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Theoretical ab Initio Calculation of Entropy, Heat Capacity, and Heat Content

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This study describes the theoretical ab initio calculation of entropy, heat capacity, and heat content for a series of alkanes by procedures that make no use of adjustable parameters. Frequencies calculated with the basis sets, 3-21G, 6-31G*, and 6-31G** and scaled by factors of 0.89 and 0.90 were used to obtain theoretical entropy values that agree well with reported values. Over a temperature range from room temperature to at least 800 K the differences between $T\Delta S$ based on calculated and literature values of ΔS are generally less than 0.3 kcal/mol. Agreement between theoretical and experimental heat capacities and heat contents ($H_T^0 - H_0^0$) is also good. Results for compounds that exist as mixtures of conformers give as good results as do compounds that exist as a single conformer.

Calculations of equilibria require free energies. Theoretical estimates of free energies are derived from theoretical estimates of enthalpies and entropies. It is important, therefore, to determine how valid are the enthalpy data and the entropy data obtainable from ab initio theoretical calculations. The primary purpose of the present study has been to evaluate the reliability of entropy values calculated by statistical methods using vibrational frequencies obtained from ab initio calculations with basis sets of modest size. This study treats alkanes having up to eight carbon atoms. In addition to entropy I have also examined the calculation of heat capacity, C_p, and of heat content ($H_T^0 - H_0^0$). The accuracy to which these latter values can be calculated provides additional evidence about the validity of scaled ab initio frequencies and of the methodology used to obtain the thermochemical values.

Alkanes have been chosen for this study since it is important to compare theoretical calculations with good experimental values, and there are more data and more reliable data for alkanes than for any other class of compounds. Moreover, alkyl components commonly occur as the framework or as substituents of many types of compounds, and the capability of getting correct values for these structural elements is essential. Work is in progress on other types of compounds and will be reported elsewhere

Issues concerning calculation of enthalpies of formation and of zero-point energies have been treated elsewhere[1−5] and will not be considered here. Recently the calculation of entropies of small molecules by ab initio methods has been treated in detail in an important study by East and Radom.[6] These authors have examined the suitability of an extensive series of basis sets and have proposed three computational protocols of differing computational requirements and accuracy. The present study is complementary in that it focuses on larger molecules, with emphasis on those that exist as mixtures of conformers. The thermochemical values reported in this study all pertain to the ideal gaseous state at 1 atm.

The theoretical thermochemical values obtained in this study have been calculated without using adjustable parameters; they are entirely ab initio. The approximations of the methodology are those of the rigid-rotor/harmonic oscillator formalism. Many compounds of interest exist as mixtures of conformers. For these compounds the thermochemical properties calculated for the reference conformer, usually the conformer of lowest energy, the global minimum, must be corrected for the contributions of the other conformers present. The necessary procedures for doing so have been developed in this study.

In the 1930s several workers pioneered the use of statistical mechanics for the theoretical estimation of entropy, heat capacity, and heat content of organic compounds.[7−12] Vibrational energy levels were estimated from Raman and infrared spectra, a remarkable achievement considering the relatively primitive state of these spectra at the time. Simultaneously great improvements were being made in the measurement of heat capacity and in the third law determination of gaseous entropies. Data were therefore at hand for evaluating the successes of the theoretical calculations.

A particular focus of theoretical treatments in the 1930s was to derive appropriate methods for calculating the contributions to the partition function due to internal rotations. Pitzer[10] pointed out that the calculated entropy of ethane based on assumed free rotation of the methyl groups was much too high in consideration of probable errors of the experimental value. In a series of papers he developed an expression for the energy component of the partition function due to internal rotation about a single bond that modeled it as a hindered rotor, that is, as a libration confined to rotational minima separated by energy barriers.[11−21] Assumption of a rotational barrier of about 3 kcal/mol gave an energy for the internal rotation term of the partition function of ethane that resulted in a value of the entropy that agreed with experiment.[10] Recently McClurg, Flagan, and Goddard[22] have described more general procedures for evaluating the contributions of hindered rotors to the partition function.

In this early work the validity of the statistical thermodynamic treatment was examined carefully for several compounds; examples are the extensive studies of ethane and of propane.[23]

Compounds having methyl free rotors are known. Examples are toluene, *m*-xylene, and *p*-xylene. For these compounds the entropy is calculated correctly using the free rotor model.[24] For toluene see ref 25, p 283.

Two parameters enter into the estimate of the energy component of the partition function for a hindered rotor, the reduced moment of inertia of the rotor and the barrier height. In turn the moment of inertia depends on the reduced masses of the rotors and on their geometries, both of which are different

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for rotation of methyl groups and for rotation about internal bonds of carbon chains. The hindered rotor model has been applied to many compounds. In the model the energies of frequencies attributable to internal rotation are replaced by energies derived from the Pitzer tables of hindered rotors,[21] making use of appropriate estimates of moments of inertia. The success of these statistical calculations depends on choosing appropriate rotational barriers. In the early work the barriers were often used as adjustable parameters chosen so as to make calculation agree with experiment.

Components of the Partition Function. Derivation of thermochemical quantities from the partition function are described in many references.[21,25−27] For the present compounds the partition function may to good approximation be separated into four components, translation, rigid-body rotation, vibration, including libration, and terms correcting for mixtures of conformers. Representations of the partition functions are approximations, though the results obtained with the approximations are often quite good.

Rotation and Translation. At room temperature and higher translation contributes $(3/2)R$ to the heat capacity, and a further $1R$ converts C_v to C_p. Overall rotation contributes an additional $(3/2)R$. For entropy the translation and rigid-body rotation contributions must be calculated individually at each temperature of interest. The translational part of the partition function depends on the mass of the molecule, and calculation of its contribution to entropy may be considered to be free of error. The rigid-body rotational component depends on the product of the principal moments of inertia and on the rotational symmetry number. Differences in calculated entropy due to differences of the assumed geometry are not likely to exceed about 0.2 cal/(K mol). For C_{2h} butane and C_{2h} octane the differences in calculated entropies of rotation are less than 0.04 cal/(K mol) for geometries optimized with 3-21G, 6-31G** and MP2/6-31G** basis sets.[28−32]

Vibrational Frequencies and Entropy, Heat Capacity, and Heat Content. Theoretically calculated entropy, heat capacity, and heat content have different sensitivities to vibrational energies. Entropy is most sensitive to low energies (low frequencies), and low-energy contributions to entropy can become very large. Heat capacity above about 250 K is most sensitive to intermediate frequencies. The limiting contribution of any one energy (frequency) to the heat capacity is 1 R, and one or more of the low frequencies may be almost at the limit. The consequence is that the calculated value of the entropy is much more sensitive to the values of the low frequencies than is heat capacity. As an example, at 298 K the two frequencies 100 and 200 cm^{-1} contribute the differing amounts of 3.45 and 2.13 cal/(K mol) to the entropy and the nearly equal amounts 1.95 and 1.84 cal/(K mol) to C_p; the C_p value is almost at the limit of 1 R.

Heat content is somewhat more sensitive to higher intermediate frequencies than is C_p. Parenthetically, the zero-point energy depends entirely on the high frequencies, being almost unaffected by frequencies below 1000 cm^{-1}; a scaling factor of 0.905 with frequencies calculated with the 6-31G* and 6-31G** basis sets gives better estimates of zero-point energies than does a scaling factor of 0.90.[3]

Vibrational frequencies obtained by HF calculations with the basis sets 3-21G, 6-31G*, and 6-31G** are on average about 10% too high.[28] Comparison of scaled frequencies with experimental frequencies as in the Shimanouchi[33,34] compilations shows that deviations occur in both directions with all choices of scaling. Results of this study support the current recommendation to use a scaling factor of 0.90 as a useful compromise, but 0.89 is about as good for heat capacity calculations.

In contrast to the limiting value of $1R$ for the vibrational contribution to C_p, a free rotor such as the methyl group of toluene makes a contribution of $(1/2)R$ to the heat capacity. A methyl free rotor makes a contribution of 2.95 cal/(K mol) at 298 K to the entropy ($\sigma = 3$) (ref 27, p 524). The contribution of a free rotor to entropy depends on moments of inertia, symmetry number, geometry, and temperature. If the energy due to the lowest frequency vibration of ethane is replaced by the energy estimated for a free rotor, the calculated entropy is too high and the calculated C_p is too low. Treatment as a hindered rotor corrects both the entropy and the heat capacity.

For ethane and propane the vibrations associated with the lowest frequencies do indeed correspond to libration of the methyl groups. However, for butane and higher alkanes the lowest frequency corresponds to a more complex vibration including libration about interior carbon−carbon bonds which accompanies libration of methyl groups. The two AU vibrations of butane at 116 and 214 cm^{-1} (6-31G** frequencies scaled by 0.90) do not involve methyl librations, while the BG vibration at 246 cm^{-1} does involve methyl group librations.

For isobutane the lowest frequency involves libration of all three methyl groups, and the next lowest involves only two. The third lowest does not involve any methyl librations. For neopentane the lowest frequency involves libration of all four methyl groups, the next lowest involves just three methyl groups, and the third lowest involves none.

For most alkanes the actual vibrational patterns of the low frequencies do not map well to the simplified hindered rotation models; the hindered rotor model has little relationship to actual vibrational modes of most alkanes.

Comparisons of Entropy Calculated by the Hindered Rotor Model with Entropy Calculated Using the Harmonic Oscillator Model. It is of interest to compare values reported for the component of the entropy ascribed to hindered rotors with the corresponding values derived from the harmonic oscillator model. Such comparisons are limited to a very few examples since references do not usually provide the individual values attributed to hindered rotors.

Pitzer[20] reported that the contribution to the entropy of ethane by a rotor with a barrier of 3050 cal/mol is within 0.04 of the value calculated for a harmonic oscillator of 290 or 270 cm.^{-1}

Pitzer[17] reports 0.40 cal/(K mol) for the vibrational contribution to the entropy of propane at 180 K and 1.98 for the hindered rotor contribution. The two lowest frequencies of propane calculated using the 6-31G* basis set and scaled by 0.90 are 211 and 264 cm^{-1}; these correspond to harmonic oscillator entropy contributions of 1.87 and 0.84 for a total of 2.01; the other remaining vibrations contribute 0.32. At 231.1 K the hindered rotor value is 2.88 and the 6-31G* frequency value is 2.79. At 231.1 K the other vibrational contribution reported by Pitzer is 1.02 and the 6-31G* frequencies give 1.14. Experimental low frequencies of propane are not useful because they are uncertain.[33,35] At both temperatures the estimated entropy component is the same whether based on frequencies or on the hindered rotor model.

In the present study some compounds have low-frequency contributions to the entropy that are well outside the entropy values in the hindered rotor tables. Yet for such examples the calculated entropies of the compounds based on the harmonic oscillator model correspond closely to experimental entropies.

Suggested Treatment for Compounds Having Unusually Low Frequencies. For all but one of the alkanes listed in the

TABLE 1: Theoretical Entropy of Alkanes That Exist as a Single Conformer

compound	temp (K)	basis[a] set	scale factor	σ	entropy trans + rotation	entropy vibration	entropy total	entropy lit.[b]	diff of entropy	scalar[c] std dev entropy	diff of $T\Delta S$	scalar[c] std dev $T\Delta S$	number
ethane	298.15	3-21G	0.90	6	52.41	2.19	54.60	54.85	0.25	0.39	0.07	0.21	7
ethane	298.15	6-31G*	0.90	6	52.39	2.15	54.54	54.85	0.31	0.41	0.09	0.21	7
ethane	298.15	6-31G**	0.90	6	52.39	2.16	54.55	54.85	0.30	0.36	0.09	0.17	7
ethane	298.15	shimano	1.00	6	52.48	2.22	54.70	54.85	0.15	0.24	0.04	0.13	7
ethane	1000.00	3-21G	0.90	6	62.03	17.01	79.04	79.39	0.35		0.35		
ethane	1000.00	6-31G*	0.90	6	62.01	17.11	79.12	79.39	0.27		0.27		
ethane	1000.00	6-31G**	0.90	6	62.00	17.25	79.25	79.39	0.14		0.14		
ethane	1000.00	shimano	1.00	6	62.10	17.17	79.27	79.39	0.12		0.12		
propane	298.15	3-21G	0.90	2	58.58	5.87	64.45	64.51	0.06	0.30	0.02	0.18	8
propane	298.15	6-31G*	0.90	2	58.56	5.89	64.45	64.51	0.06	0.26	0.02	0.15	8
propane	298.15	6-31G**	0.90	2	58.56	5.95	64.51	64.51	0.00	0.14	0.00	0.08	8
propane	298.15	shimano	1.00	2	58.58	6.17	64.75	64.51	−0.24	0.24	−0.07	0.06	8
propane	1000.00	3-21G	0.90	2	68.20	31.28	99.48	99.76	0.28		0.28		
propane	1000.00	6-31G*	0.90	2	68.17	31.44	99.61	99.76	0.15		0.15		
propane	1000.00	6-31G**	0.90	2	68.17	31.70	99.87	99.76	−0.11		−0.11		
propane	1000.00	shimano	1.00	2	68.20	31.71	99.91	99.76	−0.15		−0.15		
2-methylpropane	298.15	3-21G	0.90	3	60.50	9.71	70.21	70.42	0.21	0.60	0.06	0.35	6
2-methylpropane	298.15	6-31G*	0.90	3	60.49	9.93	70.42	70.42	0.00	0.31	0.00	0.19	6
2-methylpropane	298.15	6-31G**	0.90	3	60.49	10.03	70.52	70.42	−0.10	0.13	−0.03	0.07	6
2-methylpropane	1000.00	3-21G	0.90	3	70.11	46.09	116.20	116.71	0.51		0.51		
2-methylpropane	1000.00	6-31G*	0.90	3	70.10	46.50	116.60	116.71	0.11		0.11		
2-methylpropane	1000.00	6-31G**	0.90	3	70.10	46.86	116.96	116.71	−0.25		−0.25		
2,2-dimethylpropane	298.15	3-21G	0.90	12	59.52	13.46	72.98	73.23	0.25	0.89	0.07	0.54	6
2,2-dimethylpropane	298.15	6-31G*	0.90	12	59.51	13.86	73.37	73.23	−0.14	0.43	−0.04	0.27	6
2,2-dimethylpropane	298.15	6-31G**	0.90	12	59.51	14.01	73.52	73.23	−0.29	0.25	−0.09	0.13	6
2,2-dimethylpropane	1000.00	3-21G	0.90	12	69.13	61.09	130.22	131.43	1.21		1.21		
2,2-dimethylpropane	1000.00	6-31G*	0.90	12	69.12	61.75	130.87	131.43	0.56		0.56		
2,2-dimethylpropane	1000.00	6-31G**	0.90	12	69.12	62.20	131.32	131.43	0.11		0.11		
2,2-dimethylbutane	298.15	3-21G	0.90	1	66.17	19.46	85.63	85.62	−0.01	0.38	0.00	0.23	6
2,2-dimethylbutane	298.15	6-31G*	0.90	1	66.17	19.81	85.98	85.62	−0.36	0.24	−0.11	0.08	6
2,2-dimethylbutane	298.15	6-31G**	0.90	1	66.17	19.87	86.04	85.62	−0.42	0.36	−0.13	0.16	6
2,2-dimethylbutane	298.15	pitzer	1.00	1	66.07	20.35	86.42	85.62	−0.80	0.56	−0.24	0.18	6
2,2-dimethylbutane	1000.00	3-21G	0.90	1	75.79	77.73	153.52	153.69	0.17		0.17		
2,2-dimethylbutane	1000.00	6-31G*	0.90	1	75.79	78.32	154.11	153.69	−0.42		−0.42		
2,2-dimethylbutane	1000.00	6-31G**	0.90	1	75.79	78.72	154.51	153.69	−0.82		−0.82		
2,2-dimethylbutane	1000.00	pitzer	1.00	1	75.69	78.25	153.94	153.69	−0.25		−0.25		
2,2,3-trimethylbutane	298.15	3-21G	0.90	2	67.44	24.31	91.75	91.61	−0.14	0.30	−0.04	0.18	6
2,2,3-trimethylbutane	298.15	6-31G*	0.90	2	67.44	24.61	92.05	91.61	−0.44	0.31	−0.13	0.10	6
2,2,3-trimethylbutane	298.15	6-31G**	0.90	2	67.44	24.72	92.16	91.61	−0.55	0.51	−0.16	0.24	6
2,2,3-trimethylbutane	1000.00	3-21G	0.90	2	77.05	93.57	170.62	170.66	0.04		0.04		
2,2,3-trimethylbutane	1000.00	6-31G*	0.90	2	77.05	94.12	171.17	170.66	−0.51		−0.51		
2,2,3-trimethylbutane	1000.00	6-31G**	0.90	2	77.05	94.63	171.68	170.66	−1.02		−1.02		

[a] Shiminouchi,[33,34] Pitzer.[19] [b] All values in the table are from Stull, Westrum, Sinke.[36] The standard deviations include comparisons between additional calculated values and experimental values from other sources: ethane,[51,59] propane,[17] 2,2-dimethylbutane.[60] [c] Standard deviations are for temperatures ≤700 K.

tables the lowest frequency after scaling was 46 cm^{-1} or greater and the calculated entropies agree well with the reported values. The exception is 2,2,3-trimethylbutane. For this compound the lowest ab initio frequencies were 25 cm^{-1} (3-21G, default optimization limits), 4 cm^{-1} (3-21G with "tight" optimization limits), −11 cm^{-1} (6-31G* default, imaginary), 16 cm^{-1} (6-31G*, "tight"), and 1 cm^{-1} (6-31G** default). Application of the harmonic oscillator model to these low frequencies cannot be expected to provide a meaningful estimate of entropy.

A further examination with the 3-21G basis set showed that the eclipsed conformer is a transition state with an energy 7.0 kcal higher than that of the global minimum staggered conformer. As expected on qualitative grounds, steric hindrance precludes free rotation about the central carbon−carbon bond. However, the torsional energy well for libration about the central carbon−carbon bond is very shallow: the energy of a conformer having the central torsion "frozen" 10° from that of the minimum geometry is only 0.14 kcal/mol higher than the minimum energy.

A reasonable work-around is to replace the very low frequency with a value comparable to the lowest frequencies calculated for other alkanes. I selected an unscaled value of 67 cm,$^{-1}$ which scaled to 60 cm.$^{-1}$ For comparison the respective unscaled lowest frequencies obtained with the 6-31G** basis set for butane, 2-methylbutane, 2,2-dimethylbutane, 2,3-dimethylbutane, and 2,2,3,3-tetramethylbutane are 127, 96, 75, 63, and 107 cm^{-1}. The entropy contribution of a frequency of 60 cm^{-1} is 4.44 cal/(K mol); of 75 cm^{-1} 4.1; and of 50 cm^{-1} 4.8. Within the error limits of the present methodology, use of any of these frequency values would give a reasonable total entropy for 2,2,3-trimethylbutane.

For the compounds I have examined to date (including also those having functional groups), it is alkanes such as octanes and larger that tend to have low vibrational frequencies. The octane entropy values in Table 2 are correct; these are based on use of the lowest scaled 3-21G (and also 6-31G**) frequency of 46 cm.$^{-1}$ The best general way to calculate entropies for compounds that have very low frequencies (less than 50 cm^{-1}) has yet to be determined.

Results: Theoretically Derived Entropies of Compounds That Exist as a Single Conformer. Table 1 shows theoretically

TABLE 2: Theoretical Entropy for Alkanes That Exist as a Mixture of Conformers

compound	temp (K)	basis[a] set	scale factor	σ	entropy trans + rotation	entropy vibration	entropy mixing + S_{avg}	entropy total	entropy lit.[b]	diff of entropy	scalar[c] std dev entropy	diff of $T\Delta S$	scalar[c] std dev $T\Delta S$	number
butane	298.15	3-21G	0.90	2	61.25	10.97	1.84	74.06	74.12	0.06	0.33	0.02	0.19	7
butane	298.15	6-31G*	0.90	2	61.23	11.01	1.84	74.08	74.12	0.04	0.27	0.01	0.16	7
butane	298.15	6-31G**	0.90	2	61.23	11.03	1.84	74.10	74.12	0.02	0.17	0.01	0.09	7
butane	298.15	shimano	1.00	2	61.23	11.36	1.84	74.43	74.12	−0.31	0.25	−0.09	0.08	7
butane	1000.00	3-21G	0.90	2	70.87	47.00	2.15	120.02	120.16	0.14		0.14		
butane	1000.00	6-31G*	0.90	2	70.85	47.18	2.15	120.18	120.16	−0.02		−0.02		
butane	1000.00	6-31G**	0.90	2	70.85	47.44	2.15	120.44	120.16	−0.28		−0.28		
butane	1000.00	shimano	1.00	2	70.85	47.57	2.15	120.57	120.16	−0.41		−0.41		
pentane	298.15	3-21G	0.90	2	63.45	16.57	3.51	83.53	83.40	−0.13	0.21	−0.04	0.12	6
pentane	298.15	6-31G*	0.90	2	63.42	16.60	3.51	83.53	83.40	−0.13	0.16	−0.04	0.08	6
pentane	298.15	6-31G**	0.90	2	63.42	16.78	3.51	83.71	83.40	−0.31	0.28	−0.09	0.13	6
pentane	1000.00	3-21G	0.90	2	73.07	63.22	4.11	140.40	140.09	−0.31		−0.31		
pentane	1000.00	6-31G*	0.90	2	73.04	63.40	4.11	140.55	140.09	−0.46		−0.46		
pentane	1000.00	6-31G**	0.90	2	73.04	63.88	4.11	141.03	140.09	−0.94		−0.94		
2-methylbutane	298.15	3-21G	0.90	1	64.79	15.43	1.97	82.19	82.12	−0.07	0.21	−0.02	0.12	9
2-methylbutane	298.15	6-31G*	0.90	1	64.78	15.59	1.97	82.34	82.12	−0.22	0.18	−0.07	0.06	9
2-methylbutane	298.15	6-31G**	0.90	1	64.78	15.63	2.18	82.59	82.12	−0.47	0.39	−0.14	0.14	8
2-methylbutane	298.15	wadding	1.00	1	64.78	16.06	1.97	82.81	82.12	−0.69	0.81	−0.21	0.39	9
2-methylbutane	1000.00	3-21G	0.90	1	74.41	62.44	2.15	139.00	139.01	0.01		0.01		
2-methylbutane	1000.00	6-31G*	0.90	1	74.40	62.79	2.15	139.34	139.01	−0.33		−0.33		
2-methylbutane	1000.00	6-31G**	0.90	1	74.40	63.11	2.18	139.69	139.01	−0.68		−0.68		
2-methylbutane	1000.00	wadding	1.00	1	74.40	63.98	2.16	140.54	139.01	−1.53		−1.53		
hexane	298.15	3-21G	0.90	2	65.18	22.65	5.07	92.90	92.83	−0.07	0.21	−0.02	0.11	6
hexane	298.15	6-31G*	0.90	2	65.15	22.67	5.07	92.89	92.83	−0.06	0.17	−0.02	0.08	6
hexane	298.15	6-31G**	0.90	2	65.15	22.92	5.07	93.14	92.83	−0.31	0.33	−0.09	0.19	6
hexane	1000.00	3-21G	0.90	2	74.80	79.91	6.13	160.84	160.19	−0.65		−0.65		
hexane	1000.00	6-31G*	0.90	2	74.77	80.08	6.13	160.98	160.19	−0.79		−0.79		
hexane	1000.00	6-31G**	0.90	2	74.77	80.69	6.13	161.59	160.19	−1.40		−1.40		
2,3-dimethylbutane	298.15	3-21G	0.90	2	64.94	20.66	2.16	87.76	87.42	−0.34	0.26	−0.10	0.08	9
2,3-dimethylbutane	298.15	6-31G*	0.90	2	64.94	20.83	2.18	87.95	87.42	−0.53	0.47	−0.16	0.18	9
2,3-dimethylbutane	298.15	6-31G**	0.90	2	64.94	20.83	2.18	87.95	87.42	−0.53	0.53	−0.16	0.23	9
2,3-dimethylbutane	1000.00	3-21G	0.90	2	74.56	78.67	2.18	155.41	154.82	−0.59		−0.59		
2,3-dimethylbutane	1000.00	6-31G*	0.90	2	74.56	79.04	2.18	155.78	154.82	−0.96		−0.96		
2,3-dimethylbutane	1000.00	6-31G**	0.90	2	74.56	79.37	2.18	156.11	154.82	−1.29		−1.29		
heptane	298.15	3-21G	0.90	2	66.70	28.91	6.61	102.22	102.27	0.05	0.22	0.01	0.11	7
heptane	298.15	6-31G*	0.90	2	66.68	28.94	6.61	102.23	102.27	0.04	0.20	0.01	0.09	7
heptane	298.15	6-31G**	0.90	2	66.68	28.98	6.61	102.27	102.27	0.00	0.18	0.00	0.12	7
heptane	1000.00	3-21G	0.90	2	76.32	96.80	8.16	181.28	180.29	−0.99		−0.99		
heptane	1000.00	6-31G*	0.90	2	76.30	96.97	8.16	181.43	180.29	−1.14		−1.14		
heptane	1000.00	6-31G**	0.90	2	76.29	97.39	8.16	181.84	180.29	−1.55		−1.55		
octane	298.15	3-21G	0.90	2	67.96	35.39	8.16	111.51	111.55	0.04	0.20	0.01	0.10	6
octane	298.15	6-31G*	0.90	2	67.96	35.41	8.16	111.53	111.55	0.02	0.20	0.01	0.12	6
octane	298.15	6-31G**	0.90	2	67.96	35.49	8.16	111.61	111.55	−0.06	0.33	−0.02	0.22	6
octane	1000.00	3-21G	0.90	2	77.58	113.89	10.17	201.64	200.23	−1.41		−1.41		
octane	1000.00	6-31G*	0.90	2	77.58	114.06	10.17	201.81	200.23	−1.58		−1.58		
octane	1000.00	6-31G**	0.90	2	77.58	114.56	10.17	202.31	200.23	−2.08		−2.08		
2,2,3,3-tetramethylbutane	298.15	3-21G	0.90	6	64.87	26.88	1.38	93.13	93.06	−0.07	1.31	−0.02	0.82	6
2,2,3,3-tetramethylbutane	298.15	6-31G*	0.90	6	64.86	26.76	1.38	93.00	93.06	0.06	1.28	0.02	0.80	6
2,2,3,3-tetramethylbutane	298.15	6-31G**	0.90	6	64.87	26.91	1.38	93.16	93.06	−0.10	0.96	−0.03	0.61	6
2,2,3,3-tetramethylbutane	1000.00	3-21G	0.90	6	74.48	107.34	1.38	183.20	185.45	2.25		2.25		
2,2,3,3-tetramethylbutane	1000.00	6-31G*	0.90	6	74.48	107.49	1.38	183.35	185.45	2.10		2.10		

[a] Shiminouchi,[33,34] Waddington.[38] [b] All literature values in the table are from Stull, Westrum, Sinke.[36] The standard deviations include comparisons between additional calculated values and experimental values from other sources: butane,[18] 2-methylbutane,[38] 2,3-dimethylbutane,[61] heptane.[16] [c] Standard deviations are for temperatures ≤800 K.

derived entropies for several alkanes that exist as a single conformer. The table includes calculations based on sets of experimental frequencies derived from infrared and Raman spectra as well as calculations based on scaled frequencies obtained theoretically with the basis sets 3-21G, 6-31G*, and 6-31G**. Entropies were calculated for several temperatures: 298.15 K and from 300 to 1000 K at 100 K intervals, and in some cases they have been calculated at other temperatures for which experimental entropies have been reported. Calculations of vibrational entropy in this study are based on the harmonic oscillator approximation using all frequencies; the hindered rotor formalism was not used.

For alkanes the vibrational component of entropy constitutes from about 4% of the total with small molecules at moderate temperatures to somewhat more than 50% of the total for larger molecules and higher temperatures. In the tables differences between calculated and experimental entropies are reported in four ways: as the scalar difference between the theoretical and experimental value for a single temperature, basis set, and scale factor; as the standard deviation of the scalar differences for a set of values for temperatures up to 800 K for a given compound, basis set, and scaling factor; as the resultant scalar difference in $T\Delta S$; and as the standard deviation of all $T\Delta S$ values in the set from the literature values. In Table 7S are reported relative standard deviations of the vibrational component of the entropy, assigning all differences between calculated and reported ΔS values to the vibrational term. It is the $T\Delta S$ quantity that is the most direct measure of the usefulness of the theoretical entropies. The number of entries in the sets is also shown.

Experimental entropies in Table 1 come from the compilation of Stull, Westrum, and Sinke[36] and go back to the compilations of Rossini et al.[37] The averages shown for the sets in Table 1 include in addition the few individually reported entropy values at various temperatures; references are listed in the footnotes. Agreement between theoretical entropies and experimental values of entropies is comparable for all of the experimental data.

No one basis set or scaling factor consistently gives the smallest differences between the calculated and the observed entropies. Moreover, entropies based on experimental frequencies do not uniformly show smaller differences from reported entropies than do those based on ab initio frequencies. For frequencies obtained with either the 6-31G* or the 6-31G** basis sets and scaled by a factor of 0.90 the absolute values of the scalar differences between calculated and experimental entropies at 298.15 K are mostly smaller than 0.3 cal/(K mol). Standard deviations of scalar differences at all temperatures from 298 to 800 K are from 0.25 to 0.6, while the percent differences for just the vibrational component alone for all temperatures are less than 2%. With few exceptions the differences in $T\Delta S$ are considerably less than 0.3 kcal/mol, and most of the values at moderate temperatures have differences well below 0.3 kcal/mol. An exception is 2,2,3,3-tetramethylbutane, which has larger divergences above 500 K, although theoretical values of the entropy at lower temperatures agree well with the reported values. A difference of 0.25 kcal/mol in $T\Delta S$ corresponds to a difference in $\log(K_{\mathrm{eq}})$ of 0.18, or a 50% difference in K_{eq}, that is, lower than a factor of 2 difference. This is smaller than the usual differences between experimental $\Delta H_{\mathrm{f}}°$ and theoretical estimates of $\Delta H_{\mathrm{f}}°$.

Results: Theoretically Derived Entropies of Compounds That Exist as Mixtures of Conformers. For compounds that consist of mixtures of conformers the calculation of thermochemical properties is done in two stages. The first is to estimate the properties of the reference conformer, usually the conformer of lowest energy, although any conformer may be selected as the reference conformer.

The second stage is to calculate correction terms which allow for the contributions of the other conformers present at a given temperature. Two procedures were used to make corrections. The first procedure is based on the *mixture of components model*; corrections to the entropy consist of two parts, the average difference between the entropies of the other conformers and the entropy of the reference conformer and the entropy of mixing term. Alternatively the correction may be based on the *partition function model*. In this model the partition function of the reference conformer is augmented by adding terms for the energies of the ot her conformers. Details of both procedures are presented below.

Theoretically derived entropy values for alkanes that exist as mixtures of conformers are given in Table 2. These calculated entropies show the same excellent agreement with reported values as was found for the five alkanes in Table 1. All corrections for conformer mixtures are derived using free energies of conformers to calculate mole fractions.

Tables 1S and 2S in the Supporting Information provide additional examples. We may conclude that entropy contributions to free energy may be estimated very well by the procedures described.

Results: Theoretically Derived Heat Capacities. Heat capacity calculations use the same protocol: calculation of the heat capacity of the reference conformer and calculation of a correction for the contributions of the other conformers.

Table 3 shows heat capacities of alkanes that exist as single conformers; these are derived from the same frequency data as used for calculating the entropies. Differences between calculated and observed C_p values at 298.15 K are mostly less than 0.5 cal/(K mol). For calculation of standard deviations the data were divided into two sets, one set containing data up to and including 500 K, the other including data from 500 to 1000 K. The scalar standard deviations of calculated values for temperatures up to 500 K are mostly less than 0.5 cal/(K mol). Relative standard deviations based on the vibrational component alone are 2−3%. These values are listed on the 298.15 K lines. The deviations at higher temperatures are somewhat larger and are illustrated by selected values for 1000 K. The standard deviations for the high-temperature sets are listed on the 1000 K lines.

Table 4 shows heat capacities calculated for compounds existing as mixtures of conformers. Details of the calculation of the corrections for the contributions of the rest of the conformers in the mixture are described later. Agreement between theoretical and experimental data is comparable to those of the Table 3 sets.

Theoretical heat capacities based on the harmonic oscillator treatment of the vibrational component tend to be smaller than the experimental values at temperatures below 400 K and larger at higher temperatures. At 1000 K the five lowest frequencies of butane contribute more than 1.9 cal/(K mol) each to the heat capacity, with 1.987 being the saturation maximum. In fact there is only a gradual falloff in contribution on proceeding to the higher frequencies. With octane at 1000 K some 13 frequencies contribute more than 1.9 cal/(K mol) each. At temperatures above 500 K experimental frequencies for butane by Shimanouchi,[33,34] for 2-methylbutane by Waddington,[38] and for 2,2-dimethylbutane by Pitzer[19] give no better agreement than do the theoretical frequencies.

Supplementary Tables 3S and 4S provide additional examples.

Results. Theoretically Derived Heat Content. Heat content is a fundamental thermochemical value; it is the difference between the value of the enthalpy at 0 K and at T K, ($H_T^0 - H_0^0$). Data are presented in Table 5 for alkanes that exist as single conformers and in Table 6 for those that exist as mixtures of conformers. The correction for the mixture of conformers is labeled SMG in the tables. SM and SMG are explained below (eqs 2−7). For butane they are equal.

Inspection of the tables shows that the agreement is about the same as for entropy and for heat capacity. Supplementary Tables 5S and 6S provide additional data.

Supplementary Table 7S summarizes standard deviations of entropy, heat capacity, and heat content and includes values for additional scale factors.

Illustration of Method of Calculation of Corrections for the Presence of Multiple Conformers. The general treatment may be illustrated by the example of butane, which consists of a mixture of three conformers, anti, gauche+, and gauche−. The enthalpy, entropy, and heat capacity are calculated for the conformer of lowest energy, the anti conformer. At 298 K the gauche conformers contribute about 0.27 kcal/mol to the enthalpy of the actual mixture of conformers; that is, the enthalpy of the mixture is about 0.3 kcal/mol more positive than the value calculated for a hypothetical substance consisting entirely of the anti conformer. This correction has been called SM (statistical mechanical correction) in other papers.[3,39−42] It is defined in eqs 2−4 below.

TABLE 3: Theoretical Heat Capacity (C_p) for Alkanes That Exist as One Conformer

compound	temp (K)	basis[a] set	scale actor	heat capacity total	heat capacity lit.[b]	difference	scalar std dev[c]	relative std dev[c]	number
ethane	298.15	3-21G	0.90	12.24	12.58	0.34	0.36	0.033	12
ethane	298.15	6-31G*	0.90	12.29	12.58	0.29	0.27	0.025	12
ethane	298.15	6-31G**	0.90	12.35	12.58	0.23	0.20	0.019	12
ethane	298.15	shimano	1.00	12.26	12.58	0.32	0.29	0.027	12
ethane	1000.00	3-21G	0.90	29.82	29.33	−0.49	0.32	0.017	8
ethane	1000.00	6-31G*	0.90	29.91	29.33	−0.58	0.35	0.017	8
ethane	1000.00	6-31G**	0.90	30.02	29.33	−0.69	0.44	0.021	8
ethane	1000.00	shimano	1.00	29.86	29.33	−0.53	0.33	0.016	8
propane	298.15	3-21G	0.90	17.07	17.57	0.50	0.46	0.029	17
propane	298.15	6-31G*	0.90	17.14	17.57	0.43	0.38	0.024	17
propane	298.15	6-31G**	0.90	17.23	17.57	0.34	0.28	0.018	17
propane	298.15	shimano	1.00	17.07	17.57	0.50	0.42	0.026	17
propane	1000.00	3-21G	0.90	42.68	41.83	−0.85	0.48	0.015	9
propane	1000.00	6-31G*	0.90	42.78	41.83	−0.95	0.54	0.017	9
propane	1000.00	6-31G**	0.90	42.93	41.83	−1.10	0.68	0.021	9
propane	1000.00	shimano	1.00	42.77	41.83	−0.94	0.55	0.017	9
2-methylpropane	298.15	3-21G	0.90	22.50	23.14	0.64	0.82	0.035	4
2-methylpropane	298.15	6-31G*	0.90	22.62	23.14	0.52	0.65	0.027	4
2-methylpropane	298.15	6-31G**	0.90	22.75	23.14	0.39	0.46	0.020	4
2-methylpropane	1000.00	3-21G	0.90	55.63	54.40	−1.23	0.83	0.018	5
2-methylpropane	1000.00	6-31G*	0.90	55.75	54.40	−1.35	0.94	0.020	5
2-methylpropane	1000.00	6-31G**	0.90	55.94	54.40	−1.54	1.13	0.025	5
2,2-dimethylpropane	298.15	3-21G	0.90	28.27	29.07	0.80	1.27	0.039	4
2,2-dimethylpropane	298.15	6-31G*	0.90	28.45	29.07	0.62	1.01	0.031	4
2,2-dimethylpropane	298.15	6-31G**	0.90	28.61	29.07	0.46	0.61	0.020	4
2,2-dimethylpropane	1000.00	3-21G	0.90	68.65	67.80	−0.85	0.79	0.016	5
2,2-dimethylpropane	1000.00	6-31G*	0.90	68.78	67.80	−0.98	0.73	0.014	5
2,2-dimethylpropane	1000.00	6-31G**	0.90	69.02	67.80	−1.22	0.81	0.014	5
2,2-dimethylbutane	298.15	3-21G	0.90	33.37	33.91	0.54	0.74	0.019	9
2,2-dimethylbutane	298.15	6-31G*	0.90	33.51	33.91	0.40	0.54	0.014	9
2,2-dimethylbutane	298.15	6-31G**	0.90	33.66	33.91	0.25	0.73	0.019	9
2,2-dimethylbutane	298.15	pitzer	1.00	33.05	33.91	0.86	1.44	0.039	9
2,2-dimethylbutane	1000.00	3-21G	0.90	81.46	79.70	−1.76	1.23	0.017	5
2,2-dimethylbutane	1000.00	6-31G*	0.90	81.60	79.70	−1.90	1.35	0.019	5
2,2-dimethylbutane	1000.00	6-31G**	0.90	81.46	79.70	−1.76	1.23	0.017	5
2,2-dimethylbutane	1000.00	pitzer	1.00	81.17	79.70	−1.47	1.05	0.015	5
2,2,3-trimethylbutane	298.15	3-21G	0.90	38.86	39.33	0.47	0.77	0.017	10
2,2,3-trimethylbutane	298.15	6-31G*	0.90	38.99	39.33	0.34	0.56	0.012	10
2,2,3-trimethylbutane	298.15	6-31G**	0.90	39.18	39.33	0.15	0.28	0.006	10
2,2,3-trimethylbutane	1000.00	3-21G	0.90	94.35	92.32	−2.03	1.34	0.016	5
2,2,3-trimethylbutane	1000.00	6-31G*	0.90	94.50	92.32	−2.18	1.47	0.018	5
2,2,3-trimethylbutane	1000.00	6-31G**	0.90	94.82	92.32	−2.50	1.78	0.021	5

[a] Shiminouchi.[33,34] [b] All literature values in the table are from Stull, Westrum, Sinke.[36] The standard deviations include comparisons between additional calculated values and experimental C_p values from other sources: ethane,[51,59] propane,[17] 2,2-dimethylbutane.[60] [c] scalar SD and relative SD shown on 298.15 lines are for data at temperatures ≤500, on 1000 lines are for temperatures >500.

At 298 K the entropy of the conformer mixture is 1.84 cal/(K mol) greater than that calculated for the hypothetical pure anti conformer. For butane this correction arises solely from the entropy of mixing. The correction for average entropy is zero since all three conformers have nearly the same entropy. The heat capacity is 0.65 cal/(K mol) higher for the mixture, and the heat content is 0.27 kcal/mol greater. The latter value is the same SM quantity that corrects the enthalpy of formation.

Models for Derivation of Corrections for Mixtures of Conformers. In the present study two models were used to derive the corrections for the contributions of multiple conformers. One is the *partition function model*. The terms of the mixture component of the partition function, Q(conformer mixture), shown in eq 1 are to be added to the partition function of the reference conformer: $Q = Q(\text{translation}) + Q(\text{rotation}) + Q(\text{vibration})$. E_i is $(e_i - e_1)$, the energy of conformer i minus the energy of conformer 1, the reference conformer, and m_i is a multiplicity term. The use of m_i may best be illustrated by example. Among the nine nominal staggered conformers of pentane conformer g+(2,3) and g+(4,5) are identical, and m_i is, therefore, 2 for g+(2,3) pentane; m_i is also 2 for the corresponding g− conformer. The g+ and the g− conformers are, however, distinct, although they have the same energy. Apart from the critical multiplicity factor, eq 1 is the same as F_{steric} as defined by Pitzer.[14]

$$Q(\text{conformer mixture}) = \sum m_i \exp(-E_i/RT) \qquad (1)$$

An alternative model, the *mixture of components model*, treats the mixture of conformers as made up of a set of individual components (conformers) each having its own value of enthalpy, entropy, and heat capacity. The properties of the actual compound, a mixture of conformers, are then calculated as the average of those of the individual components. The entropy correction also includes an entropy of mixing term.

The two methods give the same values for the corrections if all conformers have the same entropy. They give slightly different values if significant fractions of the conformers have different entropies.

Identification of Conformers. For either model it is necessary to identify all conformers accurately and to obtain estimates of their energies. This step is required for either of the two models described in this study, the *partition function*

TABLE 4: Theoretical Heat Capacity C_p of Alkanes That Exist as Mixtures of Conformers

compound	temp (K)	basis[a] set	scale factor	heat capacity glob min	heat cap of confs	heat capacity total	heat capacity lit.[b]	difference	std dev[c]	rel std dev	number
butane	298.15	3-21G	0.90	22.06	0.65	22.71	23.29	0.58	0.88	0.037	8
butane	298.15	6-31G*	0.90	22.12	0.65	22.77	23.29	0.52	0.77	0.033	8
butane	298.15	6-31G**	0.90	22.22	0.65	22.87	23.29	0.42	0.62	0.026	8
butane	298.15	shimano	1.00	22.04	0.65	22.69	23.29	0.60	0.80	0.034	8
butane	1000.00	3-21G	0.90	55.53	0.06	55.59	54.22	−1.37	0.78	0.019	9
butane	1000.00	6-31G*	0.90	55.64	0.06	55.70	54.22	−1.48	0.82	0.019	9
butane	1000.00	6-31G**	0.90	55.83	0.06	55.89	54.22	−1.67	0.94	0.021	9
butane	1000.00	shimano	1.00	55.67	0.06	55.73	54.22	−1.51	0.86	0.020	9
pentane	298.15	3-21G	0.90	27.05	0.69	27.74	28.73	0.99	0.97	0.037	4
pentane	298.15	6-31G*	0.90	27.10	0.69	27.79	28.73	0.94	0.89	0.034	4
pentane	298.15	6-31G**	0.90	27.26	0.69	27.95	28.73	0.78	0.70	0.027	4
pentane	1000.00	3-21G	0.90	68.38	0.30	68.68	66.55	−2.13	1.60	0.028	5
pentane	1000.00	6-31G*	0.90	68.50	0.30	68.80	66.55	−2.25	1.73	0.030	5
pentane	1000.00	6-31G**	0.90	68.73	0.30	69.03	66.55	−2.48	2.00	0.035	5
2-methylbutane	298.15	3-21G	0.90	27.54	0.32	27.86	28.39	0.53	0.69	0.022	9
2-methylbutane	298.15	6-31G*	0.90	27.63	0.32	27.95	28.39	0.44	0.55	0.018	9
2-methylbutane	298.15	6-31G**	0.90	27.75	0.01	27.76	28.39	0.63	0.60	0.021	9
2-methylbutane	298.15	wadding	1.00	28.08	0.32	28.40	28.39	−0.01	0.21	0.006	9
2-methylbutane	1000.00	3-21G	0.90	68.47	0.05	68.52	67.12	−1.40	0.99	0.017	5
2-methylbutane	1000.00	6-31G*	0.90	68.59	0.05	68.64	67.12	−1.52	1.12	0.019	5
2-methylbutane	1000.00	6-31G**	0.90	68.82	0.00	68.82	67.12	−1.70	1.32	0.023	5
2-methylbutane	1000.00	wadding	1.00	68.82	0.05	68.87	67.12	−1.75	1.52	0.027	5
hexane	298.15	3-21G	0.90	32.05	1.31	33.36	34.20	0.84	0.70	0.021	9
hexane	298.15	6-31G*	0.90	32.09	1.31	33.40	34.20	0.80	0.62	0.019	9
hexane	298.15	6-31G**	0.90	32.28	1.31	33.59	34.20	0.61	0.47	0.014	9
hexane	1000.00	3-21G	0.90	81.23	0.51	81.74	78.89	−2.85	2.23	0.032	5
hexane	1000.00	6-31G*	0.90	81.35	0.51	81.86	78.89	−2.97	2.38	0.034	5
hexane	1000.00	6-31G**	0.90	81.63	0.51	82.14	78.89	−3.25	2.69	0.039	5
2,3-dimethylbutane	298.15	3-21G	0.90	33.03	0.00	33.03	33.59	0.56	0.71	0.019	9
2,3-dimethylbutane	298.15	6-31G*	0.90	33.11	0.01	33.12	33.59	0.47	0.56	0.015	9
2,3-dimethylbutane	298.15	6-31G**	0.90	33.26	0.01	33.27	33.59	0.32	0.34	0.009	9
2,3-dimethylbutane	1000.00	3-21G	0.90	81.39	0.00	81.39	79.10	−2.29	1.62	0.023	5
2,3-dimethylbutane	1000.00	6-31G*	0.90	81.51	0.00	81.51	79.10	−2.41	1.76	0.025	5
2,3-dimethylbutane	1000.00	6-31G**	0.90	81.79	0.00	81.79	79.10	−2.69	2.07	0.030	5
heptane	298.15	3-21G	0.90	37.04	1.83	38.87	39.67	0.80	0.58	0.015	9
heptane	298.15	6-31G*	0.90	37.08	1.83	38.91	39.67	0.76	0.53	0.014	9
heptane	298.15	6-31G**	0.90	37.25	1.83	39.08	39.67	0.59	0.42	0.010	9
heptane	1000.00	3-21G	0.90	94.08	0.78	94.86	91.20	−3.66	2.95	0.036	5
heptane	1000.00	6-31G*	0.90	94.21	0.78	94.99	91.20	−3.79	3.10	0.038	5
heptane	1000.00	6-31G**	0.90	94.53	0.78	95.31	91.20	−4.11	3.46	0.043	5
octane	298.15	3-21G	0.90	42.03	2.40	44.43	45.14	0.71	0.56	0.013	6
octane	298.15	6-31G*	0.90	42.07	2.40	44.47	45.14	0.67	0.54	0.012	6
octane	298.15	6-31G**	0.90	42.26	2.40	44.66	45.14	0.48	0.52	0.010	6
octane	1000.00	3-21G	0.90	106.93	1.02	107.95	103.60	−4.35	3.11	0.033	6
octane	1000.00	6-31G*	0.90	107.07	1.02	108.09	103.60	−4.49	3.26	0.035	6
octane	1000.00	6-31G**	0.90	107.43	1.02	108.45	103.60	−4.85	3.63	0.039	6
2,2,3,3-tetramethylbutane	298.15	3-21G	0.90	44.53	0.00	44.53	46.03	1.50	2.54	0.047	4
2,2,3,3-tetramethylbutane	298.15	6-31G*	0.90	44.65	0.00	44.65	46.03	1.38	2.31	0.043	4
2,2,3,3-tetramethylbutane	298.15	6-31G**	0.90	44.86	0.00	44.86	46.03	1.17	1.96	0.036	4
2,2,3,3-tetramethylbutane	1000.00	3-21G	0.90	107.31	0.00	107.31	106.60	−0.71	1.70	0.022	5
2,2,3,3-tetramethylbutane	1000.00	6-31G*	0.90	107.47	0.00	107.47	106.60	−0.87	1.51	0.019	5
2,2,3,3-tetramethylbutane	1000.00	6-31G**	0.90	107.84	0.00	107.84	106.60	−1.24	1.30	0.016	5

[a] Shiminouchi,[33,34] Waddington.[38] [b] All literature values in the table are from Stull, Westrum, Sinke.[36] The standard deviations include additional comparisons between calculated C_p values and experimental C_p values from other sources: butane,[62] 2-methylbutane,[38] hexane,[60] 2,3-dimethylbutane,[38,61] heptane,[63] 2,2,3-trimethylbutane,[63] octane.[64] [c] Scalar SD and relative SD shown on 298.15 lines are for data at temperatures ≤ 500, on 1000 lines are for temperatures >500.

model or the *mixture of components model*. Identification of conformers is a nontrivial task. The issues have been discussed by Noyes[43] in terms of the theory underlying treatment of entropy of mixing and the "Gibb's paradox".

The description of a molecule such as butane in terms of anti, gauche+, and gauche− conformers, each having a distinct structure and a definable energy, is an approximation that works rather well in practice for many compounds. Nevertheless, the description is a gross simplification of a system that is actually made up of a complex mixture of molecules existing at a given instant in almost a continuum of geometric quantum states. There are two boundary conditions for the validity of the conformer description of a compound. On one hand the barriers between conformers must be large enough so that the conformers represent distinct energy minima, and on the other the barriers between the minima must be small enough to permit equilibration within some time period, usually assumed to be a fraction of a second. If the barriers are large, then the substance is best described as a mixture of isolable compounds. If the barrier between two or more assumed conformers is too small, then the conformer description no longer applies to these candidate conformers.

In a few cases conformers have been identified experimentally and their energies and populations have been estimated by NMR

TABLE 5: Theoretical Heat Content of Alkanes That Exist as a Single Conformer

compound	temp (K)	basis set[a]	scale factor	heat content total	heat content lit.[37]	difference	std dev[b]	rel std dev[b]	number
ethane	298.15	3-21G	0.90	2.81	2.86	0.05	0.10	0.07	9
ethane	298.15	6-31G*	0.90	2.81	2.86	0.05	0.07	0.07	9
ethane	298.15	6-31G**	0.90	2.81	2.86	0.05	0.07	0.06	9
ethane	298.15	shimano	1.00	2.81	2.86	0.05	0.07	0.06	9
ethane	1000.00	3-21G	0.90	18.25	18.28	0.03			
ethane	1000.00	6-31G*	0.90	18.33	18.28	−0.05			
ethane	1000.00	6-31G**	0.90	18.42	18.28	−0.14			
ethane	1000.00	shimano	1.00	18.33	18.28	−0.05			
propane	298.15	3-21G	0.90	3.48	3.51	0.03	0.14	0.03	9
propane	298.15	6-31G*	0.90	3.49	3.51	0.02	0.10	0.02	9
propane	298.15	6-31G**	0.90	3.50	3.51	0.01	0.09	0.02	9
propane	298.15	shimano	1.00	3.51	3.51	0.00	0.08	0.02	9
propane	1000.00	3-21G	0.90	25.64	25.67	0.03			
propane	1000.00	6-31G*	0.90	25.73	25.67	−0.06			
propane	1000.00	6-31G**	0.90	25.85	25.67	−0.18			
propane	1000.00	shimano	1.00	25.75	25.67	−0.08			
2-methylpropane	298.15	3-21G	0.90	4.22	4.28	0.06	0.19	0.03	9
2-methylpropane	298.15	6-31G*	0.90	4.25	4.28	0.03	0.12	0.02	9
2-methylpropane	298.15	6-31G**	0.90	4.27	4.28	0.01	0.12	0.01	9
2-methylpropane	1000.00	3-21G	0.90	33.27	33.31	0.04			
2-methylpropane	1000.00	6-31G*	0.90	33.41	33.31	−0.10			
2-methylpropane	1000.00	6-31G**	0.90	33.58	33.31	−0.27			
2,2-dimethylpropane	298.15	3-21G	0.90	4.97	5.05	0.08	0.42	0.03	9
2,2-dimethylpropane	298.15	6-31G*	0.90	5.02	5.05	0.03	0.28	0.02	9
2,2-dimethylpropane	298.15	6-31G**	0.90	5.04	5.05	0.01	0.17	0.01	9
2,2-dimethylpropane	1000.00	3-21G	0.90	41.06	41.51	0.45			
2,2-dimethylpropane	1000.00	6-31G*	0.90	41.26	41.51	0.25			
2,2-dimethylpropane	1000.00	6-31G**	0.90	41.46	41.51	0.05			
2,2-dimethylbutane	298.15	3-21G	0.90	5.86	5.91	0.05	0.19	0.02	9
2,2-dimethylbutane	298.15	6-31G*	0.90	5.90	5.91	0.01	0.15	0.01	9
2,2-dimethylbutane	298.15	6-31G**	0.90	5.91	5.91	0.00	0.19	0.02	9
2,2-dimethylbutane	298.15	pitzer	1.00	5.91	5.91	0.00	0.24	0.02	9
2,2-dimethylbutane	1000.00	3-21G	0.90	48.67	48.60	−0.07			
2,2-dimethylbutane	1000.00	6-31G*	0.90	48.86	48.60	−0.26			
2,2-dimethylbutane	1000.00	6-31G**	0.90	48.67	48.60	−0.07			
2,2-dimethylbutane	1000.00	pitzer	1.00	48.51	48.60	0.09			
2,2,3-trimethylbutane	298.15	3-21G	0.90	6.65	6.70	0.05	0.18	0.012	9
2,2,3-trimethylbutane	298.15	6-31G*	0.90	6.69	6.70	0.01	0.14	0.007	9
2,2,3-trimethylbutane	298.15	6-31G**	0.90	6.71	6.70	−0.01	0.22	0.005	9
2,2,3-trimethylbutane	1000.00	3-21G	0.90	56.36	56.30	−0.06			
2,2,3-trimethylbutane	1000.00	6-31G*	0.90	56.55	56.30	−0.25			
2,2,3-trimethylbutane	1000.00	6-31G**	0.90	56.80	56.30	−0.50			

[a] Shiminouchi,[33,34] Pitzer.[19] [b] 298−1000 K.

or other spectroscopic techniques.[44] The measurements for butane and pentane have been reviewed.[45,46] More generally, energies of conformers have been estimated by molecular mechanics.[39,47] If the number of conformers is small enough, ab initio calculations of conformer energies are practical.

For large acyclic alkanes such as octane with 273 staggered conformers (not all unique) a counting procedure may be used to list conformers and their energies. In this study I assigned an energy to a conformer based on a count of gauche interactions, using the value of 0.70 kcal/mol for each gauche interaction of the same handedness. Thus *n* interactions of the same handedness contribute $n \times 0.70$. Each adjacent pair of gauche interactions of opposite handedness contributes an additional 1.90; or 3.3 kcal/mol total for each g+/g− interaction.

The energies of the 27 nominal conformers of hexane assigned by the above counting procedure may be compared with energies obtained by the detailed ab initio calculations for all conformers of hexane (and of butane and pentane) by Osawa's group.[46] Details are presented in Table 7. The differences between the corrections calculated by the two sets of conformer energies are negligible.

Some precautions must be followed in counting conformers and in assigning energies. The highly crowded 2,2,3,3-tetramethylbutane exists as a mixture of two chiral conformers having C−C−C−C torsions of 166° and 194° (instead of existing as the nominal single conformer with a torsion of 180°); both must be included. The counting method does not give correct energies for the conformers of 2,3-dimethylbutane nor for conformers of other alkanes with adjacent methyl substituents. The C_{2h} conformer of 2,3-dimethylbutane has two gauche interactions and the C_2 conformer has three, but the two conformers have almost the same free energy.[44,45] This pattern can readily be identified qualitatively; the C_{2h} conformer is in a “locked” position, while the C_2 conformer can undergo a slight torsional distortion that partly diminishes the van der Waals repulsions. In the tables the calculations for 2,3-dimethylbutane are, therefore, based on a population of three conformers of equal energy and all having $\sigma = 2$. All calculations reported in this study are based on free energies except where explicitly noted otherwise.

Entropies of Conformers. Calculation of mole fractions using Boltzmann distribution equations is easier in terms of energies (enthalpies) than in terms of free energies, which requires estimates of relative entropies. In this study I have used both calculations in order to determine how much difference is made by the free energy calculation. For alkanes other than the *n*-alkanes the differences are small. Such may not be true for molecules containing functional groups.

TABLE 6: Theoretical Heat Content of Alkanes That Exist as Mixtures of Conformers

compound	temp (K)	basis set[a]	scale factor	heat content of conf	SMG (SM)	heat content total	heat content lit.[37]	difference	std dev[b]	rel std dev[b]	number
butane	298.15	3-21G	0.90	4.29	0.27	4.56	4.64	0.08	0.18	0.033	9
butane	298.15	6-31G*	0.90	4.30	0.27	4.57	4.64	0.07	0.15	0.028	9
butane	298.15	6-31G**	0.90	4.30	0.27	4.57	4.64	0.07	0.15	0.024	9
butane	298.15	shimano	1.00	4.32	0.27	4.59	4.64	0.05	0.14	0.023	9
butane	1000.00	3-21G	0.90	33.17	0.41	33.58	33.54	−0.04			
butane	1000.00	6-31G*	0.90	33.26	0.41	33.67	33.54	−0.13			
butane	1000.00	6-31G**	0.90	33.41	0.41	33.82	33.54	−0.28			
butane	1000.00	shimano	1.00	33.31	0.41	33.72	33.54	−0.18			
pentane	298.15	3-21G	0.90	5.17	0.56	5.73	5.63	−0.10	0.37	0.022	9
pentane	298.15	6-31G*	0.90	5.14	0.56	5.70	5.63	−0.07	0.25	0.015	9
pentane	298.15	6-31G**	0.90	5.16	0.56	5.72	5.63	−0.09	0.37	0.021	9
pentane	1000.00	3-21G	0.90	41.04	0.94	41.98	41.19	−0.79			
pentane	1000.00	6-31G*	0.90	40.82	0.94	41.76	41.19	−0.57			
pentane	1000.00	6-31G**	0.90	41.03	0.94	41.97	41.19	−0.78			
2-methylbutane	298.15	3-21G	0.90	5.07	0.09	5.16	5.30	0.14	0.21	0.032	9
2-methylbutane	298.15	6-31G*	0.90	5.09	0.09	5.18	5.30	0.12	0.17	0.027	9
2-methylbutane	298.15	6-31G**	0.90	5.10	0.03	5.13	5.30	0.17	0.21	0.038	9
2-methylbutane	298.15	wadding	1.00	5.15	0.09	5.24	5.30	0.06	0.47	0.033	9
2-methylbutane	1000.00	3-21G	0.90	40.85	0.18	41.03	41.01	−0.02			
2-methylbutane	1000.00	6-31G*	0.90	40.98	0.18	41.16	41.01	−0.15			
2-methylbutane	1000.00	6-31G**	0.90	41.16	0.03	41.19	41.01	−0.18			
2-methylbutane	1000.00	wadding	1.00	41.43	0.18	41.61	41.01	−0.60			
hexane	298.15	3-21G	0.90	5.99	0.78	6.77	6.62	−0.15	0.42	0.024	9
hexane	298.15	6-31G*	0.90	6.00	0.78	6.78	6.62	−0.16	0.48	0.026	9
hexane	298.15	6-31G**	0.90	6.02	0.78	6.80	6.62	−0.18	0.62	0.032	9
hexane	1000.00	3-21G	0.90	48.31	1.42	49.73	48.85	−0.88			
hexane	1000.00	6-31G*	0.90	48.41	1.42	49.83	48.85	−0.98			
hexane	1000.00	6-31G**	0.90	48.65	1.42	50.07	48.85	−1.22			
2,3-dimethylbutane	298.15	3-21G	0.90	5.89	0.12	6.01	5.92	−0.09	0.20	0.015	9
2,3-dimethylbutane	298.15	6-31G*	0.90	5.92	0.03	5.95	5.92	−0.03	0.21	0.008	9
2,3-dimethylbutane	298.15	6-31G**	0.90	5.93	0.03	5.96	5.92	−0.04	0.32	0.011	9
2,3-dimethylbutane	1000.00	3-21G	0.90	48.58	0.13	48.71	48.24	−0.47			
2,3-dimethylbutane	1000.00	6-31G*	0.90	48.71	0.03	48.74	48.24	−0.50			
2,3-dimethylbutane	1000.00	6-31G**	0.90	48.92	0.03	48.95	48.24	−0.71			
heptane	298.15	3-21G	0.90	6.86	0.98	7.84	7.62	−0.22	0.62	0.030	9
heptane	298.15	6-31G*	0.90	6.86	0.98	7.84	7.62	−0.22	0.67	0.031	9
heptane	298.15	6-31G**	0.90	6.88	1.26	8.14	7.62	−0.52	0.83	0.051	9
heptane	1000.00	3-21G	0.90	55.90	1.85	57.75	56.52	−1.23			
heptane	1000.00	6-31G*	0.90	56.00	1.85	57.85	56.52	−1.33			
heptane	1000.00	6-31G**	0.90	56.24	1.85	58.09	56.52	−1.57			
octane	298.15	3-21G	0.90	7.73	1.19	8.92	8.61	−0.31	0.85	0.037	9
octane	298.15	6-31G*	0.90	7.74	1.19	8.93	8.61	−0.32	0.91	0.038	9
octane	298.15	6-31G**	0.90	7.75	1.19	8.94	8.61	−0.33	1.06	0.042	9
octane	1000.00	3-21G	0.90	63.49	2.32	65.81	64.18	−1.63			
octane	1000.00	6-31G*	0.90	63.59	2.32	65.91	64.18	−1.73			
octane	1000.00	6-31G**	0.90	63.86	2.32	66.18	64.18	−2.00			
2,2,3,3-tetramethylbutane	298.15	3-21G	0.90	7.30	0.00	7.30	7.40	0.10	0.99	0.037	9
2,2,3,3-tetramethylbutane	298.15	6-31G*	0.90	7.31	0.00	7.31	7.40	0.09	0.89	0.034	9
2,2,3,3-tetramethylbutane	298.15	6-31G**	0.90	7.34	0.00	7.34	7.40	0.06	0.71	0.027	9
2,2,3,3-tetramethylbutane	1000.00	3-21G	0.90	64.02	0.00	64.02	65.30	1.28			
2,2,3,3-tetramethylbutane	1000.00	6-31G*	0.90	64.19	0.00	64.19	65.30	1.11			
2,2,3,3-tetramethylbutane	1000.00	6-31G**	0.90	64.49	0.00	64.49	65.30	0.81			

[a] Shiminouchi,[33,34] Pitzer.[19] [b] 298−1000 K.

The “intrinsic” entropies of alkanes are approximately the same for all conformers. The “intrinsic" entropy is entropy corrected for differences in symmetry numbers among conformers. The entropy of a conformer having C_2 symmetry ($\sigma = 2$) is less than that of a conformer of C_1 symmetry ($\sigma = 1$) by R ln(2) or 1.38 cal/(K mol). For butane the “intrinsic” entropies of anti and gauche conformers are the same within 0.05 cal/(K mol) based on frequencies derived with HF calculations using either the 3-21G or the 6-31G* basis set (both conformers have $\sigma = 2$). For hexane the intrinsic entropies of the anti and of the gauche(2−3) conformer (ttg) are the same within 0.03 cal/(K mol) based on HF 3-21G frequencies. Osawa reports a difference of 1.39 cal/(K mol) between anti and gauche butane,[46] but this looks like an error in assignment of symmetry number since the value reported for the entropy of anti butane is the same as the 3-21G value. There also appear to be errors in deriving symmetry numbers for some of the hexane conformers; the reported entropy for ttt-hexane agrees exactly with the 3-21G value, but the reported entropy of ttg-hexane is 1.40 cal/(K mol) higher than the 3-21G value. In this study I assume that the intrinsic entropies of all alkane conformers are the same and that differences in actual entropies are due entirely to differences in symmetry numbers.

Evaluation of SM and of SMG. It is useful to begin with the calculation of corrections to heat content for conformer mixtures; these are SM and SMG. These same quantities also enter into calculation of corrections for entropy and for heat capacity. Equations 2−4 define SM and eqs 5−7 define SMG.

TABLE 7: Examples of Calculation of Corrections for Conformer Mixtures

Butane conformer data from counting algorithm
Temperature 298.15 K. Conformer labels: 1=t, 2=g+, 3=g−

number	energy of conformer	entropy of conformer	fract f_{gi}	$S_i f_{gi}$	free energy of conformer	conformer label	σ
1	0.00	0	0.6197	0	0.00	1	2
2	0.70	0	0.1901	0	0.70	2	2
3	0.70	0	0.1901	0	0.70	3	2

Corrections for mixture calculated using mixture of components model

temp	SM	C_p(corr)	S(mix)	S(avg)	S(tot)
298.15	0.27	0.654	1.843	0	1.843

Corrections for mixture calculated using partition function model

temp	SM	C_p(corr)	S(p_fun)
298.15	0.27	0.654	1.843

Hexane conformer data from counting algorithm
Temperature 298.15 K. Conformer labels: 1=t, 2=g+, 3=g−

number	energy of conformer	entropy of conformer	fraction of conformer	$S_i f_{gi}$	free energy of conformer	conformer label	σ
1	0.00	0.00	0.1824	0.00	0.00	111	2
2	0.70	1.38	0.2238	0.31	0.29	211	1
3	0.70	1.38	0.2238	0.31	0.29	311	1
4	0.70	0.00	0.0560	0.00	0.70	121	2
5	1.40	1.38	0.0687	0.09	0.99	221	1
6	3.30	1.38	0.0028	0.00	2.89	321	1
7	0.70	0.00	0.0560	0.00	0.70	131	2
8	3.30	1.38	0.0028	0.00	2.89	231	1
9	1.40	1.38	0.0687	0.09	0.99	331	1
10	1.40	0.00	0.0172	0.00	1.40	212	2
11	1.40	1.38	0.0687	0.09	0.99	312	1
12	2.10	0.00	0.0053	0.00	2.10	222	2
13	4.00	1.38	0.0009	0.00	3.59	322	1
14	5.90	0.00	0.0000	0.00	5.90	232	2
15	4.00	1.38	0.0009	0.00	3.59	332	1
16	1.40	0.00	0.0172	0.00	1.40	313	2
17	5.90	0.00	0.0000	0.00	5.90	323	2
18	2.10	0.00	0.0053	0.00	2.10	333	2

Corrections for mixture calculated using mixture of components model

temp	SM	C_p(corr)	S(mix)	S(avg)	S(tot)
298.15	0.78	1.312	4.162	0.910	5.072
500.00	1.03	0.924	4.630	1.004	5.634

Corrections for mixture calculated using partition function model

temp	SM	C_p(corr)	S(p_fun)
298.15	0.69	1.74	4.899
500.00	0.96	1.07	5.599

Hexane conformer data of Osawa, ref 46. MP4SDQ/6-31G*//6-31G*
Conformers have same numbering as above set. Temperature 298.15 K

number	energy of conformer	entropy of conformer	fract of conformer f_{gi}	$S_i f_{gi}$	free energy of conformer	conformer label	σ
1	0.00	0.00	0.1834	0.00	0	ttt	2
2	0.72	1.38	0.2176	0.30	0.31	g+tt	1
3	0.72	1.38	0.2176	0.30	0.31	g−tt−	1
4	0.73	0.00	0.0535	0.00	0.73	tg+t	2
7	0.73	0.00	0.0535	0.00	0.73	tg−t	2
5	1.30	1.38	0.0817	0.11	0.89	g+g+t	1
9	1.30	1.38	0.0817	0.11	0.89	g−g−t	1
10	1.44	0.00	0.0161	0.00	1.44	g+tg+	2
16	1.44	0.00	0.0161	0.00	1.44	g−tg−	2
11	1.56	1.38	0.0527	0.07	1.15	g−tg+	2
12	1.84	0.00	0.0082	0.00	1.84	g+g+g+	2
18	1.84	0.00	0.0082	0.00	1.84	g−g−*g*−	2
6	3.12	1.38	0.0038	0.01	2.71	g−g+t	1
8	3.12	1.38	0.0038	0.01	2.71	g+g−t	1
13	3.87	1.38	0.0011	0.00	3.46	g−g+g+	1
15	3.87	1.38	0.0011	0.00	3.46	g−g−g+	1
14	5.92	0.00	0.0000	0.00	5.92	g+g−g+	1
17	5.92	0.00	0.0000	0.00	5.92	g−g+g−	1

TABLE 7 (Continued)

Corrections for mixture calculated using mixture of components model

temp	SM	C_p(corr)	S(mixing)	S(avg)	S(total)
298.15	0.80	1.343	4.215	0.910	5.126
500.00	1.05	0.900	4.685	1.004	5.689

Corrections for mixture calculated using partition function model

temp	SM	C_p(corr)	S(p_fun)
298.15	0.71	1.786	4.952
500.00	0.98	1.042	5.654

TABLE 8: Illustration of Application of Corrections to Entropy Shown in Table 7 (Examples from Table 2)

compound	temp (K)	basis set	scale factor	σ	entropy trans + rotation	entropy vibration	entropy mixing + conf	entropy total	entropy lit.	diff	scalar std dev	rel std dev	number
butane	298.15	6-31G*	0.90	2	61.23	11.01	1.84	74.08	74.12	0.04	0.24	0.010	10
hexane	298.15	6-31G*	0.90	2	65.15	22.67	5.07	92.89	92.83	−0.06	0.37	0.006	9

Calculation of SM uses estimates of Boltzmann mole fractions based on enthalpies (energies) of conformers,[3,48] while calculation of SMG uses estimates of mole fractions based on free energies. Ab initio energies are internal energies; at a given pressure differences of internal energies are equal to differences of enthalpies. Since all energy quantities in this study are based on energy differences, it is justifiable to use energy and enthalpy interchangeably. If all conformers have the same entropy, then SM and SMG are equal.

$$\mathrm{SM} = \sum (h_i - h_1)\, f_{hi} \tag{2}$$

$$f_{hi} = m_i \exp((h_1 - h_i)/RT)/\mathrm{denomh} \tag{3}$$

$$\mathrm{denomh} = \sum m_i \exp((h_1 - h_i)/RT) \tag{4}$$

$$\mathrm{SMG} = \sum (h_i - h_1)\, \mathrm{f}_{gi} \tag{5}$$

$$f_{gi} = m_i \exp((g_1 - g_i)/RT)/\mathrm{denomg} \tag{6}$$

$$\mathrm{denomg} = \sum m_i \exp((g_1 - g_i)/RT) \tag{7}$$

In eqs 2−7 h_i is enthalpy (equals energy), g_i is free energy, and m_i is multiplicity of conformer i as defined above for Q(conformer mixture); $g_i = h_i - T\Delta S_i$. Assuming equal intrinsic entropies for all conformers, ΔS_i, the relative entropy of conformer i will be 0 or $\pm R \ln(2)$. If the conformer set includes some members having $\sigma = 1$ and some having $\sigma = 2$, then some conformers have a nonzero relative entropy.

SM has been defined in earlier studies for use in converting the enthalpy calculated for the reference conformer to the enthalpy of the actual conformer mixture, eq 8. SM values have been reported for many compounds.[39−42] In principle the correction SM is analogous to the POP correction used in MM2 and MM3 molecular mechanics programs, but for some reason POP values differ appreciably from SM values.[3,49]

$$\Delta H_f^\circ(\text{for the compound}) = \Delta H_f^\circ(\text{reference conformer}) + \mathrm{SM} \tag{8}$$

Although calculated mole fractions of conformers are sensitive to what energy is assigned to gauche interactions, the derived SM values are not very sensitive to the assigned gauche energies. For butane the SM value is 0.27 whether the assigned gauche interaction is 0.70 or 0.90 kcal/mol. The reason for insensitivity is that there is a strong compensation: the higher the energy of a conformer, the smaller the calculated fraction, and the product $f_i\mathrm{E}_i$ remains relatively constant.

Corrections to Entropy. Equations 9−11 show the calculation of S_{mcorr}, the correction to the entropy based on the *mixture of components model*. S_{mcorr} is the sum of two terms, the average difference of the entropies of the conformers and the entropy of the reference conformer plus the entropy of mixing. S_i is the entropy of conformer i and f_{gi} the mole fraction based on free energies.

$$\mathrm{S}_{\mathrm{avg}} = \sum S_i f_{gi} \tag{9}$$

$$S_{\mathrm{mixing}} = -R \sum f_{gi} \ln(f_{gi}) \tag{10}$$

$$S_{\mathrm{mcorr}} = S_{\mathrm{avg}} + S_{\mathrm{mixing}} \tag{11}$$

Equation 12 is S_{pcorr} for the *partition function model* (eq 1); S_{pcorr} is based on enthalpies.

$$S_{\mathrm{pcorr}} = R \ln(\mathrm{denomh}) + 1000\mathrm{SM}/T \tag{12}$$

The entropy of the compound is $S_{\mathrm{total}} = S_{\mathrm{reference}} + S_{\mathrm{corr}}$. If all conformers have the same entropy, then $S_{\mathrm{mcorr}} = S_{\mathrm{pcorr}}$.

Corrections to Heat Capacity, C_p. Equation 13 is the general definition of the correction, and eq 14 is the correction for both models. Terms 1 and 2 are given by eqs 15 and 16 for the *mixture of components model* and by eqs 17 and 18 for the *partition function model.*

$$C_p(\mathrm{corr}) = \partial(\mathrm{SM})/\partial(T) \tag{13}$$

$$C_p(\mathrm{corr}) = (\mathrm{term1} - \mathrm{term2})/(RT^2) \tag{14}$$

$$\mathrm{term1} = \sum (h_i - h_1)(g_i - g_1) f_{gi} \tag{15}$$

$$\mathrm{term2} = \mathrm{SM} \times \mathrm{SMG} \tag{16}$$

$$\mathrm{term1} = \sum (h_i - h_1)(h_i - h_1) f_{hi} \tag{17}$$

$$\mathrm{term2} = \mathrm{SM} \times \mathrm{SM} \tag{18}$$

Table 7 shows worked out examples of calculations for butane and hexane, and Tables 8−10 show how the corrections are applied. The examples in Tables 8−10 were abstracted from Tables 2, 4, and 6 and from Tables 2S, 4S, and 6S in the Supporting Information. Two sets of values are given for hexane, one based on counting, and the other based on the ab

TABLE 9: Illustration of Application of Heat Capacity Corrections Shown in Table 7 (Examples from Table 4)

compound	temp (K)	basis set	scale factor	heat capacity glob min	heat cap confs	heat capacity total	heat capacity lit.	difference	std dev	rel std dev	number
butane	298.15	6-31G*	0.90	22.12	0.65	22.77	23.29	0.52	0.77	0.033	8
hexane	298.15	6-31G*	0.90	32.09	1.31	33.40	34.20	0.80	0.62	0.019	9

TABLE 10: Illustration of Application of Heat Content Corrections Shown in Table 7 (Examples from Table 6)

compound	temp (K)	basis set	scale factor	heat content of conf	SMG	heat content total	heat content lit.	difference	std dev	rel std dev	number
butane	298.15	6-31G*	0.90	4.30	0.27	4.57	4.64	0.07	0.15	0.028	9
hexane	298.15	6-31G*	0.90	6.00	0.78	6.78	6.62	−0.16	0.48	0.026	9

initio energies reported by Osawa.[46] The corrections are virtually the same using either representation of conformer energies. The entropy values listed are R ln(2) for each conformer of symmetry number 1 and 0 for each conformer of symmetry number 2. (The reference conformer has the symmetry number 2.) As discussed above, these assignments assume that the intrinsic entropies are the same for all conformers. The entropy values reported by Osawa are of little use due to the inconsistencies discussed above.

Assumptions. The theoretical calculation of thermochemical values from frequencies depends on three principal types of assumptions.

The first type includes those assumptions inherent in ab initio calculations with various basis sets. This type includes also the assumption that suitable sets of frequencies may be obtained by applying an appropriate constant scaling factor to the ab initio frequencies.

Shimanouchi[33,34] assigns uncertainties for IR and Raman frequencies in terms of classes A through E. The maximum difference for class E is given as 30 cm^{-1}, for D as 15, and for C as 6. The differences in published sets of frequencies and those from the ab initio calculations are sometimes larger. It should be noted that entropies calculated with the observed frequencies are similar to those calculated using ab initio frequencies. See, for example, the butane data in Table 2.

The second type of assumption is that the partition function may be approximated adequately by use of the usual rigid-rotor−harmonic oscillator model, neglecting effects of anharmonicity and of rotational−vibrational interactions. The neglected effects may be most significant in the differences in heat capacity estimates at high temperatures or at very low temperatures.

The third type of assumption concerns treatment of compounds that exist as a mixture of conformers. The equations for calculating the corrections are exact, but the identification of conformers and assignment to them of energies is usually an approximation, as described above.

The largest potential source of uncertainty in the present method of calculation of entropies occurs if the reference conformer has low frequencies that have to be modified because they are less than about 45 cm.^{-1} This substitution will not affect the estimates of C_p since the contribution of the low frequencies is already at the R limit.

Accuracy. As for the accuracy of the experimental data, Pitzer[16] suggests uncertainties averaging about 0.25 cal/(K mol) for C_p values of the *n*-alkanes. The scatter of the C_p data for ethane[50] indicates a precision of perhaps 0.2 cal/K/mol; the standard deviation of smoothed values would be a little smaller; the accuracy is not known. Dailey and Felsing[51] suggest that the "maximum experimental difference" for their heat capacities for the ethane, propane, and butane data is 1%. This would amount to 0.25 to 0.45 cal/(K mol) scalar. In some papers no difference estimates are given. The tables in Chao et al.[23] indicate a standard deviation of C_p for ethane of less than 0.1 cal/(K mol) and for propane of 0.18 (omitting early measurements which show larger deviations).

Since a great deal of development of refined techniques has gone into the determination of heat capacities, it appears that many of the experimental data are reliable to within the above limits.

The experimental determination of entropy is more difficult. It requires precise heat capacity measurements from temperatures below 10 K along with evaluation of phase transitions in the solid, heat of melting, and heat of vaporization. The number of really good entropy measurements is rather small. Entropy values at a series of temperatures are obtained from the benchmark value by integration of suitable $C_p\, dT$ expressions or more commonly by application of the equations of statistical mechanics to sets of assigned frequencies. Since most C_p measurements are at temperatures below 600 K, the extrapolation of entropies to higher temperatures involves some uncertainty.

The experimentally evaluated entropies for methane, pentane, hexane, and heptane reported in Table 5 of Pitzer and Kilpatrick[18] are closely reproduced by the ab initio calculations based on 3-21G, 6-31G*, and 6-31G** frequencies scaled by 0.90.

Kilpatrick and Pitzer[19] report that the entropy of 2,2-dimethylbutane at 298.16 is 85.72 ± 0.2. Stull et al.[36] report 85.62. The values obtained in this study are reported in Table 1 and deviate by less than 0.4 cal/(K mol), while the standard deviation of $T\Delta S$ is about 0.2 kcal/mol. Entropy values based on the frequencies reported by Kilpatrick and Pitzer frequencies are higher by about 0.7 cal/(K mol). The calculation reported by Kilpatrick and Pitzer, however, is right on because it involved an adjustable barrier height chosen to make calculations agree with experiment.

Scott et al.[52] made careful third law heat capacity measurements on 2,2,3,3-tetramethylbutane and calculated the entropy at 298.16 K as 93.05 ± 0.30 cal/(K mol). They report assignment of 43 frequencies (out of the 72 that exist) and state with minimal detail that a hindered rotor estimate was performed for five torsions. They report a table of thermochemical values up to 1500 K. It is difficult to assess the uncertainties in these calculations from the data provided. The scaled frequencies from 3-21G, 6-31G*, and 6-31G** all exactly reproduce the 298.15 K entropy value. There is, however, divergence at the higher temperatures between the ab initio values and the Scott et al. values, and it is not clear which, if any, of these several calculated values is correct.

Considering the uncertainties of several critical "experimental" frequencies, it is fair to conclude that entropies and heat capacities derived from ab initio frequencies are as reliable as those derived from "experimental" frequencies.

Calculations. Calculations were made with the Gaussian suite of programs, Gaussian90, Gaussian92, and Gaussian94.[53−55] Special ad hoc programs were developed to process the data including those for calculating thermochemical properties at a series of special temperatures, programs to generate conformer sets of alkanes, programs to assign symmetry numbers to conformers of alkanes having large numbers of conformers, and programs to calculate corrections for contributions due to conformer mixtures by both models, the partition function model and the mixture of compounds model.

Some of the special programs were originally written in FORTRAN, but most are now in Microsoft BASIC. Programs in interpreted BASIC run so fast on modern PCs that there is little need to consider compilation.

SM6.BAS carries out computations of the corrections with both models, using symmetry numbers to estimate entropies of conformers.

TM1.BAS is coded to allow incorporation of calculated entropy data in getting S_{avg}.

ENTRVTMP.BAS carries out calculations of entropies, heat capacities, and heat content values at any desired set of temperatures.

STATEN.BAS counts conformers and assigns energies for alkanes and polymethyl-substituted alkanes.

NALKAN.BAS lists all conformers of a chain of up to 10 carbon atoms.

Upon request these programs can be made available as is, that is, without support. While heavily commented on and thoroughly tested, the text has not been prettied up and many finish with a "read past end of file" message.

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Supporting Information Available: The Supporting Information is organized into two sections (104 pages). The first contains an extended set of tables of entropy, heat capacity, and heat content. The second includes for each compound representative lists of frequencies calculated with the 3-21G and the 6-31G** basis sets along with Gaussian ARC summaries that list Cartesian coordinates for all atoms after geometry optimization together with ab initio energies and other information. These data are sufficient to permit recalculation of geometry optimized energies with relatively little computation. Selections of the Gaussian output data can be made available to anyone interested in specific compounds. It should be noted that many of the compressed files are too large for $3^1/_2$ in. floppies. Ordering information is given on any current masthead page.

Appendix: Symmetry Considerations

Calculation of entropy of overall rigid-body rotation and of internal free rotation requires correct use of symmetry numbers. Treatment of this topic in the literature is sometimes confusing, sometimes incorrect. Symmetry numbers for the several point groups are tabulated by Herzberg[27] (Table 140, p 508); this table is reproduced by Benson[26] (Table 2.3, p 49). It is usually best to list separately the rotational symmetry number of the molecule and the symmetry numbers of any free rotors present. Some authors combine the two symmetry numbers and list the overall symmetry.

Often the symmetry number is easily determined. *n*-Alkanes in the extended conformer have either C_{2h} symmetry (even number of carbon atoms) or C_{2v} symmetry. In either case the symmetry number is 2 for the extended conformer, the global minimum. The symmetry of some gauche conformers is also C_2; an example is g+g+ pentane.

Ethane has D_{3v} symmetry in the staggered form, D_{3h} symmetry in the eclipsed form, and D_3 symmetry in any other rigid torsional conformation. For all these possibilities the symmetry number of the molecule as a rigid rotor is 6. If the methyl groups had no barrier to rotation, that is, if the rotation were free, then one methyl group has three equivalent rotational phases with respect to the other, and the symmetry number for free rotation is 3. Some authors combine the two numbers and say that ethane with freely rotating methyl groups has a symmetry number of 18. Providing that the calculations are performed consistently, it is proper to use either formalism. However, no alkane has free rotors, and it is inappropriate to use the free rotor approximation to describe the symmetry. It is inappropriate, for example, to say that all *n*-alkanes have a symmetry number of 18 and that tetramethylmethane has a symmetry number of 972. The correct symmetry number of tetramethylmethane is 12, that of tetrahedral symmetry.

The methyl group of toluene is a free rotor. Toluene with a "frozen" methyl group has a symmetry number of 1. However, a freely rotating methyl group has a symmetry number of 3, and moreover, the free rotation now makes the two faces of the benzene ring rotationally equivalent and introduces a further symmetry number of 2. In this example it is necessary to be clear as to how the symmetry numbers are applied. One option is to treat the overall symmetry number as 6 in applying the free rotor component of entropy. Another option is to treat the symmetry number of the free rotor methyl group as 3 and then to calculate the rotational contribution of the whole molecule with a symmetry number of 2; the overall result is a combined symmetry number of 6. The similar systems CH_3BF_2 and CH_2NO_2 both with overall symmetry number 6 are described by Wilson et al. (refs 56, 57, and 58, p 288).

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