 std deviation. See Table 2b for the estimates of the uncertainties of the data in this table.

calculated values of C_p and of entropy. Also shown in Table 2 are estimates of the uncertainties of differences of experimental values minus calculated values; these latter include the uncertainties of the experimental data.

In parts a and b of Tables 1, the reported rms values for the differences (observed value minus calculated value) are flagged with "*i*" if the rms value is larger than one standard deviation from the expected rms value but less than two standard deviations. A flag of "*j*" signifies that the rms value exceeds two standard deviations. The absence of a "*i*" or "*j*" flag signifies that the rms value is within one standard deviation of the estimated uncertainty. Most rms values fall within less than one standard deviation.

Tables 3a through 20a show calculated values of C_p at representative temperatures for which there are experimental values. Calculated C_p values are shown for each set of frequencies, and details of the corrections, including a column showing corrections for hindered methyl rotors, are shown for the SF 0.90 set. If several conformers are present, details are shown for the conformer of lowest energy along with the dXE_g/dT values. The rms for the experimental minus calculated values is shown in the next to the last line of the entries for the

TABLE 2: Sensitivity Analysis: Uncertainty in Calculated (a) C_p and (b) S Owing to Uncertainties in Component Terms (cal K^{-1} mol^{-1})

(a) Uncertainty in Calculated C_p

	no. hindered Me rotors	total uncertainty hindered Me rotors	uncertainty of dXE_g/dT[a]		uncertainty of calculated C_p[b]		uncertainty of C_p(exptl)	uncertainty of C_p(exptl) − C_p(calcd)	
uncertainty per Me rotor	0.07	0.07	298.15 K	500.00 K	298.15 K	500.00 K		298.15 K	500.00 K
ethane	1	0.07			0.21	0.21	0.05	0.22	0.22
cyclopropane	0	0.00			0.20	0.20	0.05	0.21	0.21
propane	2	0.10			0.22	0.22	0.15	0.27	0.27
1,3-butadiene	0		0.30	0.30	0.36	0.36	0.10	0.37	0.37
2-butyne	free rotor	0.05			0.21	0.21	0.10	0.23	0.23
cyclobutane	0				0.20	0.20	no exptl		
butane	2	0.10	0.11	0.07	0.25	0.23	0.15	0.29	0.28
isobutane	3	0.12			0.23	0.23	0.15	0.27	0.27
pentane	2	0.10	0.05	0.05	0.23	0.23	0.07	0.24	0.24
2-methylbutane	3	0.12	0.18	0.10	0.30	0.25	0.15	0.33	0.30
neopentane	4	0.14			0.24	0.24	0.07	0.25	0.25
cyclohexane	0		0.50[c]	0.50[c]	0.54	0.54	0.50	0.73	0.73
2,2-dimethylbutane	4	0.14			0.24	0.24	0.20	0.31	0.31
2,3-dimethylbutane	4	0.14	0.01	0.01	0.24	0.24	0.20	0.31	0.31
toluene	free rotor	0.05			0.21	0.21	0.32	0.38	0.38
methylcyclohexane	1	0.07	0.04	0.03	0.22	0.21	0.50	0.54	0.54
trimethylbutane	5	0.16			0.26	0.26	0.10	0.28	0.28
tetramethylbutane	6	0.17			0.26	0.26	no exptl		
rms					0.27	0.27		0.34	0.34
uncertainty C(vib)	0.20								

(b) Uncertainty in Calculated S

	no. hindered Me rotors	total uncertainty hindered Me rotor	uncertainty of S(mixing)		uncertainty of calcd S[d]		uncertainty S(exptl)	uncertainty of S(exptl) − S(calcd)	
uncertainty per rotor	0.07		298.15 K	500 K	298.15 K	500 K		298.15 K	500 K
ethane	1	0.07			0.33	0.33	0.20	0.39	0.39
cyclopropane	0				0.30	0.30	0.20	0.36	0.36
propane	2	0.14			0.36	0.36	0.10	0.37	0.37
1,3-butadiene	0		0.20	0.24	0.36	0.39	0.20	0.42	0.44
2-butyne	free rotor	0.05			0.30	0.30	0.20	0.36	0.36
cyclobutane	0				0.30	0.30	0.20	0.36	0.36
butane	2	0.14	0.12	0.05	0.38	0.36	0.30	0.48	0.47
isobutane	3	0.21			0.38	0.38	0.15	0.41	0.41
pentane	2	0.14	0.05	0.05	0.36	0.36	0.20	0.41	0.41
2-methylbutane	3	0.21	0.12	0.05	0.40	0.38	0.20	0.44	0.43
neopentane	4	0.28			0.40	0.40	0.60	0.72	0.72
cyclohexane	0		0.01	0.03	0.30	0.31	0.20	0.36	0.37
2,2-dimethylbutane	4	0.28			0.40	0.40	0.20	0.45	0.45
2,3-dimethylbutane	4	0.28	0.10	0.10	0.41	0.41	0.20	0.46	0.46
toluene	Free Rot	0.05			0.30	0.31	0.15	0.34	0.34
methylcyclohexane	1	0.07	0.05	0.05	0.33	0.33	0.30	0.45	0.45
trimethylbutane	5	0.35			0.42	0.42	0.15	0.45	0.45
tetramethylbutane	6	0.42			0.44	0.44	0.30	0.53	0.53
rms					0.36	0.36		0.44	0.44
uncertainty S(vib) =	0.30								
uncertainty S(rot) =	0.05								

[a] Depends on energies assigned to the conformers. [b] Estimated uncertainty of calculated C_p combines uncertainties of C(vib), C(hr), and $C(dXE_g/dT)$. [c] Principal source of error in dXE_g/dT arises from uncertainties in the energy values used in calculating $\Delta G = \Delta H - T\Delta S$ for each conformer. ΔG is used in estimating fg(tb), the fraction of the twist boat conformer. XE_g = sum over conformers of Δefg (here $\Delta H = \Delta e$) where Δe is the E(tb) − E(chair). This XE_g value is the heat contributed by the enantiomeric tb conformers, and dXE_g/dT is the heat capacity contribution. [d] Estimated uncertainty of calculated S combines uncertainties of S(overallrot), S(vib), S(hind rotor), S(mix).

calculations based on each frequency, and these rms values have been transferred to the summary table, Table 1a for C_p.

Tables 3c through 20c show calculated values of the entropy. Details are provided for the SF 0.90 frequency set for the conformer of lowest energy, along with S(corrn) (the conformer correction for S), S(mixing), and the values of the hindered rotor corrections. The rms for the experimental minus calculated values is shown in the next to the last line of the entries for the calculations based on each frequency, and these rms values have been transferred to the summary table, Table 1b for entropy.

Parts a and b of Table 23 summarize comparisons between calculations that treat multiple conformers by assignment of a global function to represent all torsions simultaneously and calculations that treat multiple conformers as mixtures of transiently stable molecules (this work). For the compounds that are found in both studies, results are generally comparable.

Evaluation of the Results. (a) The most important conclusion is that it is possible to obtain useful values of heat capacities and of entropies of representative hydrocarbons over a temperature range of at least 200−600 K by the methodology used in the present study. Over this temperature range, the average predicted uncertainty of calculated C_p values is 0.27 cal K^{-1} mol^{-1} and of entropy values is 0.36 cal K^{-1} mol^{-1}

(b) As can be seen on comparing rms values with averages for differences (experimental−calculated) values, the precision of the calculations is good, but many of the calculated values are biased in comparison with reported experimental values. For most compounds, 6-31G(d,p) frequencies scaled by 0.91 agree more closely with experimental values than do frequencies scaled by 0.90, but there are exceptions such as ethane, 2-butyne, and toluene among others. And with cyclohexane, the Shimanouchi experimental frequencies perform poorly; correspondingly, experimental cyclohexane frequencies do not agree well with calculated frequencies. These results suggest that there are problems with some Shimanouchi frequencies or with some calculated frequencies.

One anomaly was encountered, namely the value of the lowest frequency found for 2,2,3-trimethylbutane. The lowest frequency found with MP2/6-31G(d,p)//MP2/6-31G(d,p) is about 50 cm^{-1}, a not unusual value, but with 6-31G(d,p)//6-31G(d,p), the lowest frequency varied from about -5 to $+5$ cm^{-1} depending on the cut-off used. A relaxed frequency scan showed no unusually shallow minimum. The reason for this behavior has not been determined.

With energies derived with MP2/6-311+G(2df,2p)//6-31G-(d,p), barriers for methyl hindered rotation range from 2.9 to 3.2 kcal/mol for *n*-alkanes, increasing to 3.6 for isoalkanes, to 4 for neoalkanes. To get good agreement between calculation and experiment, most earlier workers used adjusted values that are larger by more than 0.5 kcal/mol. This difference can lead to differences of more than 1 cal in calculated values.

(c) Calculations that treat multiple conformers by a function that simultaneously includes all possible multiple rotations provides an alternative to treating them as mixtures of quasi-stable molecules as has been done in this study. It is reassuring that the two methods give comparable results for the four compounds that have been treated by both methods, Table 23a,b.

(d) For most compounds, the treatment of contributions to C_p of hindered methyl rotors by the Pitzer−Gwinn formalism markedly improves on the values obtained by the rrho method. Column 6 of Table 1a shows rms values for rrho calculations; these may be compared with the rms values in column 4 that report values corrected for hindered rotation. There are so few examples of experimental entropy values that averages can be calculated for only a few compounds. However, the several entropy tables show the rrho values of entropy and the corrected values.

The method of treating the hindered rotor correction for methyl groups by simple summation tends to magnify errors as the number of methyl groups increases. A 0.1 cal K^{-1} mol^{-1} error in estimation of the hindered rotor contribution leads to a 0.2 cal error for a compound with two methyl groups and to a 1.2 cal error for a compound with six methyl groups.

Examples of Calculated Heat Capacities and Entropies of Individual Compounds. All tables have been labeled sequentially. The following sections point out special aspects of the calculations for the individual compounds. Tables and discussions for most of the compounds will be found in the Supporting Information.

Propane. Heat capacity calculations are shown in Table 5a,b. Table 5b provides an example of the method used to calculate hindered rotor corrections. The estimated uncertainty of the calculated C_p is 0.22 and for the difference of experimental and calculated C_p it is 0.27 (Table 2a). All calculated values fall within the 0.27 uncertainty. However, in contrast to the results with ethane, the rms of calculated C_p values derived from SF 0.90 frequencies is larger than for the calculated values based on experimental frequencies.

Parts c and d of Table 5 show calculation of the entropy. As summarized in Table 2b, the uncertainty of the calculated entropy is 0.36 and of the differences between calculated and experimental S values is 0.37. Root mean square values for all calculated values are 0.13 or less.

Vansteenkiste et al.[20] in their Table 3 show a value of C_p for propane of 17.45 at 298.15 K calculated by a full analysis of hindered rotation based on B3LYP/6-311G(d,p) frequencies and geometries. The calculated value obtained in this study (Table 5a) is 17.71. The experimental value is 17.56, obtained by interpolation of the data of Kistiakowsky et al.[49] Calculated values of S are 64.77 using B3LYP/6-311G(d,p)[20] and 64.70 (this study). The experimental value of Kemp and Egan[50] is 64.70.

1,3-Butadiene. Three conformers of 1,3-butadiene are energy minima, the anti or trans conformer with a C═C−C═C torsion of 180 and two g+ and g− conformers with torsions of +39 and −39 (from 6-31G(d,p) geometries). The relative MP2/6-311+G(2df,2p)//6-31G(d,p) energies are 0 for the anti conformer, the global minimum, and 2.95 kcal mol^{-1} for the gauche conformer. The cis form is a transition state between g+ and g− and has a relative energy of 3.77 kcal mol^{-1}. The transition state between anti and g is at 102 and has a relative energy of 6.43. These values differ appreciably from those reported earlier by Aston et al.,[26] Bock et al.,[51] and Compton et al.[52] Because the gauche conformer is present in low concentration (3% at 298 K and 19% at 500 K for a gauche−anti conformer energy difference of 2.95 kcal mol^{-1}), it has been very difficult to obtain definitive spectroscopic evidence for the gauche conformer.

In addition, there was uncertainty in the early studies as to whether the minor conformer was cis or gauche, and the energy assignments sometimes had the cis conformer at lower energy than the gauche. In spite of these several major difficulties, the authors all claimed to obtain calculated C_p and S values that almost exactly reproduce experimental values. Such calculations are an example of successful but arbitrary curve fitting by adjusting frequencies and energies. The several authors emphasized the need to include more than one conformer in the calculations, that is, to make a dXE_g/dT correction, but the published formalism for making this calculation is incorrect, and moreover, the energies needed for making the correction were not available at the time

Calculations of heat capacity are shown in Table 6a. The expected uncertainty (Table 2a) for C_p(calcd) at 298 K is 0.36 and of the C_p(exptl) − C_p(calcd) is 0.37. The rms values for C_p(exptl) − C_p(calcd) are within these limits except for those based on the MP2 geometries and frequencies; these are within twice the uncertainty. The C_p values shown in the last column of Table 5a illustrate the sensitivity of the calculated C_p values to the assigned energy difference between the gauche and anti conformers. C_p values based on an energy difference having the arbitrary value 3.6 (in place of the MP2/6-311+G(2df,2p)//6-31G(d,p) value of 2.95 used for the other calculations) reduces the rms value by a factor of 3.

Entropy calculations are reported in Table 6b. The estimated uncertainty in S(calcd) is 0.36 and of the difference between S(exptl) and S(calcd) is 0.42. Except for values based on MP2 frequencies, the calculated values fall within the estimated range.

Cyclobutane. There are no experimental values of C_p in the gas phase. Table 8a (Supporting Information) presents C_p(rrho) estimates using 6-31G(d,p) frequencies scaled by 0.90 and by 0.91. Dorofeeva et al.[53] and Rathjens et al.[54] calculated values of C_p with explicit treatment of ring puckering. Differences between the rrho results in this study and those of Rathjen et al. (corrected for ring puckering) are less than 0.15; differences with the Dorofeeva et al. values are larger.

TABLE 5: Propane: (a) Heat Capacity, (b) Hindered Rotor *C* Corrections, (c) Entropy, (d) Hindered Rotor *S* Corrections

(a) Propane: Heat Capacity

temp (K)	C_p(rrho)[a]	C(hr corrn) SF 0.90	C_p(hr corrected) SF 0.90	C_p(lit)	C_p[b] Chao value	C_p(hr corrn)[c] Shimanouchi	C_p(hr corrn) SF 0.91	C_p(hr corrected)[i] MP2
213.90	13.70	0.43	14.13	14.03[d]	13.93	13.97	14.08	14.01
259.00	15.50	0.55	16.05	15.89[d]	15.79	15.81	15.95	15.90
298.15	17.23	0.63	17.86	17.56[e]	17.59	17.62	17.71	17.69
334.05	18.93	0.65	19.58	19.25[f]	19.30	19.34	19.43	19.38
368.55	20.62	0.64	21.26	20.90[f]	20.97	21.01	21.07	21.03
500.00	26.82	0.33	27.15	27.05[h]	26.91	26.96	26.91	26.90
521.15	27.75	0.29	28.04	27.89[g]	27.77	27.83	27.78	27.78
603.25	31.11	0.01	31.12	30.75[g]	30.88	30.94	30.87	30.85
693.20	34.39	−0.26	34.13	33.61[g]	33.88	33.96	33.87	33.86
1000.00	42.93	−0.93	42.00	41.83[h]	41.73	41.83	41.76	41.73
rms[j]			0.29		0.13	0.15	0.14	0.12
av[j]			−0.25		0.00	−0.04	−0.07	−0.04

(b) Propane: Hindered Rotor *C* Corrections

temp (K)	*C*(vib)[k] 207 cm^{-1}	*C*(vib)[k] 262 cm^{-1}	*C*(hr)[l]	*C*(hr corrn)[m]
213.90	1.69	1.54	1.83	0.43
259.00	1.78	1.67	2.00	0.55
298.15	1.83	1.74	2.10	0.63
334.05	1.86	1.79	2.15	0.65
368.55	1.88	1.82	2.17	0.64
500.00	1.93	1.90	2.08	0.33
521.15	1.93	1.90	2.06	0.29
603.25	1.95	1.92	1.94	0.01
693.20	1.96	1.94	1.82	−0.26

(c) Propane: Entropy

temp (K)	*S*(trans)	*S*(rot)	*S*(vib) SF 0.90	*S*(rrho) SF 0.90	*S*(hr corrn)	*S*(hr corrected) SF 0.90	*S*(lit)	S[n] Chao values	*S*(hr corrected) Shimanouchi[o]	*S*(hr corrected) SF 0.91	*S*(hr corrected) MP2[s]
180.00	34.77	19.78	2.62	57.16	0.02	57.18	57.04[p]		57.15	57.17	57.16
231.04	36.01	20.53	3.98	60.51	0.11	60.62	60.45[q]		60.56	60.6	60.57
298.15	37.27	21.29	5.95	64.51	0.25	64.76	64.70[q]	64.58	64.62	64.7	64.67
500.00	39.84	22.51	13.04	75.71	0.49	76.20	75.90[r]	75.93	75.92	76.03	75.99
1000.0	43.28	24.89	31.7	99.88	−0.14	99.74	99.76[r]	99.72	99.36	99.41	99.36
rms[t]						0.13[u]			0.10[v]	0.11	0.10
av[t]						−0.12			−0.05	−0.09	−0.07

(d) Propane: Hindered Rotor *S* Corrections

temp	*S*(vib)[w] 207 cm^{-1}	*S*(vib)[w] 262 cm^{-1}	*S*(vib)[x] hindered rotor	*S*(hr) corrn
180.00	1.20	0.84	1.03	0.02
231.09	1.61	1.22	1.47	0.11
298.15	2.07	1.64	1.98	0.25
500.00	3.04	2.59	3.06	0.49
1000.00	4.40	3.94	4.10	−0.14

[a] Using 6-31G(d,p)//6-31G(d,p) geometry with frequencies scaled by 0.90. [b] Chao et al.[43] [c] Shimanouchi frequencies.[34] [d] Kistiakowsky et al.[49] [e] Interpolated using $C_p = 2.5974 + 0.048568T + 4.2905216 \times 10^4/T^2$. [f] Kistiakowsky and Rice.[63] [g] Dailey and Felsing.[64] [h] Stull et al.[16] [i] MP2/6-31G(d,p) geometry and frequencies SF 0.95/0.923. [j] Omitting nonexperimental values for C_p at 1000 K. [k] *C*(vib) at lowest two 6-31G(d,p) frequencies with SF 0.90. [l] Calculated from *I*(red) 4.49 × 10^{-40} g cm^2 and *V* 3.28 kcal mol^{-1} (from MP2/6-311+G(2df,2p)//6-31G(d,p) energies). Chao et al.[43] used *I*(red) 4.42 × 10^{-40} g cm^2 and *V* 3.29 kcal mol^{-1}. Pitzer Table 2[40] used *I*(red) 4.7 × 10^{-40} g cm^2 and *V* 3.40 kcal mol^{-1}. Kemp and Egan[50] used *I*(red) 4.35 × 10^{-40} and *V* 3.30 kcal mol^{-1}. Dailey and Felsing[64] used *I*(red) 4.4 × 10^{-40} g cm^2 *V* 3.300 kcal mol^{-1}. [m] 2*C*(hindered rotor) − *C*(207) − *C*(262) for 6-31G(d,p) SF 0.90 frequencies. Appropriate hr corrections were calculated for each set of frequencies shown in Table 5a. [n] Chao et al.[43] [o] Shimanouchi frequencies.[34] [p] Pitzer, Table 2, exptl.[65] [q] Kemp and Egan, exptl.[50] [r] Stull et al., calcd.[16] [s] MP2/6-31G(d,p) geometry and frequencies. [t] Omitting nonexperimental values for *S* at 500 K, 1000 K. [u] For rho, rms = 0.13 and av = 0.00. [v] For rho, rms = 0.30 and av = −0.26. [w] *S*(vib) at lowest two 6-31G(d,p) frequencies SF 0.90. [x] Footnotes, Table 5c.

There is a single measurement of the entropy; it is by Rathjens and Gwinn[55] at 285.67 and has an estimated uncertainty of 0.2. The estimated uncertainty of the calculated *S*(rrho) for SF 0.90 is 0.30 and of the difference between experimental and calculated entropy is 0.36 (Table 2b). The calculated values of *S*(rrho) are within this estimated uncertainty except for the value based on MP2/6-31G(d,p)//MP2/6-31G(d,p) geometry and frequencies.

Vansteenkiste et al.[23] report an extensive investigation of cyclobutane ring puckering using the 6-31+G(d,p) basis set along with various DFT functionals. With the mPW1P95 functional, they report *S*(rrho) 62.72 cal and *S*(1D-HR) (corrected for ring puckering) 63.03 at 298.15 K. With 6-31G(d,p) frequencies and SF 0.91 S(rrho) is 63.13 (Table 8b); the experimental value is 63.43.[56] It is not clear that making a correction for ring puckering improves the calculated entropy

TABLE 6: 1,3-Butadiene: (a) Heat Capacity, (b) Entropy

(a) 1,3-Butadiene: Heat Capacity

temp (K)	C_p(rrho)	dXE_g/dT SF 0.90	C_p(rrho)[a] SF 0.90	C_p(lit)	C_p(rrho)[a] SF 0.91	C_p(rrho)[b] Shimanouchi 2.95	C_p(rrho)[c] MP2	C_p(rrho)[d] Shimanouchi 3.6
243.15	15.39	0.74	16.13	15.98[e]	16.01	16.21	16.41	15.71
283.15	17.30	1.26	18.56	18.21[e]	18.41	18.74	18.84	18.02
298.15	18.04	1.45	19.49	19.08[e]	19.33	19.72	19.78	18.94
323.15	19.27	1.76	21.03	20.51[e]	20.86	21.31	21.31	20.48
363.15	21.23	2.19	23.41	22.76[e]	23.22	23.74	23.66	22.94
403.15	23.13	2.49	25.62	24.88[e]	25.41	25.94	25.86	25.27
423.15	24.03	2.61	26.64	25.85[e]	26.41	26.93	26.86	26.36
500.00	27.27	2.69	29.96		29.74	30.22	30.21	30.08
1000.00	40.62	1.10	41.72		41.52	41.74	41.81	42.25
rms[f]			0.52		0.36	0.76	0.76	0.27
av[f]			−0.52		−0.34	−0.76	−0.79	−0.06

(b) 1,3-Butadiene: Entropy

temp (K)	S(tran)	S(rot)	S(vib)[g] SF 0.90	S(mix)	S(corrn)	S(rrho) SF 0.90	S(lit)	S(rrho)[g] SF 0.91	S(rrho)[h] Shimanouchi	S(rrho)[i] MP2	S(rrho)[j] Shimanouchi 3.6
203.15	35.98	21.02	3.53	0.05	0.01	60.58	60.33[k]	60.52	60.37	60.72	60.32
243.15	36.87	21.56	4.70	0.13	0.02	63.27	63.00[k]	63.19	63.06	63.46	62.95
283.15	37.63	22.01	5.98	0.25	0.04	65.91	65.60[k]	65.80	65.72	66.13	65.51
298.15	37.88	22.17	6.48	0.31	0.05	66.89	66.56[k]	66.78	66.71	67.13	66.46
323.15	38.28	22.41	7.34	0.42	0.07	68.52	68.16[k]	68.40	68.36	68.78	68.05
363.15	38.86	22.76	8.77	0.61	0.12	71.11	70.68[k]	70.97	70.98	71.40	70.58
403.15	39.38	23.07	10.26	0.80	0.17	73.68	73.17[k]	73.51	73.57	73.99	73.09
423.15	39.62	23.21	11.02	0.89	0.20	74.94	74.40[k]	74.76	74.85	75.27	74.34
500.00	40.45	23.71	13.97	1.22	0.31	79.66		79.45	79.61	80.03	79.05
1000.00	43.89	25.78	32.06	2.08	0.83	104.64		104.28	104.63	105.17	104.37
rms[l]						0.39		0.26	0.26	0.59	0.07
av[l]						−0.38		−0.25	−0.21	−0.57	0.06

[a] 6-31G(d,p) frequencies g−a energy 2.95. [b] Shimanouchi[36] with g−a energy difference 2.95. [c] MP2/6-31G(d,p)//MP2/6-31G(d,p) geometry and frequencies. [d] Shimanouchi frequencies with g−a energy 3.6 to illustrate sensitivity to (all the others are 2.95). [e] Scott et al.[66] smoothed experimental data. [f] Omitting nonexperimental values for C_p at 500 K, 1000 K. [g] 6-31G(d,p) freqs E(g) − E(a) 2.95 kcal mol^{-1} [h] Shimanouchi.[36] [i] MP2/6-31G(d,p)//MP2/6-31G(d,p) geometry and frequencies. [j] Shimanouchi frequencies with E(g) − E(a) 3.6 kcal mol^{-1} (all the others are 2.95). [k] Scott et al.[66] smoothed experimental data. [l] Omitting nonexperimental values of S at 500 K, 1000 K.

at 298.15 K. There are no experimental C_p data for cyclobutane; however, the C(rrho) values calculated with PW1P95/6-31+G-(d,p) are about 1 cal lower than C_p(rrho) calculated with 6-31G-(d,p).

Butane. Butane exists as a mixture of anti and gauche conformers, and calculations of C_p and S need to include both conformers. The heat capacity estimates were corrected by a dXE_g/dT term, while the entropy was corrected by an entropy of mixing term. The final result is an estimate of C_p(rrho) and of S(rrho) for the compound (a mixture of conformers). To these values was applied a single overall hindered rotor correction for methyl group libration. Libration about the central C−C bond was treated as a vibration.

Calculations of the heat capacity of butane are shown in parts a and b of Table 9 (Table 9b is in Supporting Information). The estimated uncertainty of C_p(calcd) is 0.25 and of C_p(exptl) − C_p(calcd) is 0.29. Root mean square for the SF 0.90 frequencies is within this uncertainty range; the rms values for the other sets of frequencies are within twice the stated uncertainty.

Many estimates have been made of the difference of energies of the gauche and the anti conformers of butane. Examples pertinent to the present study are the following: Benson[1] used 0.8 kcal mol^{-1} for group increment calculations, DeTar used 0.7[24] in calculations of entropy and heat capacity of butane, Chen et al. used 0.76,[44] Chen et al. also provided an extensive bibliography of earlier estimates. Recently Smith and Jaffe[57] carried out extensive calculations and obtained an energy difference of 0.59 using CCISD(T)/cc-pVTZ//MP2/6-311G-(2df,p). The difference based on MP2/6-31G(d,p)//6-31G(d,p) is 0.68, while the difference obtained with the standard used for this study, MP2/6-311+G(2df,2p)//6-31G(d,p), is 0.63. Herrebout et al.[58] report an experimental value of 0.669 ± 0.096.

Assigned gauche−anti energy differences have an effect on estimates of C_p, particularly in the dXE_g/dT term; to a minor extent, they affect Boltzmann fractions of anti and gauche forms in the averaging of C(vib) and of S(rot) and S(vib). In Table 9e (Supporting Information) are shown calculated values of C_p-(rrho) and values of S(rrho) that are obtained for different assigned energy differences of the two conformers.

Chen et al.[44] present three sets of calculations of C_p, two in their Tables 5 and 8 for the C_p of the mixture of conformers (that is, for the compound to which the experimental values apply) and separate Tables 6 and 7 for the individual anti and the gauche conformers. The two sets of calculations are not entirely consistent. As summarized in Table 9a of the present study, the C_p values in the Chen et al. Tables 5 and 8 have an rms error of 0.11 cal, while those represented in the Chen et al. Tables 6 and 7 define C_p values for the compound with an rms of 0.44. It is noteworthy that none of the C_p calculations of Chen et al. take into account the energy changes that occur with alteration of the anti−gauche populations with temperature. This is to be found in the dXE_g/dT set of values shown in Table 9a.

Calculations of entropy are shown in parts c and d of Table 9 (for Table 9d, see Supporting Information). The estimated uncertainty of S(calcd) is 0.38 (Table 2b); Aston and Messerly[59] report an uncertainty of 0.2 for their experimental value. The value reported by Huffman et al.[60] is 0.4 higher than the Aston

TABLE 9: Butane: (a) Heat Capacity,[a] (c) Entropy[b]

(a) Butane: Heat Capacity

temp (K)	C_p(rrho)[c,d] SF 0.90	C(corrn)[e]	dXE_g/dT[f]	C_p(rrho)[g] SF 0.90	C(hr corrn)[h]	C_p(hr corrected)[c] SF 0.90	C_p(lit)	C_p(hr corrected)[j] Shimanouchi	C_p[j] Chen Tables 5,8	C_p Chen[j] Interpreted Tables 6,7	C_p(hr corrected) SF 0.91	C_p(hr corrected) MP2[r]
298.15	22.22	−0.03	0.54	22.73	0.65	23.38	23.29[k]	23.08	23.54	22.97	23.18	23.15
344.90	25.20	−0.02	0.41	25.59	0.65	26.24	26.43[l]	25.95	26.38	26.02	26.01	25.98
387.50	27.97	−0.01	0.33	28.28	0.59	28.87	29.10[l]	28.61	29.06	28.68	28.61	28.61
500.00	34.95	−0.01	0.20	35.14	0.26	35.40	35.69[m]	35.20	35.53	35.15	35.08	35.09
521.00	36.16	−0.01	0.17	36.32	0.20	36.51	36.81[l]	36.33	36.63	36.26	36.20	36.24
692.60	44.80	−0.01	0.11	44.90	−0.36	44.52	44.42[l]	44.37	44.41	44.35	44.20	44.23
1000.0	55.83	−0.01	0.05	55.87	−1.01	54.87	54.22[k]	54.70	54.34	54.15	54.55	54.58
rms[s]						0.23[n,t]		0.43	0.11	0.44[p]	0.50[q]	0.48
av[s]						0.18		0.40	0.09	0.40	0.48	0.41

(c) Butane: Entropy

temp (K)	S(t+rot)[u]	S(vib)[u]	S(mix)[u]	S(corrn)[u]	S(rrho)[u]	S(hr corrn)[v]	S(hr corrected) SF 0.90	S(lit)	S(hr corrected) Shimanouchi[w]	S[x] Chen Tables 5,8	S[x] Chen Tables 6,7	S(hr corrected) SF 0.91	S(hr corrected) MP2[bb]
272.66	60.52	9.83	1.85	−0.01	72.18	0.33	72.52	72.05[y,z]	72.45	72.10	71.96	72.42	72.25
298.15	61.23	11.03	1.90	−0.01	74.15	0.40	74.55	74.00[y,z]	74.45	74.07	74.03	74.49	74.26
500.00	65.33	21.46	2.08	−0.03	88.85	0.67	89.47	89.10[aa]	89.23	89.15	89.12	89.10	89.04
1000.0	70.85	47.44	2.16	−0.04	120.41	−0.07	120.34	120.16[aa]	119.98	120.32	120.31	120.16	119.67
rms[cc]							0.51[dd]		0.43	0.05	0.07	0.43	0.23
av[cc]							−0.51		−0.43	−0.03	0.03	−0.43	−0.22

[a] 6-31G(d,p) frequencies; E(g) − E(a) energy difference based on MP2/6-311+G(2df,2p)//6-31G(d,p) energies is 0.63 kcal mol^{-1}. [b] 6-31G(d,p) frequencies and MP2/6-31G(d,p) frequencies. [c] (40% g at 298.15 K; 51% g at 500 K, and 59% g at 1000 K). [d] For the global minimum (anti). [e] Correction for contributions of the gauche conformer. [f] Correction for change in anti−gauche population with temperature. [g] C_p(rrho) (rrho C_p of the compound). [h] Hindered rotor correction based on I(red) 4.50 × 10^{-40} g cm^2 and V 3.11; same corrections used for Shimanouchi data. [i] Using Shimanouchi frequencies[34] and $E_g - E_a$ 0.63. [j] Chen et al.[44] used E(g) − E(a) 0.76 kcal mol^{-1} (33.5% g at 298.15 K; 45% g at 500 K). Their Tables 5 and 6 give one set of calculated C_p values for the compound, while an alternative set of values of C_p for the separate anti (trans) and gauche conformers is given in Tables 6 and 7. [k] Stull et al.[16] [l] Dailey and Felsing;[67] reported uncertainty 1%. [m] From a parabolic interpolation of the Dailey and Felsing data. [n] E(g) − E(a) 0.63; for E(g) − E(a) 0.76, rms value is 0.13, for E(g) − E(a) 0.68, rms value is 0.17, for E(g) − E(a) 0.56, rms value is 0.27. [o] For E(g) − E(a) 0.63; for E(g) − E(a) 0.76, rms value is 0.30, for 0.68, rms value is 0.40, for 0.56, rms value is 0.48. [p] E(g) − E(a) 0.76. [q] E(g) − E(a) 0.63; for rrho, rms = 0.82 and av = 0.70. [r] MP2/6-31G(d,p) geometry and frequency SF 0.95, 0.923. [s] Omitting nonexperimental C_p values at 298 K, 1000 K. [t] For rrho rms = 0.66 and av = 0.45. [u] Entries for anti (trans) conformer (global minimum) for SF 0.90; S(corrn) corrects for contribution of gauche conformer, S(mix) is entropy of mixing. S(rrho) is for the mixture of conformers. The conformer populations are based on E(gauche) − E(anti) = 0.63 kcal mol^{-1}, e.g., which is the difference of the MP2/6-311+G(2df,2p)//6-31G(d,p) energies but are calculated for 0.64, which is the difference in the free energies. At 298.15 K, the fraction of trans conformer is 0.595; at 500 K, it is 0.492, at 1000 K, it is 0.412. [v] Hindered rotor corrections for the two methyl groups. [w] Based on Shimanouchi frequencies with E(gauche) − E(anti) 0.63.[34] [x] Values reported by Chen et al. use E(g) − E(a) 0.76.[44] S gauche values of Chen et al. Table 7 increased by R ln2 because authors used wrong symmetry number. Values interpolated as described for C_p above, and S(mix) calculated with E(g) − E(a) 0.76. The S interpolation for Chen Tables 6 and 7 use the appropriate interpolation function. [y] Aston and Messerly, exptl.[59] [z] Parks et al.[68] report S = 73.86 at 272.50 and 75.76 at 298.15 K. [aa] Stull et al., calcd.[16] [bb] MP2/6-31G(d,p) geometry and frequency SF 0.95, 0.923. [cc] Omitting nonexperimental S values at 500 K, 1000 K. [dd] For rrho, rms is 0.14 and av is −0.16.

and Messerly value; the experimental uncertainty is therefore of the order of at least 0.3; the expected uncertainty of S(exptl) − S(calcd) is expected to be 0.48. Root mean square values in Table 9c lie within this range.

The treatment of entropy by Chen et al.[44] is inconsistent; entropy values for the gauche conformer in their Table 7 evidently used a symmetry number of 1 instead of 2, and no mention was made of using an S(mix) term. With introduction of these editorial changes, the recalculated S values represented by their Tables 6 and 7 and those by their Tables 5 and 8 are consistent. The frequencies used by Chen et al. for butane conformers are idiosyncratic; they differ from those of Shimanouchi[34] and from those calculated by the 6-31G(d,p) basis set.

Table 4 of Vansteenkiste et al.[20] shows values of C_p and S for butane calculated by a full analysis of rotation about the hindered rotation bonds based on B3LYP/6-311G(d,p) frequencies and geometries. (There is no experimental value of C_p at 298.15 K.) At 500 K, the calculated value of C_p is 34.61,[20] while the value calculated in this study is 35.08 (Table 9a). The experimental value is 35.69. The calculated value of S at 298.15 K is 74.35,[20] and in this study, the value is 74.49 (Table 7c, Supporting Information). The experimental value is 74.00.[59] For this example, treatment of the skeletal libration as a hindered rotor gives a value of entropy only 0.14 cal different from treatment as a harmonic oscillator.

Cyclohexane. Cyclohexane has been investigated extensively, both experimentally and computationally, but the data are somewhat discordant. There are two conformers; the one of lower energy is the chair. The twist boat conformer is higher in energy; it is racemic. Experimental aspects of cyclohexane properties have been reviewed by Eliel and Wilen in section 11-4 of *Stereochemistry of Organic Compounds*.[61] The experimentally determined E(tb) − E(chair) is 4.7−6.2 kcal mol^{-1}; the value derived with MP2/6-311+G(2df,2p)//6-31G(d,p) is 6.38 kcal mol^{-1}.

Cyclohexane is also noteworthy as being the first molecule for which a heat capacity term was calculated that takes account of energy absorbed as the proportion of the higher energy conformers (enantiomeric tb) increases with increasing temper-

TABLE 14: Cyclohexane: (a) Heat Capacity, (b) Components of C_p at 500 K, Table 2 of Beckett et al.,[25] (c) Entropy

(a) Cyclohexane: Heat Capacity

temp (K)	C_p(rrho)[a]	$\mathrm{d}XE_g/\mathrm{d}T$[a]	C_p[a] (corrn) SF 0.90	C_p(lit)	C_p[b] Beckett Etb − Ec = 5.6	C_p[a] (corrn) SF 0.91	C_p[c] Shimanouchi	C_p[d] MP2/6-31G(d,p)
298.15	25.77	0.07	25.84	25.40[e]	25.33	25.52	25.27	25.62
370.00	32.94	0.37	33.31	33.00[f]	33.48	32.90	32.97	33.16
384.00	34.32	0.47	34.79	34.20[g]	35.15	34.24	34.53	34.67
390.00	34.90	0.52	35.42	35.00[f]	35.86	35.01	35.19	35.30
410.00	36.84	0.69	37.53	36.80[f]	38.29	37.11	37.44	37.46
428.00	38.54	0.88	39.42	38.67[g]	40.49	38.98	39.51	39.40
460.00	41.48	1.29	42.77	41.70[g]	44.35	42.31	43.12	42.80
495.00	44.53	1.77	46.30	45.30[g]	48.48	45.82	47.05	46.46
500.00	44.95	1.85	46.80	45.38[e]	49.05	46.31	47.59	46.97
521.00	46.69	2.17	48.86	47.00[g]	51.37	48.38	49.92	49.13
544.00	48.52	2.52	51.04	49.30[g]	53.85	50.59	52.40	51.41
1000.00	73.46	4.75	78.21	75.80[e]	77.20	77.61	78.50	78.48
rms[h]			1.10		2.65	0.71	1.70	1.23
av[h]			−0.98		−2.17	−0.52	−1.33	−1.03

(b) Cyclohexane: Components of C_p at 500 K

C(vib)[i]	$C(t + r) = 4R$	C(anharm)[j]	C(taut)[k]	C_p(total)	C_p(lit)
36.28[m]	7.95		2.31[n]	46.51	45.38[l,q]
36.28[m]	7.95		1.43[o]	45.66	
36.27[p]	7.95[p]	0.58[p]	0.68[p]	45.48	

(c) Cyclohexane: Entropy[r]

temp (K)	S(tran)	S(rot)	S(vib) SF 0.90	S(conf)	S(mix)	S(rrho) SF 0.90	S(lit)	Beckett	S(rrho) SF 0.91	Shimanouchi	S(MP2/6-31G(d,p))
298.15	39.20	22.79	9.69	0.00	0.00	71.68	71.41[70]	71.1	71.49	70.93	71.43
500.00	41.77	24.33	23.58	0.05	0.13	89.86	89.24[25]	89.21	89.44	88.87	89.51
1000.00	45.21	26.40	59.32	0.88	1.06	132.86	131.59[25]	133.37	132.13	132.79	132.77
only one experimental value[s]						0.27		0.31	0.08	0.48	0.02

[a] C_p(rrho) using 6-31G(d,p) frequencies. E(tb) − E(chair) is 6.38 kcal mol^{-1} based on MP2/6-311+G(2df,2p)//6-31G(d,p) energies. $\mathrm{d}XE_g/\mathrm{d}T$ corrects for the increasing fraction of the twist boat conformer with increasing temperature. [b] Using Beckett et al. frequencies, with $\mathrm{d}XE_g/\mathrm{d}T$ calcd for these frequencies and based on the Beckett et al. E(tb) − E(chair) 5.6 kcal mol^{-1}. [c] Shimanouchi frequencies,[34] E(tb) − E(chair) 6.38. [d] MP2/6-31G(d,p) frequencies with SF 0.95; E(tb) − E(chair) is 6.38 kcal mol^{-1}. [e] Beckett et al. calcd.[25] Value at 500 K based on interpolation equation $C_p = 8.35066 + 0.0793718T - 6.6338431 \times 10^5/T^2$, which fits experimental data with std deviation 0.18. [f] Montgomery and Devries.[69] [g] Spitzer and Pitzer.[62] [h] Omitting nonexperimental C_p value at 1000 K. [i] C(vib) based on Beckett et al. frequencies. [j] Not defined. [k] Calculated $\mathrm{d}XE_g/\mathrm{d}T$ for first 2 rows, chair to boat "taut" for third row. [l] Interpolated, Table 14a. [m] Based on Beckett et al. frequencies. [n] $\mathrm{d}XE_g/\mathrm{d}T$ calculated from Beckett et al., value of E(tb) − E(ch) 5.6. [o] Calculated from MP2/6-311+G(2df,2p) E(tb) − E(ch) of 6.38. [p] Table 2 of Beckett et al. [q] 45.6 ± 0.5.[p] [r] S(tran)s, S(rot), S(vib) are values for the chair conformer, S(conf) is contribution to entropy of twist boat conformer, S(rrho) (rigid rotor−harmonic oscillator) is entropy of the mixture of conformers. The energy of the twist boat conformer is 6.38 kcal mol^{-1} greater than that of the chair conformer, based on 6-311+G(2df,2p)/6-31G(d,p) energies. Values in the Beckett column used their value, 5.24. [s] Values at 500 K, 1000 K not experimental.

ature. This calculation is that reported by Beckett and Pitzer.[25] Other reports of calculated heat capacities have usually ignored this term.

Heat capacity calculations are shown in Table 14a. For Shimanouchi frequencies, there are, of course, no experimental frequencies for the twist boat conformer and those for the SF 0.90 set were used for that conformer. The stated accuracy of the experimental data is 0.3−0.5.[62] The estimated uncertainty of the calculated values of C_p is 0.54 and of differences between experimental and calculated values is 0.73 (Table 2a). Root mean square differences between calculated and experimental C_p values lie within this standard deviation except for the C_p values derived from the Beckett et al. frequencies and their estimate of 5.6 kcal mol^{-1} for the energy difference of the twist boat and chair conformations

The $\mathrm{d}XE_g/\mathrm{d}T$ term corrects for the increasing amounts of the higher energy twist boat conformer with increasing temperature. Calculations of the fraction of the tb conformer are based on free energies; note that, at 298 K, the entropy of the tb conformer is 3.9 cal K^{-1} mol^{-1} higher than that of the chair conformer owing both to a 3-fold difference in symmetry number and to intrinsically less restricted vibrational modes of the tb conformer. As a result of this large entropy difference, the estimate of conformer fractions using energies is considerably different from the fractions obtained by use of free energies, that is, SM is different from XE. The values of $\mathrm{d}XE_g/\mathrm{d}T$ are sensitive to the assigned value of the energy difference E(tb) − E(chair). Using Pitzer frequencies for the chair conformer and SF 0.90 for the twist boat conformer, at 500 K, $\mathrm{d}XE\mathrm{g}/\mathrm{d}T$ is 4.55 for a 5.6 kcal difference and 2.94 for a 6.38 kcal difference. With 0.90 frequencies $\mathrm{d}XE_g/\mathrm{d}T$ at 500 K is 1.82 for an energy difference of 6.38 and 1.50 for an energy difference of 6.67 (the MP2/6-31G(d,p)//6-31G(d,p) energy difference).

The value of the energy difference used for all calculations shown in Table 12a (Supporting Information), except for the column headed "Beckett," was 6.38 kcal mol^{-1}, the value estimated from MP2/6-311+G(2df,2p)//6-31G(d,p) energies; calculations for the "Beckett" column used the Beckett et al.[25] value, which is 5.6 kcal mol^{-1}. If 6.38 is used instead of 5.6, then the root mean square difference is 0.41 instead of 0.93. Thus the Beckett et al. frequencies give about the same values as do the Shimanouchi frequencies.

Parenthetically, if E(tb) − E(chair) is taken arbitrarily as 7.5, the rms for SF 0.90 frequencies drops to 0.34 and the average becomes −0.27. For uncorrected rrho values, rms is 0.41 and

TABLE 23: Comparison of Calculated (a) C_p and (b) Entropy[a] Values: Values Obtained Using the Conformer Mixture Model vs Full Rotor Model

(a) Calculated C_p Values

	C_p V[b]	C_p D[c]	C_p(exptl)[c]	exp-V[e]	exp-D[e]	temp (K)
ethane	18.21	18.60	18.67[d]	0.46	−0.07	500.00
propane	17.45	17.71	17.56[d]	0.11	−0.15	298.15
butane	34.61	35.08	35.69[d]	1.08	0.45	500.00
pentane	29.39	28.25	28.70	−0.69	0.29	298.15
cyclobutane	16.33	16.92				298.15

(b) Calculated Entropy Values

	S V[b]	S D[c]	S(exptl)[c]	exp-V[e]	exp-D[e]
ethane	54.73	54.70	54.85	0.12	0.15
propane	64.77	64.70	64.70	−0.07	0.00
butane	74.35	74.49	74.00	−0.35	−0.49
pentane	83.85	84.19	83.13	−0.72	−1.06
cyclobutane	63.03	63.13	63.43[f]	0.40	0.30

[a] All data in (b) at 298.15 K. [b] Full rotor model Vansteenkiste et al.[20,23] [c] SF 0.91; Tables 3, 5, 8, 9, 11 [d] Interpolated from experimental set having values at bracketing temperatures. [e] V. Vansteenkiste, D. DeTar [f] Rathjens et al., calcd.[56]

the average is +0.28, with differences increasing with temperature, an indication that the rrho values need correction.

Beckett et al.[25] provide a detailed calculation of C_p for cyclohexane at 500 K in their Table 2. These values may be compared with results of a recalculation using the Beckett et al. frequencies, as shown in Table 14b. C(vib) is the same, as it must be if the input data are correct. The anharmonicity term is in part a disposable parameter to make calculated C_p agree with experiment. The C(taut) is another name for the dXE_g/dT term of Table 14a. The values shown are those obtained with E(tb) − E(chair) of 5.6. If the energy difference is taken as 6.38 instead, then the 2.31 becomes 1.43 and the C_p calculated becomes 45.63, close to the experimental C_p of 45.38 reported by Beckett et al.; a better experimental value obtained by interpolation is 45.47. The 0.68 value of Beckett et al. for C(taut) corresponds to the 0.69 value obtained by calculating conformer fractions from energies rather than from free energies.

Entropy calculations are shown in Table 14c. The estimated uncertainty of the calculated entropy is 0.30 and of the difference of experimental and calculated entropies is 0.36 (Table 2b). The calculated values all lie within the standard deviation range except for those using the Shimanouchi frequencies.

Supporting Information Available: Analysis of results obtained in this study and evaluation of results reported in the prior literature for most individual compounds as well as Tables 3, 4, 7, 8, 9b,d,e, 10−13, and 15−22 showing results of calculations. References from this article plus additional references cited only in the Supporting Information are also included. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Benson, S. W. *Thermochemical Kinetics*, 2d Ed.; John Wiley & Sons: New York, 1976.

(2) Benson, S. W. *J. Phys. Chem. A* **1999**, *103*, 11481.

(3) Benson, S. W.; Cohen, N. Current Status of Group Additivity. In *Computational Thermochemistry*; Irikura, K. K., Frurip, D. J., Eds.; American Chemical Society: Washington, DC, 1997, p 20.

(4) Sumathi, R.; Cartensen, H. H.; Green, W. H. *J. Phys. Chem. A* **2001**, *105*, 8969.

(5) Scott, D. W. *J. Chem. Phys.* **1974**, *60*.

(6) Lay, T. H.; Bozzelli, J. W.; Dean, A. M.; Ritter, E. P. *J. Phys. Chem.* **1995**, *99*, 14514.

(7) Lay, T. H.; Yamada, T.; Tsai, P.-L.; Bozzelli, J. W. *J. Phys. Chem.* **1997**, *101*, 2471.

(8) Domalski, E. S.; Hearing, E. D. *J. Phys. Chem. Ref. Data* **1993**, *22*, 805.

(9) Domalski, E. S.; Hearing, E. D. *J. Phys. Chem. Ref. Data* **1988**, *17*, 1637.

(10) Domalski, E. S.; Evans, W. H.; Hearing, E. D. *J. Phys. Chem. Ref. Data* **1984**, *13*.

(11) Cohen, N.; Benson, S. W. *Chem. Rev.* **1993**, *93*, 2419.

(12) Cohen, N. *J. Phys. Chem. Ref. Data* **1996**, *25*, 1411.

(13) Chao, J.; Hall, K. R.; Marsh, K. N.; Wilhoit, R. C. *J. Phys. Chem. Ref. Data* **1986**, *46*, 1369.

(14) Wilhoit, R. C.; Zwolinski, B. J. *J. Phys. Chem. Ref. Data* **1973**, *2*, (Suppl. 1).

(15) Hayes, M. Y.; Li, B.; Rabitz, H. *J. Chem. Phys. A* **2006**, *110*, 264.

(16) Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; John Wiley & Sons: New York, 1969.

(17) Lewis, G. N.; Randall, M.; Pitzer, K. S.; Brewer, L. *Thermodynamics*; McGraw-Hill: New York, 1961.

(18) Herzberg, G. *Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules*; Van Nostrand Company: Princeton, NJ, 1945.

(19) Frankiss, S. G.; Green, J. H. S. Statistical Methods for Calculating Thermodynamic Functions. In *Chemical Thermodynamics, A Specialist Periodical Report*; McGlashan, M. L., Ed.; The Chemical Society: London, 1973; Vol. 1, pp 268.

(20) Vansteenkiste, P.; Van Speybroeck, V.; Marin, G. B.; Waroquier, M. *J. Phys. Chem. A* **2003**, *107*, 3139.

(21) Vansteenkiste, P.; Van Speybroeck, V.; Pauwels, E.; Waroquier, M. *Chem. Phys.* **2005**, *314*, 109.

(22) Van Speybroeck, V.; Vansteenkiste, P.; Van Neck, D.; Waroquier, M. *Chem. Phys. Lett.* **2005**, *402*, 479.

(23) Vansteenkiste, P.; Van Speybroeck, V.; Verniest, G.; De Kimpe, N.; Waroquier, M. *J. Phys. Chem. A* **2006**, *110*, 3838.

(24) DeTar, D. F. *J. Phys.Chem A* **2001**, *105*, 2073.

(25) Beckett, C. W.; Pitzer, K. S.; Spitzer, R. *J. Am. Chem. Soc.* **1947**, *69*, 2488.

(26) Aston, J. G.; Szasz, G.; Woolley, H. W.; Brickwedde, F. G. *J. Chem. Phys.* **1946**, *14*, 67.

(27) Grunwald, E. *Thermodynamics of Molecular Species*; John Wiley & Sons; New York, 1997.

(28) DeTar, D. F. *J. Phys. Chem. A* **1999**, *103*, 7055.

(29) Pitzer, K. S. *J. Chem. Phys.* **1936**, *4*, 749.

(30) Pitzer, K. S. *J .Chem. Phys.* **1937**, *5*, 469.

(31) Pitzer, K. S.; Gwinn, W. D. *J. Chem. Phys.* **1942**, *10*, 428.

(32) East, A. L. L.; Radom, L. *J. Chem. Phys.* **1997**, *106*, 6655.

(33) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(34) Shimanouchi, T. *Tables of Molecular Vibrational Frequencies, Part 1*; National Bureau of Standards: Washington, DC, 1967.

(35) Shimanouchi, T. *Tables of Molecular Vibrational Frequencies, Part 2*; National Bureau of Standards: Washington, DC, 1967.

(36) Shimanouchi, T. *Tables of Molecular Vibrational Frequencies, Part 3*; National Bureau of Standards: Washington, DC, 1968.

(37) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.

(38) DeTar, D. F. *J. Phys. Chem. A* **1998**, *102*, 5128.

(39) Block, D. A.; Armstrong, D. A.; Rauk, A. *J. Phys. Chem. A* **1999**, *103*, 3562.

(40) Pitzer, K. S. *J. Chem. Phys.* **1937**, *5*, 473.

(41) Green, J. H. S.; Holden, D. J. *J. Chem. Soc.* **1962**, 1794.

(42) Guthrie, J. P. *J. Phys. Chem. A* **2001**, *105*, 8495.

(43) Chao, J.; Wilhout, R. C.; Zwolinski, B. J. *J. Phys. Chem. Ref. Data* **1973**, *2*, 427.

(44) Chen, S. S.; Wilhoit, R. C.; Zwolinski, B., J. *J. Phys. Chem. Ref. Data* **1975**, *4*, 859.

(45) Kilpatrick, J. E.; Pitzer, K. S. *J. Am. Chem. Soc.* **1946**, *68*, 1066.

(46) Pople, J. A.; Scott, A. P.; Wong, M. W.; Radom, L. *Isr. J. Chem.* **1993**, *33*, 345.

(47) Del Bene, J. E.; Aue, D. H.; Shavitt, I. *J. Am. Chem. Soc.* **1992**, *114*, 1631.

(48) Salam, A.; Deleuze, M. S. *J. Chem. Phys.* **2002**, *116*, 1299.

(49) Kistiakowsky, G. B.; Lacher, J. R.; Ransom, W. W. *J. Chem. Phys.* **1940**, *8*, 970.

(50) Kemp, J. D.; Egan, C. J. *J. Am. Chem. Soc.* **1938**, *60*, 1521.

(51) Bock, C. W.; George, P.; Trachtman, M.; Zanger, M. *J. Chem. Soc., Perkin Trans. 2* **1979**, 26.

(52) Compton, D. A. C.; George, W. O.; Maddams, W. F. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1666.

(53) Dorofeeva, O. V.; Gurvich, L. V.; Jorish, V. S. *J. Phys. Chem. Ref. Data* **1986**, *15*, 437.

(54) Rathjens, G. W., Jr.; Freeman, N. K.; Gwinn, W. D.; Pitzer, K. S. *J. Am. Chem. Soc.* **1953**, *75*, 5634.

(55) Rathjens, G. W., Jr.; Gwinn, W. D. *J. Am. Chem. Soc.* **1953**, *75*, 5629.

(56) Rathjens, G. W., Jr.; Freeman, N. K.; Gwinn, W. D.; Pitzer, K. S. *J. Am. Chem. Soc.* **1953**, *75*, 5634.

(57) Smith, G. D.; Jaffe, R. L. *J. Phys. Chem.* **1996**, *100*, 18718.

(58) Herrebout, W. A.; van der Veken, B. J.; Wang, A.; Durig, J. R. *J. Phys. Chem.* **1995**, *99*, 578.

(59) Aston, J. G.; Messerly, G. H. *J. Am. Chem. Soc.* **1940**, *62*, 1917.

(60) Huffman, H. M.; Parks, G. S.; Barmore, M. *J. Am. Chem. Soc.* **1931**, *53*, 3876.

(61) Eliel, E. L.; Wilen, S. H. *Stereochemistry of Organic Compounds*; John Wiley & Sons: New York, 1994.

(62) Spitzer, R.; Pitzer, K. S. *J. Am. Chem. Soc.* **1946**, *68*, 2537.

(63) Kistiakowsky, G. B.; Rice, W. W. *J. Chem. Phys.* **1940**, *8*, 610.

(64) Dailey, W. P.; Felsing, W. A. *J. Am. Chem. Soc.* **1943**, *65*, 42.

(65) Pitzer, K. S. *J. Chem. Phys.* **1944**, *12*, 310.

(66) Scott, R. B.; Meyers, C. H.; Rands, R. D., Jr.; Brickwedde, F. G.; Bekkedahl, N. *J. Res. Natl. Bur. Stand.* **1945**, *35*, 39.

(67) Dailey, B. P.; Felsing, W. A. *J. Am. Chem. Soc.* **1943**, *65*, 44.

(68) Parks, G. S.; Schomate, C. H.; Kennedy, W. D.; Crawford, B. L., Jr. *J. Chem. Phys.* **1937**, *5*.

(69) Montgomery, J. B.; DeVries, T. *J. Am. Chem. Soc.* **1942**, *64*, 2375.

(70) Aston, J. G.; Szasz, G. J.; Fink, H. L. *J. Am. Chem. Soc.* **1943**, *65*, 1135.