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THERMODYNAMIC FUNCTIONS FOR THREE 1-HALO-2-FLUOROETHANES

G. M. Mussally, H. Aleman and J. Lielmezs
Chemical Engineering Department, The University of British Columbia, Vancouver 8, B. C. (Canada)

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ABSTRACT

Thermodynamic functions C_p°, S°, $(H^\circ - H_0^\circ)/T$, $-(F^\circ - H_0^\circ)/T$ have been calculated* for three asymmetric 1-halo-2-fluoroethanes (1-chloro-2-fluoroethane, 1-bromo-2-fluoroethane, 1-iodo-2-fluoroethane) in the ideal gas state from 298.15 to 1000°K at 1 atm pressure. The restricted internal rotational contribution for all these compounds has been treated by the Lielmezs–Bondi approximate method.

Thermodynamic functions for three 1-halo-2-fluoroethanes

Recently published spectrographic and molecular data[1,2] have made it possible to estimate thermodynamic functions, C_p°, S°, $(H^\circ - H_0^\circ)/T$ and $-(F^\circ - H_0^\circ)/T$, for the equilibrium mixture of trans and gauche form isomers for three asymmetric 1-halo-2-fluoroethanes (1-chloro-2-fluoroethane, 1-bromo-2-fluoroethane, 1-iodo-2-fluoroethane) in the ideal gas state at 1 atm pressure. The functions for each given compound were calculated by statistical-mechanical methods, treating the internal rotational barrier contribution by the Lielmezs–Bondi method[3,4]. The results presented in Table I are fitted to Eqn. 1:

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

where A is the thermodynamic function and T is the temperature (°K). The constants a, b and c (Eqn. 1) were calculated using the least squares curve-fitting method[5] and are given in Table II. Table II also lists the maximum deviation between the values listed in Table I and the corresponding values determined through the use of Eqn. 1. Table III gives the values of the molecular parameters used in 1-halo-2-fluoroethane thermodynamic function calculations. The molecular structures of the trans and gauche isomers of 1-chloro-2-fluoroethane, 1-bromo-2-fluoroethane and 1-iodo-2-fluoroethane were estimated (Table III) using structural data (bond lengths and angles) of compounds of similar configuration[6–8]. While the bond lengths were estimated with sufficient accuracy, the bond angles could only be crudely approximated.

However, it should be noted that generally the possible relatively large percentage changes in values of the moment of inertia product have little effect on the calculated thermodynamic property values. Consequently, although there are no

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*For nomenclature see p. 000.

TABLE I

HEAT CAPACITY, ENTROPY, FREE ENERGY AND ENTHALPY FUNCTIONS

Temperature (°K)	*$ClCH_2CH_2F$*	*$BrCH_2CH_2F$*	*ICH_2CH_2F*
C_p° *(cal/g-mole/°K)*			
298.15	16.21	16.65	17.18
400.00	19.93	20.29	20.69
500.00	23.24	23.53	23.84
600.00	26.03	26.27	26.51
700.00	28.35	28.54	28.73
800.00	30.30	30.45	30.61
900.00	31.94	32.07	32.20
1000.00	33.34	33.45	33.55
S° *(E. U.)*			
298.15	72.56	75.36	77.29
400.00	77.84	80.76	82.82
500.00	82.65	85.64	87.77
600.00	87.14	90.17	92.36
700.00	91.33	94.40	96.61
800.00	95.25	98.34	100.58
900.00	98.91	102.02	104.27
1000.00	102.35	105.47	107.74
$-(F^\circ - H_0^\circ)/T$ *(cal/g-mole/°K)*			
298.15	60.60	62.94	64.38
400.00	64.33	66.80	68.39
500.00	67.52	70.08	71.77
600.00	70.42	73.06	74.83
700.00	73.11	75.81	77.64
800.00	75.63	78.38	80.26
900.00	78.02	80.81	82.73
1000.00	80.28	83.10	85.06
$(H^\circ - H_0^\circ)/T$ *(cal/g-mole/°K)*			
298.15	11.96	12.42	12.91
400.00	13.51	13.96	14.43
500.00	15.13	15.56	16.00
600.00	16.72	17.11	17.53
700.00	18.22	18.59	18.97
800.00	19.62	19.96	20.32
900.00	20.89	21.21	21.54
1000.00	22.07	22.37	22.68

available experimental data, the overall relative insensitivity of the calculated thermodynamic functions, in terms of deviation in the used molecular data values (Table III), suggests that the possible maximum error should be within the range of the measurement error.

TABLE II

CALCULATED CONSTANTS *a*, *b*, AND *c* IN EQN. 1

Function	*1-Chloro-2-fluoroethane*				*1-Bromo-2-fluoroethane*				*1-Iodo-2-fluoroethane*			
	a	*b*	*c* × *10*^{4}	[a]*Standard error*	*a*	*b*	*c* × *10*^{4}	[a]*Standard error*	*a*	*b*	*c* × *10*^{4}	[a]*Standard error*
C_p°	3.1335	0.0499	−0.1983	0.0909	3.8646	0.0488	−0.1932	0.0907	4.7978	0.0472	−0.1850	0.0798
$(H^\circ - H_0^\circ)/T$	6.4511	0.0193	−0.0364	0.0681	6.9874	0.0191	−0.0365	0.0614	7.5595	0.0188	−0.0365	0.0583
$-(F^\circ - H_0^\circ)/T$	49.2372	0.0418	−0.1080	0.1144	51.1676	0.0434	−0.1154	0.1213	52.1660	0.0452	−0.1236	0.1343
S°	55.6883	0.0611	−0.1444	0.0478	58.1550	0.0624	−0.1519	0.0610	59.7255	0.0640	−0.1602	0.0774

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[a] Standard error of Y is the number, *s*. $s = \sqrt{\sum_{i=1}^{n} (Y_i - \hat{Y}_i)^2 / n - m - 1}$ where *n* is the number of the observations, *m* is the number of independent variables, Y_i is the i^{th} calculated value of Y (Table I), and $\hat{Y}_i$ is the i^{th} extrapolated value of Y (Eqn. 1).

TABLE III

MOLECULAR PARAMETERS FOR 1-HALO-2-FLUOROETHANES

1-Chloro-2-fluoroethane	*1-Bromo-2-fluoroethane*	*1-Iodo-2-fluoroethane*
Fundamental frequencies[a], *ν (cm^{-1})*		
Gauche form		
142, 290, 464, 685, 845, 963, 1040, 1073, 1197, 1257, 1305, 1390, 1429, 1459, 2894, 2915, 2918, 2978	126, 264, 451, 588, 821, 952, 1035, 1073, 1183, 1238, 1284, 2898, 1383, 1429, 1457, 2898, 2951, 2978	116, 244, 431, 526, 794, 940, 1018, 1063, 1175, 1206, 1272, 1396, 1426, 1467, 2901, 2901, 2948, 2992
Trans form		
142, 262, 383, 777, 845, 1040, 1073, 1092, 1197, 1232, 1305, 1390, 1445, 1469, 2894, 2915, 2918, 2978	126, 226, 338, 695, 821, 1035, 1073, 1094, 1183, 1223, 1284, 1383, 1457, 1458, 2898, 2898, 2951, 2978	116, 204, 313, 640, 794, 1018, 1089, 1063, 1175, 1206, 1272, 1362, 1452, 1480, 2901, 2901, 2940, 2992
Product of the principal moments of inertia, $I_A \cdot I_B \cdot I_C = I_{ABC}$ (g^3 cm^6)		
Gauche form		
4429×10^{-117}	10716×10^{-117}	18753×10^{-117}
Trans form		
3671×10^{-117}	8584×10^{-117}	14376×10^{-117}
Symmetry number, σ		
1	1	1
Rotational isomerization energy[b], *ΔE_{iso} (cal/g-mole)*		
200	300	500
Molecular weight		
82.509	126.968	173.962
Physical constants		
Ref. 9	Ref. 9	Ref. 9

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[a] All frequencies except an unknown (CH_2) stretching frequency (assigned by comparison from a similar known CH_2 stretching frequency of 2915 cm^{-1}) are from Bermani and Jonathan (Ref. 1).
[b] The isomerization energies used (ΔE_{iso}), were selected from the suggested range of ΔE_{iso} values (Ref. 1).

NOMENCLATURE

a, b, c	constants
C_p°	ideal gas heat capacity at constant pressure (cal/mole/°K)
ΔE_{iso}	isomerization energy (cal/mole)
$-(F^\circ - H_0^\circ)/T$	ideal gas free energy function (cal/mole/°K)
$(H^\circ - H_0^\circ)/T$	ideal gas enthalpy function (cal/mole/°K)
I_{ABC}	moment of inertia product (g^{3}cm^6)
I_A, I_B, I_C	principal moments of inertia (g cm^2)
M	molecular weight
S°	ideal gas entropy (E. U.)
T	absolute temperature (°K)
A	any of the thermodynamic functions (cal/mole/°K)

ν	wave number (cm^{-1})
σ	molecular symmetry number

Superscripts: $^\circ$ refers to the ideal gas state.
Subscripts: p refers to pressure.

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