Ab-Initio Calculations and Ideal Gas Thermodynamic Functions of Cyclopentadiene and Cyclopentadiene Derivatives

Cite as: Journal of Physical and Chemical Reference Data **20**, 665 (1991); https://doi.org/10.1063/1.555891
Submitted: 10 September 1990 . Published Online: 15 October 2009

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Received September 10, 1990; revised manuscript received May 6, 1991

Structures, frequencies and energies, ideal gas thermodynamic properties and values, have been calculated for cyclopentadiene, cyclopentadienols, and a number of radicals derived from them. The necessary molecular information for these calculations was found by *ab-initio* molecular orbital calculations. The geometries, vibrational frequencies and moments of inertia of 8 species are reported. In order to estimate the accuracy of the computations the molecular parameters were compared with known values reported in the literature whenever those were available.

Key words: cyclopentadiene; ideal gas thermodynamic properties; molecular orbital calculations; moments of inertia.

Contents

List of Tables

List of Figures

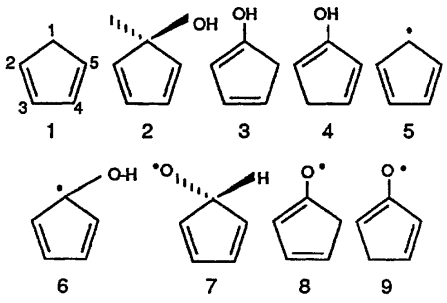
1. Introduction

Detailed investigations of the chemical kinetics of combustion processes of fuels have lately focused attention on fuel molecules other than normal chain hydrocarbons. Thus, the combustion properties and kinetics of benzene and toluene have been investigated [1,2]. Detailed kinetic schemes for the combustion of a species, necessitate the knowledge not only of its thermodynamic properties but also those of all the radicals that are formed during the chaotic combustion process. Among those radicals many are simple derivatives of the parent molecule; thus, for benzene, the most abundant are the phenyl and phenoxy radicals. While the thermodynamic properties of most stable organic species can be calculated from available spectroscopic data, the absence of the latter makes it impossible to do so for complex organic radicals.

Methods for estimating the unavailable spectroscopic data of radicals, and thus calculating approximate thermodynamic values, have been reviewed [3], and were applied in a small number of cases [4,5]. While estimated spectroscopic data provide a fair approximation, a better approach to computing thermodynamic values is to employ *ab-initio* molecular orbital calculations which yield more consistent information on the spectroscopic constants. Analysis of recent experiments in combustion kinetics of cyclopentene [6], requires knowledge of the thermodynamic parameters of cyclopentadienyl radicals. Therefore we have undertaken to calculate molecular parameters for some unknown cyclopentadienyl radicals using *ab-initio* methods. In order to evaluate the accuracy of the calculations, the molecular properties of a few stable molecules were calculated as well by the same *ab-initio* methods and compared with experimental results.

2. Methods of Calculation

The molecules and radicals investigated are: *cyclopentadiene* (1); *2,4-cyclopentadiene-1-ol* (2); *1,3-cyclopentadiene-1-ol* (3); and, *1,4-cyclopentadiene-1-ol* (4); *cyclopentadienyl radical* (5); *1-hydroxy-2,4-cyclopentadiene-1-yl radical* (6); *1-oxy-2,4- cyclopentadiene radical* (7); *1-oxy-1,3-cyclopentadiene radical* (8) and *1-oxy-1,4-cyclopentadiene radical* (9). For comparison purposes thermodynamic properties and vibrational frequencies were calculated also for the following species: CH_3·, CH_4, ethylene (C_2H_4), ethyl radical (C_2H_5·), ethane (C_2H_6), propene (C_3H_6), vinyl alcohol ($H_2C=CHOH$), vinyl radical ($H_2C=CH$·), ethyl alcohol (C_2H_5OH) and propenyl radical ($CH_2=C(CH_3)$·) .



Ab-initio Calculations:

The total molecular energies, vibrational frequencies and moments of inertia were calculated by standard *ab-initio* SCF-MO methods using Gaussian 82 series of programs [7]. The molecular geometries were optimized by gradient minimization techniques for geometry optimization [8a] with split valence 3-21G basis set [8b]. The optimized structures of 1-9 are presented in Fig. 1.

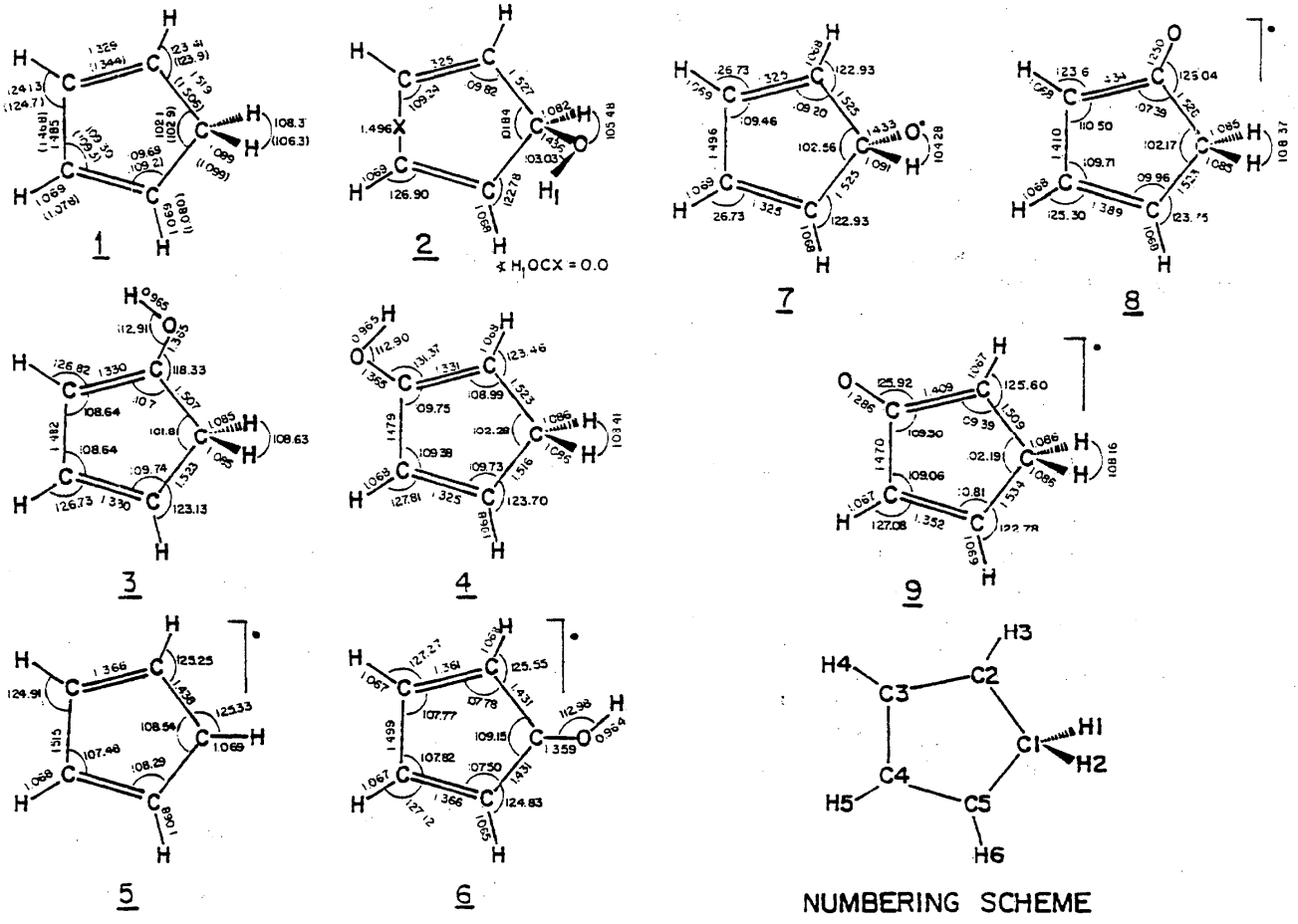


FIG. 1. Optimized geometries (at 3–21G) for species 1–9. (experimental values [29] for 1 are given in parenthesis).

The vibrational frequencies, vibrational energies at 298 K, zero point energies and moments of inertia have also been calculated with this basis set. Single point energy calculations at the best available geometries were carried out also with the polarized 6-31G* basis set [9a].

The enthalpies of formation were evaluated from the reaction energies of the isodesmic reactions presented below (eq. 1-15). An isodesmic process [10] is a reaction in which the number of electron pairs and formal chemical bond types are being conserved during the reaction; i.e., only the environment in which these bonds are located is changed. It is then assumed that many errors inherent in the heat of formation of an individual reactant or product cancel out.

3. List of Isodesmic Reactions

1) cyclo-C_5H_6 (1) + $5CH_4 \rightarrow 3C_2H_6 + 2C_2H_4$
2) cyclo-C_5H_5· (5) + $5CH_4 \rightarrow C_2H_5$· + $2C_2H_6 + 2C_2H_4$
3) 2,4-cyclo-C_5H_5OH (2) + $5CH_4 \rightarrow 2C_2H_6 + C_2H_5OH + 2C_2H_4$
4) 2,4-cyclo-C_5H_5OH (2) + $C_2H_6 \rightarrow$ cyclo-C_5H_6 (1) + C_2H_5OH
5) 1,3-cyclo-C_5H_5OH (3) + $5CH_4 \rightarrow 3C_2H_6 + C_2H_4 + H_2C{=}CHOH$
6) 1,3-cyclo-C_5H_5OH (3) + $C_2H_4 \rightarrow$ cyclo-C_5H_6 (1) + $CH_2{=}CHOH$
7) 1,4-cyclo-C_5H_5OH (4) + $5CH_4 \rightarrow 3C_2H_6 + C_2H_4 + CH_2{=}CHOH$
8) 1,4-cyclo-C_5H_5OH (4) + $C_2H_4 \rightarrow$ cyclo-C_5H_6 (1) + $CH_2{=}CHOH$
9) 2,4-cyclo-1-C_5H_4OH (6) + $5CH_4 \rightarrow C_2H_6 + 2C_2H_4 + C_2H_5OH + C_2H_5$·
10) 2,4-cyclo-1-C_5H_5O· (7) + $5CH_4 \rightarrow 2C_2H_6 + 2C_2H_4 + C_2H_5O$·
11) 2,4-cyclo-1-C_5H_5O· (7) + $C_2H_6 \rightarrow$ cyclo-C_5H_6 (1) + C_2H_5O·
12) 1,3-cyclo-1-C_5H_5O· (8) + $5CH_4 \rightarrow 2C_2H_6 + 2C_2H_4 + C_2H_5O$·
13) 1,3-cyclo-1-C_5H_5O· (8) + $C_2H_6 \rightarrow$ cyclo-C_5H_6 (1) + C_2H_5O·
14) 1,4-cyclo-1-C_5H_5O· (9) + $5CH_4 \rightarrow 2C_2H_6 + 2C_2H_4 + C_2H_5O$·
15) 1,4-cyclo-1-C_5H_5O· (9) + $C_2H_6 \rightarrow$ cyclo-C_5H_6 (1) + C_2H_5O·

The total energy ΔE was calculated by *ab-initio* methods for each reactant and product participating in the isodesmic reactions.

Knowing ΔE for the individual reactants and products, the reaction energy can be evaluated.

$$\Delta E_r = \Sigma\Delta E(\text{products}) - \Sigma\Delta E\ (\text{reactants})$$
$$\Delta H_r = \Sigma\Delta_f H(\text{products}) - \Sigma\Delta_f H\ (\text{reactants})$$
$$\Delta H_r = \Delta E_r + \Delta nRT$$

Since only one value in each reaction has an unknown experimental heat of formation it can be easily deduced from the calculated reaction energy and the known experimental heats of formation of the other species. Also, since we are comparing experimental values and calculated ones the fact that thermochemical experiments are performed under different conditions from those assumed by *ab-initio* calculations must be taken into account. Theoretical energies are calculated by *ab-initio* methods for isolated molecules at 0 K with stationary nuclei, while thermochemical measurements are carried out with vibrating molecules at higher temperatures (usually 298 K). A comparison of theoretical and experimental results requires therefore corrections for zero point energies and changes in enthalpies with temperature. These corrections were performed using the following equations [11,12].

$$\Delta H(T) = \Delta H_{trans}(T) + \Delta H_{rot}(T) + \Delta H_{vib}(T) + RT$$
$$\Delta H_{trans} = \frac{3}{2}RT$$
$$\Delta H_{rot} - \frac{3}{2}RT$$

If $\Delta n = 0$ and $\Delta E = \Delta H$ then:

$$\Delta H_{vib} = H_{vib}(T) - H_{vib}(0) = N \sum_{i}^{modes} \frac{h\nu_i}{e^{h\nu_i/kT} - 1}$$
$$H_{vib}(0) = \text{Zero Point Energy } (ZPE) = \frac{1}{2}\sum_i h\nu_i \ .$$

Zero point energies $H_{vib}(0)$ and $H_{vib}(T)$ are evaluated using the frequencies calculated by the Gaussian program with the 3–21G basis set. Those frequencies are known to be higher than the experimental values by 10% on the average [13,14] and were therefore multiplied by a factor of 0.89 which gave the best agreement with literature values. In Table 1 calculated vibrational frequencies for test species are listed and compared with available experimental values. The percent deviation is shown as well.

Table 2 compares thermodynamic values calculated using *ab-initio* and experimental vibrational frequencies. The agreement between the two sets of values is good with deviations of $\pm 1-4\%$.

The calculated heats of formation at the 3–21G and 6–31G* levels of theory are listed in Table 3. The estimated error in the reported values is ± 4 kJ/mol.

Calculations of Thermodynamic Properties:

The thermodynamic calculations were performed using the NASA code PAC90 [15]. The Rigid Rotor Harmonic Oscillator (RRHO) method was used. The data used by the program were molecular frequencies moments of inertia and enthalpies of formation calculated as described before and internal rotation barrier energies and internal molecular moments of inertia taken from molecules of similar structure 2-propanol and phenol (see Table 4). The PAC90 version of the thermodynamic program [15] includes the ability to calculate internal rotation barrier contributions. This routine was developed by Lanne *et al.*, [16] and is included in the program. The temperature range (0–5000 K) the pressure of one bar and the number of significant figures in the values reported in Table 5 conform to the JANAF [17] and NASA convention [15] which is similar to the Soviet Academy of Science convention [18,19]. The RRHO approximation is used as part of the convention for lack of detailed unharmonicity information.

The fundamental constants used in the PAC90 program were published by Cohen and Taylor [20] and the atomic weights were those of the IUPAC Commission of 1987 [21]. The reference elements used in our calculation were graphite taken from TRC 1983 [22] H_2 taken from

Cyclopentadienyl radical is a Jahn-Teller species and can not have a D_{5h} symmetry [27,28] and therefore distorts to C_{2v} symetry.

The structure of species 6 is very similar to that of species 5 though a hydroxy group is attached to C(1). The C(1)—O bond is much shorter than the corresponding one in its precusor 2 due to resonance effects described above and is similar to a C—O bond of an hydroxy group

any small variation in the values of the frequencies is averaged out. This can be seen from the values of the zero point energies in Table 6 which are practically identical with deviations from the mean of a small fraction of a percent. On the other hand, $\Delta_f H_T^\circ$ varies significantly. The nature of the bonds dictates the thermochemistry which dictates the values of $\Delta_f H_T^\circ$.

5. Tables

TABLE 1. Calculated and experimental frequencies

ν	CH_4			C_2H_4			C_2H_6		
	Calc[1] cm^{-1}	Exp[2] cm^{-1}	%Diff	Calc[1] cm^{-1}	Exp[2] cm^{-1}	%Diff	Calc[1] cm^{-1}	Exp[3] cm^{-1}	%Diff
1	1353	1306	3.5	840	826	1.6	820(2)	822(2)	−2.5
2	1548	1534	0.9	992	943	5.2	894	995	−10.2
3	2836	2917	−2.8	1029	949	8.5	1203(2)	1190(2)	1.1
4	2919	3018	−3.3	1038	1023	1.4	1399	1379	1.4
5				1235	1236	−0.1	1398	1388	0.7
6				1355	1342	1.0	1494(2)	1469(2)	1.7
7				1459	1444	1.0	1493(2)	1468(2)	1.7
8				1640	1623	1.0	2845	2896	−1.8
9				2942	2989	−1.6	2848	2954	−3.6
10				2962	3026	−2.1	2884(2)	2969(2)	−2.9
11				3001	3103	−3.3	2908(2)	2985(2)	−2.6
12				3029	3106	−2.5			

ν	C_2H_5·			C_3H_6			C_2H_5OH		
	Calc[1] cm^{-1}	Exp[4] cm^{-1}	%Diff	Calc[1] cm^{-1}	Exp[5] cm^{-1}	%Diff	Calc[1] cm^{-1}	Exp[6] cm^{-1}	%Diff
1	396	485	−18.3	423	428	−1.26	380	427	−11.1
2	796	980	−18.8	583	575	1.3	800	801	− 0.1
3	931	990	− 6.0	847	912	−7.1	851.	877	− 3.1
4	989	990	− 0.12	954	919	3.76	1010	1040	− 2.9
5	1174	1050	11.8	987	935	5.5	1033	1067	− 3.3
6	1402	1390	0.8	1022	990	3.2	1103	1104	− 0.1
7	1421	1440	− 1.3	1083	1045	3.6	1264	1242	1.7
8	1477	1440	2.6	1170	1178	−0.7	1327	1270	4.5
9	1482	1440	2.9	1307	1298	0.7	1373	1320	4.0
10	2802	2960	− 5.3	1406	1378	2.0	1406	1391	1.0
11	2865	2960	− 3.2	1433	1414	1.3	1481	1456	1.6
12	2895	2960	− 2.2	1475	1443	2.2	1488	1456	2.2
13	2929	3100	− 5.5	1484	1459	1.7	1508	1456	3.6
14	3022.	3100	− 2.5	1656	1653	0.2	2838	2789	1.7
15				2832	2932	−3.4	2846	2789	2.0
16				2875	2953	−2.6	2889	2989	−3.3
17				2885	2973	−3.0	2915	2989	−2.5
18				2943	2991	−1.6	2928	2989	−2.1
19				2955	3022	−2.2	3435	3689	−6.9
20				3014	3091	−2.5			

ν	C_5H_6			ν	C_5H_6		
	Calc[1] cm^{-1}	Exp[7] cm^{-1}	%Diff		Calc[1] cm^{-1}	Exp[7] cm^{-1}	%Diff
1	348.	350.	−0.5	15	1150.	1106.	4.0
2	518.	516.	0.4	16	1240.	1239.	0.1
3	684.	664.	3.0	17	1293.	1292.	0.1
4	755.	700.	7.9	18	1348.	1365.	−1.3
5	798.	802.	−0.1	19	1414.	1378.	2.6
6	802.	805.	−0.3	20	1520.	1500.	1.3
7	837.	891.	−6.1	21	1591.	1580.	0.7
8	910.	915.	−0.5	22	2833.	2886.	−1.8
9	913.	925.	−1.3	23	2861.	2900.	−1.3
10	920.	941.	−2.3	24	3016.	3043.	−0.8
11	999.	959.	4.2	25	3023.	3075.	−1.7
12	1003.	994.	0.9	26	3040.	3091.	−1.6
13	1100.	1090.	0.9	27	3051.	3105.	−1.8
14	1114.	1100.	1.2				

[1]Frequencies calculated by Gaussian 82 and multiplied by 0.89 (see text).
[2]T.Shimanouchi, NSRDS–NBS 39, 1972.
[3]J.Chao, R.C.Wilhoit & B.J.Zwolinski, J. Phys. Chem. Ref. Data, 2 (1973) 427.
[4]Estimated from other compounds by J.H. Purnell & C.P. Quinn, J. Chem. Soc. (1964) 4049.
[5]J.Chao & B.J.Zwolinski, J. Phys. Chem. Ref. Data, 4 (1975) 251.
[6]J.H.S.Green, Trans Faraday Soc. 57 (1961) 2132.
[7]O.V. Dorofeeva, L.V. Gurvich, & V.S. Jorish, J. Phys. Chem. Ref. Data, 15 (1986) 437.

TABLE 2. Comparison of thermodynamic values using experimental vs. calculated frequencies

		C_2H_4			C_2H_6		
	T K	$X^{a,1}_{exp}$	X^{b}_{calc}	%Diff	$X^{a,2}_{calc}$	X^{b}_{calc}	%Diff
C_p[c]	500	62.4	61.5	1.5	78.0	77.5	0.6
C_p[c]	1000	93.9	93.9	0.0	122.6	123.0	−0.3
C_p[c]	2000	118.4	118.6	−0.2	158.0	158.5	−0.3
$H-H_0$[d]	500	21.17	20.91	1.2	25.06	24.97	0.4
$H-H_0$[d]	1000	61.16	60.67	0.8	76.35	76.27	0.1
$H-H_0$[d]	2000	169.9	169.6	0.2	220.4	220.9	−0.2
S[e]	500	246.1	245.3	0.3	262.3	262.9	−0.1
S[e]	1000	300.3	299.1	0.4	331.6	332.2	−0.1
S[e]	2000	374.7	373.6	0.3	430.1	431.1	−0.2

		C_3H_6			Cyclopentadiene		
	T K	$X^{a,3}_{exp}$	X^{b}_{calc}	%Diff	$X^{a,4}_{exp}$	X^{b}_{calc}	%Diff
C_p[c]	500	95.2	94.5	1.0	126.4	125.9	0.4
C_p[c]	1000	144.4	144.8	−0.03	191.6	191.7	−0.05
C_p	2000	181.9	182.4	−0.3	234.0	234.3	−0.1
$H-H_0$[d]	500	29.74	29.56	0.6	34.19	34.01	0.5
$H-H_0$[d]	1000	91.08	90.81	0.3	116.22	115.94	0.2
$H-H_0$[d]	2000	258.3	258.5	0.0	333.82	333.81	0.0
S[e]	500	307.4	307.8	−0.1	325.9	326.2	−0.2
S[e]	1000	390.5	390.7	0.0	437.0	437.2	−0.05
S[e]	2000	504.9	505.5	−0.1	586.2	586.5	−0.05

[a]Calculations based on experimental values of vibrational frequencies and moments of inertia.
[b]Calculations based on values of the vibrational frequencies calculated in the present work.
[c]Units J/mol/K.
[d]Units kJ/mol.
[e]Units J/mol/K.
[1]J.L.Duncan et. al, J. Mol. Spectros. **61** (1976) 470.
[2]J.Chao, R.C.Wilhoit & B.J.Zwolinski J. Phys. Chem. Ref. Data **2** (1973) 427.
[3]J.Chao and B.J.Zwolinski J. Phys. Chem. Ref. Data **4**, (1975) 251.
[4]O.V.Dorofeeva, L.V.Gurvich, & V.S.Jorish, J. Phys. Chem. Ref. Data **15** (1986) 437.

TABLE 3. Enthalpies of formation (kJ/mol)of the investigated molecules[a] (1–9)

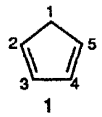
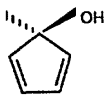
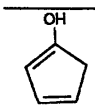
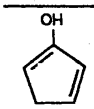
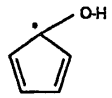
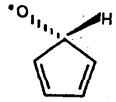
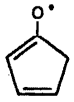
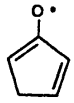
Species	Reaction	T K	$\Delta_f H$ 3-21G	$\Delta_f H$ 6-31G*	$\Delta_f H$ Experimental
 1	1	298	140.2	139.3	133.5[b]
		0	157.3	156.5	151.0[b]
 5	2	298	266.1	266.5	292.7 ± 21,[c] 264.4[d]
		0	284.9	279.1	
 2	3	298	13.4	15.5	
		0	31.0	33.0	
	4	298	5.0	7.9	
		0	24.7	28.0	
 3	5	298	−20.9	−17.2	
	6	298	−28.9	−24.3	

TABLE 3. Enthalpies of formation (kJ/mol)of the investigated molecules[a] (1–9) — Continued

Species	Reaction	T	$\Delta_f H$		
		K	3-21G	6-31G*	Experimental
 4	7	298	−22.2	−19.7	
	8	298	−30.5	−27.2	
 6	9	298	87.4	87.4	
		0	100.4	100.8	
 7	10[e]	298	225.1	222.6	
	11[e]	298	232.2	230.5	
 8	12	298	73.6	52.3	
	13	298	80.8	59.8	
 9	14	298	106.7	96.2	
	15	298	113.0	103.3	

[a]Reaction enthalpies at 298 K were calculated from reaction enthalpies at 0 K corrected for zero point energy and change of enthalpy with temperature as described in the text.
[b]K. B. Wiberg, J. J. Wendlosky, J. Am. Chem. Soc. **104**, (1982), 5679.
[c]P. Bishof, J. Am. Chem. Soc. **99**, (1977), 8145.
[d]D. J. DeFrees, R. T. McIveer and W. J. Hehre, J. Am. Chem. Soc. , **102**, (1980), 3334.
[e]Zero point energies have been estimated because direct calculations were impossible.

TABLE 4. Data used for thermodynamic calculations

Cyclopentadiene (1)[a]

Vibrations 350, 516, 664, 700, 802, 805, 891, 915, 925, 941, 959, 994, 1090, 1100, 1106, 1239, 1292, 1365, 1378, 1500, 1580, 2886, 2900, 3043, 3075, 3091, 3105
Moments of Inertia $I_A I_B I_C = 19.96 \times 10^{-115}$ g^{3}cm^6
Statistical Weight = 1.
Symmetry Number = 2.
$\Delta_f H_{298}$ = 134.3 kJ/mol[b].

2,4-cyclopentadiene-1-ol (2)

Vibrations 300, 368, 520, 543, 706, 769, 792, 810, 842, 889, 980, 1013, 1018, 1019, 1097, 1118, 1207, 1241, 1291, 1335, 1344, 1540, 1603, 2890, 3022, 3030, 3049, 3058, 3437.
Moments of Inertia I_A = 12.54 I_B = 24.83 I_C = 33.92 g cm^2 $\times 10^{-39}$
Internal rotation[c] B_R = 21.07 cm^{-1} $V(1)=30.4$, $V(2)=-86.18$, $V(3)=401.$ cm^{-1}
Rotational Symmetry = 1.
Statistical Weight = 1.
Symmetry Number = 1.
$\Delta_f H_{298}$ = 7.9 kJ/mol.

TABLE 4. Data used for thermodynamic calculations – Continued

1,3-cyclopentadiene-1-ol (3)

Vibrations 342, 363, 424, 527, 603, 714, 793, 865, 875, 887, 928, 935, 1002, 1089, 1119, 1151, 1207, 1254, 1312, 1383, 1412, 1545, 1606, 2867, 2900, 3022, 3033, 3053., 3466.
Moments of Inertia $I_A = 10.76$ $I_B = 26.59$ $I_C = 36.79$ g cm^2 $\times 10^{-39}$
Internal rotation[d] Ir = .1336 g cm^2 $\times 10^{-39}$ $V(2) = 1212.95$ cm^{-1}
Rotational Symmetry = 2.
Statistical Weight = 1.
Symmetry Number = 1.
$\Delta_f H_{298} = -24.3$ kJ/mol.

1,4-cyclopentadiene-1-ol (4)

Vibrations 336, 369, 379, 607, 616, 743, 795, 795, 850, 889, 926, 935, 999, 1075, 1112, 1148, 1196, 1252, 1298, 1387, 1422, 1550, 1626, 2852, 2880, 3030, 3037, 3058, 3472.
Moments of Inertia $I_A = 10.99$ $I_B = 26.45$ $I_C = 36.88$ g cm^2 $\times 10^{-39}$
Internal rotation[d] Ir = 0.1336 g cm^2 $\times 10^{-39}$ $V(2) = 1212.95$ cm^{-1}
Rotational Symmetry = 2.
Statistical Weight = 1.
Symmetry Number = 1.
$\Delta_f H_{298} = -27.2$ kJ/mol.

Cyclopentadienyl radical (5)

Vibrations 484, 497, 653, 702, 710, 767, 815, 834, 894, 903, 917, 955, 982, 1080, 1201, 1275, 1337, 1364, 1404, 3024, 3029, 3039, 3048, 3061.
Moments of Inertia $I_A = 9.75$ $I_B = 10.68$ $I_C = 20.44$ g cm^2 $\times 10^{-39}$
Statistical Weight = 2.
Symmetry Number = 2.
$\Delta_f H_{298} = 266. \pm 4.$ kJ/mol[e]

1-hydroxy-2,4 cyclopentadiene-1-yl radical (6)

Vibrations 296, 366, 510, 593, 615, 681, 717, 725, 832, 885, 898, 906, 939, 1061, 1067, 1209, 1273, 1275, 1365, 1504, 1467, 3028, 3044, 3054, 3075, 3483.
Moments of Inertia $I_A = 10.74$ $I_B = 24.95$ $I_C = 35.69$ g cm^2 $\times 10^{-39}$
Internal rotation[d] Ir = 0.1336 g cm^2 $\times 10^{-39}$ $V(2) = 1212.95$ cm^{-1}
Rotational Symmetry = 2.
Statistical Weight = 2.
Symmetry Number = 1.
$\Delta_f H_{298} = 87.4$ kJ/mol.

1-oxy-1,3 cyclopentadiene radical (8)

Vibrations 191, 386, 418, 521, 607, 637, 775, 788, 797, 868, 900, 926, 989, 1024, 1129, 1150, 1218, 1267, 1322, 1342, 1375, 1422, 2868, 2901, 3025, 3037, 3051.
Moments of Inertia $I_A = 11.15$ $I_B = 21.98$ $I_C = 35.27$ g cm^2 $\times 10^{-39}$
Statistical Weight = 2.
Symmetry Number = 1.
$\Delta_f H_{298} = 59.8$ kJ/mol

TABLE 4. Data used for thermodynamic calculations – Continued

1-oxy-1,4 cyclopentadiene radical (9)

Vibrations 225, 339, 410, 563, 620, 653, 724, 751, 826, 862, 896, 921, 939, 1038, 1144, 1145, 1198, 1243, 1285, 1337, 1386, 1433, 2854, 2882, 3027, 3046, 3056.
Moments of Inertia $I_A = 11.18$ $I_B = 24.93$ $I_C = 35.55$ g cm$^2 \times 10^{-39}$
Statistical Weight = 2.
Symmetry Number = 1.
$\Delta_f H_{298} =$ 103.3 kJ/mol

[a]All the values reported for Cyclopentadiene are experimental and were taken from O. V. Dorofeeva, L. V. Gurvich & V. S. Jorish, J. Phys. Chem. Ref. Data **15** (1986), 437.
[b]J. B. Pedley, R. D. Naylor & S. P. Kirby, Thermochemical Data of Organic Compounds Chapman & Hall 1986, London.
[c]Values for internal rotational constants and internal rotational barrier were taken from 2-Propanol given by J. Chao *et al.*, J. Phys. Chem. Ref. Data **15** (1986), 1425.
[d]Values for internal moments of inertia and internal rotational barrier were taken from Phenol given by A. Burcat, F. Zeleznik & B. J. McBride, NASA TM-83800 1985.
[e]Experimental value given by D. J. DeFrees, R. T. McIveer & W. J Hehre, J. Am. Chem. Soc. 102, (1980), 3334 is 264. 4 kJ/mol.

TABLE 5. Thermodynamic values for cyclopentadiene and cyclopentadiene derivatives and radicals

Cyclopentadiene C_5H_6

T K	C_p° J/mol·K	$H_T^\circ - H_{298}^\circ$ KJ/mol	S_T° J/mol·K	$-(G_T^\circ - H_{298}^\circ)/T$ J/mol·K	H_T° KJ/mol	$\Delta_f H_T^\circ$ KJ/mol	$\log_{10} K_p$
0	-------	−13.536	-------	-------	120.764	151.436	-------
100	35.046	−10.177	221.921	323.695	124.123	145.490	−80.4321
200	49.527	−6.079	249.768	280.163	128.221	139.872	−42.9986
298.15	75.368	0.000	274.154	274.154	134.300	134.300	−31.1835
300	75.894	0.140	274.622	274.155	134.440	134.202	−31.0385
400	103.302	9.125	300.279	277.468	143.425	129.354	−25.2961
500	126.452	20.653	325.908	284.602	154.953	125.480	−21.9667
600	145.034	34.262	350.668	293.565	168.562	122.414	−19.8079
700	160.047	49.541	374.192	303.419	183.841	120.018	−18.3002
800	172.415	66.183	396.396	313.667	200.483	118.195	−17.1894
900	182.777	83.958	417.319	324.033	218.258	116.874	−16.3368
1000	191.555	102.686	437.043	334.357	236.986	115.970	−15.6611
1100	199.046	122.226	455.661	344.547	256.526	115.423	−15.1118
1200	205.470	142.460	473.263	354.547	276.760	115.167	−14.6556
1300	211.000	163.290	489.933	364.325	297.590	115.144	−14.2703
1400	215.778	184.635	505.749	373.867	318.935	115.297	−13.9394
1500	219.922	206.425	520.781	383.165	340.725	115.598	−13.6526
1600	223.528	228.601	535.092	392.216	362.901	115.999	−13.4006
1700	226.678	251.115	548.740	401.026	385.415	116.475	−13.1774
1800	229.439	273.924	561.777	409.597	408.224	117.002	−12.9781
1900	231.870	296.992	574.248	417.937	431.292	117.561	−12.7991
2000	234.017	320.288	586.197	426.053	454.588	118.131	−12.6371
2100	235.920	343.787	597.662	433.954	478.087	118.703	−12.4899
2200	237.613	367.465	608.676	441.647	501.765	119.263	−12.3553
2300	239.125	391.304	619.273	449.141	525.604	119.804	−12.2319
2400	240.479	415.285	629.479	456.443	549.585	120.314	−12.1183
2500	241.696	439.394	639.320	463.563	573.694	120.789	−12.0133
2600	242.792	463.620	648.822	470.507	597.920	121.224	−11.9161
2700	243.784	487.950	658.004	477.282	622.250	121.611	−11.8258
2800	244.682	512.374	666.886	483.895	646.674	121.952	−11.7417
2900	245.499	536.883	675.486	490.354	671.183	122.235	−11.6632
3000	246.244	561.471	683.822	496.665	695.771	122.459	−11.5895
3100	246.924	586.130	691.908	502.834	720.430	122.628	−11.5208
3200	247.547	610.854	699.757	508.866	745.154	122.729	−11.4561
3300	248.119	635.638	707.384	514.766	769.938	122.767	−11.3955
3400	248.644	660.475	714.798	520.541	794.775	122.737	−11.3383
3500	249.129	685.365	722.013	526.195	819.665	122.637	−11.2846
3600	249.577	710.301	729.038	531.732	844.601	122.463	−11.2336
3700	249.992	735.280	735.882	537.157	869.580	122.218	−11.1857
3800	250.376	760.298	742.554	542.475	894.598	121.895	−11.1403
3900	250.732	785.354	749.062	547.689	919.654	121.498	−11.0975
4000	251.064	810.442	755.414	552.804	944.742	121.018	−11.0568
4100	251.373	835.565	761.618	557.821	969.865	120.464	−11.0185
4200	251.662	860.717	767.678	562.746	995.017	119.827	−10.9820
4300	251.931	885.897	773.603	567.581	1020.197	119.108	−10.9474
4400	252.183	911.103	779.398	572.329	1045.403	118.306	−10.9146
4500	252.420	936.333	785.068	576.994	1070.633	117.423	−10.8836
4600	252.641	961.586	790.618	581.578	1095.886	116.454	−10.8541
4700	252.850	986.861	796.054	586.084	1121.161	115.404	−10.8260
4800	253.046	1012.156	801.380	590.514	1146.456	114.269	−10.7994
4900	253.230	1037.469	806.599	594.870	1171.769	113.050	−10.7742
5000	253.405	1062.803	811.717	599.157	1197.103	111.749	−10.7502

2,4 Cyclopentadiene-1-ol C_5H_5OH

T K	C_p° J/mol·K	$H_T^\circ - H_{298}^\circ$ KJ/mol	S_T° J/mol·K	$-(G_T^\circ - H_{298}^\circ)/T$ J/mol·K	H_T° KJ/mol	$\Delta_f H_T^\circ$ KJ/mol	$\log_{10} K_p$
0	-------	−16.726	-------	-------	−8.826	26.186	-------
100	43.498	−12.839	238.461	366.854	−4.939	19.318	−18.1903
200	63.605	−7.573	274.171	312.038	0.327	13.411	−13.7498
298.15	91.437	0.000	304.610	304.610	7.900	7.900	−12.8062
300	91.987	0.170	305.177	304.611	8.070	7.804	−12.7977
400	120.413	10.818	335.614	308.569	18.718	3.134	−12.5540
500	144.261	24.095	365.141	316.952	31.995	−0.521	−12.5183
600	163.326	39.510	393.193	327.344	47.410	−3.360	−12.5514
700	178.661	56.636	419.563	338.655	64.536	−5.538	−12.6066
800	191.249	75.151	444.267	350.329	83.051	−7.156	−12.6661
900	201.770	94.817	467.419	362.067	102.717	−8.288	−12.7222
1000	210.677	115.451	489.151	373.700	123.351	−9.018	−12.7724
1100	218.279	136.909	509.597	385.134	144.809	−9.403	−12.8162
1200	224.805	159.071	528.876	396.317	166.971	−9.505	−12.8537
1300	230.430	181.840	547.098	407.221	189.740	−9.381	−12.8856
1400	235.298	205.132	564.357	417.834	213.032	−9.089	−12.9118
1500	239.526	228.878	580.738	428.153	236.778	−8.654	−12.9343
1600	243.211	253.019	596.318	438.180	260.919	−8.123	−12.9526
1700	246.435	277.505	611.161	447.923	285.405	−7.522	−12.9676
1800	249.266	302.293	625.328	457.388	310.193	−6.876	−12.9798
1900	251.760	327.346	638.873	466.586	335.246	−6.203	−12.9899
2000	253.966	352.635	651.844	475.526	360.535	−5.523	−12.9980
2100	255.923	378.131	664.283	484.221	386.031	−4.849	−13.0045
2200	257.667	403.813	676.230	492.679	411.713	−4.193	−13.0096
2300	259.225	429.659	687.719	500.911	437.559	−3.563	−13.0135
2400	260.621	455.652	698.781	508.926	463.552	−2.969	−13.0166
2500	261.877	481.778	709.446	516.735	489.678	−2.419	−13.0189
2600	263.009	508.023	719.740	524.346	515.923	−1.916	−13.0207
2700	264.034	534.376	729.685	531.768	542.276	−1.469	−13.0220
2800	264.963	560.827	739.304	539.009	568.727	−1.076	−13.0230
2900	265.809	587.367	748.617	546.077	595.267	−0.746	−13.0236
3000	266.579	613.986	757.641	552.979	621.886	−0.485	−13.0237
3100	267.284	640.679	766.394	559.724	648.579	−0.286	−13.0241
3200	267.929	667.440	774.891	566.316	675.340	−0.161	−13.0241
3300	268.522	694.264	783.145	572.762	702.164	−0.107	−13.0242
3400	269.067	721.143	791.169	579.068	729.043	−0.128	−13.0243
3500	269.570	748.075	798.976	585.240	755.975	−0.226	−13.0244
3600	270.034	775.056	806.577	591.283	782.956	−0.404	−13.0244
3700	270.464	802.082	813.982	597.203	809.982	−0.660	−13.0246
3800	270.863	829.148	821.199	603.003	837.048	−1.001	−13.0250
3900	271.233	856.253	828.240	608.688	864.153	−1.422	−13.0254
4000	271.578	883.394	835.111	614.263	891.294	−1.932	−13.0259
4100	271.898	910.567	841.821	619.732	918.467	−2.523	−13.0268
4200	272.198	937.773	848.377	625.098	945.673	−3.202	−13.0275
4300	272.479	965.008	854.786	630.365	972.908	−3.968	−13.0285
4400	272.741	992.268	861.053	635.537	1000.168	−4.824	−13.0297
4500	272.986	1019.555	867.185	640.617	1027.455	−5.766	−13.0312
4600	273.216	1046.864	873.187	645.608	1054.764	−6.801	−13.0328
4700	273.433	1074.197	879.066	650.513	1082.097	−7.920	−13.0345
4800	273.637	1101.550	884.824	655.335	1109.450	−9.132	−13.0364
4900	273.829	1128.925	890.469	660.076	1136.825	−10.430	−13.0387
5000	274.010	1156.317	896.003	664.739	1164.217	−11.818	−13.0410

TABLE 5. Thermodynamic values for cyclopentadiene and cyclopentadiene derivatives and radicals — Continued

1,3-cyclopentadiene−1-ol C_5H_5OH

T K	C_p° J/mol·K	$H_T^\circ - H_{298}^\circ$ KJ/mol	S_T° J/mol·K	$-(G_T^\circ - H_{298}^\circ)/T$ J/mol·K	H_T° KJ/mol	$\Delta_f H_T^\circ$ KJ/mol	$\log_{10} K_p$
0	-------	−16.399	-------	-------	−40.699	−5.687	-------
100	39.331	−12.952	238.380	367.902	−37.252	−12.995	−1.3165
200	64.743	−7.824	272.915	312.037	−32.124	−19.040	−5.3403
298.15	94.957	0.000	304.343	304.343	−24.300	−24.300	−7.1790
300	95.529	0.176	304.932	304.345	−24.124	−24.389	−7.2053
400	124.433	11.212	336.481	308.450	−13.088	−28.671	−8.3554
500	148.061	24.883	366.888	317.122	0.583	−31.933	−9.1456
600	166.722	40.658	395.598	327.834	16.358	−34.411	−9.7226
700	181.650	58.103	422.460	339.456	33.803	−36.270	−10.1621
800	193.875	76.899	447.540	351.417	52.599	−37.608	−10.5069
900	204.084	96.811	470.982	363.414	72.511	−38.494	−10.7830
1000	212.724	117.663	492.944	375.280	93.363	−39.006	−11.0079
1100	220.098	139.314	513.573	386.924	115.014	−39.198	−11.1937
1200	226.427	161.648	533.003	398.296	137.348	−39.128	−11.3487
1300	231.884	184.570	551.347	409.370	160.270	−38.851	−11.4796
1400	236.605	208.000	568.709	420.137	183.700	−38.421	−11.5901
1500	240.706	231.871	585.176	430.595	207.571	−37.862	−11.6854
1600	244.281	256.124	600.828	440.750	231.824	−37.218	−11.7672
1700	247.408	280.712	615.733	450.608	256.412	−36.515	−11.8379
1800	250.154	305.593	629.954	460.180	281.293	−35.776	−11.8996
1900	252.572	330.731	643.544	469.475	306.431	−35.018	−11.9538
2000	254.712	356.098	656.555	478.506	331.798	−34.261	−12.0014
2100	256.611	381.666	669.029	487.284	357.366	−33.515	−12.0436
2200	258.302	407.413	681.007	495.819	383.113	−32.793	−12.0810
2300	259.812	433.320	692.523	504.122	409.020	−32.101	−12.1145
2400	261.167	459.371	703.609	512.205	435.071	−31.451	−12.1446
2500	262.384	485.549	714.296	520.076	461.249	−30.849	−12.1716
2600	263.483	511.843	724.608	527.745	487.543	−30.297	−12.1962
2700	264.476	538.242	734.571	535.222	513.942	−29.803	−12.2187
2800	265.377	564.735	744.206	542.515	540.435	−29.367	−12.2392
2900	266.197	591.315	753.533	549.632	567.015	−28.998	−12.2579
3000	266.944	617.972	762.570	556.579	593.672	−28.699	−12.2750
3100	267.627	644.701	771.335	563.367	620.401	−28.464	−12.2912
3200	268.253	671.495	779.841	569.999	647.195	−28.307	−12.3061
3300	268.828	698.350	788.105	576.484	674.050	−28.221	−12.3201
3400	269.356	725.260	796.138	582.826	700.960	−28.211	−12.3333
3500	269.844	752.220	803.953	589.033	727.920	−28.282	−12.3457
3600	270.294	779.227	811.561	595.109	754.927	−28.433	−12.3574
3700	270.711	806.277	818.973	601.060	781.977	−28.665	−12.3686
3800	271.098	833.369	826.198	606.890	809.069	−28.980	−12.3793
3900	271.457	860.496	833.244	612.604	836.196	−29.379	−12.3896
4000	271.791	887.659	840.122	618.207	863.359	−29.867	−12.3995
4100	272.102	914.854	846.836	623.701	890.554	−30.436	−12.4092
4200	272.392	942.079	853.397	629.092	917.779	−31.095	−12.4184
4300	272.664	969.333	859.810	634.384	945.033	−31.842	−12.4275
4400	272.918	996.611	866.081	639.579	972.311	−32.681	−12.4364
4500	273.156	1023.915	872.217	644.680	999.615	−33.606	−12.4452
4600	273.380	1051.242	878.223	649.693	1026.942	−34.623	−12.4538
4700	273.590	1078.590	884.105	654.618	1054.290	−35.727	−12.4623
4800	273.787	1105.960	889.867	659.459	1081.660	−36.922	−12.4706
4900	273.973	1133.346	895.514	664.219	1109.046	−38.208	−12.4791
5000	274.149	1160.754	901.051	668.900	1136.454	−39.581	−12.4873

TABLE 5. Thermodynamic values for cyclopentadiene and cyclopentadiene derivatives and radicals — Continued

1,4-cyclopentadiene−1-ol C_5H_5OH

T K	C_p° J/mol·K	$H_T^\circ - H_{298}^\circ$ KJ/mol	S_T° J/mol·K	$-(G_T^\circ - H_{298}^\circ)/T$ J/mol·K	H_T° KJ/mol	$\Delta_f H_T^\circ$ KJ/mol	$\log_{10} K_p$
0	-------	−16.413	-------	-------	−43.613	−8.601	-------
100	39.562	−12.959	238.538	368.128	−40.159	−15.902	0.2101
200	64.682	−7.823	273.145	312.259	−35.023	−21.938	−4.5714
298.15	95.023	0.000	304.565	304.565	−27.200	−27.200	−6.6594
300	95.598	0.176	305.154	304.567	−27.024	−27.289	−6.6888
400	124.622	11.226	336.743	308.677	−15.974	−31.557	−7.9648
500	148.269	24.917	367.195	317.360	−2.283	−34.798	−8.8302
600	166.914	40.713	395.942	328.087	13.513	−37.257	−9.4569
700	181.817	58.176	422.832	339.724	30.976	−39.098	−9.9317
800	194.020	76.987	447.932	351.699	49.787	−40.420	−10.3028
900	204.210	96.913	471.390	363.709	69.713	−41.292	−10.5993
1000	212.833	117.777	493.364	375.588	90.577	−41.792	−10.8404
1100	220.194	139.438	514.004	387.242	112.238	−41.974	−11.0394
1200	226.512	161.781	533.441	398.624	134.581	−41.895	−11.2053
1300	231.959	184.711	551.792	409.707	157.511	−41.610	−11.3455
1400	236.673	208.148	569.159	420.481	180.948	−41.173	−11.4640
1500	240.767	232.025	585.630	430.947	204.825	−40.607	−11.5661
1600	244.335	256.284	601.286	441.108	229.084	−39.958	−11.6538
1700	247.457	280.877	616.194	450.972	253.677	−39.250	−11.7298
1800	250.198	305.762	630.417	460.549	278.562	−38.507	−11.7961
1900	252.613	330.906	644.011	469.850	303.706	−37.744	−11.8545
2000	254.749	356.276	657.023	478.885	329.076	−36.983	−11.9059
2100	256.644	381.847	669.499	487.667	354.647	−36.233	−11.9515
2200	258.333	407.598	681.478	496.206	380.398	−35.509	−11.9920
2300	259.841	433.508	692.995	504.514	406.308	−34.814	−12.0282
2400	261.193	459.560	704.083	512.599	432.360	−34.161	−12.0609
2500	262.409	485.741	714.770	520.474	458.541	−33.556	−12.0903
2600	263.505	512.038	725.084	528.146	484.838	−33.001	−12.1171
2700	264.498	538.440	735.048	535.626	511.240	−32.505	−12.1415
2800	265.397	564.934	744.683	542.921	537.734	−32.069	−12.1639
2900	266.215	591.516	754.011	550.040	564.316	−31.697	−12.1844
3000	266.961	618.174	763.048	556.990	590.974	−31.396	−12.2031
3100	267.644	644.906	771.814	563.779	617.706	−31.159	−12.2208
3200	268.269	671.702	780.321	570.414	644.502	−31.000	−12.2371
3300	268.843	698.559	788.586	576.901	671.359	−30.913	−12.2524
3400	269.370	725.468	796.619	583.246	698.268	−30.902	−12.2668
3500	269.857	752.431	804.435	589.454	725.231	−30.971	−12.2805
3600	270.307	779.440	812.043	595.532	752.240	−31.120	−12.2932
3700	270.723	806.491	819.455	601.484	779.291	−31.352	−12.3055
3800	271.109	833.583	826.680	607.316	806.383	−31.666	−12.3172
3900	271.467	860.712	833.727	613.031	833.512	−32.064	−12.3284
4000	271.800	887.874	840.604	618.635	860.674	−32.552	−12.3392
4100	272.111	915.071	847.319	624.131	887.871	−33.119	−12.3498
4200	272.401	942.297	853.880	629.523	915.097	−33.777	−12.3599
4300	272.673	969.551	860.293	634.816	942.351	−34.524	−12.3697
4400	272.926	996.830	866.564	640.012	969.630	−35.362	−12.3793
4500	273.164	1024.136	872.701	645.115	996.936	−36.285	−12.3889
4600	273.387	1051.463	878.707	650.128	1024.263	−37.302	−12.3981
4700	273.597	1078.813	884.589	655.054	1051.613	−38.405	−12.4073
4800	273.794	1106.182	890.351	659.896	1078.982	−39.600	−12.4162
4900	273.980	1133.572	895.999	664.657	1106.372	−40.883	−12.4252
5000	274.155	1160.977	901.535	669.340	1133.777	−42.258	−12.4340

TABLE 5. Thermodynamic values for cyclopentadiene and cyclopentadiene derivatives and radicals – Continued

Cyclopentadienyl Radical C_5H_5·

T K	C_p° J/mol·K	$H_T^\circ - H_{298}^\circ$ KJ/mol	S_T° J/mol·K	$-(G_T^\circ - H_{298}^\circ)/T$ J/mol·K	H_T° KJ/mol	$\Delta_f H_T^\circ$ KJ/mol	$\log_{10} K_p$
0	-------	−13.521	-------	-------	252.581	279.019	------
100	34.149	−10.184	227.508	329.343	255.919	274.552	−144.9229
200	49.590	−6.164	254.771	285.589	259.939	270.202	−73.6565
298.15	76.605	0.000	279.485	279.485	266.102	266.102	−50.5828
300	77.128	0.142	279.960	279.486	266.245	266.033	−50.2953
400	103.285	9.203	305.845	282.838	275.305	262.714	−38.7841
500	124.071	20.616	331.226	289.994	286.718	260.186	−31.9550
600	140.096	33.858	355.325	298.895	299.960	258.218	−27.4415
700	152.712	48.522	377.904	308.588	314.624	256.675	−24.2396
800	162.945	64.321	398.986	318.585	330.424	255.486	−21.8512
900	171.445	81.053	418.684	328.625	347.156	254.610	−20.0009
1000	178.617	98.566	437.129	338.563	364.669	253.992	−18.5250
1100	184.726	116.741	454.447	348.319	382.844	253.600	−17.3199
1200	189.963	135.482	470.751	357.849	401.585	253.391	−16.3168
1300	194.473	154.710	486.139	367.131	420.812	253.325	−15.4688
1400	198.372	174.357	500.697	376.156	440.459	253.362	−14.7414
1500	201.756	194.367	514.501	384.923	460.470	253.487	−14.1114
1600	204.703	214.693	527.618	393.435	480.796	253.664	−13.5595
1700	207.279	235.295	540.108	401.698	501.398	253.875	−13.0722
1800	209.539	256.139	552.021	409.721	522.241	254.103	−12.6386
1900	211.530	277.194	563.404	417.513	543.297	254.335	−12.2504
2000	213.289	298.437	574.300	425.082	564.539	254.557	−11.9007
2100	214.849	319.845	584.745	432.438	585.948	254.761	−11.5840
2200	216.238	341.401	594.772	439.590	607.504	254.938	−11.2958
2300	217.479	363.088	604.412	446.548	629.191	255.083	−11.0326
2400	218.590	384.893	613.692	453.320	650.995	255.187	−10.7912
2500	219.590	406.803	622.636	459.915	672.905	255.247	−10.5689
2600	220.491	428.807	631.266	466.340	694.910	255.260	−10.3638
2700	221.305	450.898	639.603	472.604	717.000	255.220	−10.1740
2800	222.044	473.065	647.665	478.713	739.168	255.128	−9.9977
2900	222.716	495.305	655.468	484.674	761.407	254.977	−9.8337
3000	223.328	517.607	663.029	490.494	783.709	254.765	−9.6804
3100	223.887	539.968	670.362	496.178	806.070	254.494	−9.5375
3200	224.400	562.383	677.478	501.733	828.485	254.157	−9.4036
3300	224.870	584.846	684.390	507.164	850.949	253.755	−9.2780
3400	225.303	607.355	691.110	512.476	873.457	253.288	−9.1600
3500	225.702	629.906	697.647	517.673	896.008	252.750	−9.0490
3600	226.071	652.495	704.010	522.762	918.597	252.142	−8.9442
3700	226.412	675.120	710.209	527.744	941.222	251.463	−8.8455
3800	226.728	697.777	716.251	532.626	963.879	250.710	−8.7522
3900	227.022	720.464	722.144	537.410	986.567	249.885	−8.6640
4000	227.295	743.180	727.896	542.101	1009.283	248.982	−8.5804
4100	227.550	765.923	733.511	546.701	1032.025	248.006	−8.5014
4200	227.787	788.690	738.998	551.214	1054.792	246.952	−8.4263
4300	228.009	811.479	744.360	555.644	1077.581	245.820	−8.3549
4400	228.217	834.291	749.604	559.993	1100.393	244.610	−8.2872
4500	228.412	857.122	754.735	564.264	1123.224	243.322	−8.2229
4600	228.594	879.972	759.758	568.459	1146.075	241.954	−8.1617
4700	228.766	902.841	764.676	572.582	1168.943	240.509	−8.1034
4800	228.928	925.726	769.494	576.634	1191.829	238.985	−8.0479
4900	229.080	948.626	774.215	580.618	1214.728	237.380	−7.9950
5000	229.223	971.541	778.845	584.537	1237.644	235.697	−7.9445

TABLE 5. Thermodynamic values for cyclopentadiene and cyclopentadiene derivatives and radicals — Continued

1-Hydroxy-2,4-Cyclopentadiene 1-yl Radical C_5H_4OH

T K	C_p° J/mol·K	$H_T^\circ - H_{298}^\circ$ KJ/mol	S_T° J/mol·K	$-(G_T^\circ - H_{298}^\circ)/T$ J/mol·K	H_T° KJ/mol	$\Delta_f H_T^\circ$ KJ/mol	$\log_{10} K_p$
0	-------	−16.484	-------	-------	70.961	101.739	-------
100	39.524	−13.026	243.743	374.002	74.420	95.942	−55.3072
200	65.114	−7.891	278.320	317.776	79.554	91.252	−30.7437
298.15	95.621	0.000	310.016	310.016	87.446	87.446	−23.0466
300	96.178	0.177	310.609	310.018	87.623	87.384	−22.9521
400	123.447	11.209	342.155	314.134	98.654	84.550	−19.2079
500	144.602	24.660	372.083	322.763	112.105	82.530	−17.0257
600	160.699	39.960	399.934	333.334	127.406	81.041	−15.6013
700	173.251	56.682	425.686	344.712	144.127	79.928	−14.6003
800	183.371	74.530	449.504	356.341	161.975	79.119	−13.8587
900	191.754	93.298	471.600	367.935	180.744	78.576	−13.2868
1000	198.829	112.837	492.180	379.343	200.283	78.253	−12.8316
1100	204.866	133.030	511.421	390.485	220.475	78.123	−12.4605
1200	210.058	153.782	529.475	401.323	241.228	78.150	−12.1512
1300	214.544	175.018	546.470	411.841	262.464	78.301	−11.8896
1400	218.437	196.671	562.515	422.035	284.117	78.537	−11.6643
1500	221.827	218.689	577.704	431.912	306.134	78.846	−11.4689
1600	224.789	241.022	592.117	441.478	328.468	79.196	−11.2969
1700	227.386	263.634	605.824	450.745	351.080	79.569	−11.1445
1800	229.672	286.490	618.887	459.727	373.935	79.950	−11.0083
1900	231.690	309.560	631.360	468.434	397.005	80.326	−10.8860
2000	233.477	332.820	643.290	476.881	420.265	80.682	−10.7753
2100	235.066	356.248	654.721	485.079	443.694	81.011	−10.6748
2200	236.483	379.827	665.689	493.041	467.272	81.303	−10.5830
2300	237.751	403.540	676.230	500.778	490.985	81.556	−10.4989
2400	238.889	427.373	686.374	508.301	514.819	81.760	−10.4217
2500	239.913	451.314	696.146	515.621	538.759	81.909	−10.3504
2600	240.837	475.352	705.574	522.746	562.797	82.003	−10.2846
2700	241.674	499.478	714.679	529.687	586.924	82.036	−10.2236
2800	242.434	523.684	723.482	536.452	611.130	82.009	−10.1670
2900	243.126	547.963	732.002	543.049	635.408	81.914	−10.1142
3000	243.757	572.308	740.255	549.486	659.753	81.750	−10.0649
3100	244.334	596.712	748.257	555.770	684.158	81.519	−10.0192
3200	244.863	621.172	756.023	561.906	708.618	81.213	−9.9763
3300	245.349	645.683	763.565	567.904	733.129	80.835	−9.9362
3400	245.796	670.241	770.897	573.767	757.687	80.385	−9.8987
3500	246.209	694.841	778.027	579.501	782.287	79.856	−9.8636
3600	246.590	719.482	784.969	585.113	806.927	79.249	−9.8305
3700	246.943	744.158	791.730	590.606	831.604	78.564	−9.7996
3800	247.270	768.869	798.320	595.986	856.315	77.800	−9.7705
3900	247.575	793.612	804.747	601.257	881.057	76.956	−9.7433
4000	247.858	818.383	811.018	606.423	905.829	76.027	−9.7176
4100	248.122	843.183	817.142	611.488	930.629	75.021	−9.6937
4200	248.368	868.007	823.124	616.456	955.453	73.929	−9.6710
4300	248.599	892.857	828.971	621.330	980.302	72.755	−9.6498
4400	248.814	917.727	834.689	626.114	1005.172	71.494	−9.6298
4500	249.016	942.619	840.283	630.812	1030.064	70.151	−9.6112
4600	249.206	967.529	845.758	635.425	1054.975	68.721	−9.5937
4700	249.384	992.459	851.119	639.958	1079.904	67.209	−9.5773
4800	249.552	1017.405	856.371	644.412	1104.851	65.612	−9.5618
4900	249.710	1042.370	861.519	648.791	1129.815	63.932	−9.5475
5000	249.859	1067.346	866.565	653.096	1154.791	62.164	−9.5340

TABLE 5. Thermodynamic values for cyclopentadiene and cyclopentadiene derivatives and radicals – Continued

1-Oxyl-1,3-Cyclopentadiene Radical C_5H_5O·

T K	C_p° J/mol·K	$H_T^\circ - H_{298}^\circ$ KJ/mol	S_T° J/mol·K	$-(G_T^\circ - H_{298}^\circ)/T$ J/mol·K	H_T° KJ/mol	$\Delta_f H_T^\circ$ KJ/mol	$\log_{10} K_p$
0	-------	−15.915	------	-------	43.885	74.663	-------
100	40.066	−12.398	244.231	368.206	47.402	68.925	−41.1698
200	61.548	−7.419	277.893	314.988	52.381	64.078	−23.6693
298.15	90.023	0.000	307.695	307.695	59.800	59.800	−18.3246
300	90.567	0.167	308.253	307.697	59.967	59.728	−18.2600
400	118.121	10.638	338.185	311.591	70.438	56.333	−15.7307
500	140.576	23.617	367.054	319.820	83.417	53.842	−14.2913
600	158.201	38.591	394.307	329.988	98.391	52.027	−13.3693
700	172.185	55.136	419.783	341.017	114.936	50.737	−12.7304
800	183.527	72.941	443.541	352.365	132.741	49.884	−12.2614
900	192.901	91.776	465.716	363.742	151.576	49.409	−11.9013
1000	200.755	111.470	486.458	374.988	171.270	49.241	−11.6151
1100	207.394	131.887	505.912	386.015	191.687	49.334	−11.3812
1200	213.043	152.916	524.207	396.776	212.716	49.638	−11.1854
1300	217.875	174.468	541.455	407.248	234.268	50.106	−11.0187
1400	222.029	196.469	557.757	417.422	256.269	50.688	−10.8738
1500	225.614	218.855	573.201	427.297	278.655	51.368	−10.7472
1600	228.723	241.576	587.863	436.878	301.376	52.104	−10.6347
1700	231.430	264.586	601.812	446.173	324.386	52.876	−10.5339
1800	233.797	287.850	615.109	455.192	347.650	53.665	−10.4429
1900	235.875	311.336	627.806	463.945	371.136	54.456	−10.3604
2000	237.707	335.017	639.952	472.444	394.817	55.233	−10.2851
2100	239.328	358.870	651.590	480.699	418.670	55.987	−10.2160
2200	240.769	382.876	662.757	488.723	442.676	56.707	−10.1522
2300	242.053	407.018	673.489	496.524	466.818	57.389	−10.0933
2400	243.201	431.282	683.815	504.114	491.082	58.023	−10.0387
2500	244.233	455.655	693.765	511.503	515.455	58.605	−9.9879
2600	245.161	480.125	703.362	518.698	539.925	59.131	−9.9406
2700	246.000	504.684	712.630	525.710	564.484	59.597	−9.8965
2800	246.760	529.323	721.591	532.547	589.123	60.003	−9.8552
2900	247.450	554.034	730.262	539.216	613.834	60.340	−9.8165
3000	248.079	578.811	738.662	545.725	638.611	60.607	−9.7800
3100	248.653	603.648	746.805	552.080	663.448	60.808	−9.7460
3200	249.179	628.540	754.709	558.290	688.340	60.935	−9.7139
3300	249.660	653.482	762.384	564.359	713.282	60.988	−9.6838
3400	250.104	678.471	769.844	570.293	738.271	60.969	−9.6554
3500	250.512	703.502	777.099	576.099	763.302	60.871	−9.6287
3600	250.889	728.572	784.162	581.781	788.372	60.693	−9.6034
3700	251.238	753.678	791.041	587.344	813.478	60.439	−9.5797
3800	251.561	778.819	797.745	592.793	838.619	60.104	−9.5573
3900	251.862	803.991	804.284	598.132	863.791	59.689	−9.5362
4000	252.141	829.191	810.664	603.366	888.991	59.189	−9.5163
4100	252.400	854.418	816.893	608.499	914.218	58.610	−9.4976
4200	252.643	879.669	822.978	613.533	939.469	57.945	−9.4799
4300	252.869	904.946	828.926	618.474	964.746	57.198	−9.4631
4400	253.081	930.242	834.741	623.323	990.042	56.364	−9.4475
4500	253.280	955.562	840.431	628.084	1015.362	55.449	−9.4328
4600	253.466	980.899	846.000	632.761	1040.699	54.445	−9.4190
4700	253.641	1006.254	851.453	637.357	1066.054	53.359	−9.4059
4800	253.806	1031.627	856.795	641.873	1091.427	52.188	−9.3936
4900	253.961	1057.016	862.030	646.312	1116.816	50.932	−9.3823
5000	254.107	1082.419	867.162	650.678	1142.219	49.591	−9.3715

TABLE 5. Thermodynamic values for cyclopentadiene and cyclopentadiene derivatives and radicals – Continued

1-Oxyl-1,4-Cyclopentadiene Radical C_5H_5O·

T K	C_p° J/mol·K	$H_T^\circ - H_{298}^\circ$ KJ/mol	S_T° J/mol·K	$-(G_T^\circ - H_{298}^\circ)/T$ J/mol·K	H_T° KJ/mol	$\Delta_f H_T^\circ$ KJ/mol	$\log_{10} K_p$
0	-------	−15.905	-------	-------	87.395	118.173	-------
100	39.685	−12.420	244.293	368.495	90.880	112.403	−63.8762
200	61.681	−7.449	277.886	315.131	95.851	107.548	−35.0226
298.15	90.479	0.000	307.805	307.805	103.300	103.300	−25.9396
300	91.028	0.168	308.367	307.807	103.468	103.229	−25.8281
400	118.719	10.693	338.454	311.722	113.993	99.888	−21.4042
500	141.172	23.733	367.458	319.993	127.033	97.458	−18.8266
600	158.743	38.764	394.815	330.208	142.064	95.700	−17.1448
700	172.662	55.360	420.370	341.284	158.660	94.461	−15.9623
800	183.943	73.209	444.187	352.676	176.509	93.652	−15.0853
900	193.264	92.084	466.408	364.093	195.384	93.216	−14.4076
1000	201.073	111.812	487.186	375.374	215.112	93.082	−13.8670
1100	207.673	132.258	506.669	386.434	235.558	93.205	−13.4249
1200	213.290	153.314	524.986	397.225	256.614	93.536	−13.0554
1300	218.095	174.889	542.253	407.723	278.189	94.026	−12.7417
1400	222.224	196.910	558.570	417.920	300.210	94.630	−12.4707
1500	225.790	219.315	574.027	427.817	322.615	95.327	−12.2349
1600	228.881	242.052	588.700	437.417	345.352	96.080	−12.0266
1700	231.573	265.078	602.658	446.730	368.378	96.868	−11.8413
1800	233.927	288.355	615.962	455.765	391.655	97.670	−11.6753
1900	235.993	311.853	628.667	464.533	415.153	98.474	−11.5256
2000	237.815	335.546	640.819	473.046	438.846	99.262	−11.3897
2100	239.428	359.410	652.462	481.314	462.710	100.027	−11.2658
2200	240.860	383.425	663.633	489.349	486.725	100.756	−11.1523
2300	242.138	407.577	674.369	497.162	510.877	101.447	−11.0479
2400	243.280	431.848	684.699	504.762	535.148	102.089	−10.9516
2500	244.306	456.229	694.651	512.159	559.529	102.679	−10.8624
2600	245.229	480.706	704.251	519.364	584.006	103.212	−10.7797
2700	246.063	505.271	713.522	526.385	608.571	103.684	−10.7028
2800	246.819	529.917	722.485	533.229	633.217	104.096	−10.6311
2900	247.505	554.633	731.158	539.905	657.933	104.439	−10.5640
3000	248.131	579.415	739.560	546.421	682.715	104.711	−10.5010
3100	248.702	604.257	747.705	552.783	707.557	104.918	−10.4423
3200	249.225	629.154	755.609	558.998	732.454	105.050	−10.3869
3300	249.704	654.101	763.286	565.074	757.401	105.107	−10.3350
3400	250.145	679.094	770.747	571.014	782.394	105.092	−10.2861
3500	250.551	704.129	778.004	576.824	807.429	104.997	−10.2400
3600	250.926	729.202	785.068	582.512	832.502	104.824	−10.1964
3700	251.273	754.313	791.948	588.080	857.613	104.573	−10.1554
3800	251.594	779.457	798.653	593.533	882.757	104.241	−10.1166
3900	251.893	804.630	805.192	598.876	907.930	103.829	−10.0800
4000	252.170	829.834	811.573	604.115	933.134	103.332	−10.0452
4100	252.429	855.065	817.803	609.251	958.365	102.757	−10.0125
4200	252.670	880.320	823.889	614.289	983.620	102.096	−9.9814
4300	252.896	905.598	829.837	619.233	1008.898	101.350	−9.9519
4400	253.106	930.898	835.653	624.085	1034.198	100.519	−9.9240
4500	253.304	956.219	841.344	628.851	1059.519	99.606	−9.8977
4600	253.489	981.558	846.913	633.531	1084.858	98.605	−9.8727
4700	253.663	1006.916	852.367	638.129	1110.216	97.521	−9.8490
4800	253.827	1032.291	857.709	642.648	1135.591	96.352	−9.8265
4900	253.981	1057.682	862.944	647.091	1160.982	95.099	−9.8053
5000	254.126	1083.086	868.077	651.460	1186.386	93.759	−9.7851

TABLE 6. Thermodynamic properties of molecular and radical isomers

Compound	Zero point energy cm^{-1}	C_p J/mol K 1000 K	C_p J/mol K 3000 K	S_T J/mol K 1000 K	S_T J/mol K 3000 K	$\Delta_f H_T^\circ$ kJ/mol 1000 K	$\Delta_f H_T^\circ$ kJ/mol 3000 K
2	20416	210.7	266.6	489.3	757.8	−9.0	−0.5
3	20339	212.7	266.9	492.9	762.6	−39.0	−28.7
4	20317	212.8	267.0	493.4	763.0	−41.8	−31.4
6	17439	198.9	243.8	492.2	740.2	78.3	81.8
8	17469	200.8	248.1	486.5	738.7	49.2	60.6
9	17400	201.1	248.1	487.2	739.6	93.1	104.7

6. Acknowledgement

This work was supported by the United States - Israel Bi-National Science Foundation The German - Israel Foundation for Scientific Research and Development and by the Technion fund for the promotion of Research.

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