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Note

Thermodynamic functions for 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane and 1-chloro-2,2,3,3-tetrafluorocyclobutane

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The recent publication of the needed vibrational spectra data[1] for 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane and 1-chloro-2,2,3,3-tetrafluorocyclobutane has made it possible to continue the calculation of the ideal gas state thermodynamic functions, heat capacity, enthalpy, entropy and free energy for halogenated small ring systems[2,3]. The functions for each given compound were calculated by means of the well-known statistical mechanical methods.

TABLE 1

HEAT CAPACITY, ENTROPY, FREE ENERGY AND ENTHALPY FUNCTIONS

Thermodynamic function	*Temp. (K)*	*c*-$C_4ClF_3H_3$	*c*-$C_4Cl_4F_4$
Heat capacity	273.15	28.51	40.45
C_p° (cal mol^{-1} K^{-1})	298.15	30.41	42.39
	350.00	34.68	45.91
	400.00	37.24	48.74
	450.00	40.04	51.09
	500.00	42.49	53.06
	550.00	44.62	54.70
	600.00	46.48	56.07
	650.00	48.11	57.23
	700.00	49.55	58.21
	750.00	50.82	59.04
	800.00	51.95	59.75
	850.00	52.97	60.36
	900.00	53.88	60.88
	950.00	54.71	61.34
	1000.00	55.46	61.74
Entropy	273.15	87.58	102.30
S° (e.u.)	298.15	90.30	106.08
	350.00	95.73	113.42
	400.00	100.72	119.96
	450.00	105.46	126.04
	500.00	109.99	131.70

(Table continued on p. 122)

TABLE 1 (*continued*)

Thermodynamic function	*Temp. (K)*	*c*-$C_4ClF_5H_3$	*c*-$C_4Cl_4F_4$
Entropy	550.00	114.40	136.99
$S°$ (e.u.)	600.00	118.40	141.96
	650.00	122.32	146.63
	700.00	126.06	151.03
	750.00	129.64	155.19
	800.00	133.06	159.13
	850.00	136.34	162.87
	900.00	139.49	166.43
	950.00	142.52	169.82
	1000.00	145.43	173.06
Free energy function	273.15	69.27	76.72
$-(F°-H°_0)/T$	298.15	70.92	79.02
(cal mol^{-1} K^{-1})	350.00	74.20	83.58
	400.00	77.20	87.72
	450.00	80.08	91.65
	500.00	82.85	95.37
	550.00	85.51	98.92
	600.00	88.08	102.30
	650.00	90.57	105.53
	700.00	92.97	108.63
	750.00	95.30	111.59
	800.00	97.55	114.44
	850.00	99.74	117.18
	900.00	101.86	119.82
	950.00	103.92	122.36
	1000.00	105.92	124.82
Enthalpy function	273.15	18.31	25.58
$(H°-H°_0)/T$	298.15	19.38	27.06
(cal mol^{-1} K^{-1})	350.00	21.53	29.84
	400.00	23.52	32.24
	450.00	25.38	34.39
	500.00	27.14	36.33
	550.00	28.79	38.07
	600.00	30.32	39.66
	650.00	31.75	41.10
	700.00	33.09	42.40
	750.00	34.34	43.60
	800.00	35.51	44.69
	850.00	36.60	45.69
	900.00	37.63	46.61
	950.00	38.60	47.46
	1000.00	39.51	48.24

The presented results (Table 1) were fitted[4] to eqn (1):

$$A = a + bT + cT^2 \qquad (1)$$

where A is the thermodynamic function at the temperature (K). The constants, a, b, and c (eqn (1)) were obtained using least squares curve fitting methods[4] and are given

in Table 2. Finally, Table 3 presents the values of the molecular parameters used in the presented thermodynamic function calculations.

TABLE 2

CALCULATED CONSTANTS a, b AND c IN EQN (I)

Function	a	$b \times 10^2$	$c \times 10^5$	*Standard error*[a]
c-C_4 Cl F_4 H_3				
C_p°	7.4713	9.1100	−4.3660	0.3768
$-(F^\circ - H_0^\circ)/T$	50.9801	7.2300	−1.7530	0.0867
S°	56.3258	12.5200	−3.6330	0.1478
$(H^\circ - H_0^\circ)/T$	5.3457	5.2800	−1.8810	0.0650
c-C_4 Cl_4 F_4				
C_p°	21.8619	8.3600	−4.4520	0.5280
$-(F - H_0^\circ)/T$	51.0141	10.3200	−2.9690	0.1631
S°	60.8434	17.0300	−5.8670	0.3899
$(H^\circ - H_0^\circ)/T$	9.8293	6.7000	−2.8970	0.2268

[a] Standard error is the number S where:

$$S = \sum_{i=1}^{n} (Y_i - \hat{Y}_i)^2 / n - m - l;$$

such that n is the number of observations, m is the number of independent variables, Y_i is the calculated value of Y (Table 1); and $\hat{Y}_i$ is the value of extrapolated value of Y (Eqn (1)).

TABLE 3

SUMMARY OF DATA

c-$C_4ClF_4H_3$	c-$C_4Cl_4F_4$
Fundamental frequencies (cm^{-1})[a]	
3038, 3013, 2983, 1423, 1351, 1300, 1271, 1213, 1180, 1125, 1035, 1020, 947, 898, 785, 738, 655, 618, 510, 485, 443, 336, 274, 225, 225, 211, 186, 102, 1223, 485.	1195, 948, 814, 600, 517, 400, 290, 248, 190, 1245, 848, 331, 230, 211, 143, 94, 1255, 851, 355, 248, 220, 166, 1362, 895, 831, 735, 580, 355, 290, 190.
Principal moments of inertia, I_A, I_B and I_C, g-$cm^2 \times 10^{39}$[b]	
$I_A = 44.11$; $I_B = 100.22$; $I_C = 111.04$	$I_A = 137.44$; $I_B = 145.11$; $I_C = 155.57$
Molecular symmetry number	
1	1

[a] All frequencies from ref. 1. [b] Moments of inertia values calculated, this work, using structural data of ref. 5.

DISCUSSION

1,1,2,2-Tetrachloro-3,3,4,4-tetrafluorocyclobutane

The thermodynamic functions of 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane (Table 1) were calculated using the fundamental vibration frequency assign-

ments as given by Harris and Yang[1]. These authors also presented evidence that the c–$C_4Cl_2F_4$ structure may be apparently planar since only indirect evidence for a 94 cm^{-1} ring-puckering band could be found for this substance. In view of this, the presented thermodynamic functions (Table 1) were calculated assuming that the c–$C_4Cl_2F_4$ molecule has a planar structure.

1-Chloro-2,2,3,3-tetrafluorocyclobutane

The thermodynamic functions for 1-chloro-2,2,3,3-tetrafluorocyclobutane (Table 1) were calculated using the fundamental frequency values as assigned by Harris and Yang[1]. These authors also found an interesting although weak, ring-puckering mode of c–$C_4ClF_4H_3$ centered at 102 cm^{-1} in the infrared spectrum of the molecule. However, lacking other corroborative structural evidence of the puckered c–$C_4ClF_4H_3$ structure; as well as noting the relative weakness of this observed puckering-band; the ring-puckering effect was neglected and the thermodynamic functions were calculated assuming planar c–$C_4ClF_4H_3$ molecular structure.

Accuracy

Literature search did not reveal any availability of experimental data; hence it is not possible to compare the calculated thermodynamic function values with experimental results. An indirect estimate, however, may be obtained if we consider the overall accuracy of the used structural and spectroscopic data (Table 3). If, additionally in our error estimate we include the neglected possible isomer existence for c–$C_4ClF_4H_3$ molecule[1]; as well as the assumed molecular skeleton planarity for both compounds; it is still felt that the presented results will be within 1–2% error estimate limit.

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