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IDEAL GAS STATE THERMODYNAMIC FUNCTIONS FOR A SERIES OF HALOGENATED PROPENES

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ABSTRACT

The thermodynamic functions, C_p°, S°, $-(F_0^\circ - H^\circ)/T$ and $(H^\circ - H_0^\circ)/T$ have been calculated in the ideal gas state at one atmosphere for the following halogenated propenes: *cis*-1-chloropropene; *trans*-1-chloropropene; *cis*-1-bromopropene; *trans*-1-bromopropene; 2-fluoropropene; 2-chloropropene; 2-bromopropene; 2-iodopropene; *cis*-3-fluoropropene; gauche-3-fluoropropene; isomeric-3-fluoropropene mixture; *cis*-3-chloropropene; gauche-3-chloropropene; isomeric-2-chloropropene mixture; *cis*-3-bromopropene; gauche-3-bromopropene; isomeric-3-bromopropene mixture; *cis*-3-iodopropene; gauche-3-iodopropene and isomeric-3-iodopropene mixture. The agreement with other results, whenever available, is very good.

INTRODUCTION

The available spectroscopic and structural data for a series of halogenated propenes have made it possible to calculate the thermodynamic properties—heat capacity, entropy, enthalpy and free energy function for *cis*-1-chloropropene; *trans*-1-chloropropene; *cis*-1-bromopropene; *trans*-1-bromopropene; 2-fluoropropene; 2-chloropropene; 2-bromopropene; 2-iodopropene; *cis*-3-fluoropropene; gauche-3-fluoropropene; *cis*- and gauche-3-fluoropropene equilibrium mixture; *cis*-3-chloropropene; gauche-3-chloropropene; *cis*- and gauche-3-chloropropene equilibrium mixture; *cis*-3-bromopropene; gauche-3-bromopropene; *cis*- and gauche-3-bromopropene equilibrium mixture; *cis*-3-iodopropene; gauche-3-iodopropene; *cis*- and gauche -3-iodopropene equilibrium mixture. The presented thermodynamic functions (Table 1) were calculated by means of the well-known statistical–mechanical methods. The internal rotational barrier contribution was treated by means of the Pitzer–Gwinn or Lielmezs–Bondi[2,3] method depending on the availability of the experimental data. The presented results (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 linear least squares curve fitting methods[4] and are

TABLE 1

HEAT CAPACITY, ENTROPY, FREE ENERGY AND ENTHALPY FUNCTION

Thermodynamic function	*Temperature (K)*	*cis-1-Chloropropene*	*trans-1-Chloropropene*	*cis-1-Bromopropene*	*trans-1-Bromopropene*	*2-Fluoropropene*	*2-Chloropropene*	*2-Bromopropene*	*2-Iodopropene*	*cis-3-Fluoropropene*	*gauche-3-Fluoropropene*	*Isomeric mixture of cis- and gauche-3-fluoropropenes*
Heat capacity C_p° (cal mol^{-1} K^{-1})	298.15	16.19	17.24	16.42	17.94	18.27	18.74	19.23	19.40	16.76	16.80	16.80
	400.00	20.60	21.37	20.84	21.99	22.30	22.82	23.19	23.30	21.15	21.12	21.11
	500.00	24.40	24.97	24.60	25.47	25.69	26.22	26.49	26.55	25.00	24.96	24.94
	600.00	27.57	28.01	27.74	28.40	28.54	28.99	29.23	29.28	28.23	28.20	28.17
	700.00	30.22	30.56	30.35	30.88	30.95	31.35	31.55	31.60	30.93	30.90	20.88
	800.00	32.45	32.73	32.56	32.99	33.01	33.37	33.53	33.58	33.21	33.19	33.16
	900.00	34.36	34.59	34.45	34.80	34.79	35.11	35.25	35.29	35.15	35.14	35.11
	1000.00	35.99	36.19	36.07	36.36	36.34	36.62	36.74	36.78	38.81	36.80	36.78
Entropy, S° (e.u.)	298.15	70.22	69.74	72.79	72.55	68.79	70.84	73.71	75.59	67.92	69.10	70.88
	400.00	75.60	75.39	78.24	78.39	74.73	76.93	79.93	81.85	73.46	74.65	76.46
	500.00	80.62	80.55	83.31	83.68	80.08	82.39	85.47	87.41	78.60	79.79	81.62
	600.00	85.36	85.38	88.08	88.59	85.03	87.43	90.55	92.50	83.46	84.63	86.48
	700.00	89.81	89.89	92.56	93.17	89.61	92.08	95.23	97.19	88.02	89.19	91.04
	800.00	94.00	94.12	96.76	97.43	93.88	96.40	99.58	101.54	92.30	93.47	95.32
	900.00	97.93	98.09	100.70	101.42	97.87	100.43	103.63	105.60	96.33	97.49	99.35
	1000.00	101.64	101.82	104.42	105.17	101.62	104.21	107.42	109.39	100.12	101.28	103.14
Free energy function $-(F-H_0^\circ)/T$ (cal mol^{-1} K^{-1})	298.15	58.89	57.93	61.46	60.33	56.62	58.49	60.96	62.64	56.39	57.32	58.51
	400.00	62.47	61.67	65.04	64.19	60.49	62.42	65.01	66.75	60.04	61.03	62.38
	500.00	65.59	64.93	68.19	67.57	63.88	65.88	68.57	70.33	63.24	64.28	65.72
	600.00	68.50	67.95	71.11	70.67	67.00	69.06	71.81	73.61	66.21	67.27	68.78
	700.00	71.22	70.76	73.85	73.56	69.91	72.02	74.82	76.65	69.00	70.08	71.63
	800.00	73.81	73.42	76.45	76.29	72.64	74.80	77.65	79.49	71.65	72.74	74.33
	900.00	76.27	75.95	78.93	78.86	75.23	77.42	80.31	82.17	74.17	75.27	76.89
	1000.00	78.63	78.35	81.29	81.30	77.68	79.92	82.84	84.71	76.58	77.68	79.33

TABLE 1 (*continued*)

Thermodynamic function	*Temperature (K)*	*cis-1-Chloropropene*	*trans-1-Chloropropene*	*cis-1-Bromopropene*	*trans-1-Bromopropene*	*2-Fluoropropene*	*2-Chloropropene*	*2-Bromopropene*	*2-Iodopropene*	*cis-3-Fluoropropene*	*gauche-3-Fluoropropene*	*Isomeric mixture of cis- and gauche-3-fluoropropenes*
Enthalpy function $(H^\circ - H_0^\circ)/T$ (cal mol^{-1} K^{-1})	298.15	11.33	11.81	11.33	12.22	12.17	12.35	12.75	12.95	11.53	11.77	12.37
	400.00	13.13	13.72	13.20	14.20	14.24	14.51	14.92	15.10	13.42	13.62	14.09
	500.00	15.03	15.62	15.12	16.11	16.20	16.51	16.90	17.08	15.36	15.51	15.90
	600.00	16.86	17.43	16.97	17.92	18.03	18.37	18.74	18.89	17.25	17.36	17.70
	700.00	18.59	19.13	18.11	19.61	19.70	20.06	20.41	20.54	19.01	19.11	19.41
	800.00	20.19	20.70	20.31	21.14	21.24	21.60	21.93	22.05	20.65	20.73	20.99
	900.00	21.66	22.14	21.77	22.56	22.64	23.01	23.32	23.43	22.16	22.23	22.46
	1000.00	23.01	23.47	23.13	23.87	23.94	24.29	24.58	24.68	23.54	23.60	23.81

Thermodynamic function	*Temperature (K)*	*cis-3-Chloropropene*	*gauche-3-Chloropropene*	*Isomeric mixture of cis- and gauche-3-chloropropenes*	*cis-3-Bromopropene*	*gauche-3-3-Bromo propene*	*Isomeric mixture of cis- and gauche-3-bromopropenes*	*cis-3-Iodopropene*	*gauche-3-Iodopropene*	*Isomeric mixture of cis- and gauche-3-iodopropenes*
Heat capacity, C_p° (cal mol^{-1} K^{-1})	298.15	17.82	17.73	17.94	18.10	18.15	18.86	18.38	18.51	20.26
	400.00	22.21	22.09	22.18	22.44	22.47	22.80	22.74	22.80	24.08
	500.00	25.93	25.83	25.87	26.13	26.15	26.32	26.41	26.45	27.25
	600.00	29.02	28.94	28.96	29.18	29.20	29.28	29.43	29.45	29.95
	700.00	31.59	31.52	31.53	31.72	31.74	31.78	31.93	31.95	32.25
	800.00	33.76	33.70	33.70	33.87	33.88	33.89	34.05	34.06	34.25
	900.00	35.61	35.56	35.56	35.70	35.72	35.71	35.86	35.87	35.98
	1000.00	37.20	37.16	37.15	37.28	37.29	37.28	37.42	37.43	37.48

(*Continued on p. 336*)

TABLE 1 (*continued*)

Thermo-dynamic function	*Temper-ature (K)*	*cis-3-Chloro-propene*	*gauche-3-Chloro-propene*	*Isomeric mixture of cis- and gauche-3-chloro-propenes*	*cis-3-Bromo-propene*	*gauche-3-3-Bromo propene*	*Isomeric mixture of cis- and gauche-3-bromo-propenes*	*cis-3-Iodo-propene*	*gauche-3-Iodo-propene*	*Isomeric mixture of cis- and gauche-3-iodo-propenes*
Entropy, S° (e.u.)	298.15	71.43	72.43	74.15	74.22	75.20	76.57	75.67	77.01	77.15
	400.00	77.29	78.26	80.07	80.16	81.15	82.76	81.69	83.06	83.83
	500.00	82.66	83.60	85.46	85.57	86.57	88.29	87.17	88.55	89.69
	600.00	87.66	88.59	90.48	90.62	91.62	93.39	92.26	93.65	95.00
	700.00	92.34	93.25	95.15	95.31	96.31	98.12	96.99	98.38	99.87
	800.00	96.70	97.61	99.51	99.69	100.70	102.53	101.40	102.79	104.36
	900.00	100.79	101.69	103.60	103.79	104.80	106.64	105.51	106.91	108.53
	1000.00	104.62	105.52	107.44	107.63	108.64	110.50	109.38	110.77	112.44
Free energy function $-(F-H_0^\circ)/T$ (cal mol^{-1} K^{-1})	298.15	59.19	60.08	60.89	61.73	62.57	62.82	63.06	64.16	63.48
	400.00	63.06	63.98	65.03	65.68	66.55	67.12	67.05	68.21	67.83
	500.00	66.45	67.37	68.58	69.12	70.02	70.81	70.53	71.74	71.62
	600.00	69.57	70.50	71.82	79.29	73.21	74.15	73.73	74.97	75.09
	700.00	72.50	73.42	74.82	75.25	76.18	77.24	76.72	77.98	78.28
	800.00	75.25	76.18	77.63	78.03	78.97	80.13	79.53	80.81	81.27
	900.00	77.86	78.79	80.30	80.67	81.61	82.85	82.20	83.48	84.06
	1000.00	80.35	81.27	82.82	83.17	84.13	85.43	84.72	86.02	86.71
Enthalpy function $(H^\circ-H_0^\circ)/T$ (cal mol^{-1} K^{-1})	298.15	12.23	12.35	13.26	12.49	12.63	13.75	12.60	12.85	13.67
	400.00	14.22	14.28	15.04	14.48	14.60	15.64	14.64	14.85	16.00
	500.00	16.20	16.23	16.88	16.45	16.55	17.48	16.64	16.82	18.07
	600.00	18.09	18.09	18.66	18.33	18.41	19.24	18.53	18.68	19.92
	700.00	19.84	19.83	20.33	20.06	20.14	20.88	20.27	20.40	21.58
	800.00	21.45	21.44	21.88	21.66	21.73	22.40	21.86	21.98	23.09
	900.00	22.92	22.90	23.30	23.12	23.18	23.79	23.32	23.43	24.47
	1000.00	24.27	24.25	24.61	24.46	24.52	25.07	24.65	24.75	25.73

TABLE 2

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

Function	*a*	$b \times 10^2$	$c \times 10^5$	*Standard error*[a]	*Function*	*a*	$b \times 10^2$	$c \times 10^5$	*Standard error*[a]
cis-1-Chloropropene					2-Fluoropropene				
C_p°	1.0142	5.82	−2.341	0.1132	C_p°	4.7675	5.17	−2.035	0.1123
$(H^\circ - H_0^\circ)/T$	4.9099	2.25	−0.435	0.0642	$(H^\circ - H_0^\circ)/T$	5.1759	2.54	−0.660	0.0154
$-(F^\circ - H_0^\circ)/T$	47.9898	3.96	−0.905	0.0726	$-(F^\circ - H_0^\circ)/T$	44.6459	4.37	−1.076	0.0761
S°	52.8998	6.21	−1.340	0.0148	S°	49.8218	6.91	−1.736	0.0676
trans-1-Chloropropene					2-Chloropropene				
C_p°	2.9558	5.45	−2.146	0.0946	C_p°	5.2035	5.21	−2.093	0.1397
$(H^\circ - H_0^\circ)/T$	5.2272	2.34	−0.515	0.0381	$(H^\circ - H_0^\circ)/T$	5.0922	2.65	−0.731	0.0113
$-(F^\circ - H_0^\circ)/T$	46.4586	4.18	−1.001	0.0752	$-(F^\circ - H_0^\circ)/T$	46.2785	4.46	−1.101	0.0743
S°	51.6858	6.52	−1.516	0.0392	S°	51.3707	7.10	−1.832	0.0751
cis-1-Bromopropene					2-Bromopropene				
C_p°	1.3417	5.79	−2.339	0.1226	C_p°	6.0660	5.06	−2.012	0.1254
$(H^\circ - H_0^\circ)/T$	4.7477	2.33	−0.483	0.0536	$(H^\circ - H_0^\circ)/T$	5.5143	2.65	−0.744	0.0107
$-(F^\circ - H_0^\circ)/T$	50.4878	3.98	−0.910	0.0675	$-(F^\circ - H_0^\circ)/T$	48.3722	4.61	−1.171	0.0816
S_p°	55.2356	6.31	−1.392	0.0190	S°	53.8865	7.25	−1.915	0.0874
trans-1-Bromopropene					2-Iodopropene				
C_p°	4.1233	5.28	−2.076	0.0976	C_p°	6.3945	4.99	−1.968	0.1145
$(H^\circ - H_0)/T$	5.4942	2.42	−0.579	0.0245	$(H^\circ - H_\circ^\circ)/T$	5.7886	2.62	−0.735	0.0132
$-(F^\circ - H_0^\circ)/T$	48.3992	4.35	−1.074	0.0773	$-(F^\circ - H_0^\circ)/T$	49.8798	4.67	−1.203	0.0832
S°	53.8935	6.77	−1.654	0.0558	S°	55.6684	7.30	−1.938	0.0932
cis-3-Fluoropropene					*cis*-3-Chloropropene				
C_p°	1.5714	5.81	−2.296	0.1207	C_p°	2.9920	5.70	−2.299	0.1545
$(H^\circ - H_0^\circ)/T$	4.8709	2.35	−0.478	0.0685	$(H^\circ - H_0^\circ)/T$	5.3316	2.47	−0.573	0.0468
$-(F^\circ - H_0^\circ)/T$	45.2660	4.03	−0.910	0.0856	$-(F^\circ - H_0^\circ)/T$	47.3104	4.33	−1.029	0.0922
S°	50.1369	6.38	−1.388	0.0218	S°	52.6421	6.79	−1.601	0.0488
gauche-3-Fluoropropene					gauche-3-Chloropropene				
C_p°	1.7125	5.76	−2.258	0.1081	C_p°	2.8852	5.70	−2.290	0.1471
$(H^\circ - H_0^\circ)/T$	5.3534	2.26	−0.430	0.0715	$(H^\circ - H_0^\circ)/T$	5.6081	2.40	−0.531	0.0537
$-(F^\circ - H_0^\circ)/T$	45.9952	4.12	−0.956	0.0918	$-(F^\circ - H_0^\circ)/T$	48.1475	4.35	−1.045	0.0966
S°	51.3485	6.38	−1.387	0.0233	S°	53.7556	6.75	−1.576	0.0462

(*Continued on p. 338*)

TABLE 2 (*continued*)

Function	*a*	*b×10²*	*c×10⁵*	*Standard error*[a]	*Function*	*a*	*b×10²*	*c×10⁵*	*Standard error*[a]
Isomeric mixture of *cis*- and gauche-3-fluoro-propenes					Isomeric mixture of *cis*- and gauche-3-chloro-propenes				
C_p°	1.7605	5.74	−0.245	0.1080	C_p°	3.3606	5.58	−2.217	0.1276
$(H^\circ-H_0^\circ)/T$	6.2542	2.13	−0.367	0.0847	$(H^\circ-H_0^\circ)/T$	6.9865	2.21	−0.447	0.0637
$-(F^\circ-H_0^\circ)/T$	46.7562	4.30	−1.047	0.1113	$-(F^\circ-H_0^\circ)/T$	48.2511	4.64	−1.193	0.1225
S°	53.0105	6.42	−1.414	0.0297	S°	55.2376	6.85	−1.637	0.0622
cis-3-Bromopropene					*cis*-3-Iodopropene				
C_p°	3.4371	5.64	−2.272	0.1555	C_p°	3.7557	5.64	−2.289	0.1701
$(H^\circ-H_0^\circ)/T$	5.5907	2.47	−0.580	0.0444	$(H^\circ-H_0^\circ)/T$	3.5713	2.53	−0.619	0.0410
$-(F^\circ-H_0^\circ)/T$	49.6086	4.42	−1.073	0.0967	$-(F^\circ-H_0^\circ)/T$	50.8075	4.47	−1.086	0.0974
S°	55.1993	6.89	−1.653	0.0564	S°	56.3789	7.00	−1.705	0.0632
gauche-3-Bromopropene					gauche-3-Iodopropene				
C°	3.5268	5.62	−2.261	0.1513	C_p°	4.0373	5.57	−2.247	0.1613
$(H^\circ-H_0^\circ)/T$	5.8104	2.44	−0.565	0.0454	$(H^\circ-H_0^\circ)/T$	5.9420	2.48	−0.596	0.0404
$-(F^\circ-H_0^\circ)/T$	50.3409	4.46	−1.094	0.1006	$-(F^\circ-H_0^\circ)/T$	51.7051	4.55	−1.129	0.1033
S°	56.1513	6.90	−1.659	0.0575	S°	57.6471	7.03	−1.725	0.0668
Isomeric mixture of *cis*- and gauche-3-bromopropenes					Isomeric mixture of *cis*- and gauche-3-iodopropenes				
C_p°	5.1439	5.22	−2.020	0.1012	C_p°	7.7153	4.80	−1.833	0.1292
$(H^\circ-H_0^\circ)/T$	7.3122	2.30	−0.524	0.0347	$(H^\circ-H_0^\circ)/T$	6.0426	2.83	−0.862	0.0460
$-(F^\circ-H_0^\circ)/T$	49.6391	4.85	−1.282	0.1297	$-(F^\circ-H_0^\circ)/T$	49.9492	4.96	−1.296	0.1065
S°	56.9513	7.15	−1.806	0.0963	S°	55.9918	7.79	−2.158	0.1516

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

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

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 $\bar{Y}_i$ is the extrapolated value of Y (eqn (1)).

TABLE 3

SUMMARY OF USED FREQUENCIES AND STRUCTURAL DATA

cis-1-Chloropropene	*trans-1-Chloropropene*	*cis-1-Bromopropene*	*trans-1-Bromopropene*
Fundamental frequencies (cm^{-1})			
3098,[a] 3045, 2982	3073,[a] 3034, 2976	3102,[c] 3034, 2978	3078,[c] 3029,[b] 2980
2960, 2934, 1640	2960, 2934, 1649	2960, 2947, 1638	2961, 2937, 1637
1454, 1448, 1383	1456, 1446, 1380	1456, 1444, 1388	1461, 1446, 1387
1332, 1217, 1070	1296, 1247, 1105	1312, 1212, 1070	1292, 1225, 1087
1033, 937, 933	1044, 960, 930	1041, 936, 925	1041, 952, 931
797, 759, 690	876, 806, 757	765, 684, 677	743, 729, 677
564, 398, (225)	422, 270, (220)	494, 382, (194)	355, 250, (210)
Principal moments of inertia ($gcm^2 \times 10^{39}$)			
I_A = 5.9193[d]	I_A = 2.0141[d]	I_A = 6.7549[e]	I_A = 2.0555[e]
I_B = 23.1014	I_B = 34.3407	I_B = 32.1740	I_B = 49.6844
I_C = 28.5356	I_C = 35.8338	I_C = 38.4095	I_C = 51.2285
Reduced moment of inertia ($gcm^2 \times 10^{39}$)			
I_{red} = 0.4661[f]	I_{red} = 0.4696[f]	I_{red} = 0.4695[f]	I_{red} = 0.4717[f]
Internal rotational barrier height ($cal\ mol^{-1}$)			
602[g]	2170[g]	230[g]	2120[g]
Isomerization energy ($cal\ mol^{-1}$)			
—	—	—	—
Symmetry number, σ			
1	1	1	1
Molecular weight			
		120	120.99

2-Fluoropropene	*2-Chloropropene*	*2-Bromopropene*	*2-Iodopropene*
Fundamental frequencies (cm^{-1})			
3141,[h] 3059, 3012	3121,[i] 3025, 2992	3115,[j] 3010, 2987	3103,[k] 2994, 2974
2975, 2942, 1687	2973, 2940, 1645	2972, 2930, 1640	2928, 2967, 1627
1448, 1448, 1429	1450, 1450, 1412	1443, 1439, 1405	1457, 1436, 1406
1401, 1270, 1048	1382, 1184, 1046	1379, 1170, 1045	1377, 1159, 1056
1008, 944, 862	999, 926, 879	996, 925, 883	991, 926, 893
846, 629, 472	692, 641, 434	680, 551, 414	701, 514, 389
404, 352, (191)	396, 343, (196)	335, 301, (196)	318, 271, (195)
Principal moments of inertia ($gcm^2 \times 10^{39}$)			
I_A = 17.077[l]	I_A = 17.125[m]	I_A = 35.625[n]	I_A = 8.957[o]
I_B = 9.395	I_B = 8.927	I_B = 8.949	I_B = 35.850
I_C = 8.198	I_C = 25.536	I_C = 27.192	I_C = 44.291

(*Continued on p. 340*)

TABLE 3 (*continued*)

2-Fluoropropene	*2-Chloropropene*	*2-Bromopropene*	*2-Iodopropene*
Reduced moment of inertia ($\text{gcm}^2 \times 10^{39}$)			
$I_{\text{red}} = 0.553^{l}$	$I_{\text{red}} = 0.576^{m}$	$I_{\text{red}} = 0.584^{n}$	$I_{\text{red}} = 0.589^{o}$
Internal rotational barrier height (cal mol^{-1})			
2440^{p}	2671^{p}	2695^{p}	2700^{r}
Isomerization energy (cal mol^{-1})			
—	—	—	—
Symmetry number, σ			
1	1	1	1
Molecular weight			
60.07	76.53	120.99	167.98

cis-3-Fluoropropene	*gauche-3-Fluoropropene*	*cis-3-Chloropropene*	*gauche-3-Chloropropene*
Fundamental frequencies (cm^{-1})			
$3092,^{s}$ 3026, 2990	$3092,^{s}$ 3026, 2990	$3091,^{t}$ 3021, 3018	$3091,^{t}$ 3021, 3018
2990, 2957, 1652	2990, 2939, 1630	2987, 2940, 1647	2987, 2958, 1642
1468, 1413, 1383	1459, 1426, 1362	1445, 1430, 1291	1445, 1412, 1291
1289, 1240, 1107	1289, 1240, 1163	1290, 1177, 1050	1257, 1201, 1100
1027, 989, 989	989, 916, 1027	1050, 931, 923	987, 938, 933
925, 901, 601	1006, 935, 642	795, 712, 550	896, 738, 590
352, 273, (163)	432, 345, (85)	513, 253, (94)	409, 290, (56)
Principal moments of inertia ($\text{gcm}^2 \times 10^{39}$)			
$I_A = 4.835^{u}$	$I_A = 2.982^{u}$	$I_A = 19.345^{v}$	$I_A = 29.724^{v}$
$I_B = 13.917$	$I_B = 19.605$	$I_B = 6.708$	$I_B = 3.985$
$I_C = 18.223$	$I_C = 20.271$	$I_C = 25.522$	$I_C = 30.620$
Reduced moment of inertia ($\text{gcm}^2 \times 10^{39}$)			
$I_{\text{red}} = 1.194^{u}$	$I_{\text{red}} = 1.544^{u}$	$I_{\text{red}} = 1.046^{v}$	$I_{\text{red}} = 1.710^{v}$
Internal rotational barrier height (cal mol^{-1})			
—	—	—	—
Isomerization energy (cal mol^{-1})			
306^{u}	—	500^{v}	—
Symmetry number, σ			
1	1	1	1
Molecular weight			
60.07	60.07	76.53	76.53

TABLE 3 (*continued*)

cis-3-Bromopropene	*gauche-3-Bromopropene*	*cis-3-Iodopropene*	*gauche-3-Iodopropene*
Fundamental frequencies (cm^{-1})			
3088,[i] 3021, 3010 2983, 2966, 1645 1463, 1408, 1295 1249, 1154, 1042 1040, 926, 921 810, 698, 543 456, 215, (89)	3088,[i] 3021, 3010 2983, 2966, 1631 1442, 1408, 1295 1211, 1192, 1072 986, 935, 929 867, 690, 536 392, 252, (55)	3092,[s] 3016, 2984 2984, 2968, 1645 1444, 1420, 1307 1201, 1088, 1022 981, 932, 920 825, 669, 540 420, 197, (107)	3092,[t] 3016, 2984 2984, 2968, 1632 1439, 1405, 1292 1187, 1150, 1050 981, 932, 920 825, 669, 491 380, 232, (54)
Principal moments of inertia ($gcm^2 \times 10^{39}$)			
I_A = 29.524[v] I_B = 7.240 I_C = 36.233	I_A = 43.755[v] I_B = 4.417 I_C = 45.034	I_A = 7.262[s] I_B = 38.188 I_C = 49.919	I_A = 3.488[t] I_B = 60.393 I_C = 62.948
Reduced moment of inertia ($gcm^2 \times 10^{39}$)			
I_{red} = 1.113[v]	I_{red} = 1.959[v]	—	—
Internal rotational barrier height (cal mol^{-1})			
—	—	—	—
Isomerization energy (cal mol^{-1})			
850[w]	—	1600[w]	—
Symmetry number, σ			
1	1	1	1
Molecular weight			
120.99	120.99	167.89	167.89

[a] All frequency values obtained from ref. 5. [b] This is liquid state (Raman spectra) frequency; the same given reference. [c] All frequency values obtained from ref. 8. [d] Moments of inertia values calculated; this work. Structural data taken from ref. 5. [e] Moments of inertia values calculated; this work. Structural data—see ref. 8. [f] Reduced moment of inertia values calculated; this work. Structural data taken from refs. 5, 7, and 8. [g] Internal rotational barrier values taken from refs. 6 and 9. [h] All frequencies taken from ref. 11. [i] All frequencies taken from ref. 14. [j] All frequencies taken from ref. 15. [k] All frequencies taken from ref. 16. [l] Calculated, this work. Structural data from ref. 13. [m] Calculated, this work. Structural data from refs. 13 and 14. [n] Calculated, this work. Structural data from refs. 13 and 15. [o] Calculated, this work. Structural data from refs. 13 and 16. [p] See ref. 12. [r] Estimated; this work. See the appropriate discussion in the text. [s] All frequency and structural data from refs. 19 and 20. [t] All frequency and structural data from refs. 19 and 23. [u] Structural and isomerization energy data from ref. 20. [v] Structural and isomerization energy data from ref. 23. [w] Isomerization energy calculated from mass equilibrium data. See also ref. 23. [x] Calculated using estimated mass equilibrium data. See refs. 19 and 23.

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

DISCUSSION

1-Chloro- and 1-bromopropenes

The thermodynamic functions for 1-chloro- and 1-bromopropenes (Table 1) were calculated using the infrared frequency assignments of Berg and Elst[5]; the internal rotational barrier values indicated by Good et al.[6] and the available structural data as listed by Beaudet[7] for the gaseous state *cis*- and *trans*-1-chloropropenes. The infrared vibrational frequency data of Elst et al.[8] supplemented with the internal rotational barrier values as compiled by Good et al.[6] and structural data given by Beaudet[9] again for the gaseous state, were used to calculate the thermodynamic functions for *cis*- and *trans*-1-bromopropenes.

TABLE 4

COMPARISON OF S° (cal K^{-1} mol^{-1}) VALUES AT 298.15 K

Compound	*S° (cal K^{-1} mol^{-1}) at 298.15 K*		
	This work (Table 1)	*Ref. 10*	*Ref. 21*
cis-1-Fluoropropene	—	69.0	—
trans-1-Fluoropropene	—	69.0	—
cis-1-Chloropropene	70.22	71.5	—
trans-1-Chloropropene	69.74	71.5	—
cis-1-Bromopropene	72.79	74.5	—
trans-1-Bromopropene	72.55	74.5	—
cis-1-Iodopropene	—	76.7	—
trans-1-Iodopropene	—	76.7	—
cis-3-Fluoropropene	67.92	—	—
gauche-3-Fluoropropene	69.10	—	—
Isomer-3-Fluoropropene	70.88	70.6	72.35
cis-3-Chloropropene	71.43	—	—
gauche-3-Chloropropene	72.43	—	—
Isomer-3-Chloropropene	74.15	73.3	—
cis-3-Bromopropene	74.22	—	—
gauche-3-Bromopropene	75.20	—	—
Isomer-3-Bromopropene	76.57	75.8	—
cis-3-Iodopropene	75.67	—	—
gauche-3-Iodopropene	77.01	—	—
Isomer-3-iodopropene	77.15	77.9	—

If we compare (Table 4) our calculated entropy values (at 298.15 K) with those given by Alfassi et al.[10], we note that our values for both 1-chloro- and 1-bromopropenes are smaller. However, Alfassi et al.[10] present the same entropy values for both 1-halopropene isomers (*cis*- and *trans*-forms). This and the somewhat unclear use of the additivity methods to obtain their[10] presented entropy values (Table 4) mar the credibility of their results. Thus it seems preferable to use thermodynamic property values obtained directly from gaseous state spectroscopic calculations (Tables 1–3). It should be noted that the contribution to the internal restricted rotation for these 1-halopropenes was calculated by means of the Pitzer–Gwinn method[1].

In view of these considerations, the overall calculated thermodynamic function (Table 1) accuracy is estimated to be within 1–2% interval; that is within the experimental error range.

2-Halopropenes

Thermodynamic functions for 2-halopropenes (Table 1) were calculated using the following gaseous state vibrational frequency and structural data values; for 2-fluoropropene the frequency assignments made by Crowder and Smyrl[11]; the internal rotational barrier value from Benz et al.[12]; while the needed C–F distances from the compilation of Bondi and Lielmezs[13]. For the case of 2-chloropropenes, the frequency values were taken from Meyer et al.[14], while the internal rotational barrier were taken from Benz et al. [12]. For 2-bromopropene the vibrational frequency assignments made by Meyer and Guenthard[15] were used with the internal barrier value again taken from Benz et al.[12]. Finally, for 2-iodopropene the vibrational frequency assignments of Meyer et al.[16] were used while the value of internal rotational barrier was estimated from the known barriers of 2-fluoro-, 2-chloro- and 2-bromopropenes using the observation made by Lielmezs and coworkers[17,18] that the internal rotational barriers may be correlated with the corresponding substituent atom ionization potentials within the given compound series. The contribution to the internal restricted rotation for all 2-halopropenes was obtained by means of the Pitzer–Gwinn method[1].

Considering the overall reliability of the used spectroscopic and structural data, it is estimated that thermodynamic function values have 1–2% accuracy; that is, the calculated values should be within the experimental error range.

3-Halopropenes

Thermodynamic functions of the 3-halopropenes were calculated for *cis*- and *trans*-forms and the isomeric *cis*- and *trans*-form mixtures (Table 1). As there were not available sufficiently reliable internal rotational barrier values; but rather it was possible to obtain isomerization energy and torsional frequency values (Table 3) for all 3-halopropenes; the thermodynamic functions (Table 1) were then calculated by means of the Lielmezs–Bondi[2,3] method.

For 3-fluoropropenes, the vibrational frequencies were taken from McLachlan and Nyquist[19] while the isomerization energy, the structural data and the torsional frequency values were taken from Hirota[20]. Table 4 compares the calculated entropy value at 298.15 K between our work; the value obtained by Alfassi et al.[10] using the additivity method; and value estimated by Bryce and Lielmezs[21]. The agreement between this work and that of Alfassi et al.[10] is excellent. The deviation found in the work of Bryce and Lielmezs[21] is explainable noting that Bryce and Lielmezs estimated the fundamental deformation frequencies of 3-fluoropropene from a set of experimental frequency values of 3-chloro-, 3-bromo- and 3-iodopropene as given by Thompson and Torkington[22]. Even so Bryce's and Lielmezs[21] results were within their estimated 2–3% uncertainty range.

For 3-chloro, 3-bromo- and 3-iodopropenes we used vibrational frequency data, mainly in the liquid state from McLachlan and Nyquist[19] and from Sourisseau and Pasquier[23]; while the needed isomerization energies were calculated from the known isomer mass ratios[19,20,23]. All the calculated thermodynamic functions are found in Table 1; while the used spectroscopic, thermodynamic and structural data are given in Table 3. Again, Table 4 shows the comparison between our calculated entropy values for all 3-halopropenes and the values obtained by Alfassi et al.[10] using the group additivity method. The agreement for all 3-halopropenes is very good; and we estimate that our results (Table 1) will be well within the error (less than ±1%) of our experimental determination.

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