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Note

Thermodynamic functions for 1,1,2,2-tetrafluorocyclobutane and perfluorocyclopentene

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The recent availability[1–3] of the needed spectroscopic and structural data for 1,1,2,2-tetrafluorocyclobutane and perfluorocyclopentene 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 compounds[4]. The functions for each given compound were calculated by means of the well-known statistical mechanical methods.

The results presented in Table 1 were fitted[5] to eqn (1):

$$A = a + bT + cT^2 \tag{1}$$

where A is the thermodynamic function at temperature T (K). The constants a, b and c

TABLE 1
HEAT CAPACITY, ENTROPY, FREE ENERGY AND ENTHALPY FUNCTION

Thermodynamic function	*Temp. (K)*	*1,1,2,2-Tetra fluorocyclobutane*	*Perfluorocyclopentene*
Heat capacity C_p° (cal mol^{-1} K^{-1})	273.15	24.55	36.21
	298.15	26.46	38.50
	350.00	30.21	42.76
	400.00	33.50	46.31
	450.00	36.45	49.38
	500.00	39.04	52.02
	550.00	41.34	54.30
	600.00	43.37	56.25
	650.00	45.15	57.94
	700.00	46.74	59.39
	750.00	48.17	60.64
	800.00	49.44	61.73
	850.00	50.59	62.68
	900.00	51.64	63.51
	950.00	52.58	64.24
	1000.00	53.45	64.88

(*Table continued on p. 85*)

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TABLE 1 (continued)

Thermodynamic function	*Temp. (K)*	*1,1,2,2-Tetra fluorocyclobutane*	*Perfluorocyclopentene*
Entropy S° (e.u.)	273.15	80.55	94.17
	298.15	82.92	97.58
	350.00	87.73	104.4
	400.00	92.20	110.5
	450.00	96.51	116.4
	500.00	100.7	121.9
	550.00	104.7	127.1
	600.00	108.5	132.1
	650.00	112.2	136.8
	700.00	115.7	141.2
	750.00	119.1	145.5
	800.00	122.3	149.5
	850.00	125.5	153.4
	900.00	128.5	157.1
	950.00	131.4	160.7
	1000.00	134.2	164.1
Free energy function, $-(F^\circ - H_0^\circ)/T$ (cal mol^{-1} K^{-1})	273.15	64.72	72.54
	298.15	66.15	74.50
	350.00	68.99	78.42
	400.00	71.61	82.05
	450.00	74.14	85.55
	500.00	76.59	88.90
	550.00	78.96	92.14
	600.00	81.26	95.26
	650.00	83.50	98.28
	700.00	85.67	101.2
	750.00	87.79	104.0
	800.00	89.85	106.7
	850.00	91.85	109.4
	900.00	93.80	111.9
	950.00	95.70	114.4
	1000.00	97.56	116.8
Enthalpy function $(H^\circ - H_0^\circ)/T$ (cal mol^{-1} K^{-1})	273.15	15.83	21.63
	298.15	16.77	23.08
	350.00	18.75	25.94
	400.00	20.59	28.48
	450.00	22.37	30.81
	500.00	24.04	32.98
	550.00	25.70	34.96
	600.00	27.23	36.80
	650.00	28.66	38.48
	700.00	30.02	40.04
	750.00	31.29	41.49
	800.00	32.49	42.82
	850.00	33.62	44.07
	900.00	34.69	45.21
	950.00	35.69	46.28
	1000.00	36.64	47.28

TABLE 2

CALCULATED CONSTANTS *a*, *b* AND *c* IN EQN (1)

Function	*a*	$b \times 10^2$	$c \times 10^5$	*Standard error*[a]
1,1,2,2-Tetrafluorocyclobutane				
C_p°	2.658	9.38	−4.358	±0.337
$-(F^\circ - H_0^\circ)/T$	48.924	6.19	−1.335	±0.059
S°	52.662	11.05	−2.900	±0.067
$(H^\circ - H_0^\circ)/T$	3.698	4.85	−1.565	±0.030
Perfluorocyclopentene				
C_p°	12.406	10.48	−5.305	±0.50
$-(F^\circ - H_0^\circ)/T$	50.307	8.77	−2.138	±0.08
S°	55.254	15.71	−4.870	±0.23
$(H^\circ - H_0^\circ)/T$	4.947	6.94	−2.730	±0.15

[a] Standard error of Y is the number S, where:

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

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 Y_i is the value of extrapolated value of Y (eqn (1)).

TABLE 3

SUMMARY OF DATA

1,1,2,2-Tetrafluorocyclobutane	*Perfluorocyclopentene*
Fundamental frequencies (cm^{-1})	
2981[a], 2981, 1454, 1220, 1220, 1181 1122, 912, 905, 733, 606, 511, 465, 322 264, 90, 3039, 2984, 1425, 1352, 1300, 1240, 1055, 998, 947, 667, 606, 420, 360, 200.	3070[b], 2995, 2857, 1617, 1473, 1448, 1302, 1109, 962, 933, 896, 2926, 1130, 1099, 803, 609, 387, 3062, 2914, 1445, 1349, 1275, 1203, 1043, 905, 695, 2933, 2857, 1025, 876, 775, 603, 127.
Principal moments of inertia, I_A, I_B *and* I_C, $g^3\ cm^6 \times 10^{117}$	
$I_A{}^c = 32.6$; $I_B = 41.6$; $I_C = 43.7$	$I_A{}^d = 84.9$; $I_B = 98.8$; $I_C = 138.1$
Molecular symmetry number	
1	1
Molecular weight	
128.07	212.03

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[a] All frequencies from Durig and Harris[1]. [b] All frequencies from Harris and Longshore[2]. [c] Moments of intertia values taken from Durig and Harris[1]. [d] Moments of inertia values calculated, this work, using structural data as given by Chang and Bauer[3].

(eqn (1)) were obtained using least squares curve fitting methods[5] and are found in Table 2. On the other hand, Table 3 presents the values of the molecular parameters used in thermodynamic function calculations.

DISCUSSION

1,1,2,2-Tetrafluorocyclobutane

The thermodynamic functions of 1,1,2,2-tetrafluorocyclobutane (Table 1) were calculated using the fundamental vibration frequency assignments and the structural data as given by During and Harris[1]. These authors presented evidence that 1,1,2,2-tetrafluorocyclobutane exists as a puckered small ring structure with C_2 symmetry and an estimated barrier to planarity of 140 ± 50 cm^{-1} as evidenced by the fundamental ring-puckering mode of 90 cm^{-1}; i.e. $2 \leftarrow 1$ transition of 90 ± 10 cm^{-1} in 1,1,2,2-tetrafluorocyclobutane is consistent[1] with an inversion barrier of 140 ± 50 cm^{-1}.

In order to calculate the presented thermodynamic functions (Table 1); the used moment of inertia values[1] did include the non-planarity of the molecule; while the anharmonic ring-puckering behavior was approximated to classical harmonic oscillator mode (Table 3). Introducing this approximation, the thermodynamic function values (Table 1) then were calculated by means of the classical statistical mechanical methods.

Perfluorocyclopentene

The thermodynamic functions for perfluorocyclopentene (Table 1) were calculated using the fundamental frequency values as assigned by Harris and Longshore[2]. In accordance with Harris and Longshore's suggestions[2], stating that the symmetrical shape of the ring-puckering fundamental band of 100 cm^{-1} indicates that this vibration may be essentially harmonic in nature and that therefore the ring skeleton is planar; in this calculation we assumed (even if gas phase electron diffraction studies by Chang and Bauer[3] indicate that the five-member carbon ring is somewhat non-planar) that indeed the perfluorocyclopentene ring puckering may be negligible.

The movement of inertia values for perfluorocyclopentene were established using the molecular structural data obtained by Chang and Bauer[3] (Table 3).

Accuracy

Since there was not available experimental evidence; it is not possible to compare the calculated thermodynamic function values with the experimental data. However, an indirect estimate of the presented thermodynamic function (Table 1) accuracy may be obtained if we recall that the used structural and spectroscopic data (Table 3) are highly accurate. Even if the introduced ring planarity assumptions and the neglected pseudo-rotation may be caused for some uncertainty in the calculated thermodynamic function values, it is still felt that the presented results will be within the experimental accuracy limit.

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