# Thermodynamic Properties of Twenty-One Monocyclic Hydrocarbons

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The available structural parameters, fundamental frequencies, and relative energies of different stable conformers, if any, for cyclopropane, cyclopropene, cyclobutane, cyclobutene, 1,3-cyclobutadiene, cyclopentane, cyclopentene, 1,3-cyclopentadiene, cyclohexane, cyclohexene, 1,3-cyclohexadiene, 1,4-cyclohexadiene, cycloheptane, cycloheptene, 1,3-cycloheptadiene, 1,3,5-cycloheptatriene, cyclooctane, cyclooctene, 1,3-cyclooctadiene, 1,5-cyclooctadiene, and 1,3,5,7-cyclooctatetraene were critically evaluated and the recommended values selected. Molecular constants for some molecules were estimated as the experimental values for these compounds are not available. This information was utilized to calculate the ideal gas thermodynamic properties $C_p^\circ$, $S^\circ$, $-(G^\circ - H_0^\circ)/T$, $H^\circ - H_0^\circ$, and $\log K_f$ from 100 to 1500 K. The thermal functions were obtained using the rigid-rotor harmonic-oscillator approximation. The contributions derived for the inversion motion of cyclobutane and cyclopentene were obtained from energy levels calculated with the potential functions. For cyclopentane the pseudorotational contributions to thermal functions were calculated by assuming the pseudorotation as the free rotation of the molecule. The calculated values of the thermal functions are compared with those reported in other work. Agreement with experimental data, where such are available, is satisfactory within the experimental uncertainties.

Key words: ideal gas thermodynamic properties; molecular structure; monocyclic hydrocarbons with carbon atom numbers from 3 to 8; vibrational assignments.

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## 1. Introduction

This report involves the calculation of the ideal gas thermodynamic properties of 21 monocyclic hydrocarbons with carbon atom numbers from 3 to 8 (cycloalkanes and their unsaturated analogs). For a few of these molecules, thermodynamic properties have been reported. Recently, more complete and reliable information has become available on the structure and vibrational assignments of monocyclic hydrocarbons. This information permits us to make more precise calculations of thermal functions of some molecules and to calculate the thermal functions of others for the first time. A number of substances, viz., 1,4-cycloheptadiene, 1,4-cyclooctadiene, 1,3,5-, and 1,3,6-cyclooctatriene were not considered in this work due to the unreliability of structural and conformational data and due to the lack of vibrational assignments.

The available data on vibrational frequencies, structural parameters, and energies of different stable conformations have been critically examined and the most reliable values have been selected. Molecular constants for some compounds were estimated in the present work as the experimental values for these molecules are not available, incomplete, or unreliable. The selected molecular constants are given in Tables 1–9.

Based on the selected values of molecular constants, the ideal gas thermal functions {heat capacity ($C_p^\circ$), entropy ($S^\circ$), Gibbs energy function [$-(G^\circ - H_0^\circ)/T$], and enthalpy ($H^\circ - H_0^\circ$)} were calculated by the standard statistical mechanical method using rigid-rotor harmonic-oscillator approximations. The enthalpy of formation ($\Delta_f H^\circ$) and the calculated thermal functions have been used to calculate the logarithm of the equilibrium constant of formation ($\log K_f$) by the usual thermodynamic formulas [subscript f denotes formation by the reaction $n\mathrm{C(c,graphite)} + m\mathrm{H_2(g)} = \mathrm{C}_n H_{2m}\mathrm{(g)}$]. The procedures for calculation of thermodynamic properties are similar to those used in *Thermodynamic Properties of Individual Substances* by Gurvich *et al.*[1] The fundamental physical constants and thermodynamic properties of the elements in their reference states used in the calculations are also taken from Ref. 1. The chemical thermodynamic property values

Table 1. Molecular and thermochemical constants for the three-membered rings

| | Cyclopropane  $C_3H_6$ | | Cyclopropene  $C_3H_4$ | |
|---|---|---|---|---|
| Molecular weight | 42.0804 | | 40.0646 | |
| Point group | $D_{3h}$ | | $C_{2v}$ | |
| Symmetry number | 6 | | 2 | |
| Ground state statistical weight | 1 | | 1 | |
| Product of the three principal moments of inertia, $g^3cm^6 \times 10^{117}$ | 117 | | 65.3 | |
| Vibrational frequencies, $cm^{-1}$: | | | | |
| $\nu_1$ | $A_1'$ | 3038 | $A_1$ | 3152 |
| $\nu_2$ | | 1479 | | 2909 |
| $\nu_3$ | | 1188 | | 1653 |
| $\nu_4$ | $A_1''$ | 1126 | | 1483 |
| $\nu_5$ | $A_2'$ | 1070 | | 1105 |
| $\nu_6$ | $A_2''$ | 3101.7 | | 905 |
| $\nu_7$ | | 854 | $A_2$ | 996 |
| $\nu_8$ | $E'$ | 3024.4 | | 815 |
| $\nu_9$ | | 1457.7 | $B_1$ | 3116 |
| $\nu_{10}$ | | 1028.4 | | 1043 |
| $\nu_{11}$ | | 868.5 | | 1011 |
| $\nu_{12}$ | $E''$ | 3082 | | 769 |
| $\nu_{13}$ | | 1188 | $B_2$ | 2995 |
| $\nu_{14}$ | | 739 | | 1088 |
| $\nu_{15}$ | | | | 569 |
| Enthalpy of formation at 298.15 K, kJ $mol^{-1}$ | 53.3 | | 277.1 | |

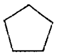
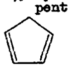
Table 2. Molecular and thermochemical constants for the four-membered rings

| | Cyclobutane  $C_4H_8$ | | Cyclobutene  $C_4H_6$ | | 1,3-Cyclobutadiene  $C_4H_4$ | |
|---|---|---|---|---|---|---|
| Molecular weight | 56.1072 | | 54.0914 | | 52.0756 | |
| Point group | $D_{2d}$ | | $C_{2v}$ | | $D_{2h}$ | |
| Symmetry number | 8[a] | | 2 | | 4 | |
| Ground state statistical weight | 1 | | 1 | | 1 | |
| Product of the three principal moments of inertia, $g^3cm^6 \times 10^{116}$ | 82 | | 55 | | 36 | |
| Vibrational frequencies, $cm^{-1}$: | | | | | | |
| $\nu_1$ | $A_1$ | 2974 | $A_1$ | 3063 | $A_g$ | 3050 |
| $\nu_2$ | | 2905 | | 2941 | | 1510 |
| $\nu_3$ | | 1469 | | 1564 | | 1120 |
| $\nu_4$ | | 1153 | | 1448 | | 900 |
| $\nu_5$ | | 1005 | | 1185 | $A_u$ | 1100 |
| $\nu_6$ | | -[b] | | 1113 | | 570 |
| $\nu_7$ | $A_2$ | 1300 | | 981 | $B_{1g}$ | 3030 |
| $\nu_8$ | | 941 | | 883 | | 1235 |
| $\nu_9$ | $B_1$ | 1234 | $A_2$ | 2955 | | 770 |
| $\nu_{10}$ | | 1142 | | 1142 | $B_{2g}$ | 900 |
| $\nu_{11}$ | | 926 | | 1000 | $B_{3g}$ | 900 |
| $\nu_{12}$ | $B_2$ | 2987 | | 909 | $B_{1u}$ | 570 |
| $\nu_{13}$ | | 2945 | | 327 | $B_{2u}$ | 3030 |
| $\nu_{14}$ | | 1454 | $B_1$ | 3056 | | 1240 |
| $\nu_{15}$ | | 883 | | 2934 | | 720 |
| $\nu_{16}$ | | 626 | | 1430 | $B_{3u}$ | 3040 |
| $\nu_{17}$ | $E$ | 2965 | | 1294 | | 1520 |
| $\nu_{18}$ | | 2887 | | 1214 | | 990 |
| $\nu_{19}$ | | 1452 | | 1013 | | |
| $\nu_{20}$ | | 1260 | | 890 | | |
| $\nu_{21}$ | | 1224 | $B_2$ | 2961 | | |
| $\nu_{22}$ | | 901 | | 1074 | | |
| $\nu_{23}$ | | 749 | | 846 | | |
| $\nu_{24}$ | | | | 636 | | |
| Enthalpy of formation at 298.15 K, $kJ\ mol^{-1}$ | 28.4 | | 156.7 | | 385 | |

[a] Although cyclobutane has the nonplanar conformation ($D_{2d}$ symmetry), the symmetry number 8 is given in the table due to the fact that the molecule is undergoing inversion through its planar configuration ($D_{4h}$ symmetry).

[b] The ring-puckering frequency $\nu_6 = 199\ cm^{-1}$ is not given in table as the contribution derived for the inversion motion of cyclobutane has been obtained by the direct summation over the energy levels.

Table 3. Molecular and thermochemical constants for the five-membered rings

| | Cyclopentane  $C_5H_{10}$ | | Cyclopentene  $C_5H_8$ | | 1,3-Cyclopentadiene  $C_5H_6$ | |
|---|---|---|---|---|---|---|
| Molecular weight | 70.134 | | 68.1182 | | 66.1024 | |
| Point group | $C_1$ | | $C_s$ | | $C_{2v}$ | |
| Symmetry number | 1 | | 2[c] | | 2 | |
| Ground state statistical weight | 1 | | 1 | | 1 | |
| Product of the three principal moments of inertia, $g^3cm^6 \times 10^{115}$ | 38.75 | | 28.39 | | 19.96 | |
| Vibrational frequencies, $cm^{-1}$: | | | | | | |
| $\nu_1$ | | 2960(5)[a] | $A_1$ | 3070 | $A_1$ | 3091 |
| $\nu_2$ | | 2880(5) | | 2903 | | 3075 |
| $\nu_3$ | | 1480(3) | | 2860 | | 2886 |
| $\nu_4$ | | 1455(2) | | 1617 | | 1500 |
| $\nu_5$ | | 1310(2) | | 1473 | | 1378 |
| $\nu_6$ | | 1285(2) | | 1448 | | 1365 |
| $\nu_7$ | | 1250(2) | | 1302 | | 1106 |
| $\nu_8$ | | 1210(2) | | 1109 | | 994 |
| $\nu_9$ | | 1160(2) | | 962 | | 915 |
| $\nu_{10}$ | | 1035(2) | | 896 | | 802 |
| $\nu_{11}$ | | 1022 | | 600 | $A_2$ | 1100 |
| $\nu_{12}$ | | 985 | $A_2$ | 2938 | | 941 |
| $\nu_{13}$ | | 949 | | 1209 | | 700 |
| $\nu_{14}$ | | 896 | | 1134 | | 516 |
| $\nu_{15}$ | | 886 | | 1047 | $B_1$ | 3105 |
| $\nu_{16}$ | | 858 | | 879 | | 3043 |
| $\nu_{17}$ | | 827 | | 390 | | 1580 |
| $\nu_{18}$ | | 770 | $B_1$ | 3068 | | 1292 |
| $\nu_{19}$ | | 617 | | 2882 | | 1239 |
| $\nu_{20}$ | | 545 | | 1438 | | 1090 |
| $\nu_{21}$ | | 283 | | 1353 | | 959 |
| $\nu_{22}$ | | -[b] | | 1268 | | 805 |
| $\nu_{23}$ | | | | 1128 | $B_2$ | 2900 |
| $\nu_{24}$ | | | | 1037 | | 925 |
| $\nu_{25}$ | | | | 933 | | 891 |
| $\nu_{26}$ | | | | 695 | | 664 |
| $\nu_{27}$ | | | $B_2$ | 2963 | | 350 |
| $\nu_{28}$ | | | | 2933 | | |
| $\nu_{29}$ | | | | 1207 | | |
| $\nu_{30}$ | | | | 1047 | | |
| $\nu_{31}$ | | | | 695 | | |
| $\nu_{32}$ | | | | 593 | | |
| $\nu_{33}$ | | | | -[d] | | |
| Enthalpy of formation at 298.15 K, $kJ\ mol^{-1}$ | -78.4 | | 32.7 | | 130.8 | |

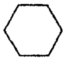
[a] Numbers in parentheses represent the accidental multiplicities since some of the close-lying frequencies were averaged due to their large uncertainty.

[b] The pseudorotational contribution was calculated by free rotation formulae[1].

[c] Although cyclopentene has the nonplanar structure ($C_s$ symmetry), the symmetry number 2 is given in the table due to the fact that the molecule is undergoing inversion through its planar configuration ($C_{2v}$ symmetry).

[d] The ring-puckering frequency $\nu_{33} = 127\ cm^{-1}$ is not given in table as the contribution due to inversion of cyclopentene was obtained by direct summation over the energy levels.

Table 4. Molecular and thermochemical constants for the six-membered rings

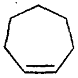
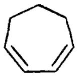
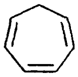
| | Cyclohexane[a]<br> $C_6H_{12}$ | Cyclohexene<br> $C_6H_{10}$ | 1,3-Cyclohexadiene<br> $C_6H_8$ | 1,4-Cyclohexadiene<br> $C_6H_8$ |
|---|---|---|---|---|
| Molecular weight | 84.1608 | 82.145 | 80.1292 | 80.1292 |
| Point group | $D_{3d}$ | $C_2$ | $C_2$ | $D_{2h}$ |
| Symmetry number | 6 | 2 | 2 | 4 |
| Number of optical isomers | 1 | 2 | 2 | 1 |
| Ground state statistical weight | 1 | 1 | 1 | 1 |
| Product of the three principal moments of inertia, $g^3 cm^6 \times 10^{114}$ | 13.35 | 10.71 | 8.517 | 9.26 |
| Vibrational frequencies | see Table 5 | see Table 5 | see Table 5 | see Table 5 |
| Enthalpy of formation at 298.15 K, kJ $mol^{-1}$ | -123.3 | -4.6 | 106.3 | 109.0 |

[a] Another stable conformer was also taken into account for cyclohexane: point group $D_2$, symmetry number 4, number of optical isomers 2, statistical weight 1, relative energy 1925 $cm^{-1}$.

Table 5. Vibrational frequencies (cm$^{-1}$) for the six-membered rings

| | Cyclohexane | | Cyclohexene | | 1,3-Cyclohexadiene | | 1,4-Cyclohexadiene | |
|---|---|---|---|---|---|---|---|---|
| $\nu_1$ | $A_{1g}$ | 2936 | $A$ | 3040 | $A$ | 3050 | $A_g$ | 3032 |
| $\nu_2$ | | 2853 | | 2940 | | 3050 | | 2822 |
| $\nu_3$ | | 1465 | | 2916 | | 2939 | | 1680 |
| $\nu_4$ | | 1158 | | 2865 | | 2838 | | 1426 |
| $\nu_5$ | | 802 | | 2839 | | 1577 | | 1197 |
| $\nu_6$ | | 384 | | 1660 | | 1444 | | 854 |
| $\nu_7$ | $A_{1u}$ | 1380 | | 1460 | | 1330 | | 530 |
| $\nu_8$ | | 1150 | | 1445 | | 1243 | $A_u$ | 1250 |
| $\nu_9$ | | 1100 | | 1353 | | 1223 | | 970 |
| $\nu_{10}$ | | 1350 | | 1343 | | 1178 | | 370 |
| $\nu_{11}$ | | 1100 | | 1240 | | 1150 | $B_{1g}$ | 1240 |
| $\nu_{12}$ | $A_{2g}$ | 2914 | | 1222 | | 1059 | | 706 |
| $\nu_{13}$ | | 2863 | | 1140 | | 994 | $B_{2g}$ | 3032 |
| $\nu_{14}$ | $A_{2u}$ | 1457 | | 1095 | | 945 | | 1377 |
| $\nu_{15}$ | | 1039 | | 1068 | | 850 | | 1280 |
| $\nu_{16}$ | | 522 | | 966 | | 753 | | 1035 |
| $\nu_{17}$ | $E_g$ | 2924 | | 905 | | 559 | | 574 |
| $\nu_{18}$ | | 2895 | | 812 | | 506 | $B_{3g}$ | 2875 |
| $\nu_{19}$ | | 1445 | | 657 | | 201 | | 1010 |
| $\nu_{20}$ | | 1347 | | 520 | $B$ | 3050 | | 985 |
| $\nu_{21}$ | | 1268 | | 392 | | 3050 | | 403 |
| $\nu_{22}$ | | 1029 | | 276 | | 2884 | $B_{1u}$ | 3042 |
| $\nu_{23}$ | | 785 | $B$ | 3078 | | 2838 | | 2840 |
| $\nu_{24}$ | | 427 | | 2960 | | 1602 | | 1439 |
| $\nu_{25}$ | $E_u$ | 2934 | | 2890 | | 1435 | | 1405 |
| $\nu_{26}$ | | 2863 | | 2878 | | 1377 | | 962 |
| $\nu_{27}$ | | 1457 | | 2858 | | 1178 | | 888 |
| $\nu_{28}$ | | 1346 | | 1455 | | 1165 | $B_{2u}$ | 2889 |
| $\nu_{29}$ | | 1260 | | 1450 | | 1100 | | 962 |
| $\nu_{30}$ | | 906 | | 1343 | | 1040 | | 625 |
| $\nu_{31}$ | | 862 | | 1325 | | 1016 | | 108 |
| $\nu_{32}$ | | 241 | | 1269 | | 927 | $B_{3u}$ | 3042 |
| $\nu_{33}$ | | | | 1215 | | 745 | | 1642 |
| $\nu_{34}$ | | | | 1140 | | 658 | | 1362 |
| $\nu_{35}$ | | | | 1039 | | 468 | | 1159 |
| $\nu_{36}$ | | | | 1009 | | 298 | | 887 |
| $\nu_{37}$ | | | | 919 | | | | |
| $\nu_{38}$ | | | | 877 | | | | |
| $\nu_{39}$ | | | | 719 | | | | |
| $\nu_{40}$ | | | | 638 | | | | |
| $\nu_{41}$ | | | | 450 | | | | |
| $\nu_{42}$ | | | | 165 | | | | |

Table 6. Molecular and thermochemical constants for the seven-membered rings

| | Cycloheptane[a]<br><br>$C_7H_{14}$ | Cycloheptene[b]<br><br>$C_7H_{12}$ | 1,3-Cycloheptadiene[c]<br><br>$C_7H_{10}$ | 1,3,5-Cyclohepta-triene<br><br>$C_7H_8$ |
|---|---|---|---|---|
| Molecular weight | 98.1876 | 96.1718 | 94.156 | 92.1402 |
| Point group | $\underline{C}_2$ | $\underline{C}_s$ | $\underline{C}_s$ | $\underline{C}_s$ |
| Symmetry number | 2 | 1 | 1 | 1 |
| Number of optical isomers | 2 | 1 | 1 | 1 |
| Ground state statistical weight | 1 | 1 | 1 | 1 |
| Product of the three principal moments of inertia, $g^3 cm^6 \times 10^{114}$ | 39.1 | 32.1 | 29.12 | 21.43 |
| Vibrational frequencies | see Table 7 | see Table 7 | see Table 7 | see Table 7 |
| Enthalpy of formation at 298.15 K, kJ $mol^{-1}$ | -118.2 | -9.4 | 94.2 | 182.8 |

Other stable conformers were also taken into account for cycloheptane, cycloheptene and 1,3-cycloheptadiene (point group, symmetry number ($\sigma$), number of optical isomers ($\underline{n}$), statistical weight ($\underline{p}$) and relative energy ($\underline{T}$) are listed for each conformer):

[a] $\underline{C}_2$, $\sigma = 2$, $\underline{n} = 2$, $\underline{p} = 1$, $\underline{T} = 1200\ cm^{-1}$;

[b] $\underline{C}_2$, $\sigma = 2$, $\underline{n} = 2$, $\underline{p} = 1$, $\underline{T} = 500\ cm^{-1}$;

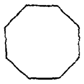
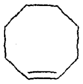
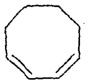
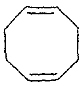
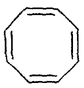
[c] $\underline{C}_1$, $\sigma = 1$, $\underline{n} = 2$, $\underline{p} = 1$, $\underline{T} = 200\ cm^{-1}$,
$\underline{C}_2$, $\sigma = 2$, $\underline{n} = 2$, $\underline{p} = 1$, $\underline{T} = 500\ cm^{-1}$.

Table 7. Vibrational frequencies (cm$^{-1}$) for the seven-membered rings

| Cycloheptane | Cycloheptene | 1,3-Cyclohepta-diene | 1,3,5-Cyclo-heptatriene |
|---|---|---|---|
| 2925(7)$^a$ | $\underline{A}'$ 3024 | $\underline{A}'$ 3018 | 3050(6)$^a$ |
| 2860(7) | 2964 | 3018 | 2950 |
| 1467 | 2926 | 2927 | 2850 |
| 1450 | 2881 | 2885 | 1650(3) |
| 1446 | 2852 | 2858 | 1450(3) |
| 1440 | 2852 | 2830 | 1400(2) |
| 1430(3) | 2837 | 1613 | 1200(3) |
| 1360 | 1656 | 1433 | 1100(2) |
| 1350 | 1457 | 1430 | 1000(4) |
| 1310(3) | 1443 | 1372 | 950(2) |
| 1285(2) | 1434 | 1356 | 900(2) |
| 1230(3) | 1339 | 1257 | 800 |
| 1210 | 1332 | 1252 | 750 |
| 1200(2) | 1252 | 1043 | 700 |
| 1125 | 1234 | 1004 | 650 |
| 1100 | 1200 | 955 | 450(3) |
| 1040 | 1072 | 882 | 350 |
| 1020 | 1042 | 856 | 300 |
| 1005(2) | 983 | 767 | 225 |
| 950 | 875 | 683 | |
| 915 | 824 | 585 | |
| 850 | 746 | 363 | |
| 830 | 691 | 347 | |
| 810 | 479 | 242 | |
| 800 | 417 | $\underline{A}''$ 3062 | |
| 735 | 353 | 3062 | |
| 690 | 190 | 2963 | |
| 650 | $\underline{A}''$ 3062 | 2905 | |
| 515 | 2963 | 1645 | |
| 490 | 2924 | 1448 | |
| 400 | 2854 | 1397 | |
| 335 | 2842 | 1341 | |
| 320 | 1447 | 1300 | |
| 273 | 1439 | 1223 | |
| 186 | 1391 | 1195 | |
| 125 | 1357 | 1153 | |
| | 1323 | 1077 | |
| | 1270 | 971 | |
| | 1234 | 895 | |
| | 1207 | 853 | |
| | 1144 | 835 | |
| | 1104 | 730 | |
| | 1024 | 577 | |
| | 985 | 377 | |
| | 960 | 165 | |
| | 889 | | |
| | 832 | | |
| | 585 | | |
| | 469 | | |
| | 312 | | |
| | 209 | | |

[a] Numbers in parentheses are the accidental multiplicities (some of the close-lying frequencies were averaged due to their large uncertainty).

Table 8. Molecular and thermochemical constants for the eight-membered rings

| | Cyclooctane[a]<br><br>$C_8H_{16}$ | Cyclooctene[b]<br><br>$C_8H_{14}$ | 1,3-Cycloocta-diene[c]<br><br>$C_8H_{12}$ | 1,5-Cycloocta-diene[d]<br><br>$C_8H_{12}$ | 1,3,5,7-Cyclo-octatetraene<br><br>$C_8H_8$ |
|---|---|---|---|---|---|
| Molecular weight | 112.2144 | 110.1986 | 108.1828 | 108.1828 | 104.1512 |
| Point group | $\underline{C}_{\underline{s}}$ | $\underline{C}_2$ | $\underline{C}_2$ | $\underline{C}_2$ | $\underline{D}_{2\underline{d}}$ |
| Symmetry number | 1 | 2 | 2 | 2 | 4 |
| Number of optical isomers | 1 | 2 | 2 | 2 | 1 |
| Ground state statistical weight | 1 | 1 | 1 | 1 | 1 |
| Product of the three principal moments of inertia, $g^3cm^6 \times 10^{114}$ | 92 | 80 | 66 | 66 | 51.67 |
| Vibrational frequencies | see Table 9 | see Table 9 | see Table 9 | see Table 9 | see Table 9 |
| Enthalpy of formation at 298.15 K, kJ $mol^{-1}$ | -124.4 | -27.0 | 80.5 | 58.6 | 297.6 |

Other stable conformers were also taken into account for cyclooctane, cyclooctene, 1,3-cyclooctadiene, and 1,5-cyclooctadiene (point group, symmetry number ($\sigma$), number of optical isomers ($\underline{n}$), statistical weight ($\underline{p}$), and relative energy ($\underline{T}$) are listed for each conformer):

[a]
$$\left.\begin{array}{l} \underline{D}_2,\ \sigma = 4,\ \underline{n} = 2 \\ \underline{C}_1,\ \sigma = 1,\ \underline{n} = 2 \\ \underline{C}_{2\underline{v}},\ \sigma = 2,\ \underline{n} = 1 \\ \underline{C}_2,\ \sigma = 2,\ \underline{n} = 2 \\ \underline{C}_1,\ \sigma = 1,\ \underline{n} = 2 \end{array}\right\}\ \underline{p} = 1,\ \underline{T} = 275\ \mathrm{cm}^{-1}$$

[b] $\underline{C}_2$ $\sigma = 2$, $\underline{n} = 2$, $\underline{p} = 1$, $\underline{T} = 1000\ \mathrm{cm}^{-1}$;

[c] $\underline{C}_1$, $\sigma = 1$, $\underline{n} = 2$, $\underline{p} = 1$, $\underline{T} = 200\ \mathrm{cm}^{-1}$;

[d]
$$\left.\begin{array}{l} \underline{C}_{2\underline{h}},\ \sigma = 2,\ \underline{n} = 1 \\ \underline{C}_{\underline{s}},\ \sigma = 1,\ \underline{n} = 1 \end{array}\right\}\ \underline{p} = 1,\ \underline{T} = 1500\ \mathrm{cm}^{-1}.$$

Table 9. Vibrational frequencies ($cm^{-1}$) for the eight-membered rings

| Cyclooctane | Cyclooctene | 1,3-Cyclooctadiene | 1,5-Cyclooctadiene | 1,3,5,7-Cyclooctatetraene | |
|---|---|---|---|---|---|
| 2933 | 3040(2)[a] | 3040(4)[a] | 3040(4)[a] | $A_1$ | 3013 |
| 2921 | 2920(4) | 2930(2) | 2910(4) | | 1651 |
| 2915(5)[a] | 2900(2) | 2900(2) | 2850(4) | | 1202 |
| 2908 | 2850(6) | 2885(2) | 1660(2) | | 873 |
| 2885(2) | 1660 | 2860(2) | 1450(4) | | 758 |
| 2880 | 1450(6) | 1635(2) | 1390(2) | | 194 |
| 2872 | 1390 | 1450(3) | 1350 | $A_2$ | 2950 |
| 2867(2) | 1350(4) | 1360(5) | 1310(2) | | 1400 |
| 2859 | 1300(3) | 1310(2) | 1260(2) | | 1000 |
| 2853 | 1240(3) | 1250(2) | 1200(3) | | 900 |
| 1483 | 1140(3) | 1200(2) | 1160(2) | | 190 |
| 1472 | 1080(3) | 1110(3) | 1060(2) | $B_1$ | 2954 |
| 1455 | 1050(2) | 1060(2) | 1020 | | 1439 |
| 1442 | 980(2) | 970(2) | 980(2) | | 994 |
| 1400(6) | 900(2) | 930(2) | 940(2) | | 967 |
| 1380(3) | 870(2) | 870(2) | 890 | | 655 |
| 1364 | 800 | 830(2) | 820(3) | | 249 |
| 1360 | 770(2) | 800 | 760 | $B_2$ | 3015 |
| 1350 | 680 | 740(2) | 720 | | 1608 |
| 1297 | 550 | 620(2) | 660 | | 1204 |
| 1291 | 460(2) | 530 | 590(2) | | 669 |
| 1260 | 350(4) | 410 | 490(2) | | 285 |
| 1250 | 300 | 370 | 380 | $E$ | 3015 |
| 1230 | 200 | 310 | 310 | | 2965 |
| 1217 | 150 | 260 | 270(2) | | 1640 |
| 1175 | | 220 | 210 | | 1400 |
| 1137 | | 190 | 120 | | 1223 |
| 1135 | | 140 | | | 967 |
| 1110 | | | | | 945 |
| 1088(2) | | | | | 800 |
| 1046 | | | | | 625 |
| 988 | | | | | 365 |
| 956 | | | | | |
| 930(2) | | | | | |
| 862 | | | | | |
| 854 | | | | | |
| 799 | | | | | |
| 768 | | | | | |
| 725(2) | | | | | |
| 691 | | | | | |
| 667 | | | | | |
| 540 | | | | | |
| 514 | | | | | |
| 478 | | | | | |
| 367 | | | | | |
| 326 | | | | | |
| 292 | | | | | |
| 255 | | | | | |
| 220 | | | | | |
| 125 | | | | | |

[a] Numbers in parentheses are the accidental multiplicities (some of the close-lying frequencies were averaged due to their large uncertainty).

at temperatures from 100 to 1500 K for a pressure of 1 atm (= 101 325 Pa) are given in Tables 10–30.

The enthalpy of formation $\Delta_f H^\circ$ (298.15 K) for all substances but 1,3-cyclobutadiene, 1,4-cyclohexadiene, and 1,3-cyclooctadiene was taken from the compilation of Pedley and Rylance.[2]

The inversion motion contributions to the thermodynamic properties for cyclobutane and cyclopentene were calculated by the use of the potential function of type $V(x) = \frac{1}{2}kx^2 + ax^4$. These potential functions are based on experimentally observed transitions and barrier heights of the inversion mode for the respective molecules. The contributions due to inversion were obtained by the summation over the energy levels calculated from the potential functions. The procedure for energy levels calculations was described previously.[3,4]

The pseudorotation contributions to the thermodynamic properties of cyclopentane were calculated using the free rotation model.[1]

The thermodynamic properties of molecules with several stable conformations were calculated by assuming the same fundamental frequencies and principal moments of inertia for all conformers (only the discrepancies in symmetry numbers and relative energies were taken into account).

It should be emphasized that the chiral conformations ($C_1$,$C_2$,$D_2$ symmetry) exist as an equimolal mixture of two enantiomeric forms. The contribution to the thermodynamic properties of two optical isomers is obtained by adding the entropy of mixing, $S^\circ_{\text{mix}} = R \ln 2$, to $S^\circ$ and $-(G^\circ - H^\circ_0)/T$, which is equivalent to assuming the effective symmetry number $\sigma_{\text{eff}} = \sigma/n$ ($\sigma$ is the symmetry number, $n = 2$ is the number of optical isomers). For that reason Tables 4, 6, and 8 show the numbers of optical isomers together with other molecular constants.

Uncertainties in the calculated thermal functions (Table 31) were obtained by taking into account the inaccuracy of selected molecular structural and spectroscopic data and inaccuracy due to the deviation from the rigid-rotor harmonic-oscillator model. The procedure for the approximate evaluation of these uncertainties was described previously.[1] Uncertainties in adopted enthalpies of formation (Table 31) for most of the substances were taken from data of Pedley and Rylance.[2] For 1,3-cyclobutadiene, 1,4-cyclohexadiene, and 1,3-cyclooctadiene uncertainties in $\Delta_f H^\circ$(298.15 K) were estimated in the present work. The selection of the enthalpy of formation values for these three substances will be described below.

Comparisons of the calculated and experimental entropy and heat capacity values are given in Tables 32 and 33, respectively.

## 2. Cyclopropane

The rotational constants $B_0$ and $C_0$ were obtained from high-resolution infrared spectra[5–7] and from pure rotational Raman spectra,[8–10] respectively. The structural parameters estimated from rotational constants[9,10] are consistent with electron diffraction data.[11] The product of the principal moments of inertia of cyclopropane (Table 1) was calculated using the more precise rotational constants of McCubbin *et al.*[7] and Butcher and Jones.[10]

Various workers have studied the infrared and Raman spectra of cyclopropane.[5–8,10,12–15] Duncan and McKean[14]

Table 10. Ideal gas thermodynamic properties for cyclopropane

| T | $C_p°$ | $-(G°-H_0°)/T$ | $S°$ | $H°-H_0°$ | log $K_f$ |
|---|---|---|---|---|---|
| K | J K$^{-1}$ mol$^{-1}$ | | | kJ mol$^{-1}$ | |
| 100 | 33.321 | 161.608 | 194.871 | 3.326 | -39.474 |
| 200 | 38.907 | 184.814 | 218.993 | 6.836 | -23.159 |
| 298.15 | 55.571 | 199.109 | 237.378 | 11.410 | -18.298 |
| 300 | 55.941 | 199.346 | 237.723 | 11.513 | -18.241 |
| 400 | 76.052 | 211.291 | 256.589 | 18.119 | -16.031 |
| 500 | 93.859 | 222.249 | 275.532 | 26.641 | -14.832 |
| 600 | 108.542 | 232.677 | 293.986 | 36.786 | -14.099 |
| 700 | 120.682 | 242.708 | 311.658 | 48.265 | -13.612 |
| 800 | 130.910 | 252.385 | 328.459 | 60.859 | -13.268 |
| 900 | 139.658 | 261.731 | 344.396 | 74.398 | -13.014 |
| 1000 | 147.207 | 270.760 | 359.510 | 88.750 | -12.817 |
| 1100 | 153.749 | 279.486 | 373.855 | 103.806 | -12.660 |
| 1200 | 159.432 | 287.923 | 387.482 | 119.471 | -12.532 |
| 1300 | 164.377 | 296.084 | 400.443 | 135.668 | -12.425 |
| 1400 | 168.688 | 303.982 | 412.787 | 152.326 | -12.332 |
| 1500 | 172.453 | 311.631 | 424.556 | 169.387 | -12.252 |

Table 11. Ideal gas thermodynamic properties for cyclopropene

| T | $C_p°$ | $-(G°-H_0°)/T$ | $S°$ | $H°-H_0°$ | log $K_f$ |
|---|---|---|---|---|---|
| K | J K$^{-1}$ mol$^{-1}$ | | | kJ mol$^{-1}$ | |
| 100 | 33.444 | 167.767 | 200.987 | 3.328 | -147.962 |
| 200 | 39.333 | 190.989 | 225.401 | 6.882 | -74.339 |
| 298.15 | 52.881 | 205.344 | 243.491 | 11.373 | -50.367 |
| 300 | 53.164 | 205.580 | 243.619 | 11.472 | -50.068 |
| 400 | 67.959 | 217.324 | 261.176 | 17.540 | -38.066 |
| 500 | 80.503 | 227.765 | 277.736 | 24.985 | -30.935 |
| 600 | 90.659 | 237.408 | 293.343 | 33.561 | -26.219 |
| 700 | 98.992 | 246.455 | 307.964 | 43.056 | -22.873 |
| 800 | 105.984 | 255.008 | 321.652 | 53.315 | -20.378 |
| 900 | 111.949 | 263.134 | 334.488 | 64.219 | -18.446 |
| 1000 | 117.084 | 270.879 | 346.556 | 75.677 | -16.907 |
| 1100 | 121.526 | 278.280 | 357.928 | 87.613 | -15.651 |
| 1200 | 125.378 | 285.370 | 368.672 | 99.963 | -14.608 |
| 1300 | 128.725 | 292.172 | 378.843 | 112.672 | -13.727 |
| 1400 | 131.639 | 298.710 | 388.491 | 125.693 | -12.973 |
| 1500 | 134.161 | 305.004 | 397.662 | 138.987 | -12.320 |

reported the complete vibrational assignment from their infrared measurements for the gaseous and solid states of cyclopropane. We have adopted the vibrational fundamentals, as shown in Table 1, of Duncan and McKean,[14] with the exception that the more precise values of $\nu_6$ and $\nu_8$–$\nu_{11}$ were taken from the high-resolution infrared spectrum of Duncan.[6] Duncan and Burns[16] confirmed their assignment by carrying out a normal coordinate analysis. More recent experimental and theoretical studies[17–20] are consistent with the vibrational assignment of Duncan.

Ideal gas thermodynamic properties for cyclopropane are listed in Table 10. The calculated value of $S°$ (298.15 K) is in good agreement with the calorimetric value of Ruehrwein and Powell[21] and with the other statistically calculated entropy values[21–23] (Table 32). The calculated values of $C_p°$ agree well with available experimental data[254,255] (Table 33). The thermal functions reported by Chang *et al.*[24] were obtained with the molecular constants estimated from molecular mechanics (empirical force field) calculation; the agreement with their functions is worse than with other calculations (for $S°$ see Table 32; the discrepancy in $C_p°$ amounted to 2 J K$^{-1}$ mol$^{-1}$ at 298.15 K). Due to the discrepancy in the molecular constants used, the agreement with the data of Karuppannan *et al.*[23] increases as the temperature increases (for $S°$ see Table 32; the discrepancy in $C_p°$ amounted to 2 J K$^{-1}$ mol$^{-1}$ at 1000 K). As we have used more reliable input data, our calculated thermodynamic properties are believed to be the most reliable.

## 3. Cyclopropene

The molecular structure of cyclopropene was investigated by electron diffraction[25] and microwave[26,27] techniques. The structural parameters obtained in these studies are mutually consistent. The rotational constants determined by Stigliani *et al.*,[27] which are believed to be more precise, were used to compute the product of the three principal moments of inertia (Table 1).

Vibrational spectra of cyclopropene were studied by various workers.[28–30] The fundamental frequencies used in our calculations (Table 1) were taken from the more reliable work of Yum and Eggers.[30] These authors observed vibrational frequencies from infrared and Raman spectra for the vapor and liquid states and carried out a normal coordinate analysis to confirm the vibrational assignment. The frequencies calculated by Wieberg *et al.*[31,256] are consistent with vibrational assignment given by Yum and Eggers.[30]

Ideal gas thermodynamic properties for cyclopropene are listed in Table 11. Unfortunately, no experimental data on gaseous $C_p°$ and $S°$ are available for comparison; however, the thermal functions computed in this work are practically identical with those reported earlier[30,32] (the comparison for $S°$ is given in Table 32).

## 4. Cyclobutane

Infrared,[33–37] Raman,[34–36] nuclear magnetic resonance,[38] and electron diffraction[39–42] studies have shown that cyclobutane undergoes inversion and the ground-state molecular structure is puckered ($D_{2d}$ symmetry). *Ab initio*[43,44] and semiempirical[45–49] calculations confirm these experimental results. Different conclusions, however, have been reported with regard to the degree of ring puckering and the value of methylene group rocking. The product of the principal moments of inertia for cyclobutane (Table 2) was calculated from electron diffraction structural data obtained by Takabayashi *et al.*,[42] except for the methylene group rocking angle. Takabayashi *et al.*[42] estimated this angle, $\tau = 6°$, assuming the linear dependence of this parameter from the ring puckering angle. We adopted $\tau = 4°$ according to data[38,44,48,49] as they appear more reliable. The ring puckering angle $\varphi = 26°$ determined by Takabayashi *et al.*[42] agrees well with the values obtained from nuclear magnetic resonance data[38] and the high quality *ab initio* calculation.[44] This result significantly differs from the previous conclusions[33–36,41] ascribing to the cyclobutane ring much higher nonplanarity of approximately 35°.

Infrared and Raman spectra for the vapor, liquid, and solid phases of cyclobutane were investigated.[33,35,36,50–53] Until recently, the vibrational frequencies determined by Miller *et al.*[52] were believed to be the most reliable. However, later Bánhegyi *et al.*[54] carried out the *ab initio* calculation and reassigned some experimental vibrational frequencies. Aleksanyan and Antipov[53] reinvestigated the infrared and

Table 12. Ideal gas thermodynamic properties for cyclobutane

| T | $C_p^\circ$ | $-(G^\circ-H_0^\circ)/T$ | $S^\circ$ | $H^\circ-H_0^\circ$ | log $K_f$ |
|---|---|---|---|---|---|
| K | J K$^{-1}$ mol$^{-1}$ | | | kJ mol$^{-1}$ | |
| 100 | 38.169 | 177.164 | 211.958 | 3.479 | -33.224 |
| 200 | 48.835 | 202.406 | 241.155 | 7.750 | -22.473 |
| 298.15 | 70.564 | 219.003 | 264.396 | 13.534 | -19.645 |
| 300 | 71.048 | 219.286 | 264.831 | 13.663 | -19.614 |
| 400 | 97.665 | 233.667 | 288.920 | 22.101 | -18.532 |
| 500 | 122.029 | 247.164 | 313.397 | 33.116 | -18.062 |
| 600 | 142.636 | 260.221 | 337.522 | 46.381 | -17.842 |
| 700 | 159.915 | 272.942 | 360.846 | 61.533 | -17.738 |
| 800 | 174.524 | 285.338 | 383.180 | 78.274 | -17.688 |
| 900 | 186.985 | 297.403 | 404.473 | 96.363 | -17.667 |
| 1000 | 197.668 | 309.131 | 424.743 | 115.612 | -17.659 |
| 1100 | 206.850 | 320.524 | 444.024 | 135.850 | -17.657 |
| 1200 | 214.761 | 331.585 | 462.368 | 156.940 | -17.658 |
| 1300 | 221.590 | 342.325 | 479.836 | 178.764 | -17.659 |
| 1400 | 227.496 | 352.745 | 496.478 | 201.226 | -17.660 |
| 1500 | 232.622 | 362.861 | 512.354 | 224.239 | -17.659 |

Raman spectra of cyclobutane in the three aggregation states and confirmed the results of Bánhegyi *et al.*[54] The vibrational frequencies given in Table 2 are those obtained by Miller *et al.*[52] from infrared and Raman spectral measurements of gaseous cyclobutane, with the exception of $\nu_4$, $\nu_7$, $\nu_8$, $\nu_{10}$, and $\nu_{15}$ modes, for which the values were taken from Refs. 53 and 54.

Cyclobutane is a molecule which undergoes inversion. The thermodynamic-property contributions due to inversion of the cyclobutane ring were obtained by the direct summation over the energy levels calculated with the potential function. The procedure for energy levels calculation was described previously.[3,4] Several investigations of the double minimum ring-puckering potential function of cyclobutane have been reported.[34–36] The potential function given by Miller and Capwell[36] was used to calculate 60 energy levels. The potential function for inversion is $V(x) = 6.932\times10^5x^4 - 3.79\times10^4x^2$ (where $x$ is the ring-puckering coordinate) with a barrier height of $(518 \pm 5)$ cm$^{-1}$. The partition function for inversion is based on these 60 levels with the first 7 levels being the experimental levels from which the potential function was derived.

Ideal gas thermodynamic properties for cyclobutane are given in Table 12. The calculated value of $S^\circ$ (298.15 K) is 1 J K$^{-1}$ mol$^{-1}$ less than that obtained from calorimetric measurements[55] (Table 32). This discrepancy is practically within uncertainties of the experimental and calculated values. Another two available calculations (Table 32) are not suitable for comparison with our result. Rathjens *et al.*[50] obtained the excellent agreement with experiment by actually fitting the vibrational assignment for cyclobutane. The discrepancy between data of Rathjens *et al.*[50] and thermal functions given in Table 12 increases significantly at higher temperatures [up to 4.2 J K$^{-1}$ mol$^{-1}$ for $S^\circ$ (1000 K) and 3 J K$^{-1}$ mol$^{-1}$ for $C_p^\circ$ (1000 K)]. As Rathjens *et al.*[50] used unreliable molecular constants and calculated inversion contributions to thermal functions by an approximate method we suppose that our data are more precise. Chang *et al.*[24] used the molecular constants evaluated from the molecular mechanics calculation. Therefore, the good agreement between their and our values of entropy (Table 32) is fortuitous (the discrepancy in $C_p^\circ$ amounted to 2.8 J K$^{-1}$ mol$^{-1}$ at 500 K).

## 5. Cyclobutene

The molecular structure of cyclobutene has been studied by the visual electron diffraction method[56] and by microwave techniques.[57,58] Cyclobutene has a planar structure. The rotational constants determined in microwave studies[57,58] agree well. Bak *et al.*[58] studied the microwave spectra of cyclobutene and four of its isotropic species. From these data they calculated the structural parameters of cyclobutene. These parameters are in good agreement with those obtained by Wieberg and Wendoloski[59] from *ab initio* calculation. The product of the principal moments of inertia, given in Table 2, was calculated using the rotational constants of Bak *et al.*[58]

Lord and Rea[60] observed both the Raman spectrum of the liquid and the infrared spectrum of gas and liquid, and made a complete assignment of the vibrational frequencies for cyclobutene. Unobserved $\nu_9$–$\nu_{12}$ modes of $A_2$ symmetry were evaluated by comparison with suitable fundamentals of $B_2$ symmetry. Sverdlov and Krainov[61] carried out the normal coordinate analysis and proposed new assignments for several frequencies. The reassignment of spectral data[60] was also made by Suzuki and Nibler[62] from their investigation of vibrational spectra of *cis*-3,4-dichlorocyclobutene. The most reliable assignment seems to be that reported by Aleksanyan and Garkusha[63] from infrared and Raman spectra of gaseous, liquid, and solid states of cyclobutene. This assignment was adopted in the present work, except for two unobserved frequencies of $A_2$ symmetry, $\nu_9$ and $\nu_{11}$ (Table 2). We have perferred the vapor phase values whenever available. For the CH$_2$-stretching mode ($\nu_9$) the value of 2955 cm$^{-1}$ was chosen in accordance with the estimation made by Lord and Rea.[60] The assignment of the CH$_2$-rocking fundamental ($\nu_{11}$) has been less certain. Lord and Rea[60] have evaluated it as 640 cm$^{-1}$, whereas Sverdlov and Krainov,[61] using a normal coordinate treatment, have assigned the band at 1276 cm$^{-1}$ to a $\nu_{11}$ fundamental. From comparison with the CH$_2$-rocking fundamentals of cyclopentene[64] we estimated this frequency as $1000 \pm 150$ cm$^{-1}$.

Table 13. Ideal gas thermodynamic properties for cyclobutene

| T | $C_p^\circ$ | $-(G^\circ-H_0^\circ)/T$ | $S^\circ$ | $H^\circ-H_0^\circ$ | log $K_f$ |
|---|---|---|---|---|---|
| K | J K$^{-1}$ mol$^{-1}$ | | | kJ mol$^{-1}$ | |
| 100 | 35.049 | 180.384 | 214.009 | 3.362 | -92.470 |
| 200 | 44.697 | 204.369 | 240.699 | 7.266 | -49.177 |
| 298.15 | 64.413 | 219.844 | 261.962 | 12.557 | -35.429 |
| 300 | 64.841 | 220.105 | 262.362 | 12.677 | -35.260 |
| 400 | 88.073 | 233.393 | 284.220 | 20.331 | -28.549 |
| 500 | 108.624 | 245.756 | 306.149 | 30.197 | -24.649 |
| 600 | 125.542 | 257.612 | 327.501 | 41.933 | -22.115 |
| 700 | 139.443 | 269.068 | 347.931 | 55.204 | -20.341 |
| 800 | 151.035 | 280.149 | 367.330 | 69.745 | -19.032 |
| 900 | 160.833 | 290.866 | 385.701 | 85.352 | -18.026 |
| 1000 | 169.184 | 301.227 | 403.090 | 101.864 | -17.228 |
| 1100 | 176.339 | 311.242 | 419.559 | 119.149 | -16.579 |
| 1200 | 182.493 | 320.925 | 435.173 | 137.098 | -16.041 |
| 1300 | 187.801 | 330.288 | 449.995 | 155.619 | -15.586 |
| 1400 | 192.393 | 339.346 | 464.085 | 174.634 | -15.197 |
| 1500 | 196.378 | 348.113 | 477.498 | 194.078 | -14.858 |

Ideal gas thermodynamic properties for cyclobutene are presented in Table 13. There are no experimental data for comparison. The thermal functions calculated by Danti[65] are different from ours by up to 3.4 J K$^{-1}$ mol$^{-1}$ for $S°$ (1000 K) and 2.7 J K$^{-1}$ mol$^{-1}$ for $C_p^\circ$(298.15 K) (see also Table 32). As we used the most recent and complete data, our thermal functions are believed to be more reliable.

## 6. 1,3-Cyclobutadiene

The question of the ground-state structure of cyclobutadiene has been of great interest to both experimental and theoretical chemists over the past 15 years. The observed infrared spectrum of matrix isolated cyclobutadiene originally has been interpreted as indicating a square-planar structure for the molecule because the number of bands agreed with the number expected,[66–68] and because the frequencies agreed with those calculated theoretically for a square ground state.[69,70] However, a number of semiempirical[71–73] and good *ab initio*[74–80] calculations of the geometry all agree in predicting a rectangular ground state instead. Masamune *et al.*[81] concluded from an improved experimental infrared spectrum that the cyclobutadiene ring is not square but most likely rectangular. This is supported by the similarity found between Masamune's and the computed infrared spectrum of rectangular cyclobutadiene.[77,79,80,82] Thus the evidence, both theoretical and experimental, leads to the conclusion that the cyclobutadiene ring in the ground state is not square but rectangular ($D_{2h}$ symmetry).

There are no experimental data on the molecular structure of cyclobutadiene. The product of the principal moments of inertia (Table 2) was calculated based on the estimated structural parameters for planar rectangular geometry:

$$r(\mathrm{C=C}) = 1.34 \pm 0.03\ \text{Å},$$

$$r(\mathrm{C\text{–}C}) = 1.55 \pm 0.03\ \text{Å},$$

$$r(\mathrm{C\text{–}H}) = 1.08 \pm 0.02\ \text{Å},$$

and

$$\sphericalangle = \mathrm{C\text{–}C\text{–}H} = 135 \pm 3°.$$

These parameters were adopted by comparing the results of *ab initio* calculations for cyclobutadiene[75,76,78,80] and semiempirical calculations for cyclobutadiene and cyclobutene.[72] (The experimental molecular structure is known for cyclobutene and it helps to estimate the uncertainty of theoretical predictions for cyclobutadiene.)

Only five vibrational fundamentals were assigned from the infrared spectrum of matrix isolated cyclobutadiene[66,81,82]: 570 cm$^{-1}$ ($\nu_{12}$, $B_{1u}$, CH wagging); 1240 cm$^{-1}$ ($\nu_{14}$, $B_{2u}$, CCH deformation); 720 cm$^{-1}$ ($\nu_{15}$, $B_{2u}$, C–C stretching); 3040 cm$^{-1}$ ($\nu_{16}$, $B_{3u}$, CH stretching); and 1520 cm$^{-1}$ ($\nu_{17}$, $B_{3u}$, C = C stretching). These values were adopted in the present work (Table 2). The vibrational spectrum of cyclobutadiene was calculated by the *ab initio* method.[77,79,80,82] While the calculated intensities were found to be in good agreement with those observed experimentally, an appreciable discrepancy exists between calculated and experimental frequency values (up to 100–250 cm$^{-1}$). To obtain more reliable data for unobserved fundamentals, a normal coordinate calculation was performed. For this purpose we used the NCA (normal coordinate analysis and force constants refinement) program by Novikov.[83] The initial force field (12 force constants) was transferred from 1,3-cyclopentadiene.[84] After force constants refinement, the five observed band positions were reproduced with an accuracy of 1 cm$^{-1}$. The uncertainties of calculated values for unobserved frequencies (except for torsion frequencies) are less than 50 cm$^{-1}$. The vibrations involving the torsion motion are not observed experimentally and their force constants therefore cannot be evaluated in the same way as the other ones. These fundamentals [$\nu_5(A_u)$, $\nu_6(A_u)$, $\nu_{10}$ ($B_{2g}$), and $\nu_{11}$ ($B_{3g}$)] were obtained by averaging the values calculated with the torsional force constants of 1,3-cyclopentadiene,[84] 1,3-cyclohexadiene,[85] and 1,3-cycloheptadiene[86]; their uncertainties were estimated to be 50–150 cm$^{-1}$.

Table 14. Ideal gas thermodynamic properties for 1,3-cyclobutadiene

| $T$ | $C_p^\circ$ | $-(G^\circ-H_0^\circ)/T$ | $S^\circ$ | $H^\circ-H_0^\circ$ | log $K_f$ |
|---|---|---|---|---|---|
| K | J K$^{-1}$ mol$^{-1}$ | | | kJ mol$^{-1}$ | |
| 100 | 33.620 | 172.314 | 205.614 | 3.330 | -204.267 |
| 200 | 42.863 | 195.772 | 230.970 | 7.040 | -102.414 |
| 298.15 | 60.968 | 210.733 | 251.328 | 12.103 | -69.161 |
| 300 | 61.332 | 210.985 | 251.706 | 12.216 | -68.745 |
| 400 | 80.069 | 223.707 | 271.974 | 19.307 | -52.047 |
| 500 | 95.643 | 235.336 | 291.578 | 28.121 | -42.098 |
| 600 | 108.029 | 246.273 | 310.154 | 38.328 | -35.503 |
| 700 | 117.980 | 256.658 | 327.581 | 49.646 | -30.814 |
| 800 | 126.171 | 266.553 | 343.887 | 61.867 | -27.310 |
| 900 | 133.025 | 276.003 | 359.155 | 74.836 | -24.593 |
| 1000 | 138.834 | 285.042 | 373.479 | 88.437 | -22.426 |
| 1100 | 143.795 | 293.701 | 386.950 | 102.575 | -20.657 |
| 1200 | 148.055 | 302.006 | 399.650 | 117.173 | -19.186 |
| 1300 | 151.725 | 309.982 | 411.649 | 132.166 | -17.943 |
| 1400 | 154.900 | 317.654 | 423.012 | 147.501 | -16.878 |
| 1500 | 157.655 | 325.040 | 433.795 | 163.132 | -15.957 |

No experimental data on the enthalpy of formation of cyclobutadiene are available, but its value was calculated by *ab initio*[78] and semiempirical[73,87] methods. We adopted the MINDO/3 value of $\Delta_f H°$(298.15 K) obtained by Kollmar *et al.*,[73] since in their opinion the extrapolation of the errors in the MINDO/3 enthalpy of formation for cyclobutane and cyclobutene suggests that the error in the case of cyclobutadiene is probably quite small.

Ideal gas thermodynamic properties for 1,3-cyclobutadiene, given in Table 14, are reported for the first time. No experimental data are available for comparison.

## 7. Cyclopentane

Kilpatrick *et al.*[88] introduced the concept of pseudorotation to explain the high gas phase entropy value of cyclopentane. The cyclopentane equilibrium conformation has been shown by Pitzer *et al.*[88,89] to be puckered in contrast with the previously assumed planar conformation ($D_{5h}$ symmetry), and to vary continuously on an equipotential energy surface. Semiempirical and *ab initio* calculations of the relative energies for different conformations of cyclopentane[90–93,257] confirmed that a pseudorotation of the ring puckering takes place. This implies a close similarity between the energies of the nonplanar half-chair ($C_2$ symmetry) and envelope ($C_s$ symmetry) conformations. The most direct evidence for pseudorotation in cyclopentane has come from spectroscopic studies.[94–96] Electron diffraction investigation[97] also agrees with the pseudorotation of cyclopentane and shows the ring to be decidedly nonplanar.

Since cyclopentane undergoes an almost unhindered pseudorotation, that is, all conformations of puckered molecule are energetically equivalent, the effective nonplanar structure ($C_1$ symmetry) is adopted for cyclopentane. The product of the principal moments of inertia, given in Table 3, was calculated from electron diffraction structural parameters obtained by Adams *et al.*[97] for nonplanar ($C_2$ and $C_s$ symmetry) conformations of cyclopentane.

The vibrational spectrum of cyclopentane based on infrared and Raman studies[98,99] was partly reassigned according to force field calculations.[92,100] The frequencies, given in Table 3, were based on the assignments proposed in Refs. 92 and 100.

The contributions of unhindered pseudorotation to the thermal functions were calculated by free rotation formulas[1] assuming the reduced moment of inertia, $I_r = 11 \cdot 10^{-40}$ g cm$^2$ (spectroscopic value[94]), and symmetry number, $\sigma_{\text{pseudo}} = 10$ [cyclopentane ring undergoes pseudorotation through its planar configuration ($D_{5h}$ symmetry)].

Ideal gas thermodynamic properties for cyclopentane are listed in Table 15. The calculated values of $S°$ at 298.15, 310.16, and 322.41 K coincide with the calorimetric entropies[88,101] [for $S°$ (298.15 K) see Table 32] and the calculated values of $C_p^\circ$ agree with experimental ones[88,101,258] within 0.1–1.1 J K$^{-1}$ mol$^{-1}$ (Table 33). The agreement of calculated values of $S°$ at 230, 260, and 323.2 K (274.4, 282.4, and 299.9 J K$^{-1}$ mol$^{-1}$, respectively) with earlier calorimetric data of Aston *et al.*[259] (273.0, 282.4, and 297.9 J K$^{-1}$ mol$^{-1}$, respectively) is not as good as with more recent experimental data.[88,101] Our thermal functions are in good agreement with those calculated by Kilpatrick *et al.*[88] and McCullough *et al.*[101] at low temperatures. The discrepancies, however, increase at higher temperatures up to 1.8 J K$^{-1}$ mol$^{-1}$ for $S°$ (1500 K)[101] and 2.7 J K$^{-1}$ mol$^{-1}$ for $C_p^\circ$(1500 K).[88] These discrepancies, as well as the discrepancies with thermal functions calculated by Chang *et al.*[24] are due to the difference in molecular constants used in calculations. As we have used more recent and reliable data, we feel our calculated values of thermodynamic properties should be more reliable.

Table 15. Ideal gas thermodynamic properties for cyclopentane

| $T$ | $C_p^\circ$ | $-(G^\circ-H_0^\circ)/T$ | $S^\circ$ | $H^\circ-H_0^\circ$ | log $K_f$ |
|---|---|---|---|---|---|
| K | J K$^{-1}$ mol$^{-1}$ | | | kJ mol$^{-1}$ | |
| 100 | 40.182 | 196.937 | 234.979 | 3.804 | 15.693 |
| 200 | 54.185 | 224.295 | 266.284 | 8.398 | -.338 |
| 298.15 | 82.759 | 242.469 | 292.857 | 15.023 | -6.567 |
| 300 | 83.388 | 242.782 | 293.371 | 15.177 | -6.652 |
| 400 | 118.150 | 258.986 | 322.122 | 25.255 | -10.268 |
| 500 | 150.053 | 274.593 | 352.001 | 38.704 | -12.671 |
| 600 | 177.072 | 289.986 | 381.820 | 55.100 | -14.396 |
| 700 | 199.703 | 305.192 | 410.866 | 73.972 | -15.694 |
| 800 | 218.795 | 320.160 | 438.814 | 94.923 | -16.704 |
| 900 | 235.021 | 334.841 | 465.546 | 117.635 | -17.511 |
| 1000 | 248.883 | 349.196 | 491.045 | 141.848 | -18.167 |
| 1100 | 260.761 | 363.205 | 515.337 | 167.346 | -18.709 |
| 1200 | 270.964 | 376.854 | 538.475 | 193.945 | -19.163 |
| 1300 | 279.750 | 390.141 | 560.519 | 221.491 | -19.546 |
| 1400 | 287.341 | 403.068 | 581.536 | 249.855 | -19.873 |
| 1500 | 293.915 | 415.639 | 601.590 | 278.926 | -20.155 |

## 8. Cyclopentene

Microwave studies,[102–104] electron diffraction investigation,[105] and analysis of the ring-puckering potential function from infrared and Raman spectra,[106–108] as well as *ab initio* calculation[257] established that cyclopentene has a nonplanar ground-state conformation (envelope, $C_s$ symmetry) and the molecule undergoes inversion through its planar configuration ($C_{2v}$ symmetry).

The values of rotational constants obtained in microwave investigations[102,103] are somewhat different. Scharpen[104] reanalyzed the data of Butcher and Costain[103] taking into account vibrational–rotational coupling and obtained good agreement with the rotational constants of Rathjens.[102] The product of the principal moments of inertia, given in Table 3, was calculated using the rotational constants of Rathjens.[102] Assuming the values of some structural parameters, Rathjens[102] evaluated the ring-puckering angle as 22°. From analysis of the ring-puckering potential of cyclopentene the dihedral angle was deduced to be 22–26°.[106,108,260] The electron diffraction value is somewhat larger (29°).[105] The value obtained by *ab initio* computation[257] is probably too small (13.6°).

Vibrational spectra of cyclopentene were studied by various workers.[64,109–113] The fundamental frequencies for gaseous cyclopentene used in our calculations (Table 3) were taken from the more detailed investigation of Villarreal *et al.*[64] These authors have measured the infrared and Raman spectra of cyclopentene and its isotopic species in all three aggregation states. In conjunction wth a normal coordinate analysis, vibrational assignments are proposed on the basis of isotopic shift ratios, group frequency considerations, relative band intensities, and shapes, as well as depolarization ratios.

The thermodynamic-property contributions due to inversion of the cyclopentene ring were obtained by direct summation over the energy levels calculated with a potential function. The procedure for energy level calculation was described previously.[3,4] Several investigations of the double minimum ring-puckering potential function of cyclopentene have been reported.[104,106–108,260] Laane and Lord[106] have reported the potential function derived from experimentally observed transition of the inversion modes for cyclopentene. This function is based on an estimated value of reduced mass. More recently, Villarreal *et al.*[261] have calculated the value of reduced mass and the potential function was recalculated. In this work the potential function given by Villarreal *et al.*[261] based on the study of Laane and Lord[106] was used to calculate 60 energy levels. The potential function for inversion is $V(x) = 7.11 \times 10^5 x^4 - 25.7 \times 10^3 x^2$ (where $x$ is the ring-puckering coordinate) with a barrier height ($232 \pm 5$) cm$^{-1}$. The partition function for inversion is based on these 60 levels with the first 12 levels being the experimental levels from which the potential function was derived.

Ideal gas thermodynamic properties for cylopentene

Table 16. Ideal gas thermodynamic properties for cyclopentene

| T | $C_p^\circ$ | $-(G^\circ-H_0^\circ)/T$ | $S^\circ$ | $H^\circ-H_0^\circ$ | log $K_f$ |
|---|---|---|---|---|---|
| K | J K$^{-1}$ mol$^{-1}$ | | | kJ mol$^{-1}$ | |
| 100 | 40.365 | 197.018 | 233.171 | 3.615 | -34.310 |
| 200 | 54.739 | 223.493 | 264.743 | 8.250 | -22.484 |
| 298.15 | 81.275 | 241.438 | 291.267 | 14.857 | -19.295 |
| 300 | 81.836 | 241.746 | 291.772 | 15.008 | -19.259 |
| 400 | 112.081 | 257.701 | 319.489 | 24.715 | -17.986 |
| 500 | 138.986 | 272.862 | 347.473 | 37.306 | -17.394 |
| 600 | 161.381 | 287.591 | 374.858 | 52.360 | -17.089 |
| 700 | 179.949 | 301.952 | 401.174 | 69.455 | -16.921 |
| 800 | 195.517 | 315.935 | 426.248 | 88.250 | -16.822 |
| 900 | 208.709 | 329.526 | 450.059 | 108.480 | -16.761 |
| 1000 | 219.961 | 342.718 | 472.646 | 129.928 | -16.721 |
| 1100 | 229.601 | 355.513 | 494.075 | 152.418 | -16.693 |
| 1200 | 237.882 | 367.915 | 514.417 | 175.802 | -16.672 |
| 1300 | 245.019 | 379.934 | 533.746 | 199.956 | -16.654 |
| 1400 | 251.186 | 391.582 | 552.136 | 224.776 | -16.639 |
| 1500 | 256.530 | 402.875 | 569.652 | 250.165 | -16.624 |

are presented in Table 16. The calculated value of $S^\circ$ (298.15 K) is 1.5 J K$^{-1}$ mol$^{-1}$ larger than that obtained from calorimetric measurements,[109] whereas the entropy values calculated in previous works[109,114,115] agree well with the experimental entropy (Table 32). Beckett *et al.*[109] and Furuyama *et al.*[114] calculated the thermal functions based on a classical partition function for inversion and unreliable vibrational frequencies. Draeger *et al.*[115] used the reduced potential function[104] based on the study of Laane and Lord,[106] and employed the same method for computing of inversion contributions as in the present work. However, the rather unreliable vibrational assignment of Furuyama *et al.*[114] was adopted by Draeger *et al.*[115] Unfortunately, Draeger *et al.*[115] have not reported the values of entropy contributions due to inversion and thus the discrepancies between their data and thermal functions given in Table 16 cannot be analyzed in detail. Nevertheless, we state that the main discrepancies between the thermal functions obtained in this work and calculated by other authors[109,114,115] [up to 6.5 J K$^{-1}$ mol$^{-1}$ for $S^\circ$ (1500 K)[115] and 2.5 J K$^{-1}$ mol$^{-1}$ for $C_p^\circ$(298.15 K)[115]] are due to the difference in the adopted vibrational frequencies. If we had adopted the same values of vibrational frequencies as Draeger *et al.*[115] had, we would have obtained the value of $S^\circ$ (298.15 K) = 290.0 J K$^{-1}$ mol$^{-1}$, which is in good agreement with the experimental value of $S^\circ$ (298.15 K) = 289.7 J K$^{-1}$ mol$^{-1}$. However, the vibrational assignment of Villarreal *et al.*[64] seems to be the most reliable (see above) and we cannot find any reason for its modification. Thus, the use of the vibrational frequencies of Villarreal *et al.*[64] has not enabled us to obtain good agreement between the calculated and experimental values of $S^\circ$ (298.15 K). One can suggest that the discrepancy between the calculated and experimental entropy values is within the experimental uncertainty. Beckett *et al.*[109] do not indicate the experimental uncertainty, but, as is seen from Table 32, it might be expected to fall within the range 0.8–1.5 J K$^{-1}$ mol$^{-1}$.

## 9. 1,3-Cyclopentadiene

Scharpen and Laurie[116] have made microwave measurements of cyclopentadiene and three of its isotopic derivatives containing $^{13}$C from which the structural parameters for the planar carbon atom ring were found. Damiani *et al.*[117] have studied the microwave spectra of five deuterated species of cyclopentadiene and have calculated the complete molecular structure using the data of Scharpen and Laurie.[116] The rotational constants obtained in this way do not significantly differ from the values reported by Scharpen and Laurie. For computation of the product of the principal moments of inertia (Table 3) the rotational constants of Damiani *et al.*[117] were used. Experimental structural parameters[116,117] are consistent with those obtained from theoretical calculations.[59,118,257]

Various workers have studied the infrared and Raman spectra of cyclopentadiene,[84,119–123] but the available vibrational assignments have differed appreciably from one another. The more reliable interpretation of the vibrational spectrum of cyclopentadiene was proposed by Gallinella *et al.*[84,122] These authors investigated the infrared spectra in the three aggregation states and the liquid- and solid-phase Raman spectra of cyclopentadiene and its deuterated species. In order to confirm the vibrational assignment they also presented the results of a normal coordinate treatment. The fundamentals, given in Table 3, are those for liquid cyclopentadiene reported by Gallinella *et al.*,[84] as the assignment for vapor phase is incomplete. The use of liquid state frequencies instead of those for the vapor state causes small errors in calculated thermal functions (the average vapor–liquid shift is found to be 5 cm$^{-1}$).

Ideal gas thermodynamic properties for 1,3-cyclopentadiene are listed in Table 17. Grant and Walsh[124] reported a measurement of the entropy of cyclopentadiene from a study of the equilibrium between $H_2$, condensed cyclopentene, and condensed cyclopentadiene (see Table 32). There are no calorimetric determinations of this entropy. The entropy values computed in this work are in good agreement with those obtained in other calculations[114,125] at low temperatures. All calculated values of $S^\circ$ (298.15 K) are different from the entropy value obtained using equilibrium data[124] (Table 32), but the inaccuracy of the latter is rather large. The difference in molecular constants used in this work and other calculations[114,125] is the reason for discrepancies in entropy

Table 17. Ideal gas thermodynamic properties for 1,3-cyclopentadiene

| T | $C_p^\circ$ | $-(G^\circ-H_0^\circ)/T$ | $S^\circ$ | $H^\circ-H_0^\circ$ | log $K_f$ |
|---|---|---|---|---|---|
| K | J K$^{-1}$ mol$^{-1}$ | | | kJ mol$^{-1}$ | |
| 100 | 35.045 | 188.227 | 221.808 | 3.358 | -78.587 |
| 200 | 49.526 | 212.372 | 249.654 | 7.456 | -42.074 |
| 298.15 | 75.367 | 228.642 | 274.039 | 13.535 | -30.560 |
| 300 | 75.892 | 228.923 | 274.507 | 13.675 | -30.419 |
| 400 | 103.300 | 243.515 | 300.164 | 22.660 | -24.830 |
| 500 | 126.449 | 257.417 | 325.792 | 34.188 | -21.594 |
| 600 | 145.032 | 270.892 | 350.552 | 47.796 | -19.498 |
| 700 | 160.045 | 283.968 | 374.075 | 63.075 | -18.033 |
| 800 | 172.413 | 296.632 | 396.279 | 79.717 | -16.953 |
| 900 | 182.774 | 308.878 | 417.202 | 97.491 | -16.125 |
| 1000 | 191.553 | 320.706 | 436.926 | 116.219 | -15.468 |
| 1100 | 199.043 | 332.126 | 455.543 | 135.759 | -14.934 |
| 1200 | 205.467 | 343.151 | 473.145 | 155.993 | -14.492 |
| 1300 | 210.997 | 353.797 | 489.815 | 176.823 | -14.118 |
| 1400 | 215.775 | 364.083 | 505.630 | 198.167 | -13.798 |
| 1500 | 219.919 | 374.024 | 520.662 | 219.956 | -13.520 |

values at high temperatures [up to 2.6 J K$^{-1}$ mol$^{-1}$ for $S^\circ$ (1000 K)[125]] and in heat capacity values [up to 3.0[125] and 4.2 J K$^{-1}$ mol$^{-1}$ [114] for $C_p^\circ$ (500 K)].

## 10. Cyclohexane

Electron diffraction studies,[126–130] analysis of vibrational spectra,[92,131–137] dynamic nuclear magnetic resonance spectroscopy,[138] and theoretical calculations[90,139–143] indicate that the chair conformation ($D_{3d}$ symmetry) is the most stable form of cyclohexane. The strain-energy calculations[90,139–143] show that there are also two conformations, twist-boat ($D_2$ symmetry) and boat ($C_2$ symmetry), with an energy of about 20–25 kJ mol$^{-1}$ above that of the chair form. The twist-boat and boat forms can interconvert by pseudorotation. Calculations suggest that the twist-boat forms are at the minima of the pseudorotation path and that the boats are the transition states about 4 kJ mol$^{-1}$ above the twist boats. Direct experimental information on the twist-boat form was obtained from nuclear magnetic resonance spectroscopy[138] and matrix-isolated infrared spectra.[136,144] In the present work the twist-boat conformation was considered together with the basic stable chair form. Relative energy of the twist-boat form, 1925 ± 70 cm$^{-1}$ (23 ± 0.8 kJ mol$^{-1}$), given in Table 4, was obtained from experimental data.[138,144] This value is in a good agreement with estimations.[90,139–143] The product of the principal moments of inertia for the chair conformation of cyclohexane (Table 4) was calculated using the structural parameters determined by Bastiansen *et al.*[129] from electron diffraction investigation.

Vibrational spectra of cyclohexane have been studied extensively.[92,131–137] Various vibrational assignments have differed slightly from one another. Fundamentals, presented in Table 5, are those (except for $\nu_7$–$\nu_{11}$) obtained by Wieberg and Shrake.[133] These authors observed in the infrared spectra of vapor and liquid and Raman spectrum of liquid cyclohexane and carried out a normal coordinate analysis. We have preferred the vapor-phase values whenever available. The frequencies $\nu_7$–$\nu_9$ of $A_{1u}$ symmetry and $\nu_{10}$, $\nu_{11}$ of $A_{2g}$ symmetry, unobserved by Wieberg and Shrake,[133] were selected according to experimental data[135,136] and calculated values.[131–133]

Ideal gas thermodynamic properties for cyclohexane are given in Table 18. The calculated standard entropy at 298.15 K is 1.5 and 0.9 J K$^{-1}$ mol$^{-1}$ less than the values obtained from the calorimetric measurements of Aston *et al.*[262] and Beckett *et al.*,[145] respectively (Table 32) and the calculated $C_p^\circ$ values are 0.2–2.7 J K$^{-1}$ mol$^{-1}$ less than the experimental data of Spitzer and Pitzer[258] (Table 33). We suppose these discrepancies are within experimental uncertainties. The molecular constants of cyclohexane are rather reliable and we cannot find any reason for their modification. (Some different vibrational assignments for cyclohexane were considered in this work and for all of them the thermal functions are less than experimental values.) Beckett *et al.*[145] have achieved the agreement with the experimental value of $S^\circ$ (298.15 K) by fitting the molecular constants unknown at the time. The largest discrepancies with thermal functions calculated by Beckett *et al.*[145] amount to 4.4 J K$^{-1}$ mol$^{-1}$ for $S^\circ$ (1500 K) and 3.9 J K$^{-1}$ mol$^{-1}$ for $C_p^\circ$ (1500 K). The thermal functions of Chang *et al.*[24] are unreliable, because the molecular parameters were obtained from molecular mechanics calculations.

**Table 18.** Ideal gas thermodynamic properties for cyclohexane

| $T$ | $C_p^\circ$ | $-(G^\circ-H_0^\circ)/T$ | $S^\circ$ | $H^\circ-H_0^\circ$ | log $K_f$ |
|---|---|---|---|---|---|
| K | J K$^{-1}$ mol$^{-1}$ | | | kJ mol$^{-1}$ | |
| 100 | 42.590 | 190.546 | 226.103 | 3.556 | 31.451 |
| 200 | 69.053 | 217.933 | 263.276 | 9.069 | 4.423 |
| 298.15 | 105.341 | 238.431 | 297.276 | 17.544 | -5.590 |
| 300 | 106.108 | 238.796 | 297.930 | 17.740 | -5.724 |
| 400 | 148.638 | 258.084 | 334.266 | 30.473 | -11.322 |
| 500 | 188.678 | 277.066 | 371.822 | 47.378 | -14.943 |
| 600 | 223.376 | 295.995 | 409.374 | 68.027 | -17.489 |
| 700 | 252.620 | 314.827 | 446.071 | 91.870 | -19.373 |
| 800 | 277.052 | 333.459 | 481.448 | 118.391 | -20.819 |
| 900 | 297.419 | 351.797 | 515.292 | 147.145 | -21.958 |
| 1000 | 314.418 | 369.772 | 547.535 | 177.763 | -22.873 |
| 1100 | 328.656 | 387.337 | 578.189 | 209.937 | -23.620 |
| 1200 | 340.645 | 404.466 | 607.315 | 243.419 | -24.239 |
| 1300 | 350.793 | 421.143 | 634.993 | 278.005 | -24.757 |
| 1400 | 359.439 | 437.366 | 661.314 | 313.528 | -25.195 |
| 1500 | 366.845 | 453.138 | 686.372 | 349.851 | -25.568 |

## 11. Cyclohexene

Half-chair form ($C_2$ symmetry) has been found to be the most stable conformation of cyclohexene by electron diffraction measurements.[146–148] Similar conclusions were reached by microwave techniques,[149,150] infrared and Raman studies,[151–153] nuclear magnetic resonance spectroscopy,[154] as well as *ab initio*[155,257] and force-field[156–160] calculations. To explain the difference between calculated and experimental values of entropy and heat capacity, Beckett *et al.*[109] have suggested that cyclohexene exists as a mixture of half-chair and half-boat ($C_s$ symmetry) conformations where the former is the predominant form and is more stable than half-boat by 11.3 kJ mol$^{-1}$. However, the more recent experimental[152,154] and force-field[156–160] results have shown that the half-boat form is approximately 20–30 kJ mol$^{-1}$ higher in energy than the half-chair. According to most of the force-field calculations[157–160] the half-boat is a transition state (an energy maximum). A metastable half-boat form (an energy minimum which lies slightly lower than the potential maximum), on the other hand, is favored by analysis of the twisting mode region of the Raman spectrum.[152] Since the energy of half-boat conformation is rather high in both cases, we have not considered this form in our calculations.

The product of the principal moments of inertia for the half-chair conformation of cyclohexene (Table 4) was calculated using the rotational constants of Scharpen *et al.*[149] The adopted rotational constants are in excellent agreement with those obtained in another microwave study.[150] From microwave data,[149,150] the molecular structure of cyclohexene was estimated assuming a number of structural parameters. All in all this structure agrees with those obtained from electron diffraction studies[147,148] and *ab initio* calculations.[155,257]

Neto *et al.*[151] reported vibrational assignment for cyclo-

Table 19. Ideal gas thermodynamic properties for cyclohexene

| $T$ | $C_p^\circ$ | $-(G^\circ-H_0^\circ)/T$ | $S^\circ$ | $H^\circ-H_0^\circ$ | log $K_f$ |
|---|---|---|---|---|---|
| K | $J\ K^{-1}\ mol^{-1}$ | | | $kJ\ mol^{-1}$ | |
| 100 | 43.061 | 204.644 | 240.867 | 3.622 | -21.844 |
| 200 | 67.349 | 232.282 | 277.521 | 9.048 | -18.943 |
| 298.15 | 101.462 | 252.593 | 310.518 | 17.270 | -18.874 |
| 300 | 102.161 | 252.952 | 311.148 | 17.459 | -18.879 |
| 400 | 139.702 | 271.804 | 345.721 | 29.567 | -19.262 |
| 500 | 173.269 | 290.080 | 380.600 | 45.260 | -19.700 |
| 600 | 201.437 | 308.028 | 414.759 | 64.039 | -20.099 |
| 700 | 224.915 | 325.641 | 447.628 | 85.391 | -20.441 |
| 800 | 244.650 | 342.865 | 478.986 | 108.897 | -20.728 |
| 900 | 261.377 | 359.660 | 508.794 | 134.221 | -20.967 |
| 1000 | 275.634 | 376.000 | 537.091 | 161.090 | -21.166 |
| 1100 | 287.829 | 391.876 | 563.948 | 189.279 | -21.331 |
| 1200 | 298.291 | 407.288 | 589.453 | 218.598 | -21.470 |
| 1300 | 307.292 | 422.241 | 613.693 | 248.889 | -21.585 |
| 1400 | 315.058 | 436.746 | 636.757 | 280.016 | -21.680 |
| 1500 | 321.782 | 450.818 | 658.729 | 311.865 | -21.760 |

Table 20. Ideal gas thermodynamic properties for 1,3-cyclohexadiene

| $T$ | $C_p^\circ$ | $-(G^\circ-H_0^\circ)/T$ | $S^\circ$ | $H^\circ-H_0^\circ$ | log $K_f$ |
|---|---|---|---|---|---|
| K | $J\ K^{-1}\ mol^{-1}$ | | | $kJ\ mol^{-1}$ | |
| 100 | 40.779 | 202.970 | 238.278 | 3.531 | -72.277 |
| 200 | 62.742 | 229.570 | 272.610 | 8.608 | -41.357 |
| 298.15 | 94.165 | 248.782 | 303.304 | 16.256 | -31.859 |
| 300 | 94.802 | 249.120 | 303.889 | 16.431 | -31.745 |
| 400 | 128.546 | 266.795 | 335.842 | 27.619 | -27.258 |
| 500 | 157.995 | 283.808 | 367.789 | 41.991 | -24.727 |
| 600 | 182.235 | 300.407 | 398.812 | 59.043 | -23.122 |
| 700 | 202.143 | 316.600 | 428.447 | 78.293 | -22.019 |
| 800 | 218.699 | 332.353 | 456.553 | 99.360 | -21.216 |
| 900 | 232.630 | 347.644 | 483.139 | 121.946 | -20.605 |
| 1000 | 244.450 | 362.462 | 508.278 | 145.815 | -20.122 |
| 1100 | 254.531 | 376.809 | 532.062 | 170.778 | -19.731 |
| 1200 | 263.164 | 390.694 | 554.589 | 196.674 | -19.407 |
| 1300 | 270.585 | 404.130 | 575.953 | 223.370 | -19.131 |
| 1400 | 276.984 | 417.134 | 596.246 | 250.757 | -18.894 |
| 1500 | 282.523 | 429.724 | 615.549 | 278.738 | -18.687 |

hexene from the the infrared measurements in the gaseous and liquid states and the Raman spectrum in the liquid state. They carried out the normal coordinate analysis to confirm their assignment. We have adopted their frequencies (with the exception of $\nu_{18}$–$\nu_{22}$ and $\nu_{39}$–$\nu_{42}$ modes) preferring the vapor-phase values whenever available. Low-frequency out-of-plane skeletal bending and twisting fundamentals $\nu_{18}$–$\nu_{22}$ and $\nu_{39}$–$\nu_{42}$ reported by Smithson and Wieser[153] from the infrared spectrum of cyclohexene in the vapor phase were used in this work.

Ideal gas thermodynamic properties for cyclohexene are given in Table 19. The calculated value of $S^\circ$ (298.15 K) coincides with the calorimetric entropy[109] (Table 32), but the calculated value of $C_p^\circ$ (400 K) is 5.3 J K$^{-1}$ mol$^{-1}$ less than the experimental value of Beckett *et al.*[109] (Table 33). In order to achieve the agreement between experimental and calculated values of $C_p^\circ$, Beckett *et al.*[109] suggested the existence of the half-boat form with relative energy of 11.3 kJ mol$^{-1}$. However, the more recent results have shown that this suggestion is not correct (see above). We think that the accuracy of the experimental value of $C_p^\circ$ is not sufficiently high to discuss the disagreement between the experimental and calculated $C_p^\circ$ values. The largest discrepancies between thermal functions calculated by Beckett *et al.*[109] and given in Table 19 are equal to 7 J K$^{-1}$ mol$^{-1}$ for $S^\circ$ (1500 K) and 5.7 J K$^{-1}$ mol$^{-1}$ for $C_p^\circ$ (500 K) and are due to the difference in adopted molecular constants.

## 12. 1,3-Cyclohexadiene

The nonplanar twisted conformation of $C_2$ symmetry was found for 1,3-cyclohexadiene from electron diffraction studies[161–163] and semiempirical[164,165] and *ab initio*[155,166] calculations. The rotational constants of 1,3-cyclohexadiene were obtained by microwave studies.[167,168] Assuming the bond distances and bond angles from related compounds, Butcher[167] estimated the dihedral angle in agreement with electron diffraction values[161–163] and showed that the moments of inertia calculated from the proposed molecular structure of $C_2$ symmetry are close to those obtained from rotational constants. The product of the principal moments of inertia, given in Table 4, was calculated using the rotational constants of Butcher.[167] These constants are consistent with those of Luss and Harmony.[168]

Carreira *et al.*[169] investigated the Raman spectrum of gaseous 1,3-cyclohexadiene and obtained the ring-twisting potential function from which the barrier to inversion of the ring through its planar configuration was determined to be 1099 ± 50 cm$^{-1}$. We do not consider the inversion motion in 1,3-cyclohexadiene because the barrier to inversion is sufficiently high.

Di Lauro *et al.*[85] reported the complete vibrational assignment for 1,3-cyclohexadiene from the infrared measurements in gaseous and liquid states and the Raman study in the liquid state as well as from a normal coordinate analysis. Some of these frequencies were reinterpreted by Warshel and Karplus[164] based on the force-field calculation. Carreira *et al.*[169] investigated the Raman spectrum of gaseous 1,3-cyclohexadiene, but no detailed assignment was proposed. Fundamentals, presented in Table 5, are those obtained by Di Lauro *et al.*[85] We prefer the vapor state values whenever available.

Ideal gas thermodynamic properties for 1,3-cyclohexadiene, given in Table 20, are reported for the first time. No experimental data are available for comparison.

## 13. 1,4-Cyclohexadiene

Over the years, conclusions regarding the equilibrium configuration of 1,4-cyclohexadiene were contradictory. An early infrared and Raman investigation[170] was interpreted on the basis of $D_{2h}$ (planar) symmetry. More recently, Stidham[171] has reinvestigated the vibrational spectra of 1,4-cyclohexadiene and supported the planar configuration, although he could not rule out a boat form ($C_{2v}$ symmetry) that inverts through the planar form. Although subsequent studies involving electron diffraction,[172] nuclear magnetic resonance,[173] and semiempirical calculations[157,174] also supported a planar conformation, there were conflicting reports involving electron diffraction,[163] nuclear magnetic resonance,[175] and semiempirical calculation,[176] which supported a boat conformation. The electron diffraction study of Oberhammer and Bauer[163] constituted the major evidence against a planar structure, but their conclusion was based on an erroneous interpretation of the experimental data.[155] The planarity of the 1,4-cyclohexadiene ring was conclusively determined by the combination of the far-infrared and Raman data for the ring-puckering mode.[169,177] The conformation of 1,4-cyclohexadiene must closely correspond to the parabolic potential energy curve involving wide amplitude vibrations around the planar form, as described from infrared and Raman spectra in the low-frequency region[169,177] and supported by the semiempirical[174,178,179] and *ab initio*[155,166,178] calculations.

The molecular structure of 1,4-cyclohexadiene was determined by electron diffraction measurements.[163,172] Although Dallinga and Toneman[172] adopted the planar structure, for a variety of reasons[162,163] their data seem to be unreliable. Oberhammer and Bauer[163] have interpreted their data for a bent structure with a dihedral angle of 159.3° because no large amplitude vibrations have been taken into account. These authors have also tested a planar structure which showed worse agreement with experimental data. For lack of more reliable data, the structural parameters of the planar model obtained by Oberhammer and Bauer[163] were used for calculation of the product of the principal moments of inertia given in Table 4.

Stidham[171] reported vibrational assignment for 1,4-cyclohexadiene on the basis of infrared spectra of gaseous and liquid phases and Raman spectrum of liquid phase. Gebhardt and Cyvin[180] reproduced completely Stidham's frequency values by the force constants refinement. Ermer and Lifson[113] reassigned the values of some frequencies arising from the force-field calculation, their results being consistent with unpublished data of Neto *et al.*, reported in Ref. 113. Most of the fundamentals, presented in Table 5, are those of Stidham.[171] We preferred the vapor-phase values whenever available. Unobserved vibrational frequencies ($\nu_8$–$\nu_{11}$, $\nu_{15}$, $\nu_{19}$) and the values of $\nu_{25}$, $\nu_{34}$, and $\nu_{36}$ were taken from the assignment of Ermer and Lifson.[113] The ring-puckering frequency, $\nu_{31}$ ($B_{2u}$), is that observed by Laane and Lord[177] from the far-infrared spectrum.

No experimental data on the enthalpy of formation of 1,4-cyclohexadiene are available. The value presented in Table 4 is based on molecular mechanics calculations[143,178] and agrees well with the value recommended by Shaw *et al.*[181]

Table 21. Ideal gas thermodynamic properties for 1,4-cyclohexadiene

| $T$ | $C_p^\circ$ | $-(G^\circ-H_0^\circ)/T$ | $S^\circ$ | $H^\circ-H_0^\circ$ | log $K_f$ |
|---|---|---|---|---|---|
| K | J K$^{-1}$ mol$^{-1}$ | | | kJ mol$^{-1}$ | |
| 100 | 42.617 | 193.232 | 230.380 | 3.715 | -74.038 |
| 200 | 63.252 | 220.991 | 265.437 | 8.889 | -42.432 |
| 298.15 | 94.051 | 240.689 | 296.225 | 16.558 | -32.702 |
| 300 | 94.675 | 241.033 | 296.809 | 16.733 | -32.585 |
| 400 | 127.751 | 258.946 | 328.630 | 27.873 | -27.982 |
| 500 | 156.822 | 276.065 | 360.352 | 42.144 | -25.382 |
| 600 | 180.966 | 292.696 | 391.149 | 59.072 | -23.733 |
| 700 | 200.940 | 308.881 | 420.593 | 78.198 | -22.601 |
| 800 | 217.630 | 324.608 | 448.546 | 99.151 | -21.777 |
| 900 | 231.710 | 339.863 | 475.015 | 121.637 | -21.150 |
| 1000 | 243.669 | 354.642 | 500.064 | 145.422 | -20.656 |
| 1100 | 253.871 | 368.950 | 523.779 | 170.312 | -20.256 |
| 1200 | 262.606 | 382.797 | 546.253 | 196.147 | -19.924 |
| 1300 | 270.111 | 396.198 | 567.577 | 222.792 | -19.642 |
| 1400 | 276.580 | 409.169 | 587.837 | 250.135 | -19.400 |
| 1500 | 282.177 | 421.728 | 607.114 | 278.080 | -19.188 |

Ideal gas thermodynamic properties for 1,4-cyclohexadiene, given in Table 21, are reported for the first time. No experimental values of $S^\circ$ and $C_p^\circ$ are available for comparison.

## 14. Cycloheptane

Extensive conformational energy calculations[90,182–184,263] have been done on cycloheptane and these have led to an identification of four basic conformations: chair ($C_s$ symmetry), boat ($C_s$ symmetry), twist-chair ($C_2$ symmetry), and twist-boat ($C_2$ symmetry). On the energy profile during pseudorotation, obtained in these studies, the twist-chair and twist-boat forms are located at the minima and the chair and boat forms at the maxima. The twist-boat form is approximately 10–15 kJ mol$^{-1}$ higher in energy than the most stable twist-chair conformation. Vibrational spectra of cycloheptane[185] were interpreted on the basis of one rigid conformation, viz., the twist-chair form. However, the best agreement with experimental electron diffraction data[186] was obtained for a mixture of two minimum-energy conformers: the most stable twist-chair form and the chair form with energy higher by 3.8 kJ mol$^{-1}$. We have performed calculations of $S^\circ$ (298.15 K) for models of the different conformational composition and made comparison of the experimental entropy with the calculated values.[187] An inspection of these values shows that an excellent agreement exists for the twist-chair conformer alone or for the mixture of twist-chair and twist-boat, while the mixture of twist-chair and chair reported in electron diffraction study[186] has a noticeable discrepancy. From these considerations only two stable conformations of cycloheptane, twist-chair, and twist-boat, were taken into account in the present work. Relative energy of the twist-boat form, 1200 cm$^{-1}$ (14 kJ mol$^{-1}$), given in Table 6, was obtained by Bocian and Strauss[184] from the strain-energy calculations.

The gaseous electron diffraction structural data of Dillen and Geise[186] for the twist-chair form were used to calculate the product of the principal moments of inertia (Table 6). These structural parameters are consistent with those obtained by the force-field calculations.[90,182–184,263]

The vibrational frequencies of cycloheptane used in our calculations (Table 7) were taken from a study by Bocian and Strauss.[185] These authors have examined in detail the vapor- and liquid-phase infrared spectra, vapor-phase far-infrared spectrum, and liquid-phase Raman spectrum; special attention has been given to the low-frequency region. In addition, a normal coordinate analysis was performed to confirm the vibrational assignment and to estimate the unobserved frequencies.

Ideal gas thermodynamic properties for cycloheptane are listed in Table 22. The calculated value of $S^\circ$ (298.15 K), as shown in Table 32, coincides with the calorimetric entropy[188] and is close to that calculated by Chang *et al.*[24] However, the discrepancies between the thermal function reported by Chang *et al.*[24] and listed in Table 22 increase to 2.3 J K$^{-1}$ mol$^{-1}$ for $S^\circ$ and 7.3 J K$^{-1}$ mol$^{-1}$ for $C_p^\circ$ as the

Table 22. Ideal gas thermodynamic properties for cycloheptane

| $T$ | $C_p^\circ$ | $-(G^\circ-H_0^\circ)/T$ | $S^\circ$ | $H^\circ-H_0^\circ$ | log $K_f$ |
|---|---|---|---|---|---|
| K | J K$^{-1}$ mol$^{-1}$ | | | kJ mol$^{-1}$ | |
| 100 | 52.126 | 213.735 | 253.285 | 3.955 | 23.380 |
| 200 | 86.837 | 245.427 | 299.578 | 10.830 | -1.733 |
| 298.15 | 132.014 | 270.263 | 342.332 | 21.487 | -11.250 |
| 300 | 132.944 | 270.710 | 343.151 | 21.732 | -11.378 |
| 400 | 183.225 | 294.436 | 388.326 | 37.556 | -16.774 |
| 500 | 228.473 | 317.804 | 434.204 | 58.200 | -20.291 |
| 600 | 266.447 | 340.982 | 479.323 | 83.005 | -22.775 |
| 700 | 298.025 | 363.875 | 522.841 | 111.276 | -24.619 |
| 800 | 324.491 | 386.365 | 564.415 | 142.440 | -26.037 |
| 900 | 346.862 | 408.364 | 603.962 | 176.038 | -27.155 |
| 1000 | 365.887 | 429.818 | 641.519 | 211.701 | -28.054 |
| 1100 | 382.126 | 450.698 | 677.174 | 249.123 | -28.789 |
| 1200 | 396.036 | 470.994 | 711.035 | 288.049 | -29.397 |
| 1300 | 407.986 | 490.707 | 743.219 | 328.265 | -29.906 |
| 1400 | 418.284 | 509.846 | 773.840 | 369.591 | -30.335 |
| 1500 | 427.191 | 528.426 | 803.010 | 411.875 | -30.700 |

Table 23. Ideal gas thermodynamic properties for cycloheptene

| $T$ | $C_p^\circ$ | $-(G^\circ-H_0^\circ)/T$ | $S^\circ$ | $H^\circ-H_0^\circ$ | log $K_f$ |
|---|---|---|---|---|---|
| K | J K$^{-1}$ mol$^{-1}$ | | | kJ mol$^{-1}$ | |
| 100 | 47.403 | 211.327 | 248.470 | 3.714 | -26.132 |
| 200 | 82.290 | 240.912 | 291.568 | 10.131 | -23.762 |
| 298.15 | 124.071 | 264.230 | 332.010 | 20.209 | -24.030 |
| 300 | 124.903 | 264.650 | 332.780 | 20.439 | -24.041 |
| 400 | 169.272 | 286.927 | 374.849 | 35.169 | -24.661 |
| 500 | 208.826 | 308.734 | 416.987 | 54.126 | -25.272 |
| 600 | 242.095 | 330.221 | 458.092 | 76.722 | -25.802 |
| 700 | 269.902 | 351.329 | 497.562 | 102.363 | -26.243 |
| 800 | 293.326 | 371.979 | 535.176 | 130.557 | -26.607 |
| 900 | 313.209 | 392.114 | 570.904 | 160.911 | -26.907 |
| 1000 | 330.170 | 411.703 | 604.805 | 193.102 | -27.154 |
| 1100 | 344.686 | 430.733 | 636.972 | 226.863 | -27.358 |
| 1200 | 357.141 | 449.203 | 667.511 | 261.970 | -27.526 |
| 1300 | 367.856 | 467.121 | 696.531 | 298.233 | -27.665 |
| 1400 | 377.107 | 484.502 | 724.139 | 335.493 | -27.780 |
| 1500 | 385.110 | 501.361 | 750.436 | 373.613 | -27.874 |

temperature increases to 500 K. These discrepancies are due to a difference in molecular constants used in calculations (Chang *et al.*[24] evaluated the molecular constants from the molecular mechanic calculations).

## 15. Cycloheptene

The conformational properties of cycloheptene have been studied experimentally by vibrational spectroscopy[189] and by nuclear magnetic resonance techniques.[190] Observed spectra were, in both cases, interpreted in terms of a $C_s$ symmetric chair form being the most stable conformation. Predictions of the conformations of the molecule have been made from force-field calculations. All recent calculations[143,157,191–193] imply that the chair conformation is only slightly more stable than the $C_2$ twist conformation (the $C_2$ twist form is 2–7 kJ mol$^{-1}$ higher in energy). Another local minimum for the boat form ($C_s$ symmetry) was supported by some workers,[157,191] but this proposal was not confirmed by more reliable calculations.[143,193] Two stable conformations of cycloheptene were considered in this work: the most stable chair form and the $C_2$ twist form with the energy higher by 500 cm$^{-1}$ ($\sim$6 kJ mol$^{-1}$). The relative energy of the $C_2$ form was estimated by averaging the values of the above parameters obtained in different force-field calculations.[143,157,191–193]

There are no direct experimental data on the molecular structure of cycloheptene. The product of the principal moments of inertia for the chair conformation of cycloheptene (Table 6) was calculated using the structural parameters obtained by Ermer and Lifson[193] from the force-field study. Adopted parameters are in good agreement with those calculated in other force-field studies[143,192] and are close to structural parameters in related compounds for which experimental data are available.

Neto *et al.*[189] have investigated the infrared spectra of cycloheptene in all three physical states and the Raman spectrum in the liquid state and carried out a normal coordinate analysis to confirm their vibrational assignment. The fundamentals, presented in Table 7, are those for liquid cycloheptene reported by Neto *et al.*[189] Vapor–liquid frequency shifts were taken into account in estimation of the inaccuracies in the vibrational frequencies.

Ideal gas thermodynamic properties for cycloheptene, given in Table 23, are reported for the first time. No experimental values of $S^\circ$ and $C_p^\circ$ are available for comparison.

## 16. 1,3-Cycloheptadiene

A number of experimental and theoretical studies have been reported on this molecule with contradictory conclusions about the most stable conformation. Electron diffraction data[194,195] indicated that the carbon skeleton is planar except for the one carbon atom ($C_s$ form). A nuclear magnetic resonance study,[196] on the other hand, was consistent with a $C_2$ twist form. Schrader and Ansmann,[197] from infrared data on stretching vibrations of the double bonds, inferred that 1,3-cycloheptadiene exists in a $C_s$ form. The vibrational spectrum of 1,3-cycloheptadiene was also interpreted in terms of a $C_s$ form.[86] Avirah *et al.*[198] investigated the microwave spectrum of 1,3-cycloheptadiene. In their opinion, the agreement between the observed and calculated rotational constants based on the electron diffraction studies argues strongly for the $C_s$ form. In addition to experimental results, molecular mechanics calculations on 1,3-cycloheptadiene have also been reported. In early work, Favini *et al.*[199,200] found for the most stable conformation a $C_2$ form, which was replaced by the $C_s$ structure in more recent studies.[201,264] The existence of three forms which are relatively close in energy was found in the later work of Favini *et al.*[264] The $C_s$ form was found to be 7.6 kJ mol$^{-1}$ more stable than the form with $C_2$ symmetry and 3.4 kJ mol$^{-1}$ more stable than the intermediate nonsymmetrical form ($C_1$). Allinger and Sprague[202] predicted that the molecule undergoes an almost unhindered pseudorotation between a $C_s$ form and an alternate nonsymmetrical form ($C_1$). This pseudorotating structure is in equilibrium with the $C_2$ form separated by a barrier of about 4 kJ mol$^{-1}$. According to *ab initio* calculations of Saebø and Boggs,[203] there are three energy-minimum conformations of 1,3-cycloheptadiene, viz., the most stable $C_s$ form and two $C_2$ forms with energies higher than that of $C_s$ by 10.5 and 60.0 kJ mol$^{-1}$, respective-

Table 24. Ideal gas thermodynamic properties for 1,3-cycloheptadiene

| $T$ | $C_p^\circ$ | $-(G^\circ-H_0^\circ)/T$ | $S^\circ$ | $H^\circ-H_0^\circ$ | log $K_f$ |
|---|---|---|---|---|---|
| K | J K$^{-1}$ mol$^{-1}$ | | | kJ mol$^{-1}$ | |
| 100 | 52.524 | 211.592 | 251.016 | 3.942 | -72.100 |
| 200 | 80.878 | 242.988 | 295.802 | 10.563 | -43.745 |
| 298.15 | 117.672 | 266.801 | 334.710 | 20.247 | -35.219 |
| 300 | 118.417 | 267.222 | 335.440 | 20.466 | -35.117 |
| 400 | 158.028 | 289.219 | 374.993 | 34.309 | -31.185 |
| 500 | 192.987 | 310.302 | 414.121 | 51.909 | -29.017 |
| 600 | 222.108 | 330.781 | 451.964 | 72.710 | -27.669 |
| 700 | 246.262 | 350.694 | 488.073 | 96.166 | -26.759 |
| 800 | 266.498 | 370.026 | 522.316 | 121.832 | -26.103 |
| 900 | 283.613 | 388.764 | 554.721 | 149.361 | -25.608 |
| 1000 | 298.162 | 406.907 | 585.377 | 178.470 | -25.218 |
| 1100 | 310.636 | 424.462 | 614.596 | 208.927 | -24.902 |
| 1200 | 321.317 | 441.446 | 641.894 | 240.538 | -24.638 |
| 1300 | 330.507 | 457.877 | 667.986 | 273.141 | -24.413 |
| 1400 | 338.439 | 473.778 | 692.776 | 306.598 | -24.218 |
| 1500 | 345.305 | 489.170 | 716.366 | 340.793 | -24.045 |

Table 25. Ideal gas thermodynamic properties for 1,3,5-cycloheptatriene

| $T$ | $C_p^\circ$ | $-(G^\circ-H_0^\circ)/T$ | $S^\circ$ | $H^\circ-H_0^\circ$ | log $K_f$ |
|---|---|---|---|---|---|
| K | J K$^{-1}$ mol$^{-1}$ | | | kJ mol$^{-1}$ | |
| 100 | 42.240 | 208.479 | 243.860 | 3.538 | -111.711 |
| 200 | 71.041 | 235.824 | 281.457 | 9.126 | -60.943 |
| 298.15 | 106.249 | 256.568 | 316.250 | 17.794 | -44.885 |
| 300 | 106.936 | 256.938 | 316.909 | 17.991 | -44.688 |
| 400 | 142.799 | 276.399 | 352.668 | 30.508 | -36.865 |
| 500 | 173.733 | 295.198 | 387.962 | 46.382 | -32.326 |
| 600 | 199.178 | 313.514 | 421.964 | 65.070 | -29.380 |
| 700 | 220.092 | 331.337 | 454.289 | 86.067 | -27.319 |
| 800 | 237.493 | 348.634 | 484.849 | 108.972 | -25.797 |
| 900 | 252.138 | 365.387 | 513.691 | 133.473 | -24.628 |
| 1000 | 264.562 | 381.591 | 540.917 | 159.325 | -23.700 |
| 1100 | 275.163 | 397.256 | 566.642 | 186.325 | -22.945 |
| 1200 | 284.244 | 412.395 | 590.984 | 214.307 | -22.318 |
| 1300 | 292.052 | 427.027 | 614.052 | 243.131 | -21.787 |
| 1400 | 298.790 | 441.175 | 635.948 | 272.682 | -21.332 |
| 1500 | 304.625 | 454.860 | 656.766 | 302.859 | -20.936 |

ly. Saebø and Boggs[203] consider their results to be close to that reported by Allinger and Sprague,[202] and believe the existence of a mixture of $C_s$ and $C_2$ forms to explain the contradiction in the interpretation of electron diffraction[194,195] and nuclear magnetic resonance[196] data. Three stable conformations of 1,3-cycloheptadiene were taken into account in this work: the most stable $C_s$ form, as well as $C_1$ and $C_2$ forms with energies higher than the $C_s$ by 200 cm$^{-1}$ ($\sim$2.4 kJ mol$^{-1}$) and 500 cm$^{-1}$ ($\sim$6 kJ mol$^{-1}$), respectively. The adopted relative energies of the $C_1$ and $C_2$ forms are intermediate between the results of Allinger and Sprague[202] and of Favini *et al.*,[264] and nearer to the latter.

The product of the principal moments of inertia, given in Table 6, was calculated using the rotational constants of Avirah *et al.*[198] This value agrees with those calculated from electron diffraction data.[194,195]

Ansmann and Schrader[86] investigated the infrared and Raman spectra of liquid 1,3-cycloheptadiene and presented the vibrational assignment on the basis of normal coordinate analysis. Their frequencies are listed in Table 7. Vapor–liquid frequency shifts were taken into account in estimating the inaccuracies in the adopted fundamentals.

Ideal gas thermodynamic properties for 1,3-cycloheptadiene, given in Table 24, are reported for the first time. No experimental data are available for comparisons.

## 17. 1,3,5-Cycloheptatriene

Cycloheptatriene has a nonplanar equilibrium conformation (boat form of $C_s$ symmetry), as shown by electron diffraction,[204] microwave,[205] infrared and Raman,[206] and nuclear magnetic resonance[207,208] measurements as well as by force-field[165,209–211] and *ab initio*[203,212] calculations. A planar structure ($C_{2v}$ symmetry) was found to be about 25 kJ mol$^{-1}$ higher in energy and to be a transition state on the energy surface, probably for interconversion of boat forms.[203,207,208,212]

Conflicting results concerning the degree of nonplanarity of the cycloheptatriene ring have been published. Traetteberg[204] determined the total molecular structure by electron diffraction and found the values of two dihedral angles to be $\alpha = 40.5°$ and $\beta = 36.5°$. Butcher[205] determined the rotational constants from microwave study of normal isotopic species of cycloheptatriene and estimated $\alpha = 29.5°$ and $\beta = 50°$, assuming bond lengths and angles, the values of dihedral angles being somewhat insensitive to the choice of structural parameters. Butcher's estimates of dihedral angles agree pretty well with theoretical results.[165,203,209–212] The product of the principal moments of inertia, given in Table 6, was calculated using the rotational constants of Butcher.[205]

Evans and Lord[213] interpreted the infrared and Raman spectra of cycloheptatriene assuming a planar structure of $C_{2v}$ symmetry. Later, La Lau and De Ruyter[206] investigated the Raman spectrum of liquid cycloheptatriene and proposed the reassignment of Evans and Lord's data[213] for $C_s$ symmetry. Paulick *et al.*[210] presented a new interpretation of vibrational spectra[206,213] on the basis of the force-field calculation. Vibrational frequencies, listed in Table 7, were obtained by means of critical comparison of experimental[206,213] and calculated[210] freqencies of cycloheptatriene with those for related compounds. The adopted vibrational assignment gives a better agreement between experimental and calculated values of $S°$ (298.15 K) than those of La Lau and Ruyter[206] or Paulick *et al.*[210]

Ideal gas thermodynamic properties for 1,3,5-cycloheptatriene are presented in Table 25. The agreement between the calorimetric entropy[188] and our calculated value is satisfactory within the experimental uncertainty (Table 32). The value of $S°$ (298.15 K) calculated by Evans and Lord[213] for a planar structure is about 2 J K$^{-1}$ mol$^{-1}$ larger than that calculated in the present work.

## 18. Cyclooctane

Some families of cyclooctane conformations were identified by conformational energy calculations.[91,139,182,214–216,263] The most stable conformation of cyclooctane is the boat–chair (BC) of $C_s$ symmetry and according to most of calculations two families of conformations are close in energy:

$$\underset{\text{boat–chair family}}{(\mathrm{BC}\rightleftarrows\mathrm{TBC})} \overset{\Delta H^{\ddagger}}{\rightleftarrows} \underset{\text{crown family}}{(\mathrm{crown}\rightleftarrows\mathrm{CC}\rightleftarrows\mathrm{TCC})}$$

[TBC: twist-boat–chair ($C_2$), crown ($D_{4d}$), CC: chair–chair ($C_{2v}$), TCC: twist-chair–chair ($D_2$)]. The energy differences among these low-energy conformers are estimated to be from 0.8 to 10 kJ mol$^{-1}$. It should be emphasized that force-field calculations give inconsistent results on the relative energies of conformers (except that for the BC form) and on the location of conformers on the potential energy surface (local minimum or saddle point). The analysis of torsional energy surfaces presented by Ivanov and Ōsawa[263] shows that even slightly different force fields exhibit significantly different pictures for the dynamic behavior of the cyclooctane molecule.

Experimental investigations have led to a variety of conclusions. Nuclear magnetic resonance experiments[217,218] provide evidence for the boat–chair and indicate the presence of a small amount of another form, probably of the crown family. The gas-phase electron diffraction data of Almenningen *et al.*[219] were not compatible with the assumption of any single geometry, but rather with a mixture of several conformations. However, good agreement between experimental and theoretical electron diffraction data was obtained for the boat–chair conformer in a recent reinvestigation by Dorofeeva *et al.*[220] An early vibrational study[221] arrived at the conclusion of a tub form for cyclooctane, which is now known to be incorrect. Pakes *et al.*[222] examined the vibrational spectra of cyclooctane, giving special attention to the low-frequency region. Agreement between calculated and observed vibrational frequencies was obtained only for the boat–chair conformer.

Although several low-energy conformers of cyclooctane were predicted from theoretical calculations, reliable experimental evidence for their existence has not been obtained. We have performed the calculations of the standard entropy of gaseous cyclooctane for models of different conformational composition[187] and have shown the value of $S^\circ$ (298.15 K) for the single boat–chair form to be 14.7 J K$^{-1}$ mol$^{-1}$ less than the experimental value. It should be noted that the set of conformers calculated by Pakes *et al.*[216] is not sufficient to reproduce the experimental entropy. A good agreement between experimental and calculated entropy values was achieved by assuming that in two above families of the cyclooctane conformers the intermediate nonsymmetrical ($C_1$) energy-minimum forms exist:

$$(\mathrm{BC}\rightleftarrows C_1\rightleftarrows\mathrm{TBC}) \overset{\Delta H^{\ddagger}}{\rightleftarrows} (\mathrm{TCC}\rightleftarrows C_1\rightleftarrows\mathrm{CC})\,.$$

(The existence of $C_1$ forms is assumed by analogy with strain-energy calculation results 1,4-cyclooctadiene.[223] The crown form is excluded from consideration because according to the calculation of Pakes *et al.*,[216] it is a saddle point. See also Ref. 187.) To calculate the thermal functions of cyclooctane, the six conformers of this molecule were taken into account (Table 8): the most stable boat–chair conformer and the five forms (TCC, $C_1$, CC, $C_1$, and TBC) with energy higher by 275 cm$^{-1}$ (3.3 kJ mol$^{-1}$). Average relative energy of the five conformers was estimated from the energies of the TCC, CC, and TBC forms calculated by Pakes *et al.*[216]

Table 26. Ideal gas thermodynamic properties for cyclooctane

| $T$ | $C_p^\circ$ | $-(G^\circ-H_0^\circ)/T$ | $S^\circ$ | $H^\circ-H_0^\circ$ | log $K_f$ |
|---|---|---|---|---|---|
| K | J K$^{-1}$ mol$^{-1}$ | | | kJ mol$^{-1}$ | |
| 100 | 64.769 | 219.700 | 262.528 | 4.283 | 19.843 |
| 200 | 99.987 | 255.803 | 318.710 | 12.581 | -6.067 |
| 298.15 | 146.194 | 284.435 | 366.725 | 24.535 | -16.010 |
| 300 | 147.189 | 284.945 | 367.633 | 24.806 | -16.145 |
| 400 | 202.155 | 311.819 | 417.501 | 42.273 | -21.857 |
| 500 | 253.069 | 338.025 | 468.208 | 65.092 | -25.624 |
| 600 | 296.638 | 363.914 | 518.311 | 92.638 | -28.307 |
| 700 | 333.376 | 389.461 | 566.877 | 124.191 | -30.314 |
| 800 | 364.461 | 414.572 | 613.479 | 159.126 | -31.865 |
| 900 | 390.901 | 439.165 | 657.974 | 196.929 | -33.094 |
| 1000 | 413.473 | 463.182 | 700.359 | 237.177 | -34.086 |
| 1100 | 432.791 | 486.592 | 740.697 | 279.515 | -34.898 |
| 1200 | 449.361 | 509.381 | 779.084 | 323.644 | -35.573 |
| 1300 | 463.605 | 531.544 | 815.629 | 369.310 | -36.137 |
| 1400 | 475.896 | 553.089 | 850.446 | 416.300 | -36.614 |
| 1500 | 486.529 | 574.028 | 883.651 | 464.434 | -37.019 |

The electron diffraction structural parameters obtained by Dorofeeva *et al.*[220] were used to calculate the product of the principal moments of inertia (Table 8). These parameters are consistent with those obtained by force-field calculations.[216,220]

The vibrational frequencies of cyclooctane used in our calculations (Table 9) were taken from the study of Pakes *et al.*[222] These authors have examined in detail the vapor and liquid-phase infrared spectra, vapor-phase far-infrared spectrum, and liquid-phase Raman spectrum, and carried out a normal coordinate analysis to confirm their vibrational assignment.

Ideal gas thermodynamic properties for cyclooctane are given in Table 26. The calculated value of $S^\circ$ (298.15 K), as shown in Table 32, coincides with the calorimetric entropy.[188] Chang *et al.*[24] have calculated the thermal functions of the $D_2$ cyclooctane conformation using the molecular constants obtained from molecular mechanics calculations. Their value of $S^\circ$ (298.15 K) is much less than the value obtained in this work (Table 32). However, this discrepancy will be markedly decreased if the $C_s$ symmetry is employed. Unfortunately, Chang *et al.*[24] did not publish the molecular constants they used and the reliability of their functions cannot be estimated.

## 19. *trans*-Cyclooctene

*Trans*-cyclooctene, which is the most stable cyclooctene isomer, can exist as the twist-chair–chair ($C_2$ symmetry) or chair ($C_2$ symmetry) form. The electron diffraction study of Gavin and Wang[224] and early force-field calculation of Buemi *et al.*[225] favored a chair conformation. Traetteberg[226] has interpreted the electron diffraction data of *trans*-cyclooctene as indicative of a twist-chair–chair conformation. The same form was also predicted by the force-field calculations.[157,160,193,201] As the reliability of electron diffraction data of Gavin and Wang[224] raise some doubts,[193,226] the most stable conformation of *trans*-cyclooctene should be twist-chair–chair. A less stable chair conformation is also

Table 27. Ideal gas thermodynamic properties for trans-cyclooctene

| $T$ | $C_p^\circ$ | $-(G^\circ-H_0^\circ)/T$ | $S^\circ$ | $H^\circ-H_0^\circ$ | $\log K_f$ |
|---|---|---|---|---|---|
| K | J K$^{-1}$ mol$^{-1}$ | | | kJ mol$^{-1}$ | |
| 100 | 52.282 | 217.505 | 256.296 | 3.879 | -24.007 |
| 200 | 93.703 | 249.271 | 304.923 | 11.130 | -25.376 |
| 298.15 | 142.912 | 275.180 | 351.225 | 22.673 | -27.063 |
| 300 | 143.904 | 275.652 | 352.112 | 22.938 | -27.093 |
| 400 | 196.926 | 300.831 | 400.841 | 40.004 | -28.514 |
| 500 | 244.054 | 325.755 | 449.991 | 62.118 | -29.642 |
| 600 | 283.393 | 350.491 | 498.077 | 88.552 | -30.531 |
| 700 | 316.026 | 374.900 | 544.290 | 118.573 | -31.236 |
| 800 | 343.353 | 398.849 | 588.326 | 151.581 | -31.799 |
| 900 | 366.444 | 422.246 | 630.137 | 187.102 | -32.254 |
| 1000 | 386.079 | 445.035 | 669.790 | 224.755 | -32.622 |
| 1100 | 402.844 | 467.192 | 707.394 | 264.223 | -32.924 |
| 1200 | 417.206 | 488.708 | 743.078 | 305.244 | -33.172 |
| 1300 | 429.546 | 509.590 | 776.972 | 347.597 | -33.377 |
| 1400 | 440.184 | 529.849 | 809.203 | 391.096 | -33.545 |
| 1500 | 449.384 | 549.504 | 839.894 | 435.586 | -33.685 |

considered in the present work (Table 8). The relative energy of this form, 1000 cm$^{-1}$ (12 kJ mol$^{-1}$), was estimated from the force-field calculations.[157,193,201]

The product of the principal moments of inertia for *trans*-cyclooctene, given in Table 8, was calculated from the electron diffraction structural parameters of Traetteberg.[226] These parameters are consistent with those obtained by force-field calculations.[160,193,226,227]

Until now no vibrational spectra of *trans*-cyclooctene have been reported. In the present work the fundamental vibrations were estimated by normal coordinate calculations. The similarity of force fields for cyclohexene,[151] cycloheptene,[189] and related compounds allows a decision to be made concerning the transferability of the force fields for cycloalkenes. Thus, the force field used was transferred from cycloheptene.[189] For normal coordinate calculations we used the NCA program written by Novikov.[83] The fundamental frequencies, given in Table 9, were selected on the basis of our calculations and the comparison with fundamentals of cyclohexene and cycloheptene; their uncertainties are estimated to be 20–50 cm$^{-1}$.

Ideal gas thermodynamic properties for *trans*-cyclooctene, given in Table 27, are reported for the first time. No experimental data are available for comparisons.

## 20. *cis,cis*-1,3-Cyclooctadiene

*Cis,cis*-1,3-cyclooctadiene is the most stable isomer of 1,3-cyclooctadiene. Braude,[228] from ultraviolet spectroscopy, and Schrader and Ansmann,[197] from infrared data on stretching vibrations of the double bonds, deduced that the diene system in *cis,cis*-1,3-cyclooctadiene must be nonplanar with a torsional angle of about 40°–45° and 38°, respectively. Traetteberg[229] has investigated the structure of *cis,cis*-1,3-cyclooctadiene in the gas phase by electron diffraction and has reported that the conformation is irregular twist-boat ($C_1$ symmetry) with a diene twist angle of 38°. Allinger *et al.*[230] studied *cis,cis*-1,3-cyclooctadiene by the iterative force-field method. The molecule is calculated to be a mixture of two conformations, one of which has a $C_2$ axis, and one is irregular. The energies of these two conformations are calculated to be very nearly the same. These results are consistent with the noniterative force-field findings.[199,200] Anet and Yavari[231] have investigated *cis,cis*-1,3-cyclooctadiene by dynamic nuclear magnetic resonance spectroscopy and have also reported iterative force-field calculations of the interconversion paths of *cis,cis*-1,3-cyclooctadiene conformations. According to their data, the compound exists as a nearly equal mixture of symmetrical ($C_2$) twist-boat–chair and unsymmetrical ($C_1$) twist-boat conformers. This is in agreement with previous calculations.[199,200,230] The mixture of the two conformers of *cis,cis*-1,3-cyclooctadiene was considered in this work (Table 8), where the twist-boat–chair is the predominant conformation and is more stable than twist-boat by 200 cm$^{-1}$ (2.4 kJ mol$^{-1}$). (Anet and Yavari[231] have estimated this energy as ~2.1 kJ mol$^{-1}$.)

Electron diffraction structural parameters of the $C_1$ conformer determined by Traetteberg[229] were used to calculate the product of the principal moments of inertia (Table 8). Allinger *et al.*[230] suppose that this structure must be some kind of average over the two conformations of *cis,cis*-1,3-cyclooctadiene.

Only infrared data on the stretching vibrations of C = C bonds have been reported for 1,3-cyclooctadiene.[197] The vibrational frequencies, given in Table 9, were estimated on the basis of normal coordinate calculations. The similarity of force fields for 1,3-cyclohexadiene,[85] 1,3-cycloheptadiene,[86] and related compounds allows a decision to be made concerning the transferability of the force fields for 1,3-cycloalkadienes. Thus, the force constants used were transferred from 1,3-cycloheptadiene.[86] For normal coordinate calculations we used the NCA program by Novikov.[83] The fundamental frequencies, given in Table 9, were selected on the basis of our calculations and the comparison with fundamentals of 1,3-cyclohexadiene and 1,3-cycloheptadiene. The uncertainties of calculated frequencies are estimated to be 20–50 cm$^{-1}$.

The enthalpy of formation, presented in Table 8, was estimated by Kozina *et al.*[232] from available experimental data.

Ideal gas thermodynamic properties for *cis,cis*-1,3-cyclooctadiene, given in Table 28, are reported for the first time. No experimental data are available for comparisons.

Table 28. Ideal gas thermodynamic properties for cis,cis-1,3-cyclooctadiene

| $T$ | $C_p^\circ$ | $-(G^\circ-H_0^\circ)/T$ | $S^\circ$ | $H^\circ-H_0^\circ$ | $\log K_f$ |
|---|---|---|---|---|---|
| K | J K$^{-1}$ mol$^{-1}$ | | | kJ mol$^{-1}$ | |
| 100 | 61.276 | 217.979 | 260.574 | 4.260 | -71.586 |
| 200 | 95.587 | 253.045 | 313.431 | 12.077 | -46.081 |
| 298.15 | 138.825 | 280.512 | 359.358 | 23.508 | -38.652 |
| 300 | 139.704 | 281.001 | 360.219 | 23.766 | -38.565 |
| 400 | 186.556 | 306.638 | 406.895 | 40.103 | -35.260 |
| 500 | 227.963 | 331.327 | 453.101 | 60.887 | -33.502 |
| 600 | 262.458 | 355.375 | 497.812 | 85.463 | -32.444 |
| 700 | 291.077 | 378.797 | 540.486 | 113.183 | -31.747 |
| 800 | 315.064 | 401.561 | 580.906 | 143.524 | -31.254 |
| 900 | 335.360 | 423.643 | 619.280 | 176.073 | -30.886 |
| 1000 | 352.644 | 445.036 | 655.532 | 210.496 | -30.598 |
| 1100 | 367.422 | 465.746 | 689.854 | 246.518 | -30.363 |
| 1200 | 380.100 | 485.789 | 722.381 | 283.910 | -30.167 |
| 1300 | 391.005 | 505.186 | 753.247 | 322.479 | -29.997 |
| 1400 | 400.418 | 523.961 | 782.576 | 362.062 | -29.846 |
| 1500 | 408.569 | 542.140 | 810.487 | 402.521 | -29.712 |

## 21. *cis,cis*-1,5-Cyclooctadiene

It is known from electron diffraction study[233] and from interpretation of the nuclear magnetic resonance spectra[234] and molecular mechanics calculations,[143,235,236] that the lowest energy form of the *cis,cis*-1,5-cyclooctadiene is the twist-boat ($C_2$ symmetry). Ermer[236] has performed the force-field calculations of the interconversion paths of *cis*, *cis*-1,5-cyclooctadiene and has shown that three conformations correspond to potential energy minima: the most stable twist-boat form and two forms of $C_{2h}$ (chair) and $C_s$ symmetry with energies higher than that of twist-boat by about 17 kJ mol$^{-1}$. This result agrees well with the interpretation of nuclear magnetic resonance spectra by Anet and Kozerski[234] but less well with Allinger and Sprague's force-field calculation.[235] In the latter work five conformations correspond to energy minima, the relative energy of chair form being ~6 kJ mol$^{-1}$. No significant evidence for the presence of the chair form was found in the electron diffraction study of Hagen *et al.*,[233] but amounts less than about 10% in an equilibrium mixture with the twist-boat form cannot be ruled out. On the basis of the above experimental and theoretical data on *cis,cis*-1,5-cyclooctadiene, three stable conformations of this molecule (twist-boat, chair, and $C_s$ form) were considered in the present work (Table 8). The relative energy of chair and $C_s$ forms, 1500 cm$^{-1}$ (18 kJ mol$^{-1}$), was adopted according to the force-field calculations of Ermer.[236]

The product of the principal moments of inertia for the twist-boat conformer, given in Table 8, was calculated from structural data obtained by electron diffraction.[233]

Infrared and Raman spectra of the liquid and solid 1,5-cyclooctadiene were reported[237,238] but no vibrational assignments were presented except for $\nu(C=C)$. To estimate a complete set of fundamentals, the normal coordinate calculations were carried out in this work. The similarity of the force fields for cyclohexene,[151] cycloheptene,[189] and *trans,trans,trans*-cyclododecatriene[239] permits the transfer of the force constants from these molecules to 1,5-cyclooctadiene. The fundamental frequencies, adopted in Table 9, were selected on the basis of normal coordinate calculations. For this purpose we used the NCA program by Novikov.[83] The uncertainties of calculated frequencies are estimated to be 20–50 cm$^{-1}$.

Ideal gas thermodynamic properties for *cis,cis*-1,5-cyclooctadiene are listed in Table 29. No experimental data are available for comparisons. The value of $S°$ (298.15 K) reported by Ermer[236] is about 2 J K$^{-1}$ mol$^{-1}$ less than that calculated in the present work (Table 32). We believe our value to be more reliable than that obtained by Ermer[236] from molecular mechanics calculations.

## 22. 1,3,5,7-Cyclooctatetraene

Cyclooctatetraene has a nonplanar equilibrium conformation (boat form of $D_{2d}$ symmetry), as shown by electron diffraction[240,241] and nuclear magnetic resonance[242] measurements as well as by *ab initio*[243] and force-field[244–246] calculations. A planar structure ($D_{4h}$ symmetry) was found to be a transition state on the energy surface for interconversion of boat forms.[242–244,246] Electron diffraction structural parameters of Traetteberg[241] were used to calculate the product of the principal moments of inertia (Table 8). Bond lengths and angles obtained by Traetteberg[241] are consistent with those determined in another electron diffraction study[240] and calculated theoretically,[243–246] but Traetteberg's degree of nonplanarity is 10°–25° less than that obtained from theoretical calculations. It is difficult to offer an explanation for this discrepancy. However, it should be emphasized that the electron diffraction model gives a better description of the electronic spectrum than theoretical models.[247]

Lippincott *et al.*[248] observed the infrared and Raman spectra of liquid and gaseous cyclooctatetraene and have made a complete vibrational assignment. Later, Popov and Kogan[249] and Traetteberg *et al.*[250] carried out a normal coordinate analysis and partly reassigned the observed spectra. The vibrational fundamentals given in Table 9 are those by Popov and Kogan.[249] Their vibrational assignment gives a better agreement with experimental entropy than the others. The adopted values of frequencies were taken from the Raman spectrum of the liquid ($A_1$ and $B_1$ modes), from in-

Table 29. Ideal gas thermodynamic properties for cis,cis-1,5-cyclooctadiene

| $T$ | $C_p°$ | $-(G°-H_0°)/T$ | $S°$ | $H°-H_0°$ | log $K_f$ |
|---|---|---|---|---|---|
| K | J K$^{-1}$ mol$^{-1}$ | | | kJ mol$^{-1}$ | |
| 100 | 53.367 | 217.343 | 257.120 | 3.978 | -60.758 |
| 200 | 91.777 | 249.596 | 305.409 | 11.163 | -40.830 |
| 298.15 | 138.304 | 275.377 | 350.508 | 22.400 | -35.277 |
| 300 | 139.226 | 275.843 | 351.367 | 22.657 | -35.214 |
| 400 | 188.010 | 300.563 | 398.183 | 39.048 | -32.862 |
| 500 | 230.946 | 324.771 | 444.885 | 60.057 | -31.672 |
| 600 | 266.581 | 348.595 | 490.247 | 84.992 | -30.988 |
| 700 | 295.898 | 371.954 | 533.615 | 113.163 | -30.552 |
| 800 | 320.197 | 394.757 | 574.762 | 144.004 | -30.252 |
| 900 | 340.521 | 416.940 | 613.684 | 177.070 | -30.030 |
| 1000 | 357.646 | 438.471 | 650.473 | 212.002 | -29.855 |
| 1100 | 372.165 | 459.340 | 685.260 | 248.512 | -29.711 |
| 1200 | 384.529 | 479.551 | 718.187 | 286.363 | -29.587 |
| 1300 | 395.109 | 499.119 | 749.395 | 325.359 | -29.478 |
| 1400 | 404.198 | 518.063 | 779.016 | 365.336 | -29.379 |
| 1500 | 412.043 | 536.406 | 807.177 | 406.157 | -29.287 |

Table 30. Ideal gas thermodynamic properties for 1,3,5,7-cyclooctatetraene

| $T$ | $C_p°$ | $-(G°-H_0°)/T$ | $S°$ | $H°-H_0°$ | log $K_f$ |
|---|---|---|---|---|---|
| K | J K$^{-1}$ mol$^{-1}$ | | | kJ mol$^{-1}$ | |
| 100 | 50.684 | 203.150 | 241.425 | 3.828 | -171.052 |
| 200 | 83.798 | 233.885 | 286.410 | 10.505 | -90.627 |
| 298.15 | 122.613 | 257.873 | 326.986 | 20.606 | -64.737 |
| 300 | 123.361 | 258.301 | 327.747 | 20.834 | -64.415 |
| 400 | 161.834 | 260.785 | 368.617 | 35.133 | -51.580 |
| 500 | 194.415 | 302.351 | 408.349 | 52.999 | -44.014 |
| 600 | 220.958 | 323.202 | 446.225 | 73.813 | -39.040 |
| 700 | 242.052 | 343.356 | 481.969 | 97.029 | -35.523 |
| 800 | 260.625 | 362.805 | 515.580 | 122.220 | -32.906 |
| 900 | 275.697 | 381.553 | 547.172 | 149.057 | -30.883 |
| 1000 | 288.444 | 399.616 | 576.898 | 177.282 | -29.270 |
| 1100 | 299.286 | 417.018 | 604.912 | 206.683 | -27.953 |
| 1200 | 308.552 | 433.789 | 631.361 | 237.087 | -26.857 |
| 1300 | 316.500 | 449.958 | 656.380 | 268.349 | -25.929 |
| 1400 | 323.345 | 465.556 | 680.092 | 300.350 | -25.133 |
| 1500 | 329.261 | 480.616 | 702.607 | 332.988 | -24.442 |

Table 31. The uncertainties of the calculated thermal functions (in J $K^{-1}$ $mol^{-1}$) and adopted enthalpies of formation (in kJ $mol^{-1}$)

| Molecule | Uncertainties in $\underline{S}^{\circ}$ | | Uncertainties in $\underline{C}_p^{\circ}$ | | Uncertainties in $\Delta_f\underline{H}^{\circ}$(298.15 K) |
|---|---|---|---|---|---|
| | 298.15 K | 1000 K | 298.15 K | 1000 K | |
| | J $K^{-1}$ $mol^{-1}$ | | | | kJ $mol^{-1}$ |
| Cyclopropane | 0.5 | 4.5 | 1.0 | 6.0 | 0.5 |
| Cyclopropene | 0.5 | 3.5 | 1.0 | 4.0 | 2.5 |
| Cyclobutane | 1.0 | 6.5 | 2.0 | 8.0 | 0.5 |
| Cyclobutene | 1.0 | 6.5 | 2.5 | 7.0 | 1.5 |
| 1,3-Cyclobutadiene | 2.0 | 9.0 | 3.0 | 6.0 | 20.0 |
| Cyclopentane | 1.5 | 9.0 | 2.5 | 11.0 | 0.8 |
| Cyclopentene | 1.5 | 8.0 | 2.5 | 9.0 | 1.7 |
| 1,3-Cyclopentadiene | 1.5 | 8.0 | 2.5 | 8.0 | 3.8 |
| Cyclohexane | 2.0 | 13.0 | 4.0 | 14.0 | 0.3 |
| Cyclohexene | 2.0 | 11.5 | 3.5 | 12.0 | 0.5 |
| 1,3-Cyclohexadiene | 2.0 | 10.5 | 3.5 | 11.0 | 0.5 |
| 1,4-Cyclohexadiene | 2.5 | 11.0 | 3.5 | 11.0 | 5.0 |
| Cycloheptane | 3.5 | 14.0 | 6.0 | 15.0 | 0.6 |
| Cycloheptene | 4.0 | 15.0 | 6.5 | 16.0 | 0.9 |
| 1,3-Cycloheptadiene | 6.0 | 17.0 | 7.5 | 18.0 | 0.9 |
| 1,3,5-Cycloheptatriene | 3.0 | 13.5 | 5.0 | 12.0 | 1.2 |
| Cyclooctane | 4.5 | 19.0 | 8.0 | 20.0 | 0.9 |
| Cyclooctene | 7.5 | 21.0 | 8.0 | 20.0 | 1.1 |
| 1,3-Cyclooctadiene | 6.5 | 18.5 | 7.0 | 17.0 | 2.0 |
| 1,5-Cyclooctadiene | 7.0 | 20.0 | 10.0 | 20.0 | 1.2 |
| 1,3,5,7-Cyclooctatetraene | 3.0 | 11.0 | 4.0 | 10.0 | 1.3 |

Table 32. Comparison of experimental[a] entropies with calculated values (in J $K^{-1}$ $mol^{-1}$)

| $\underline{S}^{\circ}$ | | | Investigator (year) | Reference |
|---|---|---|---|---|
| 298.15 K | 500 K | 1000 K | | |
| | | | **Cyclopropane** | |
| 237.4 | | | Ruehrwein and Powell (1946) | 21 |
| 237.4 | 275.9 | 360.5 | Kobe and Pennington (1951) | 22 |
| 238.9 | 277.3 | | Chang et al. (1970) | 24 |
| 237.2 | 274.7 | 357.9 | Karuppannan et al. (1981) | 23 |
| 237.4 | 275.5 | 359.5 | This work | |
| | | | **Cyclopropene** | |
| 243.5 | 277.7 | 346.5 | Yum and Eggers (1979) | 30 |
| 243.5 | 277.5 | 346.2 | Adame and Vicharelli (1979) | 32 |
| 243.5 | 277.7 | 346.6 | This work | |
| | | | **Cyclobutane** | |
| $265.4\pm0.8$ | | | Rathjens and Gwinn (1953) | 55 [b] |
| 265.4 | 315.6 | 428.9 | Rathjens et al. (1953) | 50 |
| 264.1 | 313.7 | | Chang et al. (1970) | 24 |
| 264.4 | 313.4 | 424.7 | This work | |
| | | | **Cyclobutene** | |
| 263.5 | 308.9 | 406.5 | Danti (1956) | 65 |
| 262.0 | 306.1 | 403.1 | This work | |
| | | | **Cyclopentane** | |
| 292.8 | | | Kilpatrick et al. (1947) | 88 |
| 292.9 | | | McCullough et al. (1959) | 101 |
| 292.9 | 352.0 | 491.4 | Kilpatrick et al. (1947) | 88 |
| 292.9 | 352.3 | 492.2 | McCullough et al. (1959) | 101 |
| 293.8 | 353.3 | | Chang et al. (1970) | 24 |
| 292.9 | 352.0 | 491.0 | This work | |
| | | | **Cyclopentene** | |
| 289.7 | | | Beckett et al. (1948) | 109 |
| 289.7 | 342.3 | 464.2 | Beckett et al. (1948) | 109 |
| 289.2 | | | Furuyama et al. (1970) | 114 |
| 289.1 | 343.6 | 466.5 | Draeger et al. (1983) | 115 |
| 291.3 | 347.5 | 472.6 | This work | |
| | | | **1,3-Cyclopentadiene** | |
| $270.3\pm4.0$[c] | | | Grant and Walsh (1969) | 124 |
| 274.4 | 325.0 | 434.3 | Turnbull (1967) | 125 |
| 274.5 | | | Furuyama et al. (1970) | 114 |
| 274.0 | 325.8 | 436.9 | This work | |
| | | | **Cyclohexane** | |
| $298.8\pm0.8$ | | | Aston et al. (1943) | 262 |
| 298.2 | | | Beckett et al. (1947) | 145 |
| 298.2 | 373.4 | 550.6 | Beckett et al. (1947) | 145 |
| 299.6 | 374.6 | | Chang et al. (1970) | 24 |
| 297.3 | 371.8 | 547.5 | This work | |
| | | | **Cyclohexene** | |
| 310.5 | | | Beckett et al. (1948) | 109 |
| 310.7 | 383.4 | 543.1 | Beckett et al. (1948) | 109 |
| 310.5 | 380.6 | 537.1 | This work | |
| | | | **Cycloheptane** | |
| $342.3\pm1.3$ | | | Finke et al. (1956) | 188 |
| 343.0 | 431.9 | | Chang et al. (1970) | 24 |
| 342.3 | 434.2 | | This work | |
| | | | **1,3,5-Cycloheptatriene** | |
| $315.6\pm1.0$ | | | Finke et al. (1956) | 188 |
| 318.0 | | | Evans and Lord (1960) | 213 |
| 316.3 | | | This work | |
| | | | **Cyclooctane** | |
| $366.8\pm1.3$ | | | Finke et al. (1956) | 188 |
| 353.0 | 455.5 | | Chang et al. (1970) | 24 |
| 366.7 | 468.2 | | This work | |
| | | | **1,5-Cyclooctadiene** | |
| 347.9 | | | Ermer (1976) | 236 |
| 350.3 | | | This work | |
| | | | **1,3,5,7-Cyclooctatetraene** | |
| $326.8\pm1.5$ | | | Scott et al. (1949) | 251 |
| 325.3 | 406.8 | 575.0 | Lippincott and Lord (1951) | 252 |
| 327.0 | 408.3 | 576.9 | This work | |

[a] Experimental values of $\underline{S}^{\circ}$(298.15 K) are underlined.

[b] From calorimetric measurements Rathjens and Gwinn[55] obtained the value of $\underline{S}^{\circ}$(285.67 K). On the basis of this value Stull et al.[253] calculated $\underline{S}^{\circ}$(298.15 K).

[c] The entropy value was calculated from equilibrium data.

Table 33. Comparison of experimental heat capacities with calculated values (in J $K^{-1}$ $mol^{-1}$)

| Experimental $C_p^{\circ}$ data | | Calculated $C_p^{\circ}$ data | |
|---|---|---|---|
| Cyclopropane | | | |
| $T$, K | Ref. 254 | Ref. 254 | This work |
| 272.15 | 50.6 | 50.8 | 50.5 |
| 300.48 | 56.5 | 56.4 | 56.0 |
| 333.70 | 63.2 | 63.2 | 62.8 |
| 368.46 | 70.2 | 70.4 | 69.8 |
| $T$, K | Ref. 255 [a] | Ref. 255 | This work |
| 157.6 | 35.3 | 35.0 | 35.0 |
| 223.4 | 42.6, 43.1 | 42.1 | 42.1 |
| 258.4 | 48.7, 49.6 | 48.1 | 47.9 |
| 295.4 | 55.5, 57.1 | 55.2 | 55.0 |
| 313.9 | 59.3, 61.3 | 59.1 | 58.7 |
| 325.3 | 61.3, 63.6 | 61.5 | 61.1 |
| 338.9 | 64.2 | 64.2 | 63.8 |
| Cyclopentane | | | |
| $T$, K | Ref. 258 | Ref. 88 | This work |
| 353 | 102.0 | 102.0 | 101.8 |
| 372 | 108.2 | | 108.5 |
| 395 | 117.3 | | 116.4 |
| 424 | 126.3 | | 126.2 |
| 463 | 138.7 | | 138.8 |
| 503 | 150.7 | 150.9 | 150.9 |
| 539 | 160.1 | 161.2 | 161.2 |
| $T$, K | Ref. 101 | Ref. 101 | This work |
| 329.05 | 94.0 | 93.9 | 93.4 |
| 395.05 | 117.1 | 117.1 | 116.5 |
| 463.10 | 139.5 | 139.6 | 138.8 |
| Cyclohexane | | | |
| $T$, K | Ref. 258 | | This work |
| 384 | 143.1 | | 141.9 |
| 428 | 161.8 | | 160.3 |
| 460 | 174.5 | | 173.2 |
| 495 | 189.5 | | 186.8 |
| 521 | 196.6 | | 196.4 |
| 544 | 206.3 | | 204.6 |
| Cyclohexene | | | |
| $T$, K | Ref. 109 | Ref. 109 | This work |
| 400 | 145.0 | 144.9 | 139.7 |

[a] Only a part of experimental values is included in this table

frared spectrum of the gas ($B_2$ and $E$ modes), and from calculation (unobserved $A_2$ modes).

Ideal gas thermodynamic properties for 1,3,5,7-cyclooctatetraene are given in Table 30. The calculated value of $S^\circ$ (298.15 K), as shown in Table 32, agrees well with the calorimetric entropy.[251] Lippincott and Lord[252] have calculated thermal functions for the crown structure of $D_4$ symmetry. Calculated $S^\circ$ values are somewhat lower than values obtained in this work (Table 32), while the $C_p^\circ$ values are close to those given in Table 30. The discrepancies in the entropy values are due to the different vibrational frequencies adopted for calculations (the discrepancy in symmetry numbers is compensated for the presence of optical isomers in the case of $D_4$ symmetry).

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