

SUPPORTING INFORMATION

Calculation of Entropy and Heat Capacity of Organic Compounds in the Gas Phase. Evaluation of a Consistent Method. Applications to Hydrocarbons.

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Ethane. Ethane is the classical example of a molecule for which hindered rotation about a carbon-carbon bond has been calculated and demonstrated. It is the molecule for which Pitzer began development of the theory of hindered rotation.²⁹ Actually, as can be seen from examination of the tables, the hr corrections for ethane are rather small.

Chao, et al⁴³ have made a critical survey of the literature for experimental and calculated entropy and heat capacity of ethane. They provide calculations that start with a rigid rotor-harmonic oscillator model using Shimanouchi³⁴ frequencies; the C(rrho) value for the lowest frequency is replaced with the value for a hindered rotor. Their calculated Cp values can be reproduced exactly (largest discrepancy 0.03) by using Shimanouchi frequencies and using interpolated values of the hindered rotor contribution from the Pitzer-Gwinn tables,^{17,31} using $1/Q_f$ and V/RT calculated from the reported I(red) (reduced moment of inertia) of 2.62×10^{-40} g cm² and a barrier of 2.96 kcal mol⁻¹ for rotation of a methyl group.

Table 3a shows the application of the method described in this study. Col. 2 shows the rrho values of Cp based on 6-31G(d,p) geometries with frequencies scaled by 0.90. Col. 3 shows the hindered rotor correction for rotation about the central bond; these values come from Table 3b. Values in col. 4 are the sums of the values in

cols. 2 and 3; they are Cp values corrected for hindered rotation. The last two rows of col. 4 are the RMS and the average for Cp(exp) - Cp(calc) based on the *experimental* Cp values only. Also shown are Cp values derived from frequencies scaled by 0.91, from MP2/6-31G(d,p) frequencies scaled by 0.95, and from experimental frequencies reported by Shimanouchi. The hr corrections were computed separately from the respective frequencies. For comparison col 7 shows the frequencies reported by Chao, et al. Two features may be specially noted. For ethane the SF 0.90 frequencies reproduce the experimental Cp values slightly better than do the experimental frequencies, and the Cp(rrho) values give almost as low a RMS as do the hr corrected values.

Table 3b shows details of the calculation of the corrections for hindered rotation that have been entered into col. 3 of Table 3a. In all calculations in this study the hindered rotor corrections are applied to the rrho estimates for Cp or S. This differs from the usual prior practice in which frequencies corresponding to methyl libation were simply omitted and replaced directly with the hindered rotor values.

RMS values of differences between *experimental* values minus *calculated* values, shown in the next to last row of the columns of calculated heat capacities, include the biases that arise from a constant error; this bias appears as a non-zero value for the average of the differences. The expected RMS uncertainties for the differences, shown in Table 2a, are $0.22 \text{ cal K}^{-1} \text{ mol}^{-1}$ and in this case happen to be independent of temperature. RMS values for all calculations fall within this uncertainty estimate.

Tables 3c and 3d show calculations of the entropy of ethane. There are three reported experimental values of the entropy. The values at 298.15 and at 355 were derived (eq 1) using unreported experimental Cp data. The expected uncertainty in the calculated entropy is 0.33 and that for a difference between experimental and

calculated S is 0.39 (Table 2b). The RMS values for the differences of experimental and calculated values of entropy in Table 3c lie within this estimate. The RMS for S calculated using experimental frequencies is lower than any of the others. If the hr correction is not used, then the RMS for SF 0.90 frequencies in this rho approximation is 0.29 instead of 0.12.

Table 2 of Vansteenkiste, et al²⁰ shows Cp for ethane calculated by a quantum mechanical treatment of hindered rotation based on B3LYP/6-311G(d,p) frequencies and geometries. Their value is 12.36 at 298.15; the value obtained in this study is 12.64 (Table 3a). There is no experimental Cp value at 298.15. At 500K the Cp values are 18.21²⁰ and 18.60 (this study). There is no experimental value for 500K, but a good interpolated value of 18.67 can be obtained by a parabolic fit of the Dailey and Felsing Cp data.⁶⁷ At 298.15 the values of entropy are 54.73²⁰ and 54.70 (this study). The experimental value reported by Witt and Kemp⁷¹ is 54.85.

Cyclopropane. Heat capacity calculations are shown in Table 4a. The uncertainty of the calculated Cp values is estimated to be 0.20 and the difference between experimental and calculated Cp has an uncertainty of 0.21 (Table 2a). The calculated values of Cp shown for the Shimanouchi frequencies, RMS 0.08, agree exactly with the values published by Dorofeeva, et al.⁵³

Table 4b (SI) shows calculations of the entropy of cyclopropane. There is a single experimental value, at 240.3 K; the calculated value differs from the experimental value by 0.04. The estimated uncertainty of the difference between experimental and calculated entropy is 0.36 (Table 2b).

2-Butyne. This molecule has D3d symmetry(Brauman⁷²) and has free methyl rotors (Kistiakowsky and Rice,⁷³ Yost, et al.⁷⁴) The heat capacity calculations are shown in Tables 7a and 7b (S. I.). The estimated uncertainty of calculated Cp values is 0.21 and of differences between experimental and calculated values is 0.23 (Table 2a). The RMS for Cp(exp) - Cp(calc) using 6-31G(d,p) frequencies scaled by 0.90 is 0.11. For the entropy calculations shown in Tables 7c and 7d (see S.I.) the estimated uncertainty of calculated entropy values is 0.30 and of differences between of experimental and calculated values is 0.36 (Table 2b). For SF 0.90 the RMS is 0.51, within two standard deviations. Yost, et al.⁷⁴ report a calculated entropy of 67.08 at 291 K (close to the value 66.97 in Table 7c); the error of the experimental entropy may be larger than that reported by Yost, et al. (Table 2b.)

Isobutane. Calculations of Cp are shown in Tables 10a and 10b (see S.I.). The estimated uncertainty of the calculated values is 0.23; the experimental uncertainty is estimated by Dailey and Felsing⁶⁷ as 1% or about 0.3; the estimated uncertainty of Cp(exp) - Cp(calc) is therefore 0.38 (Table 2a). The RMS values of Cp(exp) - Cp(calc) shown in Tables 10a range from 0.30 to 0.57.

Differences between the calculated Cp values obtained with the model used in this study and the values reported by Chen, et al.⁴⁴ arise in part because the frequency assignments differ and in part because different methods were used for treating the hindered rotor contributions. Analysis of the magnitude of the differing hr treatments is uncertain because the numerical hr corrections used in the Chen study have not been published. A direct comparison of the effect of frequency assignments can be made, however, by examining the C(vib) contributions of the full sets of frequencies minus those of the three lowest (which are to be replaced by the hr values for the three methyl librations). On average the Chen, et al. frequencies give C(vib) values 0.24 cal

smaller than those given by the 6-31G(d,p) frequencies. Column 6 of Table 10a reports estimates of Cp(rrho) obtained with the Chen, et al. frequencies. Column 7 reports the appropriate hindered rotor correction values calculated as the difference between the C(vib) hr value from the Pitzer and Gwinn tables using the Chen, et al. barrier and reduced moment. The corrected values are in column 8; this calculation is made in exactly the same way as has been done for all other calculations. The numbers in column 8 do not exactly match those calculated by Chen, et al. as reported in column 9.

Tables 10c and 10d (see S.I.) report the calculated entropy values. The estimated uncertainty for the calculated entropy is 0.38, the estimated uncertainty for S(exptl) minus S(calcd) is 0.41 (Table 2b). The RMS for the SF 0.91 and the MP2 frequencies lie within this range; the RMS for the SF 0.90 frequencies is slightly larger, 0.44.

Aston, et al.⁷⁵ provide details of their calculation of the entropy of isobutane, and these permit useful comparisons with the method used in this study. For example, the sums of S(tran) and S(rot) agree within 0.03 and show that the geometries used in the Aston, et al. study correspond closely with the geometries obtained with 6-31G(d,p)//6-31G(d,p). The S(vib) values (omitting those due to methyl group librations) differ by 0.2, the Aston, et al. values being smaller, a result due in part to use by the authors of *ad hoc* values for some of the frequencies.

Pentane. Calculations of heat capacity are shown in Tables 11a and 11b. Pentane exists as a mixture of seven distinct conformers t t , t g+, t g-, g+g+, g-g-, and g+g-(2 enantiomers) although there are only four distinct energy levels; t g+ and g+t are identical, but the total concentration is doubled. The Cp(hr corrected) values are

derived from relative energies of conformers of 0, 0.61, 0.96, and 2.98 based on MP2/6-311+G(2df,2p)//6-31G(d,p) energies. At 298.15 the relative fractions (based on free energies) are respectively 0.25, 0.67, 0.07 and 0.005; at 500 the relative fractions are 0.18, 0.70, 0.09, and 0.03. One set of Salam and Deleuze⁴⁸ relative energies are 0.000, 0.621, 1.065, 2.917. At 298.15 the relative fractions are 0.26, 0.67, 0.06, and 0.006 and at 500 0.18, 0.70, 0.08, and 0.03. The computed Cp values are nearly the same for either set of relative energies.

The expected uncertainties are 0.23 for the calculated Cp values and 0.07 for the experimental values. There is a precision of 0.07 for the experimental values of Hossenlopp and Scott⁷⁶ based on deviations from a parabolic fit. Cp data for pentane have also been reported by Messerly and Kennedy⁷⁷ but their values differ by more than 2 cal from those derived from the parabolic fit. The expected uncertainty of the difference is 0.24 (Table 2a). RMS values are 0.14 for the conformer energies based on MP2/6-311+G(2df,2p)/6-31G(d,p) and 0.15 for the Salam energies. The SF 0.91 frequencies give RMS 0.33.

Table 11b shows calculation of hindered rotor corrections for C and Table 11d for S. It should be noted that the lowest three frequencies of the t t conformer do not correspond to methyl group librations; the lowest at 98 cm⁻¹ involves the expected librations about the C-C bonds; 100 cm⁻¹ corresponds to wagging of the central CH₂ group, and 173 corresponds to bending about all C-C-C bonds. It is the 230 cm⁻¹ and 240 cm⁻¹ frequencies that correspond to methyl group libration, and it is the C and S values of these two frequencies that are indirectly to be replaced through application of the corrections in Tables 11b for C and 11d for S for the hindered rotors. The vibrational pattern for the predominant g t conformer is somewhat different. The lowest two frequencies at 88 and 143 cm⁻¹ correspond to complex skeletal motions. The third at 206 corresponds mostly to libration of the

gauche methyl group while the fourth at 235 corresponds mostly to libration of the other methyl group. It turns out that the substitution of C(hind rotor) values and S(hind rotor) values for these two frequencies for the g t conformer gives the same hindered rotor corrections as reported in the tables. Within the approximations inherent in the method of using the same corrections for all methyl groups and basing them on the frequencies that correspond to methyl group librations, the procedure is consistent whether applied to the t t conformer or the g t conformer.

Calculation of the entropy of pentane is shown in Table 11c. There is a single experimental value having a stated uncertainty of 0.2; the estimated uncertainty for the calculated entropy is 0.36 and that of the difference between experimental and calculated S is 0.41 (Table 2b). The RMS reported in Table 11c is within the two standard deviation bracket of 0.82 for the SF 0.90 frequencies but otherwise outside these limits.

Vansteenkiste, et al²⁰ show tables of Cp and S for pentane calculated by a full analysis of rotation about the several hindered rotation bonds based on B3LYP/6-311G(d,p) frequencies and geometries. Cp at 298.15 as reported in their Table 5 is 29.39. In this study based on 6-31G(d,p) with S.F 0.91 Cp is 28.25. Experimental Cp (Hossenlopp and Scott⁷⁶) is 28.70. In Table 5²⁰ S is 83.85; in this study (Tables 11c) S is 84.19. Experimental S is 83.13 (Messerly and Kennedy⁷⁷) At 500K S is 102.27²⁰ and 102.35 (this study). There is no experimental value for S at 500K. It appears that S calculated by treating the skeletal librations as harmonic oscillators is 0.34 cal higher than that obtained with hr treatment including all rotors; but the latter value is still 0.72 cal greater than the published experimental value.

2-Methylbutane. Heat capacity calculations are shown in Tables 12a and 12b (see S.I.). The estimated uncertainty in calculated Cp is 0.30 and of the difference between experimental and calculated Cp is 0.33 (Table 2a). The RMS values for SF 0.91 and for MP2 fall within this range, while RMS for the SF 0.90 values fall within twice the range.

Entropy calculations are shown in Tables 12c and 12d (See S.I.). The estimated uncertainty of the calculated entropy is 0.40; the uncertainty of the experimental data is not stated, but it is probably greater than 0.2. The estimated uncertainty of $S(\text{exp}) - S(\text{calc})$ is then 0.44. The RMS values for SF 0.90, 0.91, and MP2 frequencies fall within this range.

Based on energies obtained with MP2/6-311+G(2df,2p)//6-31G(d,p) the energy of the Cs conformer is 0.79 kcal mol⁻¹ higher than that of the C1 conformer. Scott, et al.⁷⁸ state that the difference is several thousand calories. In view of the gross uncertainty in the parameters used for the Scott, et al. calculations, it is interesting that the authors were able to match experimental and calculated data with uncertainties of less than 0.1 cal.

Neopentane. Heat capacity calculations are shown in Tables 13a and 13b (both in S.I.). The Cp data of Hossenlopp and Scott^{76,4778} are reproduced by the equation $13.2584 + 0.06569T - 3.59956 \times 10^5/T^2$ to a precision of 0.06. The uncertainty in calculated Cp values is estimated to be 0.24 and of differences between experimental and calculated values is 0.25 (Table 2a). The RMS estimate of the differences between experimental and calculated Cp values derived with 6-31G(d,p) frequencies scaled by 0.90 is outside of the two standard deviation range, the others are within the two standard deviation range.

Entropy calculations for neopentane are reported in Tables 13c and 13d (both in S.I.). The estimated uncertainty of calculated values of S is 0.40 and of differences between experimental and calculated S it is estimated to be 0.72 (Table 2a); there are two experimental values that differ by 0.47. The RMS of the S_{exp} - $S_{(calc)}$ values are within the estimated uncertainty. The calculated entropy of Aston and Messerly⁷⁹ uses incorrect values for $S_{(tran)} + S_{(rot)}$ and an incorrect value of $S_{(vib)}$ for the carbon skeleton, which values are copied by Enokido, et al.⁸⁰

2,2-Dimethylbutane. Heat capacity calculations are reported in Tables 15a and 15b (see S.I.). The combined literature Cp data of Pitzer⁸¹ and Waddington and Douslin⁸² are represented by the equation $11.80094 + 0.08393T - 2.66432 \times 10^5/T^2$ with a standard deviation of 0.18. The estimated uncertainty of calculated Cp values is 0.24 and of the difference of experimental and calculated Cp is 0.32 (Table 2a). The RMS uncertainty of Cp values calculated with 6-31G(d,p) SF 0.90 frequencies is due to a systematically too high calculated Cp value at each temperature. If the Kilpatrick and Pitzer approximate frequencies are used instead of the 6-31G(d,p) frequencies, the resulting RMS uncertainty is 0.08 instead; the Kilpatrick and Pitzer frequencies are slightly higher than the 6-31G(d,p) frequencies. In both calculations the skeletal torsion at 78 cm^{-1} (1.96) was treated as a harmonic oscillator; this approximation should cause little uncertainty in the Cp estimates since the related methyl hindered rotation values for C are close to $2\text{ cal K}^{-1}\text{ mol}^{-1}$.

Entropy calculations for 2,2-dimethylbutane are shown in Tables 15c and 15d. Kilpatrick and Pitzer⁴⁵ estimate the uncertainty in the experimental entropy as 0.2. The estimated uncertainty of the calculated entropy

is 0.40. The estimated uncertainty for the difference $S(\text{exptl}) - S(\text{calcd})$ is, therefore, 0.45. However, there is actually considerable uncertainty in the experimental entropy; Scott⁵ reports a value of 86.62 ± 0.1 , which differs from the Kilpatrick and Pitzer value by 0.9 cal.

In their Table XII Kilpatrick and Pitzer⁴⁵ provide details of an entropy calculation at 298.15. Having this information available, it was of interest to ascertain the origins of the differences between the calculated $S(298.15)$ 85.72 of Kilpatrick and Pitzer and the $S(298.15)$ 86.37 obtained with 6-31G(d,p) frequencies scaled by 0.90. The comparisons are summarized in Table 15e. The value shown for the methyl hindered rotors in columns 4 and 5 is four times the value shown in Table 15d. In making the calculation the frequency at 245 cm^{-1} is not replaced; this frequency comes from angle bending only. For MP2/6-31G(d,p) the frequencies for methyl libration are 206, 249, 275, and 288; the omitted frequency 252 corresponding entirely to bending vibrations.

The second column of Table 15e summarizes the K and P values given in Table XII of their paper. The third column shows values recalculated from their published frequencies and published moment of inertia and barrier; these recalculated values agree with the Table XII values, the values in columns 2 and 3 are nearly identical. The values in column 4 are based on 6-31G(d,p) geometry and frequencies scaled by 0.90, those in column 5 are based on MP2/-31G(d,p) frequencies scaled by 0.95. The $S(\text{tran})+S(\text{rot})$ in columns 4 and 5 is higher by 0.1 (15%) than the KP value because the formal geometry they used gives a lower overall moment of inertia, thus giving a lower value of $S(\text{rot})$. The hindered rotor value for the C-C-C-C torsion of KP is 0.26 (40%) less than the rrho value used for the fourth column. The value for 4 CH₃ hindered rotors in columns 3 and 4 is based on the I(red) derived from use of the Herzberg equations on the calculated 6-31G(d,p) geometries, while the value of V is derived from the MP2/6-311+G(2df,2p)//6-31G(d,p) energies. The value for the hindered methyl rotors is

0.23 (35%) less than the KP estimate which used an adjusted value of V to make the calculated entropy agree with experiment. And finally the S(vib) of columns 4 and 5 come from the frequencies of the indicated basis set, and KP S(vib) is 10% less than the value in column 4. Thus the differences of the KP values and those of the present study arise as a summation of several small differences in each term.

2,3-Dimethylbutane. Calculations of heat capacity are shown in Tables 16a and 16b. There are two conformers having nearly the same energy in a 1:2 ratio: $E(Cs) - E(C2h) = 0.12 \text{ kcal mol}^{-1}$ based on MP2/6-311+G(2df,2p)//6-31G(d,p) energies. As a result the dXE_g/dT term is very small at all temperatures.

Scott, et al.⁷⁸ report frequencies and the overall moment of inertia I(xyz), and I(red) for methyl groups. The last columns in Tables 16a and in 16c show recalculations based on their frequencies, moments and energies.

The uncertainty of the experimental Cp values is 0.2 based on fitting the experimental Cp values: the equation is $Cp=19.26052 + 0.069686T - 5.854601E5/T^2$. The estimated uncertainty of calculated values is 0.24 and of the differences experimental minus calculated is 0.32. The recalculated Cp values based on the Scott, et al. frequencies fall within the expected uncertainty, and the other calculations based on Gaussian frequencies give Cp values that fall within a range of two standard deviations. (All calculations, including those in he Scott column treat the lowest frequency as a harmonic oscillator.)

Calculations of entropy are shown in Tables 16c and 16d. The reported uncertainty of the experimental values is 0.2.⁸³ The estimate uncertainty of the calculations is 0.41. The estimated uncertainty of $S(\text{calcd}) - S(\text{exptl})$ is therefore 0.46. The values obtained with MP2/6-31G(d,p) frequencies and the recalculated Scott

entropies are somewhat out of the 0.46 range. The calculated entropy values based on SF 0.91 lie within the two standard deviation range, the value of W obtained with SF 0.90 is outside of the two standard deviation range.

Toluene. Calculations of heat capacity are shown in Table 17a. The experimental data were fitted to the equation of footnote a (eq 6-13 of Lewis, et al.¹⁷). The smoothed Cp values are listed in column 5; these have a std. dev. of 0.32, which in this case is a measure of accuracy. Calculations have an expected uncertainty of 0.21 while differences experimental minus calculated Cp values have an uncertainty of 0.38. The RMS of the calculated values fall within a range of two standard deviations. As reported in the several references the methyl group behaves as a free rotor. Table 5 of Frankiss and Green¹⁹ reports a detailed analysis of the calculation of Cp and S for toluene. The values for 427.20 in FG Table 5 and the values in Table 23a are in close agreement. Note that both sets of calculations use a symmetry number of 2 for S(overallrot) and a symmetry number of 3 for free rotation of the methyl group.

Calculations of entropy are reported in Tables 17b and 17c. The uncertainty of the calculated entropy is 0.30 and of the RMS of the observed minus calculated values is 0.34. All calculated values fall within this range. The values in FG¹⁹ Table 5 and in Table 17b are in close agreement for 298.15.

Methylcyclohexane. There are four conformers, eq chair, ax chair, eq twist boat, and axial twist boat with respective energies 0, 1.77, 6.41, and 8.15 kcal mol⁻¹. Heat capacity calculations are shown in Tables 18a and 18b. The uncertainty of the experimental values is 0.4 to 0.6;⁶² based on the fit of the four experimental values to the 3-term interpolation equation the precision is 0.2. The estimated uncertainty of the calculated Cp values is

0.22 and of experimental minus calculated values is 0.54. The SF 90 Cp is within the range while the SF 0.91 value is within twice the range

Calculations of the entropy are summarized in Tables 18c and 18d. The uncertainty of the experimental value of the entropy is not stated but is of the order of 0.3 or greater. The uncertainty of the calculated S is 0.33 and of experimental minus calculated is 0.45. The SF 0.91 S is within the range while the SF0.91 value is within twice the range.

Trimethylbutane. Calculations of heat capacity are shown in Tables 19a and 19b. The experimental Cp values shown in Table 19a (excluding the calculated values at 298.15, 500, and 1000) are reproduced by the equation $Cp = 16.53416 + 0.09343437T - 4.90209E-5/T^2$ with a std dev of 0.039 or with the equation $Cp = -3.408 + 0.16188T - 6.55619E-5T^2$ with a std dev of 0.024. The data are not reproduced by the equation $Cp = 1.800 + 0.15320T - 5.3907E-5T^2$ reported by Waddington, et al.⁸⁴ These values represent precision; accuracy is probably similar to results with other compounds, about 0.2. The uncertainty of calculations is 0.40; the uncertainty of $Cp(exp) - Cp(calc)$ is therefore 0.42. The observed differences are of the order of 1 cal or more.

Calculations of entropy are shown in Table 19c. Again the difference between experimental values and calculated values is large. To compensate for the exceptional value found for the lowest vibrational frequency it became necessary for this one compound to replace that frequency with an average value. The number selected for the scaled frequency was 100 cm^{-1} .

Scott and Waddington⁸⁵ list frequencies and moments of inertia for trimethylbutane. Their overall moment of inertia calculated from a model using standard bonds, angles and torsions is about 92% as large as the moment based on 6-31G(d,p) geometries, but the S(external rot) differs by only about 0.05.

I(red) based on 6-31G(d,p) geometry and using the Herzberg equation is 5.07E-40 g cm² and V based on MP2/6-311+G(2df,2p)//6-31G(d,p) energies is 3.41 Kcal mol⁻¹. Scott and Waddington report I(red) 5.225 and V 4.20. Since the value for S(hr) occurs five times, there is a considerable difference in the calculated values of Cp and of S based on the two different estimates of I(red) and V. At 298.15 the 5 hindered rotors amount to 10.06 (SW) and 10.54 (DFD) for C(hind rotor) and 9.14 (SW) and 10.28 (DFD) for S(hind rotor).

Excluding the lowest 6 frequencies (1 libration about central C-C bond and the 5 involving methyl group librations) the Scott and Waddington frequencies give for C(vib) at 298.15 19.08 and S(vib) 10.89. The corresponding values for frequencies derived with 6-31G(d,p) SF 0.90 are C(vib) 20.28 and S(vib) 10.75.

Recalculations based on the Scott and Waddington frequencies and moments are shown in Tables 19a and 19c. For all calculations the torsion about the central C-C bond was treated as a harmonic oscillator having a frequency of 100 cm⁻¹ scaled. For Cp in Table 19a, the difference in the hr correction of 0.49 together with the difference of 1.17 owing to differences of C(vib) account for the different calculated values of Cp. The differences in S(hind rotor) and S(vib) likewise account for the difference in the entropy calculations.

Tetramethylbutane. Calculations for the heat capacity of tetramethylbutane are shown in Tables 20a and 20b. There appear to be no experimental values for comparison. Calculations of the entropy are shown in Tables

20c and 20d. The expected uncertainty for S(exp)-S(calc) is 0.60 and the observed differences fall within this range for SF 0.90 and 0.91 and within twice the range for MP2.

Table 3a. Ethane. Heat capacity

Temp	C(rrho)	C	Cp (hr	Cp(lit)	Cp (hr	Cp ^c	Cp (hr	Cp (hr
						corrtd) ^b		
						Chao	corrtd) ^a	corrtd)
				SF 0.90	Shiman.	values	SF 0.91	MP2 ^g
298.15	12.35	0.29	12.64	12.58 ^d	12.51	12.54	12.54	12.24
359.75	14.25	0.28	14.53	14.43 ^e	14.40	14.40	14.40	14.37
373.60	14.69	0.26	14.95	14.83 ^f	14.83	14.83	14.83	14.80
500.00	18.68	0.08	18.76	18.67 ^e	18.64	18.64	18.60	18.57
561.65	20.49	-0.04	20.45	20.62 ^e	20.33	20.33	20.28	20.24
603.25	21.64	-0.09	21.55	21.62 ^e	21.42	21.41	21.37	21.34
1000.00	30.02	-0.54	29.48	29.33 ^d	29.32	29.30	29.31	29.26
RMS ^h			0.12 ⁱ		0.16	0.16	0.20 ^j	0.22
Avg ^h			-0.01		0.11	0.11	0.14	0.17

^aUsing 6-31G(d,p)//6-31G(d,p) geometry and frequencies. SF is scale factor; C(rrho) is rigid rotor-harmonic oscillator value based on *all* frequencies for SF 0.90, hr corr from Table 3b; hr corrections and C(rrho) values for Shimanouchi, Chao, SF 0.91, and MP2 are based on the respective sets of frequencies. ^bBased on Shimanouchi frequencies.³⁴ ^cCalcd values as reported by Chao, et al.⁴³ ^dStull, et al. calcd.¹⁶ ^eDailey and Felsing.⁶⁷ (Value at 500K interpolated) ^fEucken and Parts as quoted by Chao, et al. ^gMP2/6-31G(d,p) geom and freqs SF 0.95/0.923 ^hOmitting non-experimental Cp values for T=298.15, 500, 1000. ⁱFor rrho RMS=0.12, Avg=0.09. ^jFor rrho RMS= 0.26, avg=0.24.

Table 3b Ethane. Calc of hindered rotor C corr

temp	C(vib) ^a	C(hind)	C(hr)
	295 cm ⁻¹	rotor) ^b	corrn) ^c
298.15	1.68	1.97	0.29
359.75	1.77	2.05	0.28
373.60	1.79	2.05	0.26
500.00	1.87	1.95	0.08
561.65	1.90	1.86	-0.04
603.25	1.91	1.82	-0.09
1000.00	1.96	1.42	-0.54

^aC(vib) at lowest 6-31G(d,p) freq scaled by 0.90.

^bCalculated from I(red) 2.57E-40 g cm² and V

2.96 kcal mol⁻¹ (i.e., based on MP2/6-

311+G(2df,2p)// 6-31G(d,p) energies). C values

for a hindered rotor are obtained from Pitzer

tables.^{17,31} Chao, et al.⁴³ used 2.62 g cm² V 2.96

kcal mol⁻¹, which yields the same C(vib) hr

corrections. ^cFor 6-31G(d,p) SF 0.90 frequencies.

Appropriate alternative hr corrections were

calculated for each set of frequencies.

Table 3c Ethane. Entropy

Temp	S(tran) ^a	S(rot) ^a	S(vib) ^a	S(rrho) ^a	S	S(hr	S(lit)	S ^b (hr	S ^c	S(hr	S(hr
	SF 0.90				(hr corr)	corrtd)		corrtd)	Chao	corrtd)	corrtd)
					SF 0.90		Shiman.	values	SF 0.91	MP2 ^g	
184.10	33.74	14.82	0.79	49.35	0.06	49.41	49.54 ^d	49.49		49.40	49.41
298.15	36.13	16.26	2.16	54.55	0.18	54.73	54.85 ^d	54.77	54.76	54.70	54.69
355.00	37.00	16.78	3.07	56.85	0.24	57.09	57.20 ^e	57.11		57.04	57.02
500.00	38.70	17.80	5.92	62.42	0.30	62.72	62.81 ^f	62.69	62.70	62.63	62.62

1000.00	42.14	19.86	17.25	79.26	0.08	79.33	79.39 ^f	79.21	79.26	79.11	79.07
RMS ^h						0.12 ⁱ		0.08 ^j		0.15	0.16
Avg ^h						0.12		0.07		0.18	0.16

^aUsing 6-31G(d,p)//6-31G(d,p) geometry and frequencies, SF 0.90. ^bBased on Shimanouchi frequencies.³⁴ using S(vib) hindered rotor correction values of Table 3d ^cAs calculated by Chao, et al.⁴³ ^dWitt and Kemp⁷¹ ^eKemp and Pitzer⁸⁶ (reported uncertainty is 0.2.) ^fStull, et al. calc.¹⁶ ^gMP2/6-31G(d,p) freqs SF 0.95, 0.923 ^hOmitting non-experimental values for T=500, 1000. ⁱFor rrho RMS=0.29, Avg=0.28. ^jFor rrho RMS=0.15, Avg=0.13

Table 3d Ethane. Hindered Rotor S Correction

Temp	S(vib) ^a	S(hind)	S(hr)
	295 cm ⁻¹	rotor) ^b	corrn) ^c
184.10	0.72	0.78	0.06
298.15	1.45	1.63	0.18
355.00	1.75	1.99	0.24
500.00	2.37	2.67	0.30
1000.00	3.71	3.79	0.08

^aS(vib) at lowest 6-31G(d,p) freq. ^bEntropy for

hindered rotor calculated from I(red) 2.57E-40 g cm²

and V 2.96 kcal mol⁻¹ derived from MP2/6-

311+G(2df,2p)//6-31G(d,p) energies. ^cFor 6-

31G(d,p) SF 0.90 frequencies. Appropriate hr

corrections were calculated for each set of

frequencies.

Table 4a. Cyclopropane. Heat Capacity.

Temp	Cp(rrho) ^a	Cp(lit)	Cp(rrho) ^b	Cp(rrho) ^a	Cp(rrho)
	SF 0.90		Shiman.	SF 0.91	MP2 ^f
272.15	12.09	12.10 ^c	12.08	11.96	0.01
291.10	12.96	13.03 ^d	12.96	12.81	0.07
298.15	13.29	13.28 ^e	13.29	13.14	-0.01
300.48	13.40	13.50 ^c	13.40	13.24	0.10
313.90	14.04	14.13 ^d	14.05	13.88	0.09
333.70	15.00	15.10 ^c	15.01	14.82	0.10

368.46	16.67	16.77 ^c	16.70	16.47	0.10
500.00	22.39	22.43 ^e	22.44	22.18	0.04
1000.00	35.28	35.18 ^e	35.18	35.09	-0.10
RMS ^f	0.08		0.08	0.22	0.15
Avg ^f	0.07		-0.02	0.15	0.13

^a6-31G(d,p) geom freqs. SF 0.90 ^bShimanouchi freqs.³⁵ ^cKistiakowski

and Rice⁶³ ^dKistiakowski, et al.⁴⁹ ^eDorofeeva, et al., calcd.⁵³ ^fMP2/6-

31G(d,p) geom and freqs ^fOmitting non-experimental Cp values for

T=500, 1000

Table 4b. Cyclopropane. Entropy.

Temp	S(tran)	S(rot)	S(vib)	S(rrho) ^a	S(lit)	S(rrho)	S(rrho)	S(rrho)	S(rrho)
	SF 0.90	SF 0.90		Dorofeeva ^b	Shiman. ^c	SF 0.91	MP2 ^f		
240.30	36.06	17.42	0.65	54.13	54.17 ^d		54.11	54.10	54.12
298.15	37.13	18.07	1.50	56.70	56.75 ^e	56.73	56.68	56.65	56.75
500.00	39.70	19.61	6.50	65.81	65.95 ^e	65.85	65.80	65.65	65.69
1000.00	43.15	21.67	21.08	85.89	86.15 ^e	85.92	85.88	85.59	85.67
One experimental value at 240.30				0.04			0.06	0.07	0.05

^a6-31G(d,p) geom and freqs. ^bCalculated by Dorofeeva,et al.⁵³ ^cShimanouchi³⁵ ^dRuehrwein and Powell, exp⁸⁷ ^eStull, et al. calcd. ¹⁶ ^fMP2/6-31G(d,p) freqs and geometry

Table 7a. 2-Butyne Heat Capacity

Temp	Cp(rrho) SF 0.90	C(fr corrn) ^a	Cp(fr corretd) SF 0.90	Cp(lit)	Cp(fr corretd) SF 0.91
298.15	19.55	-0.99	18.56	18.63 ^a	18.43
336.07	21.05	-0.99	20.06	20.21 ^c	19.91
369.46	22.39	-0.99	21.40	21.43 ^c	21.24
500.00	27.38	-0.99	26.39	26.38 ^b	26.19
1000.00	40.41	-0.99	39.42	39.33 ^b	39.21 ^f
RMS ^e			0.11		0.25 ^f
Avg			0.09		0.25

6-31G(d,p) freqs. and MP2/6-31G(d,p) freqs. ^aFree rotor

correction; in the limit C(vib) is R and C(fr) is 0.5R; 2-butyne

has D3d symmetry (Brauman⁷²). Only one Me group is

included as free rotor; as in ethane the other rotor is the

reference ^bStull, et al.¹⁶ ¹⁰⁵² ^cKistiakowsky and Rice⁷³

^dMP2/6-31G(d,p) geom and freqs SF 0.95, 0.923 ^eOmitting

non-experimental Cp values at 298, 500, 1000. ^fRMS for

rrho=0.60.

Table 7b. 2-Butyne. Free Rotor

Corrections for Me

Temp	C(vib)	C(free	C(fr
	15 cm ⁻¹	rotor)	corrn)
298.15	1.986	0.994	-0.992
336.07	1.986	0.994	-0.992

369.46	1.987	0.994	-0.993
500.00	1.987	0.994	-0.993
1000.00	1.987	0.994	-0.993

6-31G(d,p) frequencies; I(red) 2.58E-40 g

cm² V 0.01kcal mol⁻¹

Table 7c. 2-Butyne Entropy

Temp	S(tran)	S(rot)	S(vib)	S(rrho)	S(fr	S(fr	S(lit)	S(fr
					corr)	corrctd)	corrctd)	SF 0.90
								SF 0.91
291.00	37.76	19.73	13.74	71.24	-4.27	66.97	67.48 ^a	66.94
298.15	37.88	19.81	14.02	71.71	-4.29	67.42	67.93 ^a	67.38
500.00	40.45	21.35	21.90	83.70	-4.81	78.89	79.21 ^b	78.78
1000.00	43.89	23.41	39.87	107.18	-5.55	101.63	101.94 ^b	101.35
RMS ^c						0.51		0.55
Avg ^c						0.51		0.55

6-31G(d,p) frequencies Symmetry is D3d Brauman⁷² (sigma 6) ^aYost, et al.⁷⁴ ^bStull, et al¹⁶

^cOmitting non-experimental values at 500, 1000

Table 7d. 2-Butyne Free Rotor S

Corrections for Me

Temp	S	S	S (fr
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15 cm^{-1} free rotor^a corr)

291.00	7.12	2.85	-4.27
298.15	7.17	2.88	-4.29
500.00	8.20	3.39	-4.81
1000.00	9.58	4.03	-5.55

^aSee footnotes Table 7b.

Table 8a. Cyclobutane. Heat Capacity.

Temp	Cp(rrho) ^a	Cp(lit)	Cp(rrho) ^b	Cp(rrho) ^c	Cp(rrho) ^a	Cp(rrho)
	SF 0.90		Shiman.	Dorofeeva	SF 0.91	MP2 ^e
285.67	16.34	16.46 ^d	16.23		16.14	16.52
298.15	17.13	17.26 ^d	17.02	16.87	16.92	17.31
500.00	29.71	29.86 ^d	29.86	29.17	29.41	29.38
1000.00	48.04	47.96 ^d	47.84	47.10	47.77	47.87

No experimental values available

^a6-31G(d,p) freqs.; based on sum of C_{vib} for all frequencies with no

correction for ring bending. ^bShimanouchi freqs.³⁴ ^cDorofeeva calcd.⁵³

^dRathjens, et al. calcd.⁵⁶ ^eMP2/6-31G(d,p) geom and freq, SF 0.95,0,923

Table 8b. Cyclobutane. Entropy.

Temp	S(tran)	S(rot)	S(vib)	S(rrho) ^a	S lit	S(rrho) ^b	S ^c	S(rrho)	S(rrho)
				SF 0.90		Shiman.	Dorofeeva	SF 0.91	MP2 ^d

285.67	37.78	20.70	4.04	62.52	62.72 ^d	62.35		62.43	63.26
298.15	37.99	20.83	4.42	63.23	63.43 ^e	63.43	63.19	63.13	63.98
500.00	40.56	22.37	12.23	75.16	75.42 ^e	75.42	74.90	74.92	75.99
1000.00	44.00	24.43	33.81	102.24	105.51 ^e	102.51	101.52	101.80	103.06
Only one experimental value				0.20		0.17		0.29	0.54

^a6-31G(d,p) freqs SF 0.90; no correction made for ring bending. ^bShimanouchi freqs.³⁴ ^cDorofeeva calcd.⁵³

^dRathjens, and Gwinn, exptl.⁵⁵ ^eRathjens, et al. calcd.⁵⁶

Table 9b. Butane. Hindered Rotor Correction for Cp

temp	C(vib) ^a	C(vib) ^a	C(hind	C(hr
	217 cm ⁻¹	250 cm ⁻¹	rotor) ^b	corrn)
298.15	1.82	1.76	2.12	0.65
344.90	1.86	1.82	2.16	0.65
387.50	1.88	1.85	2.16	0.59
500.00	1.92	1.90	2.04	0.26
521.00	1.93	1.91	2.02	0.20
692.60	1.95	1.94	1.77	-0.36
1000.00	1.97	1.97	1.47	-1.01

^aC(vib) for lowest second and third freqs. for anti (C2h)

conformer 6-31(d,p) SF 0.90 (Lowest freq. 114 cm⁻¹

corresponds to libration about C-C bond). ^bCalculated

using I(red) 4.45E-40 g cm² and V 3.11 kcal mol⁻¹

based on MP2/6-311+G(2df,2p)//6-31G(d,p) energies

for eclipsed Me. Chen, et al.^{Chen, 1075 #1525} used 4.74E-

40 and 3.30.

Table 9d. Butane. Hindered Rotor S Correction (anti)

Temp	S(vib)	S(vib)	S(hind	S(hr
	217 cm ⁻¹	250 cm ⁻¹	rotor) ^b	corrn)
272.66	1.82	1.57	1.86	0.33
298.15	1.98	1.73	2.06	0.40
500.00	2.95	2.68	3.13	0.62
1000.00	4.31	4.03	4.13	-0.07

^aS(vib) for lowest second and third 6-31G(d,p) freqs SF

0.90 for trans conformer. Lowest freq is 114 cm⁻¹ and

corresponds to libration about C-C bond. ^bCalculated

using I(red) 4.45E-40 g cm² and V 3.11 kcal mol⁻¹.

Table 9e. Butane. Effect on Cp and S of Value Used for

E(gauche)-E(anti)

E(g)-E(a)	S(rrho)		Cp(rrho)	
kcal mol ⁻¹	298.16	500	298.15	500

6-31G(d,p) SF 0.90 frequencies

0.56	74.20	88.87	22.58	35.09
0.63 ^a	74.15	88.85	22.67	35.17
0.68	74.10	88.84	22.74	35.21
0.76	74.03	88.81	22.85	35.27

Shimanouchi frequencies

0.56	74.50	89.06	22.35	34.93
0.63 ^a	74.44	89.04	22.44	34.99
0.68	74.40	89.02	22.52	35.03
0.76	74.32	88.99	22.62	35.09

^aFrom MP2/6-311+G(2df,2p)//6-31G(d,p) energies, used
in this study

Table 10a . Isobutane. Heat Capacity

Temp	^a corrn) ^b	Cp(rrho)		Cp(rrho) ^c Chen	Cp(rrho) ^d Chen	Cp(hr) corrctd) ^e	Cp(Chen) values) ^f	Cp(hr) corrctd)	Cp(hr) corrctd)				
		C(hr)	Cp(hr)										
Chen													
SF 0.90		SF 0.90		freqs		freqs		Chen freqs					
SF 0.91		SF 0.91		freqs		Chen freqs		SF 0.91					
MP2 ^k													
243.15	19.45	0.659	20.10	19.67 ^g	19.12	0.63	19.75	19.65	19.97				
273.15	21.21	0.805	22.01	21.50 ^g	20.89	0.76	21.65	21.49	21.85				

298.15	22.75	0.880	23.63	23.26 ^h	22.44	0.86	23.30	23.10	23.43	23.44
313.15	23.69	0.913	24.60	24.08 ^g	23.39	0.90	24.29	24.08	24.39	24.39
347.60	25.90	0.969	26.87	26.21 ⁱ	25.61	0.97	26.58	26.35	26.63	26.64
353.15	26.25	0.977	27.23	26.71 ^g	25.97	0.98	26.95	26.71	27.00	27.00
500.00	35.34	0.706	36.05	35.61 ^h	35.11	0.84	35.95	35.67	35.74	35.77
520.90	36.53	0.640	37.17	36.55 ⁱ	36.29	0.77	37.06	36.80	36.86	36.90
692.70	45.05	-0.100	44.95	44.26 ⁱ	44.81	0.10	44.91	44.71	44.62	44.67
1000.0										
0	55.94	-1.159	54.78	52.40 ^j	55.68	-0.97	54.71	54.60	54.47	54.50
RMS ^k			0.57 ^l				0.36	0.20	0.30	0.32
Avg ^k			-0.55 ^l				-0.29	-0.08	-0.29	-0.31

^aSummed over all 6-31G(d,p) frequencies. ^bFrom Table 10b using I(red) 4.96E-40 g cm² and V=3.60 kcal mol⁻¹ from MP2/6-311+G(2df,2p)//6-31G(d,p) energies. ^cDerived from frequencies of Chen et al.⁴⁴ ^dC hind rotor corrections based on Chen et al. values: I(red) 5.1364 g cm² and V=3.85. C(vib) values come from Chen et al. frequencies 220 and 256 cm⁻¹. ^eCp derived from Chen, et al., frequencies by the procedure used in this study. Sum of Cp(rrho) from column 6 and hindered rotor correction column 7. ^fValues as reported by Chen, et al.⁴⁴ ^gWacker, et al.;⁸⁸ Scott;⁵ Chen, et al.⁴⁴ ^hLinear interpolation of Dailey and Felsing data. ⁱDailey and Felsing.⁶⁷ ^jStull, et al.¹⁶ ^kOmit non-experimental Cp value at 1000. ^lFor rrho RMS=0.42 and Avg=0.19.

Table10b. Isobutane. Hindered Rotor Corrections for Cp

Temp	C(vib) ^a	C(vib) ^a	C(vib) ^a	C(hind)	C (hr)
	200 cm ⁻¹	249 cm ⁻¹	249 cm ⁻¹	rotor) ^b	corrn) ^c
243.15	1.770	1.664	1.664	1.919	0.659
273.15	1.812	1.726	1.726	2.023	0.805
298.15	1.839	1.765	1.765	2.083	0.880
313.15	1.852	1.784	1.784	2.111	0.913
347.60	1.877	1.820	1.820	2.162	0.969
353.15	1.880	1.825	1.825	2.169	0.977
500.00	1.933	1.904	1.904	2.149	0.706
520.90	1.937	1.911	1.911	2.133	0.640
692.70	1.959	1.943	1.943	1.915	-0.100
1000.00	1.973	1.966	1.966	1.582	-1.159

^aC(vib) values for lowest three frequencies. ^bC contribution of hindered Me rotor based on I(red) 4.96E-40 g cm² and V 3.60 kcal mol⁻¹ based on MP2/6-311+G(2df,2p) energies of eclipsed and staggered Me rotor. ^c3*C(hin rot) - Cv200 - 2*Cv249. ^dChen, et al. ^eChen, 1975 #1325 used I(red) 5.20E-40 g cm² and V 3.85 kcal mol⁻¹

Table10c. Isobutane. Entropy

Temp	S(tran) ^a	S(rot) ^a	S(vib) ^b	S(rrho) ^c	S (hr)	S(hr	S lit	S Chen ^g	S(hr	S (hr
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SF 0.90						corr ⁿ ^d	corrctd)	corrctd)		
						SF 0.90		SF 0.91	MP2 ⁱ	
261.44	37.44	22.00	8.24	67.88	0.151	68.03	67.54 ^e	67.72	67.75	67.74
298.15	38.10	22.39	10.03	70.52	0.285	70.81	70.43 ^e	70.60	70.71	70.69
500.00	40.66	23.93	20.71	85.31	0.600	85.91	85.45 ^f	85.61	85.66	86.66
1000.00	44.11	25.99	46.86	116.96	-0.237	116.72	116.69 ^f	116.96	116.27	116.27
RMS ^j						0.44		0.18	0.25	0.22
Avg ⁱ						-0.43		0.18	-0.24	-0.22

^aAston, et al.⁷⁵ values for S(tran)+S(rot) agree within 0.03. ^bAston S(vib) (omitting 3 methyl librations) for 261.44 and 298.15 are 0.2 less than 6-31G(d,p) S(vib). ^cS(vib) from 6-31G(d,p) frequencies, S.F. 0.90 ^dS hr correction Table 10d. Chen, et al.⁴⁴ used 5.136E-40 g cm² and V 3.85 kcal mol⁻¹. ^eAston, et al.⁷⁵ ^fPitzer and Kilpatrick⁸⁹ ^gChen, et al.⁴⁴ ^hStull, et al.¹⁶ ⁱMP2/6-31G(d,p) geom and freqs ^jOmitting non-experimental S values at 500, 1000

Table 10d. Isobutane. Hindered rotor Correction for S

Temp	S(vib) ^a	S(vib) ^a	S(vib) ^a	S	S (hr)
(hind					
200 cm ⁻¹	249 cm ⁻¹	249 cm ⁻¹	rotor) ^b	corr ⁿ ^c	

261.44	1.890	1.510	1.510	1.687	0.151
298.15	2.130	1.740	1.740	1.965	0.285
500.00	3.110	2.690	2.690	3.030	0.600
1000.00	4.460	4.040	4.040	4.101	-0.237

^aS(vib) 6-31G(d,p) geometry and freqs SF 0.90 ^bS Hin rotor

(hindered rotor) value based on I(red) 4.96E-40 g cm² and V 3.60

kcal mol⁻¹ (from MP2/6-311+G(2df,2p)//6-31G(d,p) energy of

eclipsed Me). ^c3*S Hin rotor - S200 - 2*S249. ^dS Hin rotor*3

^eusing I(red) 5.2E-40 g cm² and V 3.87 kcal mol⁻¹; Aston, et al.⁷⁵

^fusing 5.136E-40 and V 3.85 kcal mol⁻¹, Chen, et al.⁴⁴

Table 11a. Pentane. Heat Capacity

Temp	Cp ^a	C(Conf ^b)	dXE _g /dT ^c	Cp(rrho) ^d	C (hr)	Cp(hr)	Cp(lit)	Cp(hr)	Cp Salam ^f (hr)
	SF 0.90	corrn)			corrn) ^e	corrctd)		corrctd)	corrctd)
						SF 0.90		SF 0.91	SF 0.90
298.15	27.26	-0.08	0.66	27.84	0.67	28.51	28.70 ^g	28.25	28.57
331.00	29.87	-0.08	0.60	30.40	0.67	31.07	31.26 ^h	30.77	31.11
348.15	31.26	-0.07	0.57	31.77	0.66	32.43	32.48 ^g	32.10	32.47
373.15	33.29	-0.06	0.54	33.77	0.62	34.39	34.40 ^g	34.06	34.43
423.15	37.30	-0.05	0.51	37.76	0.51	38.26	38.16 ^g	37.89	38.30
427.00	37.60	-0.05	0.51	38.05	0.48	38.54	38.40 ⁱ	38.18	38.57
448.15	39.25	-0.05	0.50	39.68	0.45	40.11	40.00 ^g	49.75	40.15

500.00	43.11	-0.04	0.48	43.56	0.26	43.82	43.58 ⁱ	43.42	43.84
523.15	44.75	-0.03	0.46	45.19	0.20	45.38	45.19 ^g	44.98	45.40
1000.00	68.73	-0.01	0.28	69.12	-1.00	68.11	66.55 ^j	67.60	67.98
RMS ^k							0.14 ^{j,l}	0.33 ^m	0.15 ⁿ
Avg ^k							-0.03	0.31	-0.07

^aCp entries are based on all frequencies for the C2v conformer. Conformer population based on MP2/6-311+G(2df,2p)//6-31G(d,p) energies: t t 0.00, g t 0.61, g g 0.96, g+g- 2.98 ^bC(Conf correction) corrects for contributions to C of the other conformers. ^cdXE_g/dT is the change of C due to changes in conformer populations. ^dCp(rrho) is the heat capacity based on the harmonic oscillator model. ^ehr correction is the correction for Me hindered rotors (Table 11b). ^fSF 0.90; Salam and Deleuze energies: ⁴⁸t t 0.00, g t 0.621, g g 1.065, g+g- 2.917. ^gHossenlopp and Scott, ⁷⁶^hPitzer⁸¹ ⁱInterpolated ⁷⁶Cp=10.3920+0.06791T-1.80176E5/T² ^jStull, et al¹⁶ ^kOmitting non-experimental Cp value at 1000. ^lFor rrho RMS = 0.55 and Avg = 0.47. ^mFor rrho RMS = 0.83 and Avg = 0.77 ⁿFor rrho RMS = 0.52 and Avg = 0.43

Table11b. Pentane. Hindered Rotor Corrections(t t) for Cp

	C(vib) ^a	C(vib) ^a	C	C (hr)
	230 cm ⁻¹	240 cm ⁻¹	hind rotor ^b	corrn) ^c
298.15	1.795	1.780	2.122	0.669
331.00	1.829	1.817	2.159	0.672
348.15	1.844	1.832	2.169	0.662
373.15	1.862	1.851	2.167	0.621

423.15	1.889	1.881	2.139	0.508
427.00	1.890	1.882	2.136	0.500
448.15	1.899	1.892	2.118	0.445
500.00	1.916	1.910	2.045	0.264
523.15	1.922	1.917	2.020	0.201
1000.00	1.969	1.968	1.467	-1.003

^aS(vib) for methyl group libration frequencies. (98 +cm-1is for

libr about all C-C bonds, 100 is for wagging of central CH₂,

173 bending of all three C-C-C angles. ^bI(red) 4.45E-40 g cm²

and V 3.33 kcal mol⁻¹ from MP2/6-311+G(2df,2p)//6-31G(d,p)

energies. ^c2*C(hind rotor) - C(230) - C(240)

Table 11c. Pentane. Entropy

Temp	S(tran)	S(rot)	S(vib) ^a	S(mix)	S(con) ^b	S(rrho) ^c	S(hr	S(hr	S(lit)	S(hr	S(Salam) ^d
							corrn)	corrctd)	corrctd)	(hr corrctd)	
							SF 0.90	SF 0.90	SF 0.91	SF 0.90	
298.15	38.74	24.68	16.78	2.68	0.77	83.65	0.24	83.99	83.13 ^e	84.19	83.96
500.00	41.31	26.22	30.57	2.86	0.77	101.76	0.42	102.25	101.88 ^f	102.34	102.24
1000.00	44.75	28.29	63.88	3.14	0.78	140.85	-0.23	140.68	140.09 ^f	140.48	140.68
Only one experimental value							-0.86		-1.06	-0.83	

^aValue for the single t t conformer. S(vib) includes all frequencies. ^bContributions from the other conformers; the correction is large because t t is C2 and has symmetry number of 2, as does the g g conformer, while the other conformers have a symmetry number of 1. These values are based on MP2/6-311+G(2df,2p)//6-31G(d,p) energies. S(mix) includes all conformers (one t t , two t g, two enantiomeric g g , and two enantiomeric g+g-; for t g+ and g+t the concentration has to be doubled) in respective total fractions 25%, 67%, 7%, and 0.5% at 298.15 and 18%, 70%, 9%, and 3% at 500. ^cS(rrho) is the entropy, calculated by the rigid rotor harmonic oscillator model, for the compound, a mixture of conformers ^dSalam and Deleuze energies;⁴⁸ see footnotes Table 11a. ^eMesserly and Kennedy⁷⁷ ^fStull, et al.¹⁶

Table 11d. Pentane. Hindered rotor Corrections(t t) for S

	S(vib) ^a 230 cm ⁻¹	S(vib) ^a 240 cm ⁻¹	S (hind rotor) ^b	S (hr corrn)	S (hr corrn) ^c
298.150	1.878	1.805	2.089	0.495	0.24
500.000	2.842	2.764	3.148	0.69	0.42
1000.000	4.192	4.112	4.154	0.004	-0.23

^aS(vib) 98 cm⁻¹ libration about all C-C bonds, 108 wagging of central

CH₂, 173 bending about all 3 C-C-C angles, 230 asynch libration of Me

groups, 240 synchr libration of Me groups. ^bHindered rotor entropy

based on I(red) 4.45E-40 g cm² and V 3.11 kcal mol⁻¹ from MP2/6-

311+G(2df,2p)//6-31G(d,p) energies. ^cFrom average of t t , g t , and g g

conformers.

Table 12a. 2-Methylbutane. Heat Capacity

temp	Cp(rrho)	dXE_g/dT^b	C(hr)	Cp(hr)	Cp(lit)	Cp(hr)	Cp(hr)
				SF 0.90	corr ⁿ) ^c	corrctd)	corrctd)
					SF 0.90		SF 0.91
298.15	27.74	0.34	0.89	28.97	28.41 ^d	28.73	28.75
317.20	29.25	0.32	0.82	30.38	29.95 ^e	30.23	30.25
358.15	32.54	0.28	0.90	33.72	33.25 ^e	33.50	33.53
402.30	36.08	0.24	0.88	37.20	36.72 ^e	36.92	37.01
449.20	39.72	0.20	0.79	40.72	40.24 ^e	40.51	40.49
487.05	42.54	0.18	0.69	43.41	42.93 ^e	43.03	43.14
500.00	43.46	0.17	0.66	44.29	43.71 ^f	43.94	44.03
1000.00	68.82	0.06	-1.23	67.65	67.12 ^f	67.26	67.34
RMS ^h				0.47		0.23	0.27
Avg ^h				-0.47		-0.22	-0.26

Energy Cs-C1 = 0.75 kcal mol⁻¹ MP2/6-311+G(2df,2p)//6-31G(d,p) 88% C1 and 12%

Cs at 298; 82% C1 and 18% Cs at 500 ^aCp values for Cs and C1 conformers are the same within 0.01. ^bC due to change in conformer population with temperature. ^cTable

12b. ^dScott⁵ ^eScott, et al.⁷⁸ ^fStull,et al.¹⁶ ^gMP2/6-31G(d,p) geom and freqs 0.95,

0.923 ^hOmitting non-experimental Cp values at 298, 500, 1000

Table 12b. 2-Methylbutane. Hindered rotor Corrections for Cp

temp	C(vib) ^a 207 cm ⁻¹	C(vib) ^a 220 cm ⁻¹	C(vib) ^a 252 cm ⁻¹	C(hind rotor) ^b	C (hr corr)
298.150	1.830	1.810	1.760	2.097	0.891
317.200	1.880	1.860	1.830	2.129	0.817
358.150	1.900	1.890	1.860	2.182	0.896
402.300	1.920	1.910	1.880	2.196	0.878
449.200	1.930	1.920	1.900	2.181	0.793
487.050	1.930	1.920	1.900	2.148	0.694
500.000	1.930	1.920	1.900	2.137	0.661
1000.000	1.970	1.970	1.960	1.558	-1.226

^aC(vib) for Me groups 6-31G(d,p) frequencies S.F. 0.90. ^bI(red)4.98E-40 g cm² V 3.50 kcal mol⁻¹ (from MP2/6-311+G(2df,2p)//6-

31G(d,p) energies)

Table 12c. 2-Methylbutane. Entropy.

temp	S(tran) ^a	S(rot) ^a	S(vib) ^b	S(mix)	S(con) ^c	S(rrho) ^d SF 0.90	S (hr corr) ^e	S(hr corrtd)	S(lit) corrtd)	S(hr corrtd)	S(hr corrtd)
279.48	38.42	25.85	14.40	1.89	-0.02	80.54	0.20	80.74	80.37 ^f	80.59	80.49
298.15	38.74	26.04	15.63	1.91	-0.02	82.31	0.24	82.55	82.11 ^f	82.39	82.3

301.01	38.79	26.07	15.82	1.92	-0.02	82.58	0.27	82.85	82.39 ^f	82.69	82.538
500.00	41.31	27.58	29.66	2.05	-0.03	100.58	0.57	101.15	100.56 ^g	100.82	100.74
1000.0											
0	44.75	29.65	63.11	2.12	-0.04	139.60	-0.33	139.27	139.01 ^g	138.67	138.63
RMS ⁱ									0.41	0.27	0.16
Avg ⁱ									-0.41	-0.26	-0.16

^aValues for C1 conformer using 6-31G(d,p) geometry. ^bAll frequencies 6-31G(d,p) SF 0.90. ^cCorrection for contribution of Cs conformer. ^dFor the compound. ^eTable 12d. ^fScott, et al ⁷⁸ ^gStull, et al. ¹⁶ Scott, et al. report S=100.51 at 500K and S=139.87 at 1000K. ^hMP2/6-31G(d,p) geom and freqs 0.95, 0.923 ⁱOmitting non-experimental values at 500, 1000

Table 12d. 2-Methylbutane. Hindered Rotor Corrections for S

temp	S(vib)	S(vib)	S(vib)	S(hind	S (hr
	207 cm ⁻¹	220 cm ⁻¹	252 cm ⁻¹	rotor)	corr)
279.48	1.956	1.844	1.603	1.866	0.195
298.15	2.074	1.960	1.716	1.996	0.238
301.01	2.091	1.978	1.733	2.023	0.267
500.00	3.050	2.930	2.668	3.071	0.565
1000.00	4.406	4.283	4.014	4.125	-0.328

^aS(vib) for Me groups 6-31G(d,p) frequencies S.F. 0.90. ^bI(red)

4.98E-40 g cm² V 3.50 kcal mol⁻¹ (from MP2/6-

311+G(2df,2p)//6-31G(d,p) energies)

Table 13a. Neopentane. Heat Capacity

Temp	Cp(rrho)	C (hr	Cp (hr	Cp(lit)	Cp (hr	Cp (hr
	SF 0.90	corr) corrctd)			corrctd)	corrctd)
			SF 0.90		SF 0.91	MP2
298.15	28.61	1.090	29.70	28.88 ^a	29.45	29.49
323.15	30.61	1.182	31.79	30.97 ^a	31.52	31.57
348.15	32.62	1.259	33.88	33.08 ^a	33.59	33.65
373.15	34.62	1.325	35.95	35.15 ^a	35.62	35.70
398.15	36.59	1.350	37.94	37.16 ^a	37.61	37.70
423.15	38.52	1.357	39.88	39.08 ^a	39.54	39.63
448.15	40.41	1.324	41.73	40.98 ^a	41.37	41.48
473.15	42.25	1.265	43.52	42.77 ^a	43.14	43.26
498.15	44.02	1.207	45.23	44.56 ^a	44.86	44.97
500.00	44.15	1.202	45.35	45.00 ^b	44.98	45.09
523.15	45.74	1.118	46.86	46.22 ^a	46.48	45.59
1000.00	69.02	-1.136	67.88	67.80 ^b	67.51	67.59
RMS ^c			0.74		0.42	0.50
Avg ^c			-0.72		-0.39	-0.48

Using 6-31G(d,p) geometry and frequencies. ^aHossenlopp and Scott⁷⁶^bPitzer and Kilpatrick⁸⁹ calculated ^cOmitting non-experimental Cp value at

Table 13b. Neopentane. Hindered Rotor Corrections for Cp

Temp	C(vib) ^a	C(vib) ^b	C(hind	C (hr ^c
	195 cm ⁻¹	270 cm ⁻¹	rotor)	corr)
298.15	1.847	1.729	2.031	1.090
323.15	1.867	1.765	2.086	1.182
348.15	1.883	1.794	2.131	1.259
373.15	1.896	1.817	2.168	1.325
398.15	1.907	1.837	2.192	1.350
423.15	1.916	1.853	2.208	1.357
448.15	1.923	1.867	2.212	1.324
473.15	1.930	1.879	2.208	1.265
498.15	1.935	1.890	2.203	1.207
500.00	1.936	1.890	2.202	1.202
523.15	1.940	1.898	2.188	1.118
1000.00	1.974	1.962	1.681	-1.136

^aC(vib) of one Me ^bC(vib) of three Me ^cC(hr correction) =

4*C(hin rotor) - C195 - 3*(C270); 6-31G(d,p) frequencies

SF 0.90. C hindered rotor value calculated using I(red)

5.01E-40 g cm² and V 4.02 kcal mol⁻¹)from MP2/6-311+G(2df,2p)//6-31G(d,p) energies). Enokido, et al.⁸⁰ usedI(red) 5.14E-40 g cm² and V 4.40 kcal mol⁻¹

Table 13c. Neopentane. Entropy.

Temp	S(tran)	S(rot)	S(vib)	S(rrho)	S (hr)	S(hr)	S(lit)	S(hr)	S(hr)
	SF 0.90			corr)	corrctd)		corrctd)	corrctd)	
				SF 0.90			SF 0.91	MP2	
282.61	38.47	20.61	12.93	72.01	0.33	72.34	71.71 ^a	72.22	72.22
298.15	38.74	20.77	14.01	73.51	0.38	73.89	73.11 ^{bc}	73.76	73.25
500.00	41.31	22.31	28.45	92.07	0.81	92.88	92.17 ^{bc}	95.56	92.59
							131.41 ^b		
1000.00	44.75	24.37	62.20	131.32	0.00	131.32	^c	130.74	130.85
RMS ^d						0.71		0.59	0.58
Avg ^d						-0.71		-0.58	-0.57

^a Aston and Messerly⁷⁹ error 0.3 Enokido, et al.⁸⁰ report 71.24 ^bPitzer and Kilpatrick⁸⁹

report 73.23 at 298.15K ^cScott,⁵ Stull, et al.¹⁶ ^dOmitting non-experimental values at 500,

1000

Table 13d. Neopentane. Hindered Rotor S Corrections

Temp	S(vib)	S(vib)	S(hind	S(hr)
	195 cm ⁻¹	270 cm ⁻¹	rotor) ^a	corr) ^b
282.61	2.08	1.51	1.736	0.33
298.15	2.18	1.6	1.841	0.38
500	3.15	2.54	2.895	0.81
1000	4.52	3.88	4.041	0.004

^aI(red) 5.01E-40 g cm² V 4.02 kcal mol⁻¹ (MP2/6-311+G(2df,2p

energies) ^bS(hr correction)= 4*S(hind rotor) - S(195)-3*S(270).

Table 15a. 2,2-Dimethylbutane. Heat Capacity.

Temp	Cp	C hr	Cp hr	Cp(lit)	Cp (hr)			
							corrctd)	
					corr	corrctd	corrctd)	Pitzer
							frequencies	corrctd)
			SF 0.90		SF 0.91		^c	MP2
298.15	33.64	1.08	34.72	33.81 ^a	34.43	33.91	34.48	
341.55	37.81	1.21	39.02	38.10 ^b	38.70	37.78	38.79	
353.20	38.94	1.24	40.18	39.25 ^b	39.84	39.32	39.93	
361.00	39.69	1.25	40.94	40.40 ^c	40.60	40.08	40.69	
376.05	41.13	1.29	42.42	41.50 ^b	42.06	41.55	42.17	
391.00	42.55	1.30	43.85	42.60 ^c	43.49	42.98	43.61	
412.40	44.55	1.31	45.86	44.95 ^b	45.50	45.00	45.64	
448.00	47.79	1.33	49.12	47.80 ^c	48.68	48.27	48.83	
449.40	47.92	1.32	49.24	48.33 ^b	48.81	48.40	48.96	
500.00	52.29	1.19	53.48	52.50 ^d	53.03	52.70	53.20	
1000.00	81.88	-1.16	80.72	79.70 ^d	80.29	80.35	79.70	
RMS ^e			0.99		0.63	0.25	0.74	
Avg ^e			-0.95		-0.59	-0.10	-0.71	

^aScott⁵ ^bWaddington and Douslin⁸² ^cPitzer⁸¹ ^dStull, et al.¹⁶ ^eOmitting non-experimental Cp values at 500, 1000

Table 15b. 2,2-Dimethylbutane Hindered Rotor Correction. for Cp

	C(vib)	C(vib)	C(vib)	C(vib)	C(hind	C(hr
	199 cm ⁻¹	244 cm ⁻¹	267 cm ⁻¹	280 cm ⁻¹	rotor)	corr) ^a
298.150	1.841	1.772	1.733	1.710	2.034	1.08
341.550	1.882	1.831	1.802	1.772	2.124	1.209
353.200	1.886	1.837	1.810	1.785	2.140	1.242
361.000	1.894	1.848	1.823	1.793	2.151	1.246
376.050	1.901	1.858	1.835	1.807	2.172	1.287
391.000	1.909	1.871	1.849	1.820	2.187	1.299
412.400	1.921	1.888	1.870	1.836	2.206	1.309
448.000	1.921	1.889	1.859	1.858	2.213	1.325
449.400	1.921	1.889	1.870	1.859	2.214	1.317
500.000	1.934	1.907	1.892	1.883	2.202	1.192
1000.000	1.974	1.967	1.963	1.960	1.677	-1.156

6-31G(d,p) frequencies, SF 0.90. Note that second S 245 cm⁻¹ is a

bending mode, not a Me libration. ^a4*C(hind rotor)-C(199)-C(244)-C(267)-C(280).

Table 15c. 2,2-Dimethylbutane. Entropy.

Temp	S(tran)	S(rot)	S(vib)	S(rrho)	S(hr	S(hr	S(lit)	S(hr	S(hr ^c	S(hr
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SF 0.90				corr)	corrctd)	corrctd)	corrctd)	corrctd)	corrctd)
				SF 0.90	SF 0.90	SF 0.91	Pitzer	MP2 ^d	
298.15	39.27	26.90	19.87	86.04	0.33	86.37	85.72 ^a	86.17	85.74
500.00	41.84	28.44	37.68	107.95	0.76	108.72	107.70 ^b	108.31	107.82
1000.00	45.28	30.51	78.72	154.51	-0.07	154.44	153.69 ^b	153.71	153.03
Only one experimental value					0.65		0.45	0.02	0.54

^aKilpatrick and Pitzer:⁴⁵ ± 0.2 ; Scott⁵ report 86.62 ± 0.1 ^bStull, et al.¹⁶ ^cUsing Kilpatrick and Pitzer

frequencies and 3.658 entropy for skeletal internal rotation of Table XII of Kilpatrick and Pitzer. ^dMP2/6-31G(d,p) geom and freqs SF 0.95, 0.923

Table 15d. 2,2-Dimethylbutane. Hindered Rotor S Correction.

Temp	S(vib)	S(vib)	S(vib)	S(vib)	S	S (hr)
	199 cm ⁻¹	244 cm ⁻¹	267 cm ⁻¹	280 cm ⁻¹	(hind rotor)	corr) ^a
298.15	2.142	1.771	1.615	1.532	1.848	0.332
500	3.121	2.727	2.558	2.468	2.908	0.758
1000	4.478	4.074	3.9	3.806	4.046	-0.074

Note that second S 245 cm⁻¹ is a bending mode, not a Me libration.

^a4*S(hind rotor)-S(199)-S(244)-S(267)-S(280)

Table 15e. 2,2-Dimethylbutane. Comparison with Kilpatrick and Pitzer Calculations of S at

298.15

	Table XII ^a	KP freqs, ^b	6-31G(d,p) ^c	MP2/6-31G(d,p) ^d
		I(red) 5.02E-		
	I(red) 5.3E-40	I(red) 5.3E-40	40	I(red) 5.02E-40
	V 4.375	V 4.375	V 4.00	V 4.00
S(tran)+S(rot)	66.08	66.14	66.17	66.14
S 4 CH3 hind rotors	7.16	7.19	7.39	7.39
S vib	8.82	8.82	8.65	8.44
S tot	85.72	85.81	86.14	86.03

^aValues in Table XII of Kilpatrick and Pitzer.⁴⁵ Units are g cm² and kcal mol⁻¹ ^bRecalculated from frequencies, I(red), and V of Kilpatrick and Pitzer, but using K and P value for S internal rot. The values reproduce those of K and P. ^c6-31G(d,p) geometry and frequencies, SF 0.90; I(red) calculated by Herzberg equation p 511¹⁸ and V based on MP2/6-311+G(2df,2p)//6-31G(d,p) energies. ^dMP2/6-31G(d,p) geometry and frequencies, SF 0.95, 0.923.

Table 16a. 2,3-Dimethylbutane. Heat Capacity.

Temp	Cp(rrho) ^a	C(con)	dXE _g /dT ^b	C(hr)	Cp(hr)	Cp(lit)	Cp(hr)	Cp(hr)	Cp(hr)
	SF 0.90	corr ^a	corr ^a	corr ^c	corrctd)	corrctd)	corrctd)	corrctd)	corrctd)
					SF 0.90		SF 0.91	MP2 ^e	Scott ^f
298.15	33.26	0.04	0.02	1.28	34.59	33.59 ^g	34.30	34.32	33.34
341.60	37.43	0.02	0.02	1.24	38.71	37.78 ^d	38.36	38.44	37.63

371.20	40.28	0.01	0.02	1.15	41.46	40.68 ^d	41.09	41.17	40.55
402.30	43.24	0.01	0.01	1.00	44.27	43.63 ^d	43.86	43.98	43.66
436.00	46.37	0.01	0.01	0.80	47.19	46.73 ^d	46.77	46.91	46.72
471.15	49.51	0.00	0.01	0.56	50.08	49.77 ^d	49.64	49.80	49.86
500.00	51.99	0.00	0.01	0.39	52.39	51.94 ^g	51.93	52.10	52.30
1000.00	81.79	-0.01	0.00	-2.13	79.66	79.13 ^g	79.21	79.34	80.07
RMS ^h					0.66		0.34	0.41	0.10
Avg ^h					-0.62		-0.23	-0.34	0.04

^aData are for the C2h conformer; the energy of the C2 conformer is 0.12 kcal mol⁻¹ greater based on MP2/6-311+G(2df,2p)//6-31G(d,p) energies. C(con corr) corrects for contribution of the C2 conformer. ^bcorrects for change in conformer ratios with temperature. ^cHindered rotor correction, Table 16b. ^dScott, et al.⁷⁸ Waddington, et al.⁸³ ^eMP2/6-31G(d,p) geom and freqs SF 0.95, 0.923 ^fUsing Scott, et al. frequencies⁷⁸ ^gStull, et al.¹⁶ ^hOmitting non-experimental Cp values for 298, 500, 1000

Table 16b. 2,3-Dimethylbutane. Hindered Rotor Corrections for

Cp

Temp	C(vib)	C(vib)	C(vib)	C(vib)	C(hind)	C(hr)	C(hind)
	193 cm ⁻¹	193 cm ⁻¹	215 cm ⁻¹	233 cm ⁻¹	rotor) ^a	corr) ^b	rotor) ^b
298.15	1.85	1.85	1.82	1.79	2.15	1.28	2.03
341.60	1.88	1.88	1.86	1.84	2.18	1.24	2.12
371.20	1.90	1.90	1.88	1.86	2.17	1.15	2.17
402.30	1.91	1.91	1.89	1.88	2.15	1.00	2.20
436.00	1.92	1.92	1.91	1.91	2.12	0.80	2.21

471.15	1.93	1.93	1.92	1.91	2.06	0.56	2.22
500.00	1.94	1.94	1.92	1.92	2.03	0.39	2.21
1000.00	1.97	1.97	1.97	1.97	1.44	-2.13	1.70

^aI(red) 5.02E-40 g cm², V 3.00 (MP2(6-311+G(2df,2p)//6-31G(d,p)). ^bScott, et al.⁷⁸

used I(red) 5.2E-40 g cm², V 4.10.

Table 16c. 2,3-Dimethylbutane. Entropy.

temp	S(tran) ^a	S(rot) ^a	S(vib) ^a	S(mix)	S(con) ^b	S(rrho)	S (hr	S(hr	S(lit)	S(hr	S(hr	S(hr
	SF 0.90				SF 0.90		corr)	corrctd)	corrctd)	corrctd)	corrctd)	corrctd)
								SF 0.90	SF 0.91	MP2 ^e	Scott ^f	
298.15	39.27	25.67	20.72	2.17	-0.03	87.80	0.54	88.34	87.43 ^d	88.14	87.27	86.93
313.13	39.51	25.82	21.99	2.17	-0.03	89.47	0.61	90.08	89.12 ^d	89.87	88.92	88.6
331.15	39.79	25.98	23.54	2.17	-0.03	91.46	0.67	92.13	91.09 ^d	91.09	90.9	90.57
									109.28			
500.00	41.84	27.21	38.33	2.18	-0.02	109.54	0.83	110.37	^g	109.26	108.85	108.5
									154.82			
1000.0	45.28	29.28	79.25	2.18	-0.03	155.97	-0.74	155.23	^g	154.8	155.05	153.6
RMS ^h								0.97		0.76	0.51	0.52
Avg ^h								-0.97		-0.76	-0.48	0.52

^aData for C2h conformer. Lowest freq SF 0.90 ^bCorrects for contribution of C2 conformer. ^cScott, et al.,⁷⁸ Waddington,

et al.⁸³ ^dScott, et al.^{5,78} ^eMP2/6-31G(d,p) geom and freqs SF 0.95, 0.923 ^fUsing Scott, et al. frequencies, I(xyz) =

21,240E-117, I(red) (Me) 5.12E-40 g cm², V 4.10 ^gStull, et al.¹⁶ ^hOmitting non-experimental S values for 500, 1000

Table 16d. 2,3-Dimethylbutane. Hindered Rotor Correction. for S

Temp	S 193	S 193	S 215	S 233	S(hin rotor) ^a	S(hr corr)
	cm ⁻¹	cm ⁻¹	cm ⁻¹	cm ⁻¹		
298.150	2.202	2.198	2.001	1.859	2.199	0.536
313.130	2.293	2.289	2.091	1.937	2.305	0.610
331.150	2.398	2.393	2.194	2.049	2.427	0.674
500.000	3.185	3.180	2.973	2.822	3.247	0.828
1000.000	4.543	4.538	4.327	4.172	4.210	-0.740

^aI(red) 5.02E-40, V 3.00 (MP2/6-311+G(2df,2p)//6-31G(d,p) energies

Table 17a Toluene. Heat Capacity.

Temp	Cp(rrho)	Cp(fir corrctd) ^a	Cp(lit) raw	Cp(lit) smoothed	Cp(fir corrctd) ^a
	SF 0.90			SF 0.91	
298.15	25.89	24.90	24.77 ^b	24.75	24.61
371.20	32.20	31.21	31.09 ^c	31.40	30.86
390.00	33.75	32.76	33.50 ^d	32.91	32.41
393.00	34.00	33.01	32.80 ^e	33.14	32.65
396.20	34.26	33.25	33.19 ^c	33.39	32.91
410.00	35.36	34.35	34.99 ^e	34.45	34.02
427.20	36.70	35.71	35.65 ^c	35.00	35.35

428.00	36.77	35.78	35.70 ^e	35.79	35.41
462.20	39.31	38.32	38.32 ^c	38.25	37.96
463.00	39.37	38.38	38.00 ^e	38.31	38.01
500.20	41.96	40.97	40.98 ^c	40.88	40.60
500.00	41.95	40.96	40.58 ^b	40.86	40.59
1000.00	63.60	62.61	62.27 ^b	63.32	62.27
RMS raw exp-calcd ^f	0.34			0.50	
RMS smoothed-calcd ^f	0.11			0.41	
Avg ^f	0.01			0.37	

^afir (free internal rotor) C correction is -0.99 for all temperatures

and adds to Cp(rrho). The smoothed lit. values were derived from

Cp = 14.0987 + 0.05832T -5.98946E5/T² and have a std dev of

0.32. The average uncertainties 0.34 and 0.50 pertain to

comparisons with the raw experimental data, the 0.11 and 0.41 to

smoothed data. ^bStull, et al.¹⁶ ^cScott, et al.⁹⁰ ^dMontgomery and

DeVries⁶⁹ ^ePitzer and Scott⁹¹ ^fOmitting non-experimental values

at 298.15, 500, 1000

Table 17b. Toluene. Entropy.

Temp	S(trans)	S(rot)	S(vib)	S(rrho)	S (fir	S(fir	S(lit)	S(fir
					SF 0.90	corrn)	corrctd)	corrctd)
							SF 0.90	SF 0.91
298.15	39.47	25.57	14.57	79.61	-2.93	76.68 ^e	76.77 ^{ab}	76.54 ^e

341.27	40.14	25.97	17.24	83.35	-3.06	80.29	80.39 ^b	80.11
361.06	40.42	26.14	18.52	85.07	-3.12	81.96	82.04 ^b	81.75
383.77	40.72	26.32	20.00	87.04	-3.18	83.86	83.92 ^b	83.64
410.11	41.05	26.52	21.75	89.32	-3.24	86.08	86.08 ^b	85.83
500.00	42.04	27.83	27.83	96.98	-3.44	93.55	93.47 ^c	93.22
1000.00	45.48	29.17	59.16	133.82	-4.13	129.68	129.85 ^c	129.12
RMS ^d						0.07		0.30
Avg ^d						0.06		0.30

Geometry and frequencies 6-31G(d,p). Lowest freq. 22 cm⁻¹, S=6.46 (replaced by free internal rotor values Table 17c) Sigma 2 for S(rot). ^aPitzer and Scott⁹¹ report S=76.44 ^bScott, et al.⁹⁰

^cStull, et al.¹⁶ ^dOmitting non-experimental S values at 500, 1000. ^eEast,et al.³² report 76.85 by their E3 method.

Table 17c. Toluene. Free Internal Rotor

Correction for S

Temp	S(vib)	S (fir) ^a	
		22 cm ⁻¹	Me
298.15	6.46	3.53	-2.93
341.27	6.73	3.67	-3.06
361.06	6.84	3.72	-3.12
383.77	6.96	3.78	-3.18
410.11	7.09	3.85	-3.24

500.00 7.48 4.05 -3.44

1000.00 8.86 4.73 -4.13

^aI(red) 5.14E-40 g cm² V 0.01 kcal mol⁻¹

sigma 3

Table 18a. Methylcyclohexane. Heat Capacity

Temp	Cp(rrho)	dXE _g /dT	Cp (rrho)	C (hr	Cp (hr	Cp(lit)	Cp (hr
				(conf mixt)			
				corrn)			
298.15	31.54	0.71	32.25	0.30	32.55	32.27 ^b	32.17
398.00	42.87	0.91	43.78	0.30	44.08	44.13 ^c	43.59
439.00	47.32	1.04	48.36	0.26	48.62	48.62 ^c	48.10
480.00	51.54	1.19	52.73	0.21	52.94	53.24 ^c	52.38
500.00	53.51	1.25	54.76	0.16	54.92	55.21 ^b	54.39
527.00	56.06	1.34	57.40	0.13	57.54	57.82 ^c	57.01
1000.00	86.46	2.96	89.42	-0.46	88.96	88.79 ^b	88.44
RMS					0.21		0.72 ^d
Average					0.18		0.71

^achair eq 0.00, chair ax 1.77, tb eq 6.41, tb ax 8.15 kcal mol⁻¹ MP2/6-311+G(2df,2p)//6-31G(d,p) energies; based on conformer free energies, conformer mixture at 298.15 is 95.84% ch eq, 4.15 tb eq, 0.004% tb eq; at 500 87.27% ch eq, 12.38% ch ax, 0.30% tb eq, 0.05% tb ax. 6-31G(d,p) geometries and frequencies. Table entries are for the mixture of conformers at 298.15; Cp(rrho) values are the same for the single ch eq conformer and for the mixture of conformers ^bBeckett, et al.²⁵ calcd. ^cSpitzer and Pitzer⁶² and Beckett, et al. est uncertainty of exp 0.4 to 0.6 cal. ^dFor rrho RMS=0.93, avg 0.92

Table 18b. Methylcyclohexane. Hindered Rotor C

Correction

Temp	C(vib) ^a	C (Hin)	C (hr)
	215 cm ⁻¹	rotor) ^b	corrn)
298.15	1.819	2.114	0.295
398	1.89	2.186	0.296
439	1.907	2.164	0.257
480	1.92	2.127	0.207
500	1.935	2.099	0.164
527	1.931	2.064	0.133
1000	1.971	1.515	-0.456

^aLowest freq 146 cm⁻¹ ring librations; both 215 and

233 are composite and include both Me and ring

librations. Choice of 215 cm⁻¹ to represent Me

group libration is necessarily somewhat arbitrary.

^bI(red) 4.98R-40 g cm² and V 3.32 kcal mol⁻¹.

Table 18c. Methylcyclohexane. Entropy.

temp	S(tran)	S(rot)	S(vib)	S(mix)	S(con)	S(rrho)	S (hr	S(hr	S(lit)	S(hr
	SF 0.90				SF 0.90		corrн)	corrctd)		
							SF 0.90		SF 0.91	
298.157	39.66	27.49	15.07	0.34	-0.012	82.54	0.064	82.61	82.05 ^a	82.37
500	42.23	29.03	32.61	0.79	-0.037	104.61	0.155	104.77	104.32 ^b	104.29
1000	45.67	31.09	75.83	1.68	0.03	154.30	-0.176	154.13	154.57 ^b	153.29
Only one experimental value								0.55	0.32	
Lowest frequency SF 0.90 146 cm ⁻¹ S=2.72. ^a Beckett, et al. ²⁵ exp ^b Beckett, et al. calcd. c Stull, et al. ¹⁶										

Table 18d. Methylcyclohexane. Hindered Rotor

Corrections for S

temp	S(vib) ^a	S(hind	S(hr
	215 cm ⁻¹	rotor) ^a	corrн)

298.15	2.004	2.068	0.064
500	2.977	3.132	0.155
1000	4.331	4.155	-0.176

^aSee Table 18b footnotes.

Table 19a. Trimethylbutane. Heat Capacity.^a

Temp	Cp(rrho)	C(hr)	Cp(hr)	Cp(lit)	Cp(hr)	Cp(hr)	Cp(rrho)	C (hr)	Cp(hr)
	SF 0.90	corrn)	corrctd)		corrctd)	corrctd)	Scott,	corrn)	corrctd)
			SF 0.90			SF 0.91	MP2 ^d	Wadding ^b	SW ^b
298.15	39.18	1.57	40.75	39.33 ^b	40.36	40.46	37.97	1.09	39.06
328.80	42.61	1.65	44.26	42.74 ^c	43.84	43.97	41.23	1.29	42.52
348.85	44.86	1.68	46.54	45.09 ^c	46.09	46.26	43.39	1.39	44.78
369.20	47.14	1.67	48.81	47.39 ^c	48.34	48.52	45.60	1.49	47.09
400.40	50.57	1.58	52.15	50.92 ^c	51.66	51.85	48.97	1.56	50.53
434.30	54.19	1.45	55.64	54.54 ^c	55.13	55.35	52.56	1.61	54.17
461.80	57.03	1.27	58.30	57.36 ^c	57.78	58.02	55.40	1.58	56.98
500.00	60.81	1.02	61.84	61.04 ^b	61.29	61.55	59.20	1.50	60.70
1000.00	94.82	-2.15	92.67	92.32 ^b	92.16	92.36	93.78	-1.24	92.54
RMS omit 298, 500, 1000				1.29	0.84	1.11			0.33
Average omit 298, 500, 1000				-1.28	-0.66	-0.99			0.33

^aLowest freq reset to 100 cm⁻¹ scaled. I encountered an anomaly in the calculation of the lowest frequency of 2,2,3-trimethylbutane. Depending on cut off specifications, the lowest 6-31G(d,p) frequency was sometimes a few cm⁻¹ positive, in others a few cm⁻¹ negative. The lowest frequency with MP2/6-31G(d,p) frequencies was about 50 cm⁻¹. I ran a relaxed frequency scan about the central C-C bond, but could see no exceptional features. I have no idea why this one compound out of the total set shows this behavior. What I did in calculating Cp and S was to replace that lowest frequency with 67 cm⁻¹, which value is in the range observed for alkanes of comparable size; I did not attempt to select a value to specifically make calculated S correspond with experiment. ^bScott and Waddington;⁸⁵ Cp recalcd. using SW freqs, SW I(red) 5.225E-40 g cm², and SW V 4.20 kcal mol⁻¹; lowest freq taken as 60 cm⁻¹. ^cWaddington, et al.⁸⁴ ^dMP2/6-31G(d,p) geom and freqs SF 0.95, 0.923

Table 19b. Trimethylbutane. Hindered Rotor Corrections for Cp

temp	C(vib)	C(vib)	C(vib)	C(vib)	C(vib)	C(hind)	C (hr)
	182 cm ⁻¹	226 cm ⁻¹	227 cm ⁻¹	248 cm ⁻¹	261 cm ⁻¹	rotor) ^b	corrn)
298.15	1.86	1.80	1.80	1.77	1.74	2.11	1.57
328.80	1.88	1.83	1.83	1.80	1.78	2.16	1.65
348.85	1.90	1.85	1.85	1.82	1.80	2.18	1.68
369.20	1.91	1.86	1.86	1.84	1.82	2.19	1.67
400.40	1.92	1.88	1.88	1.86	1.85	2.19	1.58
434.30	1.93	1.90	1.90	1.88	1.87	2.18	1.45
461.80	1.94	1.91	1.91	1.89	1.88	2.16	1.27
500.00	1.94	1.92	1.92	1.90	1.90	2.12	1.02
1000.00	1.98	1.97	1.97	1.97	1.96	1.54	-2.15

^a6-31G(d,p) geometries and frequencies SF 0.90. ^bI(red) 5.07E-40 g cm² V 3.41 kcal

mol⁻¹ from MP2/6-311+G(2df,2p)//6-31G(d,p) energies.

Table 19c. Trimethylbutane. Entropy^a.

Temp	S(tran) ^b	S(rot) ^b	S(vib) ^b	S(rrho)	S (hr)	S(hr)	S(lit)	S(hr)	S(hr)	S(hr)
	SF 0.90				corr)	corctd)	corctd)	corctd)	corctd)	corctd)
					SF 0.90		SF 0.91		ScottW ^e	MP2 ^d
298.15	39.72	27.72	24.72	92.16	0.74	92.89	91.64 ^c	92.64	90.84	92.46
313.84	39.97	27.87	26.37	94.21	0.83	95.04	93.69 ^c	94.78	92.89	94.60
353.96	40.57	28.23	30.60	99.40	0.95	100.36	98.82 ^c	100.05	98.02	99.89
500.00	42.29	29.26	46.12	117.67	1.24	118.90	117.30 ^c	118.43	115.95	118.3
1000.00	45.73	31.32	94.63	171.68	-0.36	171.32	170.60 ^c	170.47	168.04	170.53
RMS ^f						1.39		1.11	0.20	0.94
Avg ^f						-1.38		-1.11	0.20	-0.93

^aUsing raw 67 cm⁻¹ (scaled 60 cm⁻¹) as lowest freq ^b6-31G(d,p) geometries and frequencies.

^cScott and Waddington⁸⁵ using S(vib) for C skeleton with 60 cm⁻¹ as lowest frequency 3.45^a I(red)

5.25E-40 g cm², V 4.2 kcal mol⁻¹, S(hr) 1.83 at 298.15 K ^dMP2/6-31G(d,p) geom and freqs SF

0.95, 0.923, using raw 67 cm⁻¹ (scaled 64) as lowest frequency. ^eUsing I(red) 5.225E-40 g cm² and

V 4.20 kcal/mol. ^fOmitting non-experimental values for 500, 1000

Table 19d Trimethylbutane Hindered Rotor Corrections for S

temp	S(vib)	S(vib)	S(vib)	S(vib)	SVib	S(hind)	S(hr)
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	182 cm^{-1}	226 cm^{-1}	227 cm^{-1}	248 cm^{-1}	261 cm^{-1}	rotor) ^a	corr)
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298.150	2.308	1.910	1.902	1.745	1.655	2.051	0.74
313.840	2.400	2.010	2.000	1.840	1.740	2.163	0.83
353.960	2.630	2.230	2.220	2.060	1.960	2.409	0.95
500.000	3.290	2.880	2.870	2.700	2.600	3.115	1.24
1000.000	4.650	4.230	4.220	4.050	3.940	4.146	-0.36

^aFor S hindered rotor 5.07E-40 g cm², V 3.41 kcal mol⁻¹, MP2/6-311+G(2df,2p)//6-31G(d,p) energies.

Table 20a Tetramethylbutane. Heat Capacity.

Temp	Cp(rrho)	C(hr corr)	Cp(hr corrtd)	Cp(lit)	Cp(hr corrtd)	Cp(hr corrtd)	Cp(hr SF 0.90)	MP2 ^b
							SF 0.91	
298.15	44.86	1.72	46.58	46.03 ^a	46.19	46.28		
500.00	69.56	1.79	71.35	71.76 ^a	70.76	71.08		
1000.00	107.84	-1.81	106.03	106.60 ^a	105.46	105.72		

There are no experimental Cp values

6-31G(d,p) geometry and frequencies. ^aScott, et al. calcd.⁹² MP@/6-

31G(d,p) geom and freqs SF 0.95, 0.923

Table 20b. Tetramethylbutane. Hindered Rotor Corrections for Cp

temp	C(vib)	C(vib)	C(vib)	C(vib)	C(vib)	C(vib)	C(hind)	C(hr corr)
	214 cm^{-1}	243 cm^{-1}	243 cm^{-1}	260 cm^{-1}	278 cm^{-1}	278 cm^{-1}	rotor) ^a	

298.15	1.82	1.78	1.78	1.75	1.71	1.71	2.04	1.72
500.00	1.93	1.91	1.91	1.90	1.88	1.88	2.20	1.79
1000.00	1.97	1.97	1.97	1.96	1.96	1.96	1.66	-1.81

6-31G(d,p) frequencies, SF 0.90. ^aI(red) 5.07E-40 g cm², V 3.94 kcal mol⁻¹ based on MP2/6-

311+G(2df,2p)//6-31G(d,p) energies

Table 20c. Tetramethylbutane. Entropy.

Temp	S(tran)	S(rot)	S(vib)	S(rrho)	S (hr)	S(hr)	S(lit)	S(hr)	S hr
	SF 0.90				corrn)	corrctd)	corrctd)	corrctd)	MP2 ^c
					SF 0.90	SF 0.90	SF 0.91		
298.15	40.11	24.76	26.91	91.77	0.95	92.72	93.05 ^a	92.44	93.06
500.00	42.68	26.30	52.02	121.00	1.55	122.55	123.20 ^b	122.00	121.26
1000.00	46.12	28.36	108.09	182.58	0.24	182.82	185.40 ^b	181.85	181.83
Only one experimental value					0.33			0.61	0.99

6-31G(d,p) geometry and frequencies. Lowest frequency SF 0.90 96 cm⁻¹ S(vib)=3.53 ^aScott,

et al. exp.⁹² ^bScott, et al. calcd. ^cMP2/6-31G(d,p) geom and freqs SF 0.95, 0.923

Table 20d. Tetramethylbutane. Hindered Rotor Corrections. for S

temp	S(vib)	S(vib)	S(vib)	S(vib)	S(vib)	S(vib)	S(hind)	S(hr)
9	214 cm ⁻¹	243 cm ⁻¹	243 cm ⁻¹	260 cm ⁻¹	278 cm ⁻¹	278 cm ⁻¹	rotor) ^a	corrn)
298.15	2.01	1.78	1.78	1.66	1.55	1.55	1.88	0.95
500.00	2.98	2.74	2.74	2.61	2.48	2.48	2.93	1.55
1000.00	4.33	4.09	4.09	3.95	3.82	3.82	4.06	0.24

6-31G(d,p) frequencies, SF 0.90. ^aI(red) 5.07E-40 g cm², V 3.94 based on MP2/6-311+G(2df,2p)//6-31G(d,p) energies

Table 21a. Difference of Summed C(vib) Values from Shimanouchi and 6-31G(d,p) Frequencies at 298.15K

	C(vib) ^a	6-31G(d,p) ^b	6-31G(d,p) ^b	MP2/6-
	Shimanouchi			31G(d,p) ^{bc}
	value	SF 0.90	SF 0.91	SF 0.95/0.923
Ethane	2.60	-0.12	-0.03	0.00
Cyclopropane	5.34	0.00	-0.15	0.13
Propane	5.47	-0.24	0.10	-0.06
1,3-Butadiene	10.15	0.06	0.22	-0.40
Cyclobutane	7.24	-0.09	0.12	-0.20
Butane t	8.49	-0.27	-0.08	0.04
Butane g	8.32	-0.35	-0.15	0.13
Cyclohexane	17.18	-0.65	-0.33	-0.39
RMS omit cyclohexane		0.21	0.11	0.12
Avg omit cyclohexane		-0.14	0.02	-0.10

^aSum of C(vib) from Shimanouchi frequencies³⁴⁻³⁶ omitting frequencies due to Me

libration, C-C-C-C libration, and cyclobutane ring pucker ^bSum of C(vib) from

Shimanouchi frequencies minus sum for 6-31G(d,p) frequencies, ^cMP2/6-31G(d,p), SF

0.95 for freqs 2000cm⁻¹ or less and 0.923 for freqs greater than 2000.

Table 21b. Difference of C(vib) Values Derived from Shimanouchi and from 6-31G(d,p)

Frequencies 500K

	C _{vib} ^a	6-31G(d,p) ^b	6-31G(d,p) ^b	31G(d,p) ^{bc}
		SF 0.90	SF 0.91	SF 0.95/0.923
Ethane	8.74	-0.12	-0.05	0.08
Cyclopropane	14.49	-0.07	0.27	0.21
Propane	14.85	-0.20	0.04	0.06
1,3-Butadiene	19.49	0.16	0.38	-0.30
Cyclobutane	19.64	0.19	-0.11	0.28
Butane t	21.02	0.19	-0.02	-0.11
Butane g	20.95	-0.23	0.09	0.05
Cyclohexane RMS omit cyclohexane	36.42	0.58 0.15	0.12 0.16	0.24 0.16
Avg omit cyclohexane		-0.10	0.14	-0.01

a See footnotes to Table 21a

Table 21c. Difference of Sums of S(vib) Values from Shimanouchi and from 6-31G(d,p)

Frequencies 298K

	S(vib) ^a	6-31G(d,p) ^b	6-31G(d,p) ^{bc}	31G(d,p) ^{bd}
		SF 0.90	SF 0.91	SF 0.95/0.923
Ethane	0.66	-0.25	-0.03	-0.02
Cyclopropane	1.48	-0.02	0.03	0.03
Propane	2.07	-0.17	-0.10	-0.09

1,3-Butadiene	6.25	-0.23	-0.38	-0.47
Cyclobutane	2.11	-0.17	-0.10	-0.09
Butane t	3.84	-0.29	-0.19	-0.11
Butane g	3.43	-0.33	-0.22	-0.18
Cyclohexane	8.93	-0.72	-0.57	-0.53
RMS omit cyclohexane		0.23	0.13	0.10
Avg omit cyclohexane		0.23	0.13	0.10

^aSum of S(vib) values, omitting values due to Me libration, C-C-C-C libration, and cyclobutane ring pucker, ^bSum of Shimanouchi S(vib)³⁴⁻³⁶ minus sum S(vib) from 6-31G(d,p) freqs with scale factor 0.90. ^cSame, SF 0.91 ^dMP2/6-31G(d,p)

Table 21d. Difference of S(vib) Values Derived from Shimanouchi and from 6-31G(d,p) Frequencies at 500

	S(vib) ^a	MP2/6-		
		6-31G(d,p) ^b	6-31G(d,p) ^b	31G(d,p) ^{bc}
		SF 0.90	SF 0.91	SF 0.95/0.923
Ethane	3.43	-0.12	-0.02	0.00
Cyclopropane	6.50	0.00	0.15	0.13
Propane	7.12	-0.29	-0.12	-0.09
1,3-Butadiene	13.81	-0.29	-0.03	-0.74
Cyclobutane	8.88	-0.29	-0.12	-0.09
Butane t	11.21	-0.41	-0.18	-0.10
Butane g	10.74	-0.86	-0.23	-0.50
Cyclohexane	22.49	-1.09	-0.69	-0.73
RMS omitting cyclohexane		0.43	0.15	0.22

Sum of residuals	0.43	0.15	0.22
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^a See footnotes Table 21c.

Table 22a. Uncertainties in Calculated C(vib) Owing to Uncertainties in Frequencies, Based on Shimanouchi Uncertainty Estimates

Differences between C(vib) based on best Shimanouchi frequencies and best Shianouchi freqs + half uncertainty

Temperature	C(vib) from	C(vib) from	delta	C(vib) from	C(vib) from	delta
	best freqs ^a	best+half		best freqs ^a	best+half	
Ethane	298	uncer ^b		500	uncer ^b	
Propane	2.597	2.558	0.039	8.743	8.664	0.079
Butane t C2h	5.471	5.431	0.040	14.845	14.786	0.059
Cyclohexane	8.491	8.373	0.118	21.020	20.896	0.124
	17.178	17.065	0.113	36.423	36.291	0.132

^aOmitting Me torsion frequencies and butane C-C-C-C torsion ^bBest frequencies increased by half the stated

uncertainty

Table 22b. Uncertainties in Calculated S(vib) Owing to Uncertainties in Frequencies, Based on Shimanouchi Uncertainty Estimates

Differences between S(vib) based on best Shimanouchi frequencies and Shianouchi freqs + half uncertainty

Temperature	S(vib) from	S(vib) from	delta	S(vib) from	S(vib) from	delta
	best freqs ^a	best+half		best freqs ^a	best+half	
Ethane	298	uncer ^b		500	uncer ^b	
	0.655	0.645	0.010	3.432	3.390	0.042

Propane	2.074	2.053	0.021	7.121	7.072	0.049
Butane t C2h	3.837	3.666	0.171	11.209	11.029	0.180
Cyclohexane	8.929	8.805	0.124	22.486	22.297	0.189

^aOmitting Me torsion frequencies and butane C-C-C-C torsion ^bBest frequencies increased by half the stated uncertainty

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