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Note

Ideal gas state thermodynamic functions for 2-chloro- and 2-bromo-3-fluoro-isopropenes

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The recent availability of molecular structural and spectroscopic data[1–3] has made it possible to estimate the thermodynamic functions, C_p°, S°, $(H^\circ - H_0^\circ)/T$ and $-(F^\circ - H_0^\circ)/T$, for the isomeric (*gauche*- and *cis*-isomers) equilibrium mixtures of 2-chloro-3-fluoro- and 2-bromo-3-fluoroisopropenes in the ideal gas state at 1 atm pressure. This work is a continuation of the ideal gas state thermodynamic function calculation for halogenated propenes[4]. Table 1 presents the calculated thermodynamic functions obtained by means of statistical mechanical calculations using the harmonic oscillator approximation while at the same time treating the internal rotational contribution by means of the Lielmezs–Bondi method[5–6]. The results presented in Table 1 are correlated 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 (eqn (1)) were obtained using the linear least squares curve fitting methods[7] and are

TABLE 1

HEAT CAPACITY, ENTROPY, FREE ENERGY AND ENTHALPY FUNCTION

Thermodynamic function	*Temp. (K)*	*Isomeric mixture of*	
		cis- and gauche-2-chloro-3-fluoroisopropene	*cis- and gauche-2-bromo-3-fluoroisopropene*
Heat capacity, C_p° (cal mol^{-1} K^{-1})	298.15	20.92	21.41
	400.00	25.22	25.43
	500.00	28.69	28.81
	600.00	31.51	31.61
	700.00	33.84	33.93
	800.00	35.78	35.88
	900.00	37.43	37.53
	1000.00	38.84	38.94

(*Table continued on p. 425*)

TABLE 1 (*continued*)

Thermodynamic function	*Temp. (K)*	*Isomeric mixture of*	
		cis- and gauche-2-chloro-3-fluoroisopropene	*cis- and gauche-2-bromo-3-fluoroisopropene*
Entropy S° (e.u.)	298.15	75.41	78.94
	400.00	82.19	85.79
	500.00	88.23	91.83
	600.00	93.74	97.33
	700.00	98.79	102.38
	800.00	103.46	107.05
	900.00	107.78	111.37
	1000.00	111.81	115.40
Free energy function, $-(F^\circ-H_0^\circ)/T$ (cal mol^{-1} K^{-1})	298.15	61.74	64.69
	400.00	66.10	69.20
	500.00	69.93	73.13
	600.00	73.45	76.13
	700.00	76.71	80.03
	800.00	79.77	83.12
	900.00	82.64	86.02
	1000.00	85.36	88.76
Enthalpy function, $(H^\circ-H_0^\circ)/T$ (cal mol^{-1} K^{-1})	298.15	13.67	14.28
	400.00	16.09	16.59
	500.00	18.30	18.70
	600.00	20.29	20.61
	700.00	22.08	22.35
	800.00	23.69	23.95
	900.00	25.14	25.35
	1000.00	26.45	26.64

TABLE 2

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

Function	*a*	*b*	*c* × *10*^{5}	*Standard error*[a]
Isomeric mixture of *cis*- and *gauche*-2-chloro-3-fluoroisopropene				
C_p°	6.8023	5.49	−2.303	0.1999
$(H^\circ-H_0^\circ)/T$	5.5313	3.01	−9.186	0.0244
$-(F^\circ-H_0^\circ)/T$	48.1748	4.96	−1.246	0.0965
S°	53.7061	7.96	−2.164	0.1167
Isomeric mixture of *cis*- and *gauche*-2-bromo-3-fluoroisopropene				
C_p°	7.8443	5.23	−2.135	0.1450
$(H^\circ-H_0^\circ)/T$	6.5008	2.86	−8.463	0.0221
$-(F^\circ-H_0^\circ)/T$	50.6673	5.14	−1.344	0.1113
S°	57.1681	8.00	−2.191	0.1326

[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 ith 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

cis-2-Chloro-3-fluoro-isopropene	*gauche-2-Chloro-3-fluoro-isopropene*	*cis-2-Bromo-3-fluoro-isopropene*	*gauche-2-Bromo-3-fluoro-isopropene*
Fundamental frequencies (cm^{-1})			
3119[a], 3039, 2995	3119[a], 3066, 3015	3113[a], 3042, 2970	3113[a], 3051, 2993
2956, 1660, 1464	2974, 1635, 1464	2935, 1649, 1465	2950, 1636, 1465
1425, 1371, 1252	1395, 1371, 1252	1409, 1363, 1244	1386, 1363, 1244
1175, 1155, 1050	1194, 1077, 1050	1145, 1108, 1054	1186, 1108, 1045
1006, 905, 896	1006, 935, 804	1045, 909, 900	1002, 934, 767
735, 472, 442	655, 587, 390	675, 389, 365	580, 547, 344
380, 249, 119	380, 225, 119	318, 223, 113	318, 203, 113
Product of principal moments of inertia[b], $I_A I_B I_C$, $g^3\ cm^6 \times 10^{117}$			
$I_A I_B I_C = 15214.4$	$I_A I_B I_C = 16677.4$	$I_A I_B I_C = 50576.3$	$I_A I_B I_C = 40299.1$
Isomerization energy[c], ΔE_{iso} (cal mol^{-1})			
1426.6	—	1733.2	—
Symmetry number:			
1	1	1	1
Molecular weight			
138.97	—	94.52	—

[a] All frequencies obtained from ref. 2. [b] All moments of inertia calculated using bond lengths from ref. 1, assuming that bond angles are either tetrahedral or 120°; and dihedral angles of 30° for *cis* and 120° for *gauche* molecules (compare with ref. 2). [c] Isomerization energy calculated from mass equilibrium data, see ref. 3.

found in Table 2. The values of the molecular parameters used for the calculation of the presented thermodynamic functions are given in Table 3.

Although there are no available experimental data, the overall reliability of the frequency assignments[1–3] suggests that the error should be within the limits of the experimental accuracy.

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