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Ideal gas thermodynamic properties of oxygen heterocyclic compounds
Part 1. Three-membered, four-membered and five-membered rings

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Abstract

The available structural parameters, fundamental frequencies and enthalpies of formation for oxirane, oxirene, dioxirane, oxetane, 1,2-dioxetane, tetrahydrofuran, 2,3-dihydrofuran, 2,5-dihydrofuran, furan, 1,2-dioxolane, 1,3-dioxolane, 1,2,3-trioxolane and 1,2,4-trioxolane were critically evaluated and recommended values were selected. Molecular constants and enthalpies of formation for some of the molecules were estimated, as experimental values for these compounds are not available. Using the rigid-rotor harmonic-oscillator approximation, this information was used to calculate the chemical thermodynamic functions $C_p^\ominus$, $S^\ominus$, $-(G^\ominus - H_0^\ominus)/T$, $H^\ominus - H_0^\ominus$, and the properties of formation, $\Delta_f H^\ominus$, $\Delta_f G^\ominus$, $\log K_f^\ominus$, to 1500 K in the ideal gas state at a pressure of 1 bar. The contributions to the thermodynamic properties of compounds having inversion motion (oxetane, 2,3- and 2,5-dihydrofuran) or pseudo-rotation (tetrahydrofuran and 1,3-dioxolane) have been computed by employing a partition function formed by the summation of the inversional or pseudo-rotational energy levels. These energy levels have been calculated by solving the wave equation using appropriate potential functions. The calculated values of the thermodynamic functions are compared with those reported in other works. Comparison with experimental data, where such are available, is also presented. The thermodynamic properties for seven of the compounds are reported for the first time.

INTRODUCTION

As an extension of our studies on the thermodynamic properties of cyclic compounds [1–3], we proceed to calculation of the thermodynamic properties of heterocyclic compounds. This report involves the calculation of the ideal gas thermodynamic properties of 13 monocyclic three-, four- and five-membered oxygen compounds. (The thermodynamic properties of 17 six-, seven- and eight-membered oxygen heterocyclic compounds will be presented in Part 2 of this series.) For half of these molecules, the thermodynamic properties have been reported previously. Recently, more complete and reliable information has become available on the structure and vibrational assignments and this information permits us to make more precise calculations of the thermodynamic functions of some molecules and to calculate the thermodynamic properties of others for the first time.

The available data on vibrational frequencies, structural parameters and enthalpies of formation have been critically examined and the most reliable values have been selected. The molecular constants and enthalpies of formation for some compounds were estimated in the present work, as the experimental values for these molecules are not available, are incomplete, or unreliable. The selected molecular constants are given in Tables 1, 2.

Based on the selected values of the molecular constants, the ideal gas thermodynamic functions (heat capacity $C_p^\ominus$, entropy $S^\ominus$, Gibbs energy $-(G^\ominus - H_0^\ominus)/T$, and enthalpy $(H^\ominus - H_0^\ominus)$ were calculated by the standard statistical mechanical method using a rigid-rotor harmonic-oscillator approximation. The enthalpy of formation $\Delta_f H^\ominus(298.15\text{ K})$ if any, was taken from the data of Pedley et al. [4]; otherwise its value was estimated in the present work using the incremental method, a variant of the group additivity approach to calculations of $\Delta_f H^\ominus$. The accepted enthalpy of formation, $\Delta_f H^\ominus(298.15\text{ K})$, and the calculated thermodynamic functions, have been used to calculate the enthalpies of formation $\Delta_f H^\ominus(T)$, the Gibbs energies of formation $\Delta_f G^\ominus(T)$, and the logarithm of the equilibrium constant of formation $\log K_f^\ominus$, by the usual thermodynamic formulae. (Subscript f denotes formation by the reaction $x\text{C(c, graphite)} + y\text{H}_2\text{(g)} + z\text{O}_2\text{(g)} = \text{C}_x\text{H}_{2y}\text{O}_{2z}\text{(g)}$). The procedures for calculation of the thermodynamic properties are similar to those used in ref. 5. The fundamental physical constants and thermodynamic properties of the elements in their reference states used in the calculations were also taken from ref. 5. The chemical thermodynamic property values for selected temperatures up to 1500 K for a pressure of 1 bar are given in Tables 3–15.

The inversion motion contributions to the thermodynamic properties for oxetane, 2,3- and 2,5-dihydrofuran were calculated by use of the potential function of type $V(x) = ax^4 + bx^2$. 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 summation over the energy levels calculated from the potential functions.

The pseudo-rotational contributions to the thermodynamic properties of tetrahydrofuran and 1,3-dioxolane were obtained by direct summation over the energy levels, calculated with the potential function of type $V(\psi) = 0.5[V_2(1 - \cos 2\psi) + V_4(1 - \cos 4\psi)]$.

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 $S_{\text{mix}}^\ominus = R \ln 2$ to $S^\ominus$ and $-(G^\ominus - H_0^\ominus)/T$, which is equivalent to assuming the effective symmetry number $\sigma_{\text{eff}} = \sigma/n$, where σ is the symme-

TABLE 1

Symmetry groups and products of three principal moments of inertia for three-, four- and five-membered ring oxygen compounds in their ground electronic state [a]

Molecule		Point group	Symmetry number, σ	Number of optical isomers, n	$I_AI_BI_C \times 10^{117}$ ($g^3 \times cm^6$)
C_2H_4O	Oxirane	C_{2v}	2	1	74.4
C_2H_2O	Oxirene	C_{2v}	2	1	45
CH_2O_2	Dioxirane	C_{2v}	2	1	55.1
C_3H_6O	Oxetane	C_{2v}	2	1	625
$C_2H_4O_2$	1,2-Dioxetane	C_{2v}	2	1	515
C_4H_8O	Tetrahydrofuran	C_2	2	1 [b]	2979
C_4H_6O	2,3-Dihydrofuran	C_1	1	1 [c]	2235
	2,5-Dihydrofuran	C_{2v}	2	1	2237
C_4H_4O	Furan	C_{2v}	2	1	1449
$C_3H_6O_2$	1,2-Dioxolane	C_2	2	2	2554
	1,3-Dioxolane	C_2	2	1 [b]	2334
$C_2H_4O_3$	1,2,3-Trioxolane	C_s	1	1	2174
	1,2,4-Trioxolane	C_2	2	2	1932

[a] Ground state statistical weight is equal to 1.

[b] Although tetrahydrofuran and 1,3-dioxolane have the non-planar structure of C_2 symmetry for which $\sigma = 2$ and $n = 2$, the number of optical isomers $n = 1$ is given in the Table due to the fact that the molecules are undergoing restricted pseudo-rotation through their planar configuration (C_{2v} symmetry, $\sigma = 2$, $n = 1$).

[c] Although 2,3-dihydrofuran has the non-planar conformation of C_1 symmetry for which $\sigma = 1$ and $n = 2$, the number of optical isomers $n = 1$ is given in the Table due to the fact that the molecule is undergoing inversion through its planar form (C_s symmetry, $\sigma = 1$, $n = 1$).

try number and n ($= 2$) is the number of optical isomers. For this reason, Table 1 shows the number of optical isomers together with other molecular constants.

Uncertainties in the calculated thermodynamic properties (Table 16) were obtained by taking into account the inaccuracy of the selected molecular structural and spectroscopic data, and the inaccuracy due to deviation from the rigid-rotor harmonic-oscillator model. The procedure for the approximate evaluation of these uncertainties was described previously [5]. Uncertainties in the adopted enthalpies of formation (Table 16) were taken from the data of Pedley et al. [4] or were estimated in the present work.

Comparisons of the calculated and experimental entropy and heat capacity values are given in Tables 17 and 18, respectively.

OXIRANE

The molecular structure of oxirane has been investigated by electron diffraction [6], microwave spectroscopy [7–9] and ab initio calculations [10–12]. From microwave measurements of rotational spectra of ten isotopic species of oxirane, Hirose [9] has determined the rotational constants and r_0, r_s, and r_m structures. These structural parameters are in good agreement with those obtained from previous microwave studies and calculated by the ab initio method. The product of the principal moments of inertia given in Table 1 was calculated using the rotational constants of Hirose [9].

The IR and Raman spectra of oxirane have both been the subject of a number of investigations [13–24]; and there have been a number of normal coordinate analysis [17,20,23,25–28] and semiempirical and ab initio calculations [11,29–33]. Until now, the vibrational assignments published by Cant and Armstead [17] have been considered the most reliable. However, different authors have proposed considerably varying values for $\nu_7(A_2)$, $\nu_8(A_2)$, and $\nu_{12}(B_1)$, for which no direct spectral evidence has been obtained. The fundamentals presented in Table 2 are those obtained by Cant and Armstead [17] (except for ν_7, ν_8 and ν_{12}). The values of ν_7 and ν_8 were estimated according to normal coordinate analysis [20] and ab initio calculations [11,31,32]. For ν_{12}, the value obtained from high-resolution IR spectrum [24] was accepted.

The enthalpy of formation for oxirane (Table 3) was taken from the data of Pedley et al. [4].

The ideal gas thermodynamic properties for oxirane are given in Table 3. The calculated value of $S^{\ominus}(298.15\ \mathrm{K})$ is in good agreement with the calorimetric values [34,35] and with other entropy values calculated by the statistical method [35–42] (Table 17). Likewise our heat capacity values are in good agreement with the experimental values [43] and with the reported statistical values [35,37,39–42] (Table 18).

OXIRENE

There are no experimental data on the rotational constants or the molecular structure of oxirene. The geometrical structure of oxirene was calculated by semiempirical [44,45] and ab initio [46–51] methods. The product of the principal moments of inertia (Table 1) was calculated using the estimated structural parameters: $r(\mathrm{C{-}O}) = 1.49 \pm 0.05$ Å; $r(\mathrm{C{-}H}) = 1.07 \pm 0.02$ Å; $r(\mathrm{C{=}C}) = 1.27 \pm 0.05$ Å; and $\angle(\mathrm{H{-}C{=}C}) = 162 \pm 5°$. These values are close to those obtained by Tanaka and Yoshimine [48] and Novoa et al. [51] from ab initio calculations. It should be noted that Tanaka and Yoshimine also calculated the rotational constants for ketene, which is isomeric with oxirene, and that these rotational constants were found to be in good agreement with those observed experimentally.

The information on the vibrational spectrum of oxirene is known from ab initio calculations [49,50] only. Based on these data, the vibrational frequencies of oxirene were estimated in the present work (Table 2). In addition to oxirene, the vibrational frequencies of ketene and thiirene were calculated in the above ab initio calculations. In the present work, the ab initio vibra-

TABLE 2

Vibrational frequencies for the reference molecules

Molecule		Frequencies (cm^{-1})
C_2H_4O	Oxirane	A_1: 3018, 1498, 1270, 1148, 877 A_2: 3073, 1150, 1025 B_1: 3006, 1472, 1151, 897 B_2: 3065, 1142, 821
C_2H_2O	Oxirene	A_1: 3150, 1750, 1000, 750 A_2: 650 B_1: 550 B_2: 3150, 950, 450
CH_2O_2	Dioxirane	A_1: 3000, 1450, 1250, 750 A_2: 950 B_1: 3050, 1050 B_2: 1200, 850
C_3H_6O	Oxetane	A_1: 2979, 2894, 1505, 1452, 1343, 1033, 909, 785 A_2: 2965, 1230, 1096, 842 B_1: 2887, 1480, 1289, 1230, 1008, 937 B_2: 3006, 2938, 1183, 1137, 703, – [a]
$C_2H_4O_2$	1,2-Dioxetane	A_1: 2903, 1517, 1203, 1072, 846, 840 A_2: 2996, 1289, 1148, 348 B_1: 2902, 1493, 1327, 998, 760 B_2: 2986, 1246, 983
C_4H_8O	Tetrahydrofuran	2976, 2964, 2938, 2924, 2865, 2861, 2847, 1487, 1481, 1458, 1444, 1366, 1332, 1288, 1240, 1238, 1185, 1177, 1140, 1108, 1076, 1030, 980, 954, 912, 909, 870, 821, 654, 581, 286, – [a]
C_4H_6O	2,3-Dihydrofuran	A: 3101, 3096, 2923, 2911, 2840, 2829, 1591, 1551, 1521, 1334, 1253, 1220, 1190, 1168, 1097, 1060, 1043, 1004, 973, 901, 845, 834, 820, 694, 603, 384, – [a]
	2,5-Dihydrofuran	A_1: 3096, 2863, 1618, 1482, 1363, 935, 920, 801, 744 A_2: 2888, 1167, 1080, 1011, 398 B_1: 3096, 2863, 1482, 1347, 1097, 982, 900, 744 B_2: 2888, 1200, 1036, 662, – [a]
C_4H_4O	Furan	A_1: 3167, 3140, 1491, 1384, 1140, 1066, 995, 871 A_2: 863, 728, 613 B_1: 3161, 3129, 1556, 1267, 1180, 1040, 873 B_2: 838, 745, 603
$C_3H_6O_2$	1,2-Dioxolane	A: 2974, 2892, 2884, 1422, 1328, 1295, 1187, 1150, 1099, 931, 908, 780, 604, 333 B: 2982, 2971, 2890, 1406, 1306, 1208, 1188, 1070, 1053, 966, 809, 635, 254
	1,3-Dioxolane	A_1: 2889, 2857, 1509, 1480, 1361, 1087, 1030, 939, 658 A_2: 2972, 1246, 1210, 1009, 260 B_1: 2889, 1480, 1397, 1327, 1158, 961, 680 B_2: 2998, 2964, 1286, 921, 723, – [a]
$C_2H_4O_3$	1,2,3-Trioxolane	A': 2969, 2892, 1339, 1318, 1155, 1042, 941, 825, 750, 501, 171 A'': 2977, 2888, 1411, 1310, 1170, 1062, 1004, 795, 543, 97
	1,2,4-Trioxolane	A: 2973, 2894, 1482, 1387, 1196, 1129, 1078, 952, 808, 737, 352 B: 2967, 2900, 1483, 1346, 1202, 1143, 1029, 926, 698, 193

[a] The ring-puckering frequency is not given in the table, because the contribution derived for the inversion motion (oxetane, 2,3- and 2,5-dihydrofuran) or for the restricted pseudo-rotation (tetrahydrofuran and 1,3-dioxolane) has been obtained by direct summation over the energy levels.

tional frequencies for ketene and thiirene were scaled by fitting to the observed spectra and the scale factors obtained for these molecules were chosen for the corresponding vibrational modes of oxirene. The uncertainties of the adopted fundamentals are estimated to be 50–150 cm^{-1}.

There are no experimental data on the enthalpy of formation of oxirene, but its value was calculated by semiempirical methods [44,45]. In Table 4, we accepted the MINDO/3 value [44] which was corrected by comparison of the experimental and MINDO/3 values of $\Delta_f H^{\ominus}(298.15\ K)$ for

TABLE 3

Ideal gas thermodynamic properties for oxirane

T (K)	$C_p^\ominus$ (J K^{-1} mol^{-1})	$S^\ominus$ (J K^{-1} mol^{-1})	$-(G^\ominus - H_0^\ominus)/T$ (J K^{-1} mol^{-1})	$H^\ominus - H_0^\ominus$ (kJ mol^{-1})	$\Delta_f H^\ominus$ (kJ mol^{-1})	$\Delta_f G^\ominus$ (kJ mol^{-1})	log $K_f^\ominus$
0	0.000	0.000	0.000	0.000	−39.988	−39.988	∞
100	33.275	202.800	169.541	3.326	−44.234	−35.514	18.550
200	36.194	226.354	192.660	6.739	−48.319	−25.244	6.593
298.15	47.032	242.607	206.486	10.770	−52.600	−13.004	2.278
300	47.287	242.899	206.709	10.857	−52.680	−12.761	2.222
400	61.661	258.464	217.709	16.302	−56.607	1.158	−0.151
500	74.895	273.683	227.389	23.147	−59.801	15.981	−1.670
600	85.970	288.349	236.336	31.208	−62.296	31.386	−2.732
700	95.137	302.312	244.773	40.277	−64.228	47.158	−3.519
800	102.813	315.531	252.799	50.186	−65.699	63.176	−4.125
900	109.321	328.027	260.470	60.801	−66.792	79.354	−4.606
1000	114.886	339.840	267.822	72.019	−67.575	95.638	−4.996
1100	119.667	351.020	274.882	83.752	−68.096	111.986	−5.318
1200	123.791	361.614	281.672	95.930	−68.395	128.373	−5.588
1300	127.357	371.666	288.211	108.492	−68.514	144.773	−5.817
1400	130.449	381.220	294.516	121.386	−68.466	161.180	−6.014
1500	133.138	390.314	300.602	134.568	−68.287	177.578	−6.184

TABLE 4

Ideal gas thermodynamic properties for oxirene

T (K)	$C_p^\ominus$ (J K^{-1} mol^{-1})	$S^\ominus$ (J K^{-1} mol^{-1})	$-(G^\ominus - H_0^\ominus)/T$ (J K^{-1} mol^{-1})	$H^\ominus - H_0^\ominus$ (kJ mol^{-1})	$\Delta_f H^\ominus$ (kJ mol^{-1})	$\Delta_f G^\ominus$ (kJ mol^{-1})	log $K_f^\ominus$
0	0.000	0.000	0.000	0.000	172.990	172.990	∞
100	34.073	200.257	166.884	3.337	171.754	170.656	−89.140
200	43.133	226.220	190.544	7.135	170.748	169.968	−44.390
298.15	54.212	245.557	205.560	11.925	170.000	169.754	−29.740
300	54.401	245.893	205.808	12.025	169.987	169.751	−29.556
400	63.250	262.819	217.993	17.930	169.425	169.763	−22.168
500	69.774	277.670	228.474	24.598	168.977	169.899	−17.749
600	74.746	290.849	237.793	31.834	168.585	170.123	−14.810
700	78.733	302.680	246.232	39.514	168.202	170.408	−12.716
800	82.066	313.418	253.969	47.559	167.821	170.750	−11.149
900	84.922	323.253	261.128	55.912	167.439	171.138	−9.932
1000	87.401	332.331	267.801	64.531	167.062	171.570	−8.962
1100	89.563	340.765	274.055	73.381	166.696	172.039	−8.169
1200	91.454	348.641	279.946	82.434	166.349	172.541	−7.510
1300	93.110	356.028	285.517	91.664	166.021	173.068	−6.954
1400	94.561	362.983	290.804	101.049	165.723	173.622	−6.478
1500	95.835	369.551	295.837	110.571	165.450	174.196	−6.066

TABLE 5

Ideal gas thermodynamic properties for dioxirane

T (K)	$C_p^\ominus$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	$S^\ominus$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	$-(G^\ominus - H_0^\ominus)/T$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	$H^\ominus - H_0^\ominus$ ($\mathrm{kJ\,mol^{-1}}$)	$\Delta_f H^\ominus$ ($\mathrm{kJ\,mol^{-1}}$)	$\Delta_f G^\ominus$ ($\mathrm{kJ\,mol^{-1}}$)	$\log K_f^\ominus$
0	0.000	0.000	0.000	0.000	42.574	42.574	∞
100	33.286	202.099	168.839	3.326	39.939	47.226	−24.668
200	35.944	225.657	191.964	6.739	37.419	55.483	−14.490
298.15	43.877	241.368	205.726	10.627	35.000	64.874	−11.366
300	44.052	241.640	205.947	10.708	34.956	65.058	−11.327
400	53.535	255.623	216.645	15.591	32.926	75.413	−9.848
500	61.823	268.489	225.744	21.373	31.393	86.221	−9.007
600	68.525	280.376	233.872	27.902	30.275	97.299	−8.471
700	73.926	291.359	241.310	35.034	29.465	108.537	−8.099
800	78.349	301.529	248.210	42.655	28.893	119.874	−7.827
900	82.030	310.976	254.665	50.680	28.508	131.272	−7.619
1000	85.130	319.783	260.742	59.042	28.273	142.705	−7.454
1100	87.763	328.024	266.488	67.690	28.160	154.153	−7.320
1200	90.012	335.759	271.941	76.582	28.151	165.610	−7.209
1300	91.943	343.042	277.133	85.682	28.222	177.060	−7.114
1400	93.606	349.918	282.089	94.961	28.368	188.505	−7.033
1500	95.046	356.427	286.830	104.396	28.568	199.937	−6.962

cyclopropene. On the other hand, nearly the same value of $\Delta_f H^\ominus(298.15\ K)$ for oxirene is obtained when one assumes that in passing from cyclopropene to oxirene, the change in $\Delta_f H^\ominus(298.15\ K)$ values will be the same as in passing from cyclopropane to oxirane.

The ideal gas thermodynamic properties for oxirene given in Table 4 are reported for the first time. No experimental data are available for comparison.

DIOXIRANE

In order to determine its molecular structure, Lovas and Suenram [52,53] have investigated the microwave spectra of several isotopic forms of dioxirane. A number of the ab initio calculations [54–61] agree well with those experimental structural data. The product of the principal moments of inertia of dioxirane (Table 1) was calculated using the rotational constants of Suenram and Lovas [53].

The ab initio calculations [58,59] were performed to provide an estimate of the as yet experimentally undetermined vibrational spectrum of dioxirane. Based on the scaled ab initio frequencies obtained in these studies, the vibrational frequencies of dioxirane were selected in Table 2; their uncertainties are estimated to be 50–150 cm^{-1}.

No experimental data on the enthalpy of formation of dioxirane are available. The value of $\Delta_f H^\ominus(0) = 17\ kJ\ mol^{-1}$ was obtained from ab initio calculation [62]. The enthalpy of formation of dioxirane was estimated in the present work (Table 5) by comparison of known values of $\Delta_f H^\ominus(298.15\ K)$ for related compounds [4]. We considered the change in $\Delta_f H^\ominus(298.15\ K)$ values with the exchange of a $-CH_2-$ unit for an $-O-$ group in aliphatic and cyclic compounds, and we believe that in passing from cyclopropane or oxirane to dioxirane, the change in $\Delta_f H^\ominus(298.15\ K)$ values might be expected to be approximately the same as in passing from butane or methoxyethane to dimethyl peroxide or as in passing from hexane or 1-ethoxypropane to diethyl peroxide (the $\Delta_f H^\ominus$ values for the above compounds may be found in ref. 4).

The ideal gas thermodynamic properties for dioxirane are presented in Table 5. These values are reported for the first time and there are no experimental data for comparison.

OXETANE

The molecular structure and evidence for the ring-puckering vibration of oxetane have been obtained from microwave studies of its rotational spectra [63–66], from far-infrared measurements of the corresponding low-frequency absorptions [67–71], from combination bands appearing in the mid-infrared regions [72–74], from Raman spectra [75,76] and from theoretical calculations [10,77–84]. According to these data, there is a double minimum potential function for the ring-puckering vibration; the barrier found experimentally is extremely low — below the puckering zero-point energy — so that the geometry can be regarded as essentially planar. The product of the principal moments of inertia for the planar configuration (C_{2v} symmetry) given in Table 1 was calculated using the rotational constants determined from microwave study [66].

Some assignments of the vibrational spectra of oxetane are known [74,76,85–89]. The fundamental frequencies listed in Table 2 were taken from the reliable interpretation of the vibrational spectra by Kydd et al. [89]. These authors investigated the IR vapour phase and solid phase spectra, and the Raman spectra of the vapours and liquids of oxetane and its deuterated derivatives. Most of the assignments of Kydd et al. [89] were confirmed by ab initio calculation [83].

The thermodynamic-property contributions due to inversion of the oxetane ring were obtained by direct summation over the energy levels calculated with the potential function. Several investigations of the double minimum ring-puckering potential functions of oxetane have been reported [63,64,68, 70,71]. The potential function given by Kydd et al. [70] was used to calculate 60 energy levels (0–13 800 cm^{-1}). The potential function for inversion is $V(x) = (7.16 \times 10^5 x^4 - 6.58 \times 10^3 x^2)\ \text{cm}^{-1}$ (where x (Å) is the ring-puckering coordinate) with a barrier height of 15.1 cm^{-1} and a reduced mass of 95.7 a.u. The partition function for inversion is based on these 60 levels with the first 11 levels being the experimental levels from which the potential function was derived.

The enthalpy of formation for oxetane (Table 6) was taken from the data of Pedley et al. [4].

The ideal gas thermodynamic properties for oxetane are given in Table 6. The calculated values of $C_p^\ominus(T)$ coincide with the calorimetric heat capacities [90] within 0.3 J K^{-1} mol^{-1} (Table 18). This discrepancy is within the uncertainties of the experimental values. Due to the discrepancy in the molecular constants used, the discrepancies with the $C_p^\ominus(T)$ and $S^\ominus(T)$ values calculated by Zürcher and Günthard [85,86] amount to 2–10 J K^{-1} mol^{-1} (Tables 17, 18). Curl et al. [91] have developed a technique for determination of the gas-state free energy functions from the absolute intensity measurements in microwave spectroscopy. The value of $-(G^\ominus - H_0^\ominus)/T$ at 298.15 K obtained by Curl et al. differs by only 0.2 J K^{-1} mol^{-1} from our calculation.

1,2-DIOXETANE

The structural parameters of 1,2-dioxetane have been obtained by ab initio calculations [92–95] only. In the present work, the product of the principal moments of inertia (Table 1) was calculated on the basis of the

TABLE 6

Ideal gas thermodynamic properties for oxetane

T (K)	$C_p^\ominus$ (J K^{-1} mol^{-1})	$S^\ominus$ (J K^{-1} mol^{-1})	$-(G^\ominus - H_0^\ominus)/T$ (J K^{-1} mol^{-1})	$H^\ominus - H_0^\ominus$ (kJ mol^{-1})	$\Delta_f H^\ominus$ (kJ mol^{-1})	$\Delta_f G^\ominus$ (kJ mol^{-1})	$\log K_f^\ominus$
0	0.000	0.000	0.000	0.000	−60.475	−60.475	∞
100	38.535	222.994	185.875	3.711	−67.397	−50.529	26.393
200	44.296	250.828	212.038	7.758	−73.870	−31.191	8.146
298.15	61.541	271.428	228.234	12.878	−80.500	−8.824	1.546
300	61.936	271.811	228.502	12.993	−80.623	−8.382	1.459
400	83.967	292.640	241.925	20.286	−86.644	16.638	−2.173
500	104.237	313.611	254.168	29.721	−91.504	43.040	−4.496
600	121.313	334.173	265.797	41.025	−95.244	70.323	−6.122
700	135.524	353.973	276.990	53.889	−98.068	98.150	−7.324
800	147.442	372.871	287.804	68.054	−100.137	126.331	−8.248
900	157.529	390.835	298.262	83.316	−101.587	154.732	−8.980
1000	166.120	407.889	308.380	99.509	−102.527	183.266	−9.573
1100	173.468	424.076	318.168	116.499	−103.043	211.874	−10.061
1200	179.772	439.447	327.640	134.169	−103.201	240.514	−10.469
1300	185.195	454.056	336.806	152.424	−103.071	269.149	−10.814
1400	189.878	467.956	345.682	171.183	−102.676	297.769	−11.110
1500	193.933	481.198	354.278	190.379	−102.075	326.353	−11.364

TABLE 7

Ideal gas thermodynamic properties for 1,2-dioxetane

T (K)	$C_p^{\ominus}$ (J K^{-1} mol^{-1})	$S^{\ominus}$ (J K^{-1} mol^{-1})	$-(G^{\ominus} - H_0^{\ominus})/T$ (J K^{-1} mol^{-1})	$H^{\ominus} - H_0^{\ominus}$ (kJ mol^{-1})	$\Delta_f H^{\ominus}$ (kJ mol^{-1})	$\Delta_f G^{\ominus}$ (kJ mol^{-1})	$\log K_f^{\ominus}$
0	0.000	0.000	0.000	0.000	25.772	25.772	∞
100	34.705	215.045	181.504	3.354	20.104	36.264	−18.942
200	42.203	241.028	205.308	7.144	14.940	54.428	−14.215
298.15	56.696	260.386	220.306	11.950	10.000	74.877	−13.118
300	57.013	260.738	220.554	12.055	9.910	75.277	−13.107
400	74.473	279.537	232.957	18.632	5.630	97.740	−12.763
500	90.263	297.899	244.119	26.890	2.319	121.167	−12.658
600	103.400	315.556	254.565	36.595	−0.112	145.182	−12.639
700	114.195	332.333	264.487	47.492	−1.844	169.541	−12.651
800	123.137	348.184	273.968	59.372	−3.012	194.111	−12.674
900	130.620	363.132	283.053	72.071	−3.725	218.798	−12.699
1000	136.933	377.230	291.773	85.457	−4.070	243.545	−12.721
1100	142.289	390.539	300.152	99.425	−4.113	268.310	−12.741
1200	146.855	403.121	308.214	113.889	−3.901	293.070	−12.757
1300	150.764	415.034	315.976	128.775	−3.488	317.799	−12.769
1400	154.125	426.333	323.459	144.023	−2.893	342.493	−12.778
1500	157.025	437.068	330.678	159.584	−2.157	367.139	−12.785

estimated geometric parameters for a planar structure: r(C–O) = 1.45 ± 0.03 Å; r(C–H) = 1.09 ± 0.01 Å; r(C–C) = 1.55 ± 0.02 Å; r(O–O) = 1.47 ± 0.03 Å; ∠(H–C–O) = 112 ± 5°; and ∠(H–C–C) = 115 ± 5°. The C–O, C–C and C–H bond lengths were assumed to be the same as in oxetane, and the O–O bond length was taken to be the same as in 1,2,4-trioxolane. The bond angles were selected by comparing the results of ab initio calculations for 1,2-dioxetane [93] with experimental data for related compounds.

The vibrational spectrum of 1,2-dioxetane was not investigated, either experimentally or theoretically. In this work the vibrational frequencies of 1,2-dioxetane (Table 2) were calculated using 19 force constants transferred from oxetane and 1,2,4-trioxolane. Normal coordinate calculations were performed for oxetane and 1,2,4-trioxolane using vibrational frequencies from Table 2 and the NCA program written by Novikov and Malyshev [96]. Simple valence force fields for oxetane and 1,2,4-trioxolane (with 18 and 16 parameters, respectively) obtained after refinements, reproduce the experimental vibrational spectra of these molecules with an average error of 18 cm^{-1}. We believe that an average uncertainty of the vibrational frequencies of 1,2-dioxetane calculated by combining the force constants of oxetane and 1,2,4-trioxolane is about 50 cm^{-1}; however, for the ring-puckering vibration the uncertainty may be much more significant.

The experimental value of $\Delta_f H^\ominus$(298.15 K) for 1,2-dioxetane has not yet been determined. The enthalpies of formation estimated from semiempirical calculations [97,98] (−98 and −18 kJ mol^{-1}, respectively) and from the group additivity scheme [99] (0 kJ mol^{-1}), differ significantly from each other. In this work, the value of $\Delta_f H^\ominus$(298.15 K) (Table 7) was estimated by comparison of known values of $\Delta_f H^\ominus$ for related compounds, as described above for dioxirane. Recently, Richardson [100] used molecular mechanics to calculate the $\Delta_f H^\ominus$(298.15 K) value of 1,2-dioxetane. His estimate (4.4 kJ mol^{-1}) is close to the value assumed in this work.

The ideal gas thermodynamic properties for 1,2-dioxetane are given in Table 7. No experimental or theoretical data are available for comparison.

TETRAHYDROFURAN

Lafferty et al. [101] interpreted the far-infrared spectrum of tetrahydrofuran in terms of a free pseudo-rotation. Later, Greenhouse and Strauss [102] re-examined the spectrum and proposed the existence of hindered pseudo-rotation in the molecule. Evidence for essentially free pseudo-rotation has been found from electron diffraction data [103,104], but a definite distinction between free pseudo-rotation and the presence of one or more static puckered conformations could not be made from the electron diffraction intensities. The conformational energy calculations [105] indicate that the half-chair (C_2 symmetry) and the envelope (C_s symmetry) conformations, and also the intermediate conformations, have nearly the same energy.

TABLE 8

Ideal gas thermodynamic properties for tetrahydrofuran

T (K)	$C_p^\ominus$ (J K^{-1} mol^{-1})	$S^\ominus$ (J K^{-1} mol^{-1})	$-(G^\ominus - H_0^\ominus)/T$ (J K^{-1} mol^{-1})	$H^\ominus - H_0^\ominus$ (kJ mol^{-1})	$\Delta_f H^\ominus$ (kJ mol^{-1})	$\Delta_f G^\ominus$ (kJ mol^{-1})	log $K_f^\ominus$
0	0.000	0.000	0.000	0.000	−156.364	−156.364	∞
100	40.344	246.441	208.107	3.833	−166.225	−141.535	73.929
200	52.147	277.310	235.551	8.352	−175.247	−113.366	29.608
298.15	76.634	302.353	253.425	14.588	−184.200	−81.071	14.203
300	77.175	302.829	253.728	14.730	−184.366	−80.436	14.005
400	107.071	329.127	269.269	23.944	−192.409	−44.533	5.815
500	134.425	356.035	283.930	36.053	−198.850	−6.793	0.710
600	157.477	382.646	298.174	50.683	−203.752	32.109	−2.795
700	176.672	408.406	312.093	67.419	−207.391	71.719	−5.352
800	192.764	433.079	325.686	85.914	−209.985	111.781	−7.298
900	206.364	456.591	338.935	105.889	−211.725	152.114	−8.828
1000	217.921	478.948	351.828	127.119	−212.763	192.602	−10.060
1100	227.781	500.192	364.359	149.417	−213.220	233.166	−11.072
1200	236.222	520.383	376.527	172.628	−213.188	273.751	−11.916
1300	243.467	539.584	388.337	196.622	−212.763	314.310	−12.629
1400	249.710	557.862	399.798	221.288	−211.980	354.826	−13.239
1500	255.106	575.278	410.921	246.535	−210.919	395.277	−13.765

Engerholm et al. [106] studied the microwave spectrum of tetrahydrofuran and interpreted it in terms of a model of restricted pseudo-rotation. Based on the variation of the dipole moment, they suggested that the twisted (C_2 symmetry) configuration had a lower energy than the bent (C_s symmetry) configuration. The hindered pseudo-rotation with the most stable, puckered C_2-symmetrical twist form has been found for tetrahydrofuran by Cremer [107] from ab initio calculations. In the present work, it is assumed that tetrahydrofuran has a non-planar twist ground-state conformation (C_2 symmetry) and that the molecule undergoes hindered pseudo-rotation through its planar configuration (C_{2v} symmetry). The product of the principal moments of inertia given in Table 1 was calculated using the reported three ground-state rotational constants [106].

The IR and Raman spectra of tetrahydrofuran have been observed by several researchers [108–110] (for the earliest work, see citations in ref. 35) and their vibrational assignments have been made on the basis of a normal coordinate analysis assuming the molecule possesses C_{2v} [111] or C_2 [109,110] symmetry. The vibrational frequencies listed in Table 2 are those obtained by Eyster and Prohofsky [111] and Derouault et al. [110] from IR and Raman spectral measurements and normal coordinate analysis.

The thermodynamic-property contributions due to restricted pseudo-rotation of the tetrahydrofuran ring were obtained by direct summation over the energy levels calculated from the potential function $V(\psi) = 0.5[-30(1-\cos 2\psi) - 40(1-\cos 4\psi)]$ cm^{-1}, where ψ is the angle of pseudo-rotation, as reported by Engerholm et al. [106]. This potential function and a pseudo-rotation constant $F = 3.27$ cm^{-1} [101] were employed to generate 132 pseudo-rotation energy levels (0–14270 cm^{-1}) for the calculation of the pseudo-rotational contributions.

The enthalpy of formation for tetrahydrofuran (Table 8) was taken from data of Pedley et al. [4].

The ideal gas thermodynamic properties for tetrahydrofuran are given in Table 8. The calculated value of $S^{\ominus}(298.15\ \text{K})$ is in good agreement with values calculated by Scott [109] and by Chao et al. [35] (Table 17). The $S^{\ominus}(298.15\ \text{K})$ value reported in the TRC Tables [42], as well as the value of $S^{\ominus}(298.15\ \text{K})$ calculated by Rehman and Lee [112] from an approximate equation based on the formulae of statistical mechanics, is about 5 J K^{-1} mol^{-1} less than the values obtained from more precise statistical calculations with evaluation of the pseudo-rotational contributions to the thermodynamic properties [35,109,this work]. However, all the calculated values are substantially higher than the calorimetric value obtained by Lebedev et al. [113] (Table 17). Although Lebedev et al. do not see any shortcomings in their calorimetric determination of entropy which could cause the discrepancy in the statistical and calorimetric values of $S^{\ominus}(298.15\ \text{K})$ by 12 J K^{-1} mol^{-1}, the calorimetric value seems to be incorrect as the statistical values of $C_p^{\ominus}(T)$ (Table 18) are in good agreement with experimental ones [90].

2,3-DIHYDROFURAN

The ring-puckering vibration in 2,3-dihydrofuran has been studied in the infrared (as difference bands between the CH stretching and ring-puckering vibrations) [72], in the far-infrared [114], in the Raman [115] and in the microwave region [116,117]. All of these studies indicate that the ring has a non-planar equilibrium conformation. The ring-puckering vibration is described by a double minimum potential function with a low barrier (around 83 cm^{-1}). The product of the principal moments of inertia for the non-planar conformation (C_1 symmetry) of 2,3-dihydrofuran given in Table 1 was calculated using the rotational constants determined from microwave study [117].

The vibrational spectrum of 2,3-dihydrofuran was not investigated, either experimentally or theoretically. In this work, the vibrational frequencies of 2,3-dihydrofuran (Table 2) were calculated using 24 force constants transferred from tetrahydrofuran, furan and 2,5-dihydrofuran. Normal coordinate calculations were carried out for the above three molecules using their fundamental frequencies from Table 2. Simple valence force fields for tetrahydrofuran, furan and 2,5-dihydrofuran (with 18, 19 and 19 parameters, respectively) obtained after refinements, reproduce the experimental vibrational spectra of these molecule with an average error of 9, 10 and 21 cm^{-1}, respectively. We believe that the average uncertainty of the vibrational frequencies obtained in this work is about 50 cm^{-1}.

The thermodynamic-property contributions due to inversion of the 2,3-dihydrofuran ring were obtained by direct summation over the energy levels calculated with the potential function. Several investigations of the double minimum ring-puckering potential function of 2,3-dihydrofuran have been reported [72,114–117]. The potential function given by Green [114] was used to calculate 60 energy levels (0–13400 cm^{-1}). The potential function for inversion is $V(x) = (1.002 \times 10^6 x^4 - 1.834 \times 10^4 x^2)\ \text{cm}^{-1}$ (where x (Å) is the ring-puckering coordinate) with a barrier height of 83 cm^{-1} and a reduced mass of 112 a.u. The partition function for inversion is based on these 60 levels with the first 13 levels being the experimental levels from which the potential function was derived.

Experimental or calculated data on the enthalpy of formation are not available for 2,3- or 2,5-dihydrofuran. The experimental values of $\Delta_f H^{\ominus}(298.15\ \text{K})$ are known for related sulphur-containing five-membered rings [4]: tetrahydrothiophene (-34.1 kJ mol^{-1}); 2,3-dihydrothiophene (90.7 kJ mol^{-1}); 2,5-dihydrothiophene (86.9 kJ mol^{-1}); and thiophene (114.9 kJ mol^{-1}). As the difference between the enthalpies of formation for tetrahydrothiophene and thiophene (-149.0 kJ mol^{-1}) is practically the same as for tetrahydrofuran and furan (-149.3 kJ mol^{-1}), one can estimate the $\Delta_f H^{\ominus}(298.15\ \text{K})$ values for 2,3- and 2,5-dihydrofuran to be about -59 and -63 kJ mol^{-1}, respectively, assuming that the difference between the

$\Delta_f H^\ominus$(298.15 K) values for 2,3- or 2,5-dihydrofuran and tetrahydrofuran will be the same as for 2,3- or 2,5-dihydrothiophene and tetrahydrothiophene. On the other hand, the value of $\Delta_f H^\ominus$(298.15 K) = −86 kJ mol^{-1} is obtained for 2,3-dihydrofuran when one assumes that in passing from cyclopentene to 2,3-dihydrofuran, the change in $\Delta_f H^\ominus$(298.15 K) will be the same as in passing from cyclohexene to 3,4-dihydro-2H-pyran. The average of these two estimates, −75 kJ mol^{-1}, was accepted for the enthalpy of formation of 2,3-dihydrofuran (Table 9). The value of $\Delta_f H^\ominus$(298.15 K) = −70 kJ mol^{-1} was assumed for 2,5-dihydrofuran.

The ideal gas thermodynamic properties for 2,3-dihydrofuran presented in Table 9 are reported for the first time. No experimental data are available for comparison.

2,5-DIHYDROFURAN

The ring-puckering motion of 2,5-dihydrofuran has been studied in detail by far-infrared [118–122], Raman [123,124] and microwave [125] spectroscopy and by gas-phase electron diffraction [126]. All of these studies have confirmed that 2,5-dihydrofuran has a planar equilibrium configuration (C_2 symmetry) and a single minimum ring-puckering potential function. The product of the principal moments of inertia for the planar conformation of 2,5-dihydrofuran given in Table 1 was calculated using the rotational constants determined from microwave study [125].

Fortunato [127] has reported the vibrational assignment for 2,5-dihydrofuran from the IR measurements in gaseous, liquid and solid states, and from the Raman study in the liquid state. This assignment has been confirmed by normal coordinate analysis [126]. The observed vibrational frequencies with minor modifications based on the normal coordinate calculation [126] are listed in Table 2.

The thermodynamic-property contributions due to ring-puckering of the 2,5-dihydrofuran were obtained by direct summation over the energy levels calculated with the potential function. Several investigations of the ring-puckering potential function of 2,5-dihydrofuran have been reported [118–122,125,126]. The potential function given by Carreira and Lord [119] was used to calculate 60 energy levels (0–13 200 cm^{-1}). The potential function for ring-puckering vibration is $V(x) = (0.12699 \times 10^7 x^4 + 0.16374 \times 10^5 x^2)$ cm^{-1} (where x (Å) is the ring-puckering coordinate) with a reduced mass of 155.7 a.u. The partition function for ring-puckering motion is based on these 60 levels with the first 13 levels being the experimental levels from which the potential function was derived.

There are no experimental or theoretical data on the enthalpy of formation of 2,5-dihydrofuran and the $\Delta_f H^\ominus$(298.15 K) value given in Table 10 was estimated in this work (see 2,3-dihydrofuran).

TABLE 9

Ideal gas thermodynamic properties for 2,3-dihydrofuran

T (K)	$C_p^\ominus$ (J K^{-1} mol^{-1})	$S^\ominus$ (J K^{-1} mol^{-1})	$-(G^\ominus - H_0^\ominus)/T$ (J K^{-1} mol^{-1})	$H^\ominus - H_0^\ominus$ (kJ mol^{-1})	$\Delta_f H^\ominus$ (kJ mol^{-1})	$\Delta_f G^\ominus$ (kJ mol^{-1})	log $K_f^\ominus$
0	0.000	0.000	0.000	0.000	−55.227	−55.227	∞
100	39.031	237.984	201.223	3.676	−62.246	−46.782	24.436
200	51.259	268.058	227.645	8.083	−68.686	−28.836	7.531
298.15	74.226	292.571	244.999	14.184	−75.000	−7.916	1.387
300	74.708	293.031	245.294	14.321	−75.117	−7.504	1.307
400	100.457	318.090	260.356	23.094	−80.696	15.909	−2.077
500	122.988	343.003	274.403	34.300	−85.116	40.589	−4.240
600	141.504	367.120	287.860	47.556	−88.464	66.067	−5.752
700	156.687	390.111	300.839	62.490	−90.967	92.027	−6.867
800	169.293	411.881	313.372	78.808	−92.785	118.303	−7.724
900	179.887	432.451	325.471	96.282	−94.052	144.768	−8.402
1000	188.860	451.881	337.150	114.731	−94.867	171.352	−8.950
1100	196.505	470.249	348.422	134.010	−95.304	197.999	−9.402
1200	203.046	487.635	359.305	153.996	−95.420	224.672	−9.780
1300	208.662	504.115	369.817	174.588	−95.275	251.337	−10.099
1400	213.501	519.760	379.973	195.702	−94.881	277.987	−10.372
1500	217.687	534.636	389.792	217.266	−94.294	304.601	−10.607

TABLE 10

Ideal gas thermodynamic properties for 2,5-dihydrofuran

T (K)	$C_p^{\ominus}$ (J K^{-1} mol^{-1})	$S^{\ominus}$ (J K^{-1} mol^{-1})	$-(G^{\ominus} - H_0^{\ominus})/T$ (J K^{-1} mol^{-1})	$H^{\ominus} - H_0^{\ominus}$ (kJ mol^{-1})	$\Delta_f H^{\ominus}$ (kJ mol^{-1})	$\Delta_f G^{\ominus}$ (kJ mol^{-1})	log $K_f^{\ominus}$
0	0.000	0.000	0.000	0.000	−50.470	−50.470	∞
100	40.448	228.379	191.584	3.679	−57.486	−41.062	21.448
200	52.342	259.289	218.267	8.204	−63.808	−22.205	5.799
298.15	75.654	284.293	235.904	14.427	−70.000	−0.448	0.079
300	76.144	284.763	236.204	14.567	−70.114	−0.021	0.004
400	102.125	310.272	251.528	23.497	−75.536	24.196	−3.160
500	124.673	335.562	265.817	34.873	−79.786	49.640	−5.186
600	143.107	359.980	279.490	48.294	−82.969	75.846	−6.603
700	158.177	383.209	292.664	63.382	−85.318	102.508	−7.649
800	170.673	405.171	305.367	79.844	−86.992	129.464	−8.453
900	181.163	425.897	317.619	97.450	−88.127	156.592	−9.088
1000	190.048	445.457	329.434	116.022	−88.818	183.824	−9.602
1100	197.615	463.935	340.830	135.416	−89.141	211.107	−10.025
1200	204.088	481.414	351.823	155.509	−89.150	238.407	−10.377
1300	209.645	497.975	362.434	176.202	−88.904	265.690	−10.675
1400	214.433	513.691	372.682	197.413	−88.413	292.952	−10.930
1500	218.574	528.630	382.585	219.068	−87.735	320.169	−11.149

TABLE 11

Ideal gas thermodynamic properties for furan

T (K)	$C_p^\ominus$ (J K^{-1} mol^{-1})	$S^\ominus$ (J K^{-1} mol^{-1})	$-(G^\ominus - H_0^\ominus)/T$ (J K^{-1} mol^{-1})	$H^\ominus - H_0^\ominus$ (kJ mol^{-1})	$\Delta_f H^\ominus$ (kJ mol^{-1})	$\Delta_f G^\ominus$ (kJ mol^{-1})	log $K_f^\ominus$
0	0.000	0.000	0.000	0.000	−21.757	−21.757	∞
100	33.531	220.603	187.316	3.329	−26.124	−18.995	9.922
200	43.598	245.960	210.748	7.042	−30.563	−10.176	2.658
298.15	65.405	267.248	225.837	12.347	−34.900	0.772	−0.135
300	65.850	267.654	226.093	12.468	−34.978	0.990	−0.172
400	88.801	289.810	239.248	20.225	−38.669	13.563	−1.771
500	107.825	311.750	251.565	30.093	−41.502	26.961	−2.817
600	122.774	332.786	263.364	41.653	−43.618	40.868	−3.558
700	134.587	352.633	274.714	54.543	−45.228	55.080	−4.110
800	144.129	371.249	285.630	68.495	−46.459	69.498	−4.538
900	152.003	388.693	296.123	83.314	−47.407	84.051	−4.878
1000	158.603	405.060	306.207	98.853	−48.127	98.700	−5.155
1100	164.197	420.466	315.900	115.001	−48.657	113.410	−5.385
1200	168.974	434.943	325.222	131.666	−49.017	128.161	−5.579
1300	173.076	448.634	334.193	148.773	−49.234	142.932	−5.743
1400	176.617	461.593	342.835	166.262	−49.303	157.718	−5.884
1500	179.687	473.886	351.165	184.081	−49.251	172.504	−6.007

The ideal gas thermodynamic properties for 2,5-dihydrofuran are given in Table 10. No experimental data are available for comparison. The calculated values of $S^{\ominus}(T)$ and $C_p^{\ominus}(T)$ are in good agreement with those calculated by other authors [35,42,112] (Tables 17, 18).

FURAN

Information on the structural parameters and rotational constants of furan has been obtained from microwave studies [128,129], high-resolution rotational spectra [130], electron diffraction data [131] and theoretical calculations [132–134]. The rotational constants determined in experimental works [128–130] are in virtual agreement and were used to calculate the product of the three principal moments of inertia (Table 1).

The vibrational spectra of furan have been investigated by many authors [29,135–144] and complete fundamental vibrational assignments have been reported. The fundamental frequencies used in our calculations (Table 2) were taken from the reliable work of Rico et al. [137]. These authors observed the vibrational frequencies for furan and some deuterated derivatives from their IR and Raman spectra for vapour and liquid states; their vibrational assignment has been confirmed by vibrational analysis [141].

The enthalpy of formation for furan (Table 11) was taken from the data of Pedley et al. [4].

The ideal gas thermodynamic properties for furan are given Table 11. The calculated value of $S^{\ominus}(298.15\ \mathrm{K})$ agrees well with the calorimetric value [145] (Table 17). The calculated entropy values are in good agreement with those obtained in other statistical calculations [35,40,42,112,145,146]. The heat capacity values also agree well with those obtained experimentally [145] and calculated theoretically [35,42,112,137,145,146] (Table 18).

1,2-DIOXOLANE

Scant information is available on the structure of 1,2-dioxolane. Kondo et al. [147] have determined the rotational constants of 1,2-dioxolane by microwave spectroscopy. The observed rotational constants were fairly well reproduced by the plausible set of bond lengths and bond angles borrowed from analogous molecules. The bond angles in the skeletal framework and the dihedral angle were allowed to adjust themselves. The dihedral angle around the peroxide bond obtained from the treatment (50 ± 2°) corresponds to the non-planar twist form. A close value for the dihedral angle was obtained from a photoelectron spectroscopic study [148]. A theoretical determination of the molecular structure and the conformation of 1,2-dioxolane has been carried out by Cremer [107] from ab initio investigation. It was established that the molecule undergoes hindered pseudo-rotation. A puckered C_2-symmetrical twist form was found to be the most stable conformation for 1,2-dioxolane. On the energy profile during pseudo-rotation, the planar (C_{2v} symmetry) and envelope (C_s symmetry) forms are located at the maxima. The calculated structural parameters are close to those estimated by Kondo et al. [147]. As the barrier to pseudo-rotation calculated by Cremer [107] is fairly high ($\approx$ 9 kJ mol^{-1}), the pseudo-rotation was not taken into account in the present work. The twist conformation of C_2 symmetry was accepted for 1,2-dioxolane and the product of the principal moments of inertia given in Table 1 was calculated using the rotational constants of Kondo et al. [147]. Recently, Carballeira et al. [149] have carried out a molecular mechanics investigation of 1,2-dioxolane. The optimisation led to a single minimum corresponding to the twist conformer; this unique conformer is the same as was obtained using ab initio methods by Cremer [107] and whose existence was deduced experimentally by Kondo et al. [147] on the basis of microwave data.

Experimental or theoretical data on the vibrational spectrum of 1,2-dioxolane are unknown. In this work, the vibrational frequencies of 1,2-dioxolane (Table 2) have been calculated using 20 force constants transferred from tetrahydrofuran and 1,2,4-trioxolane. Normal coordinate calculations were carried out for tetrahydrofuran and 1,2,4-trioxolane using vibrational assignments from Table 2. Simple valence force fields for tetrahydrofuran and 1,2,4-trioxolane with 18 and 16 parameters, respectively, obtained after refinement, reproduce the experimental vibrational spectra of these molecules with an average error of 9 and 17 cm^{-1}, respectively. An average uncertainty of the vibrational frequencies of 1,2-dioxolane calculated by combining the force constants of tetrahydrofuran and 1,2,4-trioxolane, is believed to be about 50 cm^{-1}, however, for the ring-puckering frequency the uncertainty may be much more significant.

There are no experimental or theoretical determinations of the enthalpy of formation of 1,2-dioxolane. In this work, the value of $\Delta_f H^{\ominus}$(298.15 K) (Table 12) was estimated by comparison of known values of $\Delta_f H^{\ominus}$(298.15 K) for related compounds, as described above for dioxirane.

The ideal gas thermodynamic properties for 1,2-dioxolane are given in Table 12. No experimental or theoretical data are available for comparison.

1,3-DIOXOLANE

Durig and Wertz [150] interpreted the far-infrared spectrum of 1,3-dioxolane in terms of free pseudo-rotation. Greenhouse and Strauss [102] concluded from their far-infrared study that 1,3-dioxolane has a barrier to pseudo-rotation of about 50 cm^{-1}. Baron and Harris [151] interpreted the microwave spectrum of 1,3-dioxolane in terms of restricted pseudo-rotation and concluded that the minimum in the potential energy occurs at a configuration which is approximately half bent and half twisted, and that both the bent (C_s symmetry) and twist (C_2 symmetry) forms are maxima on

TABLE 12

Ideal gas thermodynamic properties for 1,2-dioxolane

T (K)	$C_p^\ominus$ (J K^{-1} mol^{-1})	$S^\ominus$ (J K^{-1} mol^{-1})	$-(G^\ominus - H_0^\ominus)/T$ (J K^{-1} mol^{-1})	$H^\ominus - H_0^\ominus$ (kJ mol^{-1})	$\Delta_f H^\ominus$ (kJ mol^{-1})	$\Delta_f G^\ominus$ (kJ mol^{-1})	log $K_f^\ominus$
0	0.000	0.000	0.000	0.000	−67.044	−67.044	∞
100	38.109	231.197	196.776	3.442	−75.685	−50.973	26.625
200	53.355	261.819	222.092	7.945	−83.157	−23.328	6.093
298.15	76.947	287.303	239.385	14.287	−90.000	7.525	−1.318
300	77.439	287.780	239.682	14.430	−90.122	8.126	−1.415
400	103.703	313.695	254.943	23.501	−95.851	41.784	−5.456
500	126.621	339.378	269.272	35.053	−100.123	76.711	−8.014
600	145.323	364.177	283.038	48.683	−103.117	112.383	−9.784
700	160.545	387.760	296.329	64.002	−105.114	148.467	−11.079
800	173.112	410.044	309.164	80.704	−106.315	184.784	−12.065
900	183.627	431.059	321.552	98.556	−106.878	221.211	−12.839
1000	192.507	450.878	333.503	117.375	−106.924	257.673	−13.459
1100	200.053	469.590	345.032	137.013	−106.547	294.116	−13.966
1200	206.498	487.280	356.156	157.349	−105.814	330.513	−14.387
1300	212.023	504.032	366.893	178.282	−104.798	366.830	−14.739
1400	216.779	519.923	377.261	199.728	−103.524	403.064	−15.038
1500	220.889	535.023	387.279	221.616	−102.052	439.199	−15.294

TABLE 13

Ideal gas thermodynamic properties for 1,3-dioxolane

T (K)	$C_p^\ominus$ (J K^{-1} mol^{-1})	$S^\ominus$ (J K^{-1} mol^{-1})	$-(G^\ominus - H_0^\ominus)/T$ (J K^{-1} mol^{-1})	$H^\ominus - H_0^\ominus$ (kJ mol^{-1})	$\Delta_f H^\ominus$ (kJ mol^{-1})	$\Delta_f G^\ominus$ (kJ mol^{-1})	log $K_f^\ominus$
0	0.000	0.000	0.000	0.000	−275.000	−275.000	∞
100	40.669	245.241	206.945	3.830	−283.253	−259.945	135.780
200	50.896	276.015	234.387	8.326	−290.733	−233.743	61.047
298.15	71.007	299.822	252.050	14.243	−298.000	−204.207	35.776
300	71.448	300.263	252.345	14.375	−298.133	−203.629	35.455
400	95.781	324.150	267.307	22.737	−304.571	−171.118	22.345
500	118.086	347.982	281.065	33.458	−309.674	−137.143	14.327
600	136.884	371.226	294.166	46.235	−313.521	−102.251	8.902
700	152.488	393.535	306.780	60.729	−316.343	−66.804	4.985
800	165.511	414.773	318.963	76.647	−318.328	−31.012	2.025
900	176.463	434.917	330.738	93.761	−319.629	4.987	−0.289
1000	185.734	454.002	342.119	111.885	−320.370	41.103	−2.147
1100	193.617	472.085	353.119	130.863	−320.653	77.265	−3.669
1200	200.347	489.228	363.754	150.570	−320.549	113.441	−4.938
1300	206.113	505.498	374.037	170.899	−320.137	149.586	−6.010
1400	211.073	520.958	383.983	191.764	−319.444	185.696	−6.928
1500	215.355	535.671	393.610	213.091	−318.533	221.746	−7.722

the potential energy surface, with the twist form being slightly higher in energy. No attempt was made to determine the structure using rotational constants. Nuclear magnetic resonance results on 1,3-dioxolane [152] were not consistent with a planar ring structure and could only be explained in terms of appreciable ring deformations.

Shen et al. [153] have determined the gas-phase structure of 1,3-dioxolane from electron diffraction investigation. Various rigid, single conformer models, conformational mixtures of envelope (C_s symmetry) and twist (C_2 symmetry) forms of the molecule and pseudo-rotational models were tested. The best results were obtained with a pseudo-rotational model. The authors inferred from their data that there is a very small barrier to pseudo-rotation and that the C_2 form of the molecule corresponds to an energy minimum. This result agrees with ab initio calculations [107,154,155], but is in disagreement with the results of molecular mechanics calculations [153,156–159] and the microwave spectroscopic data [151]. The molecular mechanics calculations predict the C_s form of 1,3-dioxolane to be the more stable, but this result hinges critically upon the data chosen for parameterisation [155,158].

In the present work, it is assumed that 1,3-dioxolane has a twist conformation (C_2 symmetry) and that the molecule undergoes hindered pseudo-rotation through its planar (C_{2v} symmetry) form. The product of the principal moments of inertia given in Table 1 was calculated using the reported three ground-state rotational constants [151].

The IR and Raman spectra for different phases of 1,3-dioxolane were reported by Barker et al. [160]. The authors assigned 25 of the 27 normal modes of 1,3-dioxolane on the basis that the molecule possesses C_{2v} symmetry. These frequencies are presented in Table 2. The only modes which Barker et al. did not assign were the two out-of-plane skeletal bending vibrations $\nu_{14}(A_2)$ and $\nu_{27}(B_2)$. For the high-frequency puckering mode ν_{14}, the value of 260 cm^{-1} obtained by Durig and Wertz [150] from the far-infrared spectrum is assumed in Table 2. The low-frequency puckering mode ν_{27} is not given in Table 2, as the contribution due to pseudo-rotation of 1,3-dioxolane was obtained from energy levels calculated with the potential function.

The contributions of hindered pseudo-rotation to the thermodynamic properties were obtained by direct summation over the energy levels calculated with the potential function $V(\psi) = 0.5[-10.2(1 - \cos 2\psi) - 40(1 - \cos 4\psi)]$ cm^{-1}, where ψ is the angle of pseudo-rotation, as reported by Baron and Harris [151]. This potential function and a pseudo-rotation constant $F = 3.99$ cm^{-1} [151] were employed for generating 132 pseudo-rotation energy levels (0–17400 cm^{-1}) for calculation of the pseudo-rotational contributions.

The enthalpy of formation of 1,3-dioxolane (Table 13) was taken from the data of Pedley et al. [4].

The ideal gas thermodynamic properties for 1,3-dioxolane are given in

Table 13. No other statistical calculations are available for comparison. Our value of $S^\ominus(298.15\ \mathrm{K})$ is 10.8 J K^{-1} mol^{-1} less than the value obtained from the calorimetric investigation [161] (Table 17). Such a large discrepancy between the calculated and experimental values of the entropy is unlikely to be due to the uncertainty of the molecular constants assumed for statistical calculation. From the viewpoint of group additivity principles, one can reasonably suggest that the changes in $S^\ominus_{\mathrm{int}}(298.15\ \mathrm{K})$ [1] values with the exchange of a $-\mathrm{CH}_2-$ unit for an $-\mathrm{O}-$ group will be rather close to one another for five-, six- and seven-membered rings. We have in fact found that this suggestion is true, within the uncertainties of statistical calculations, for the following compounds (all values of entropy were calculated by us; for six- and seven-membered rings see Part 2 of this series):

$\Delta_5 = S^\ominus_{\mathrm{int}}(\mathrm{C_4H_8O}$, tetrahydrofuran$) - S^\ominus_{\mathrm{int}}(\mathrm{C_3H_6O_2}$, 1,3-dioxolane$)$
$= 2.5\ \mathrm{J\ K^{-1}\ mol^{-1}}$;
$\Delta_6 = S^\ominus_{\mathrm{int}}(\mathrm{C_5H_{10}O}$, tetrahydro-2H-pyran$) - S^\ominus_{\mathrm{int}}(\mathrm{C_4H_8O_2}$, 1,3-dioxane$)$
$= 5.3\ \mathrm{J\ K^{-1}\ mol^{-1}}$;
$\Delta_7 = S^\ominus_{\mathrm{int}}(\mathrm{C_6H_{12}O}$, oxepane$) - S^\ominus_{\mathrm{int}}(\mathrm{C_5H_{10}O_2}$, 1,3-dioxepane$)$
$= 3.4\ \mathrm{J\ K^{-1}\ mol^{-1}}$.

However, if we adopt the calorimetric value of entropy for 1,3-dioxolane, the Δ_5 value will be equal to -8.3 J K^{-1} mol^{-1} and group additivity will not be correct in this case. Thus, assuming group additivity to be correct, one can give preference to the calculated value of entropy.

1,2,3-TRIOXOLANE

The lowest energy oxygen envelope conformation (C_s symmetry) has been determined for gaseous 1,2,3-trioxolane from microwave spectra of five isotopic species [162,163]. This form corresponds to a conformation in which the unique oxygen is bent out of the plane defined by the remaining four ring atoms. Contrary to previous semiempirical and ab initio calculations [164–169] which are rather inconclusive with regard to the most probable 1,2,3-trioxolane conformation, the ab initio calculations performed by Cremer [107,170] and by McKee and Rohlfing [171] clearly predict the symmetrical oxygen envelope conformation to be lowest in energy which is consistent with the microwave data. The barrier to pseudo-rotation is estimated by ab initio methods [107,170] to be a fairly high (≈ 15 J K^{-1} mol^{-1}). The product of the principal moments of inertia given in Table 1 was calculated using the rotational constants of Gillies et al. [162].

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[1] The intrinsic entropy $S^\ominus_{\mathrm{int}}$ is related to the observed entropy $S^\ominus$ by the relation $S^\ominus_{\mathrm{int}} = S^\ominus + R\ \ln(\sigma/n)$, where σ is the symmetry number for the molecule and n is the number of optical isomers.

TABLE 14

Ideal gas thermodynamic properties for 1,2,3-trioxolane

T (K)	$C_p^\ominus$ (J K^{-1} mol^{-1})	$S^\ominus$ (J K^{-1} mol^{-1})	$-(G^\ominus - H_0^\ominus)/T$ (J K^{-1} mol^{-1})	$H^\ominus - H_0^\ominus$ (kJ mol^{-1})	$\Delta_f H^\ominus$ (kJ mol^{-1})	$\Delta_f G^\ominus$ (kJ mol^{-1})	log $K_f^\ominus$
0	0.000	0.000	0.000	0.000	−83.710	−83.710	∞
100	46.053	238.325	199.262	3.906	−90.277	−67.779	35.404
200	58.854	273.764	228.311	9.091	−95.502	−43.212	11.286
298.15	77.952	300.690	247.790	15.772	−100.000	−16.557	2.901
300	78.338	301.173	248.118	15.916	−100.078	−16.042	2.793
400	98.486	326.518	264.581	24.775	−103.562	12.530	−1.636
500	115.556	350.395	279.381	35.507	−105.928	41.845	−4.371
600	129.231	372.720	293.099	47.772	−107.379	71.553	−6.229
700	140.211	393.495	305.975	61.264	−108.144	101.442	−7.570
800	149.179	412.822	318.138	75.748	−108.377	131.405	−8.580
900	156.618	430.836	329.670	91.049	−108.191	161.370	−9.366
1000	162.859	447.669	340.638	107.031	−107.671	191.297	−9.992
1100	168.135	463.446	351.093	123.588	−106.881	221.156	−10.502
1200	172.622	478.273	361.080	140.632	−105.864	250.936	−10.923
1300	176.457	492.246	370.637	158.091	−104.670	280.619	−11.275
1400	179.750	505.446	379.799	175.906	−103.316	310.208	−11.574
1500	182.589	517.947	388.596	194.026	−101.842	339.696	−11.829

Kohlmiller and Andrews [172] have investigated the reaction between ozone and ethylene in solid xenon by IR spectroscopy, and seven absorptions have been assigned to 1,2,3-trioxolane. From microwave investigation, Gillies et al. [162,163] have assigned two lowest vibrational frequencies which correspond to the ring-puckering vibrations of 1,2,3-trioxolane. The vibrational frequencies listed in Table 2 have been calculated in the present work by transferring force constants from tetrahydrofuran and 1,2,4-trioxolane, except for two ring-puckering frequencies whose values have been taken from microwave data [162]. Normal coordinate calculations were performed for tetrahydrofuran and 1,2,4-trioxolane using vibrational frequencies from Table 2. Simple valence force fields for tetrahydrofuran and 1,2,4-trioxolane with 18 and 16 parameters, respectively, reproduce the experimental vibrational spectra of these molecules with an average error of 13 cm^{-1}. One can believe that an average uncertainty for the vibrational fundamentals of 1,2,3-trioxolane calculated combining the force constants of these two molecules is about 50 cm^{-1}.

There are no experimental data on the enthalpy of formation of 1,2,3-trioxolane. The value of $\Delta_f H^\ominus$(298.15 K) estimated from semiempirical [166] (-118 kJ mol^{-1}) and ab initio [62] (0 kJ mol^{-1}) calculations differ significantly from each other. An estimate for $\Delta_f H^\ominus$(298.15 K) for 1,2,3-trioxolane was obtained in the present work (Table 14) by comparison of the adopted values of the enthalpy of formation of cyclopentane, tetrahydrofuran and 1,2-dioxolane with the $\Delta_f H^\ominus$(298.15 K) values for related aliphatic compounds, as described above for dioxirane.

The ideal gas thermodynamic properties for 1,2,3-trioxolane presented in Table 14 are reported for the first time. No experimental data are available for comparison.

1,2,4-TRIOXOLANE

The half-chair (twist) conformation with C_2 symmetry has been determined from the microwave spectra of the isotopic species of 1,2,4-trioxolane [173,174]; there was no evidence for free or hindered pseudo-rotation. The twist form was found to be the most stable conformation from ab initio calculations [107,170,175]. Semiempirical methods have yielded different results for the geometry and for the relative stability of the conformers of 1,2,4-trioxolane [165]. An almost equally good agreement between the theoretical and experimental intensities has been obtained from electron diffraction data by assuming both C_2 and C_s symmetry [176], but calculations of conformational energies favoured the C_2 model [105]. The product of the principal moments of inertia given in Table 1 was calculated using the rotational constants determined from an analysis of the microwave spectra [173,174].

TABLE 15

Ideal gas thermodynamic properties for 1,2,4-trioxolane

T (K)	$C_p^\ominus$ (J K^{-1} mol^{-1})	$S^\ominus$ (J K^{-1} mol^{-1})	$-(G^\ominus - H_0^\ominus)/T$ (J K^{-1} mol^{-1})	$H^\ominus - H_0^\ominus$ (kJ mol^{-1})	$\Delta_f H^\ominus$ (kJ mol^{-1})	$\Delta_f G^\ominus$ (kJ mol^{-1})	log $K_f^\ominus$
0	0.000	0.000	0.000	0.000	−191.732	−191.732	∞
100	39.235	231.306	196.241	3.506	−198.698	−175.499	91.670
200	50.826	261.768	221.939	7.966	−204.648	−149.959	39.165
298.15	68.846	285.237	238.973	13.794	−210.000	−121.950	21.365
300	69.227	285.664	239.259	13.922	−210.095	−121.407	21.138
400	89.724	308.410	253.717	21.877	−214.481	−91.146	11.902
500	107.826	330.437	266.872	31.782	−217.675	−59.922	6.260
600	122.655	351.454	279.234	43.332	−219.841	−28.150	2.451
700	134.682	371.296	290.982	56.220	−221.210	3.915	−0.292
800	144.529	389.944	302.199	70.196	−221.951	36.133	−2.359
900	152.688	407.453	312.932	85.069	−222.193	68.413	−3.971
1000	159.512	423.904	323.215	100.689	−222.035	100.698	−5.260
1100	165.262	439.385	333.079	116.936	−221.555	132.949	−6.313
1200	170.135	453.979	342.552	133.712	−220.805	165.148	−7.189
1300	174.288	467.765	351.658	150.939	−219.844	197.269	−7.926
1400	177.843	480.815	360.422	168.550	−218.694	229.314	−8.556
1500	180.902	493.192	368.864	186.491	−217.399	261.272	−9.098

Kühne and Günthard [177] have observed the infrared and far-infrared spectra of three isotopic modifications of 1,2,4-trioxolane isolated in solid argon and have made a complete vibrational assignment based on empirical considerations and normal coordinate analysis. Several absorptions have also been assigned to 1,2,4-trioxolane from other matrix IR spectra studies [178]. The vibrational frequencies, given in Table 2, are those obtained by Kühne and Günthard [177].

There are no experimental data on the enthalpy of formation of 1,2,4-trioxolane. The values of $\Delta_f H^\ominus$ estimated from semiempirical [166] (-272 kJ mol^{-1}) and ab initio [62] (-50 kJ mol^{-1}) calculations differ significantly from each other. In the present work, the value of $\Delta_f H^\ominus$(298.15 K) for 1,2,4-trioxolane (Table 15) was estimated by comparison of the enthalpies of formation for related five-membered rings (cyclopentane, tetrahydrofuran, and 1,2- and 1,3-dioxolane) and aliphatic compounds, as described above for dioxirane.

The ideal gas thermodynamic properties for 1,2,4-trioxolane are presented in Table 15. No experimental data are available for comparison. The statistical thermodynamic functions of 1,2,4-trioxolane have been reported by Kühne and Günthard [177]. Although we used practically the same molecular constant values as Kühne and Günthard, only the values of $C_p^\ominus$ are in good agreement for the two statistical calculations (Table 18), while our $S^\ominus$ values are about 6 J K^{-1} mol^{-1} more than those of Kühne and Günthard (Table 17). We believe that the values of $S^\ominus$ calculated by Kühne

TABLE 16

The uncertainties in the calculated thermodynamic functions (J K^{-1} mol^{-1}) and adopted enthalpies of formation (kJ mol^{-1})

Molecule		Uncertanties in $-(G^\ominus - H_0^\ominus)/T$		Uncertainties in $C_p^\ominus$		Uncertainties in $\Delta_f H^\ominus$(298.15 K)
		298.15	1000 K	298.15	1000 K	
C_2H_4O	Oxirane	0.5	1.5	1.5	4.5	0.6
C_2H_2O	Oxirene	2.0	4.0	3.0	4.5	20.0
CH_2O_2	Dioxirane	2.0	4.0	3.0	4.5	30.0
C_3H_6O	Oxetane	1.5	2.5	2.0	4.5	0.6
$C_2H_4O_2$	1,2-Dioxetane	3.0	5.0	4.0	6.0	30.0
C_4H_8O	Tetrahydrofuran	1.5	3.0	3.0	5.0	0.8
C_4H_6O	2,3-Dihydrofuran	3.0	5.0	4.0	6.0	20.0
	2,5-Dihydrofuran	2.0	3.5	3.0	5.0	20.0
C_4H_4O	Furan	0.5	2.5	2.0	6.5	0.7
$C_3H_6O_2$	1,2-Dioxolane	3.0	5.0	4.0	8.5	50.0
	1,3-Dioxolane	3.0	5.0	4.0	8.5	1.4
$C_2H_4O_3$	1,2,3-Trioxolane	3.5	5.5	3.5	7.0	75.0
	1,2,4-Trioxolane	3.0	5.0	3.5	6.5	50.0

TABLE 17

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

$S^{\ominus}(T)$				Reference
298.15 K	500 K	1000 K	1500 K	
C_2H_4O Oxirane				
242.5				[34]
243.1				[35]
243.8				[36]
243.3	274.7	341.0		[37]
243.1	274.4	340.7		[38]
242.9	274.3	340.7	390.4	[39]
	274.4	340.7		[40]
245.5	277.6	344.8		[41]
243.0	274.4	340.8	391.3	[35,42]
242.6	273.7	339.8	390.3	This work
C_3H_6 Oxetane				
265.4	306.3	399.8		[85]
274.0	314.2	406.5		[86] [b]
265.0	305.0	397.3		[86] [c]
271.4	313.6	407.9	481.2	This work
C_4H_8O Tetrahydrofuran				
288 ± 1				[113]
302.4	355.7	478.3		[109]
297.2	350.7	473.3	569.8	[112]
302.4	355.7	478.1	574.2	[35]
297.3	350.8	473.6	570.0	[42]
302.4	356.0	478.9	575.3	This work
C_4H_6O 2,5-Dihydrofuran				
284.7	335.8	445.1	527.9	[112]
284.2	335.2	443.5	525.0	[35]
284.8	335.9	445.3	528.2	[42]
284.3	335.6	445.5	528.6	This work
C_4H_4O Furan				
267.3 ± 0.4				[145]
267.3	311.7	404.9	473.7	[145]
267.2	311.8	405.1		[146]
	311.9	405.2	474.4	[40]
267.1	311.5	404.8	473.6	[112]
267.2	311.7	405.1	473.9	[35,42]
267.2	311.8	405.1	473.9	This work
$C_3H_6O_2$ 1,3-Dioxolane				
310.6 ± 4.1				[161]
299.8	348.0	454.0	535.7	This work
$C_2H_4O_3$ 1,2,4-Trioxolane				
279.0	324.1	417.5	486.8	[177]
285.2	330.4	423.9	493.2	This work

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[a] Experimental values of $S^{\ominus}$(298.15 K) are italic.

[b] $\nu_{24} = 60$ cm^{-1}.

[c] $\nu_{24} = 184$ cm^{-1}.

TABLE 18

Comparison of experimental [a] heat capacities $C_p^{\ominus}(T)$ with calculated values (J K^{-1} mol^{-1})

T (K)	Literature values						
C_2H_4O Oirane							
	[43]	[37]	[39]	[40]	[41]	[35,42]	This work
298.15		48.2	47.9		48.6	47.9	47.0
307.18	*49.4*					49.1	48.3
337.04	*53.5*					53.4	52.6
371.23	*58.4*					58.3	57.5
500		75.1	75.4	75.6	76.9	75.4	74.9
1000		114.9	115.0	115.3	115.9	115.0	114.9
1500			132.8	133.2		133.2	133.1
C_3H_6O Oxetane							
	[90]	[85]	[86]	[86]			This work
298.15	*61.2*	59.4	58.7	58.2			61.5
323.15	*66.7*						67.0
348.15	*72.2*						72.5
373.15	*77.8*						78.1
398.15	*83.3*						83.6
423.15	*88.7*						88.9
448.15	*94.1*						94.1
473.15	*99.1*						99.1
498.15	*103.9*						103.8
500		102.0	100.0	99.9			104.2
523.15	*108.7*						108.5
1000		174.5	165.0	164.9			166.1
1500							193.9
C_4H_8O Tetrahydrofuran							
	[90]	[109]	[112]	[35]	[42]		This work
298.15		76.2	76.5	76.3	76.4		76.6
328.15	*85.1*		85.3	85.1			85.6

349.15	*91.4*		91.6	91.3			91.9
399.15	*106.1*		106.5	106.1			106.8
449.15	*120.4*		120.6	120.3			121.0
500		133.6	133.9	133.6	133.9		134.4
500.15	*133.7*		133.9	133.6			134.5
1000		217.3	218.1	217.3	217.9		217.9
1500			255.2	254.7	255.6		255.1
C_4H_6O 2,5-Dihydrofuran							
	[112]	[35]	[42]				This work
298.15	75.6	75.6	75.6				75.7
500	123.9	123.5	123.9				124.7
1000	189.4	186.5	189.3				190.0
1500	217.8	213.7	217.8				218.6
C_4H_4O Furan							
	[145]	[145]	[137]	[146]	[112]	[35,42]	This work
298.15		65.4		65.4	65.4	65.4	65.4
317.25	*70.3*	70.0	70.0	70.0	69.9	70.0	70.0
358.20	*80.1*	79.6	79.6		79.4	79.6	79.6
402.20	*90.0*	89.2	89.3		89.2	89.3	89.3
449.20	*99.6*	98.5	98.7		98.7	98.7	98.7
487.20	*106.5*	105.4	105.7	105.6	105.6	105.7	105.6
500		107.7		107.8	107.8	107.8	107.8
1000		158.5		158.6	158.5	158.6	158.6
1500		179.7			179.5	179.7	179.7
$C_2H_4O_3$ 1,2,4-Trioxolane							
	[177]						This work
298.15	68.6						68.8
500	107.7						107.8
1000	159.5						159.5
1500	180.8						180.9

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[a] Experimental values of heat capacity are italic.

and Günthard are incorrect because they have not taken into account the existence of optical isomers for the C_2 conformation.

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