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THERMODYNAMIC FUNCTIONS FOR n-HALOGENATED HYDROCARBONS

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ABSTRACT

Thermodynamic functions $[C_p^0, S^0, (H^0 - H_0^0)/T, -(F - H_0^0)/T]$ have been calculated for n-halogenated hydrocarbons, n-$C_mH_{2m+1}X$ (X = F, Cl, Br, I) in the ideal gas state at 1 atm pressure. The functions for the three lower members (C_1—C_3) of the series were determined by the statistical mechanical means treating the restricted internal rotational contribution by the Pitzer—Gwinn method. The applicability of CH_2-group increment values as obtained from n-alkanes to determine the thermodynamic function values for higher member n-alkyl halides was examined and a linear property increment equation was proposed to extend the thermodynamic property values for n-heptyl halides and higher. The agreement between the computed results and the available experimental data was found to be excellent

INTRODUCTION

The ideal gas state thermodynamic functions $[C_p^0, S^0, (H^0 - H_0^0)/T$, and $-(F^0 - H_0^0)/T]$ have already been calculated at 1 atm pressure for lower members of the n-alkyl halide series [1—11] defined as n-$C_mH_{2m+1}X$, where X = F, Cl, Br, I. However, recent structural and spectroscopic data [6—27] have made it possible to compare and re-assess these calculations; therefore, computations were performed for each successive member in the given series, from C_1 to C_3, inclusive *. Assuming that the interaction effects of the substituent halogen atoms become negligible only when there are more than seven carbon atoms in the straight paraffin chain [2—4; 28—32], modified CH_2-group increment values (obtained from differences of halogenated compounds, C_1—C_2 and C_2—C_3) were obtained, thus permitting to extend the calculated (C_1—C_3) thermodynamic function values from C_3 to C_7. Further extension, from C_7 to the next higher members of the n-alkyl halide series, has been made possible through the linear relation [3,4]

$$\Lambda_T = K_T + \Delta_T(n - 7) \tag{1}$$

where Λ_T = any one of the thermodynamic properties, C_p^0, $(H^C - H_0^0)/T$, S^0, and $(-F^0 - H_0^0)/T$, at given temperature T (K); K_T = homologous series constant, or axial intercept; Δ_T = thermodynamic property per methylene group [3,4] for the given n-alkyl halide series; and n = number of carbon atoms

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* Because several references (Table 4) list calculation or measurements at 298.16 K (reference to the triple point of water, 273.16 K), we have also performed calculations at this temperature. Equation (2) would allow calculation to be made at 298.15 K.

TABLE 1

Extrapolation constants for n-halogenated hydrocarbons [eqn. (1)]
(all values in cal g mole^{-1} °K^{-1})

Temp. (K)	K_T					Δ_T					
	C_n	Substituent halogens				ΔC_n	Substituent halogens				
		F	Cl	Br	I		F	Cl	Br	I	H
$\Lambda_T = C_p^o$											
298.16	C_4	24.80	25.46	25.86	26.18	C_3—C_4	5.36	5.35	5.34	5.35	
	C_5	30.21	30.86	31.26	31.59	C_4—C_5	5.41	5.40	5.40	5.41	
	C_6	35.65	36.30	36.70	37.04	C_5—C_6	5.44	5.44	5.44	5.45	
	C_7	41.11	41.77	42.17	42.51	C_6—C_7	5.46	5.47	5.47	5.47	
	C_8	46.58	47.24	47.64	47.98	C_n—C_{n+1} $n \geqslant 7$	5.47	5.47	5.47	5.47	5.47
400.00	C_4	31.45	32.21	32.46	32.80	C_3—C_4	6.95	6.94	6.90	6.90	
	C_5	38.39	39.15	39.38	39.72	C_4—C_5	6.94	6.94	6.92	6.92	
	C_6	45.33	46.09	46.32	46.66	C_5—C_6	6.94	6.94	6.94	6.94	
	C_7	52.27	53.03	53.26	53.60	C_6—C_7	6.94	6.94	6.94	6.94	
	C_8	59.29	59.97	60.02	60.54	C_n—C_{n+1} $n \geqslant 7$	6.94	6.94	6.94	6.94	6.94
500.00	C_4	37.27	38.05	38.22	38.56	C_3—C_4	8.30	8.27	8.22	8.21	
	C_5	45.55	46.31	46.44	46.78	C_4—C_5	8.28	8.26	8.22	8.22	
	C_6	53.81	54.57	54.67	55.01	C_5—C_6	8.26	8.26	8.23	8.23	
	C_7	62.07	62.82	62.91	63.25	C_6—C_7	8.26	8.25	8.24	8.24	
	C_8	70.32	71.07	71.16	71.50	C_n—C_{n+1} $n \geqslant 7$	8.25	8.25	8.25	8.25	8.25
600.00	C_4	42.19	43.00	43.14	43.48	C_3—C_4	9.42	9.42	9.39	9.39	
	C_5	51.58	52.39	52.51	52.85	C_4—C_5	9.39	9.39	9.37	9.37	
	C_6	60.95	61.76	61.87	62.21	C_5—C_6	9.37	9.37	9.36	9.36	
	C_7	70.29	71.10	71.22	71.56	C_6—C_7	9.34	9.35	0.35	9.35	
	C_8	79.63	80.44	80.56	80.90	C_n—C_{n+1} $n \geqslant 7$	9.34	9.34	9.34	9.34	9.34
$\delta\Lambda_T = (H^o - H_0^o)/T$											
298.16	C_4	16.05	16.43	16.85	16.95	C_3—C_4	3.00	3.03	3.08	3.02	
	C_5	19.22	19.61	20.07	20.15	C_4—C_5	3.17	3.18	3.22	3.20	
	C_6	22.49	22.88	23.37	23.42	C_5—C_6	3.27	3.27	3.30	3.27	

	C_7	25 81	26.20	26 69	26 74	C_6—C_7	3.32	3.32	3.32	3.32	
	C_8	29 14	29.53	30 02	30 07	C_n—C_{n+1} $n \geqslant 7$	3.33	3.33	3.33	3.33	3.33
400 00	C_4	19.15	19.60	19.96	20.12	C_3—C_4	3.82	3.82	3.84	3.82	
	C_5	23.06	23.54	23 92	24.06	C_4—C_5	3.94	3.94	3.96	3.94	
	C_6	27.11	27.56	27 94	28.08	C_5—C_6	4.02	4.02	4.02	4.02	
	C_7	31.16	31 61	31.99	32.13	C_6—C_7	4.05	4.05	4.05	4.05	
	C_8	35.22	35.67	36.05	36 19	C_n—C_{n+1} $n \geqslant 7$	4.06	4.06	4.06	4.06	4.06
500.00	C_4	22 20	22.66	23.01	23.20	C_3—C_4	4.57	4.52	4.55	4.50	
	C_5	26 89	27.29	27.68	27.80	C_4—C_5	4.69	4.63	4.67	4.60	
	C_6	31.64	31.99	32 41	32.47	C_5—C_6	4.75	4.70	4.73	4.67	
	C_7	36.41	36.73	37.18	37.20	C_6—C_7	4.77	4.74	4.77	4.73	
	C_8	41.18	41.50	41.95	41.97	C_n—C_{n+1} $n \geqslant 7$	4.77	4 77	4.77	4.77	4.77
600.00	C_4	25.07	25.76	25.93	26.18	C_3—C_4	5.22	5.35	5.22	5.22	
	C_5	30.39	31.16	31.25	31.50	C_4—C_5	5 32	5 40	5.32	5.32	
	C_6	35.78	36.60	36.64	36.89	C_5—C_6	5.39	5.44	5.39	5.39	
	C_7	41.21	42.04	42 07	42.32	C_6—C_7	5.43	5.44	5.43	5.43	
	C_8	46 45	47.48	47.51	47.76	C_n—C_{n+1} $n \geqslant 7$	5.44	5.44	5.44	5.44	5.44
$\Lambda_T = S^\circ$											
298 16	C_4	83 14	85.81	88.72	90.40	C_3—C_4	9 68	9.68	9.68	9.58	
	C_5	92.66	95.33	98.24	99.88	C_4—C_5	9 52	9.52	9.52	9.44	
	C_6	102 06	104.73	107.64	109.23	C_5—C_6	9.40	9.40	9.40	9.35	
	C_7	111 37	114.04	116 95	118.54	C_6—C_7	9.31	9.31	9 31	9.31	
	C_8	120.68	123.35	126 26	127.85	C_n—C_{n+1} $n \geqslant 7$	9.31	9.31	9.31	9.31	9.31
400.00	C_4	91.48	94.21	97 23	99.08	C_3—C_4	11.48	11 43	11.48	11.43	
	C_5	102.79	105.48	108 54	110 35	C_4—C_5	11.31	11 27	11.31	11 27	
	C_6	113.99	116.67	119.74	121.54	C_5—C_6	11 20	11 19	11.20	11.19	
	C_7	125.13	127.81	130.88	132 68	C_6—C_7	11 14	11 14	11.14	11.14	
	C_8	136.25	138.93	142.00	143 80	C_n—C_{n+1} $n \geqslant 7$	11 12	11.12	11 12	11 12	11.12
500.00	C_4	99 22	102.03	105.04	106 95	C_3—C_4	13 17	13 10	13.10	13.05	
	C_5	112 19	114.96	117.97	119 85	C_4—C_5	12 97	12.93	12 93	12 90	
	C_6	125.05	127.81	130 82	132 78	C_5—C_6	12 86	12 85	12 85	12.85	
	C_7	137.87	140.63	143 64	145.52	C_6—C_7	12 82	12 82	12.82	12 82	
	C_8	150 69	153.45	156.46	158 34	C_n—C_{n+1} $n \geqslant 7$	12.82	12 82	12.82	12 82	12 82

TABLE 1 (continued)

Temp. (K)	K_T					Δ_T					
	C_n	Substituent halogens				ΔC_n	Substituent halogens				
		F	Cl	Br	I		F	Cl	Br	I	H
600.00	C_4	106.94	109.91	112.94	114.91	C_3—C_4	15.19	15.19	15.19	15 14	
	C_5	121 97	124.94	127.97	129.91	C_4—C_5	15.03	15.03	15.03	15.00	
	C_6	136.43	139.40	142.43	144.35	C_5—C_6	14.46	14.46	14.46	14.44	
	C_7	150.84	153.81	156.86	158.76	C_6—C_7	14.41	14.41	14.41	14.41	
	C_8	165.25	168.22	171.25	173.17	C_n—C_{n+1} $n \geqslant 7$	14.41	14.41	14.41	14.41	14.41
$\Lambda_T = -(F^\circ - H_0^\circ)/T$											
298.16	C_4	67.09	69.38	71.87	73.49	C_3—C_4	6.68	6.65	6.59	6.56	
	C_5	73.44	75.22	78 17	79.73	C_4—C_5	6.35	6.34	6.30	6.24	
	C_6	79.57	81.85	84.27	85.81	C_5—C_6	6.13	6.13	6.10	6.08	
	C_7	85.56	87.84	90.26	91.80	C_6—C_7	5.99	5.99	5.99	5.99	
	C_8	91.54	93.82	96.24	97.78	C_n—C_{n+1} $n \geqslant 7$	5.98	5.98	5.98	5.98	5.98
400.00	C_4	72.33	74.01	77.27	78.96	C_3—C_4	7.66	7.61	7.64	7.64	
	C_5	79.73	81.96	84.62	86.29	C_4—C_5	7.40	7.35	7.35	7.33	
	C_6	86.88	89.11	91.80	93.46	C_5—C_6	7.15	7.15	7.18	7.17	
	C_7	93.97	96.20	98.89	100.55	C_6—C_7	7.09	7.09	7.09	7.09	
	C_8	101.03	103.26	105.95	107.61	C_n—C_{n+1} $n \geqslant 7$	7.06	7.06	7.06	7.06	7.06
500.00	C_4	77.02	79.37	82.03	83.75	C_3—C_4	8.60	8.58	8.55	8.55	
	C_5	85.30	87.67	90.29	92.05	C_4—C_5	8.28	8.30	8.26	8.30	
	C_6	93.41	95.82	98.41	100.23	C_5—C_6	8.11	8.15	8.12	8.18	
	C_7	101.46	103.90	106.46	108.32	C_6—C_7	8.05	8.08	8.05	8.09	
	C_8	109.51	111.95	114.51	116.37	C_n—C_{n+1} $n \geqslant 7$	8.05	8.05	8.05	8.05	8.05
600.00	C_4	81.87	84.15	87.01	88 73	C_3—C_4	9.97	9.84	9.97	9.92	
	C_5	91.58	93.78	96.72	98.41	C_4—C_5	9.71	9.63	9.71	9.68	
	C_6	100.65	102.80	105.79	107.46	C_5—C_6	9.07	9.02	9.07	9.05	
	C_7	109.63	111 77	114.77	116.44	C_6—C_7	8.98	8.97	8.99	8.98	
	C_8	118.60	120.74	123.74	125.41	C_n—C_{n+1} $n \geqslant 7$	8.97	8.97	8.97	8.97	8.97

(per molecule) in a straight unbranched chain issuing from the functional group.

Equation (1) can be generalized for the multi-substituted *n*-alkyl halides. The constants needed for the application of eqn. (1) are given in Table 1. Several Λ_T—n relations are shown in Figs. 1 and 2. The internal rotational barrier contribution was treated by means of the Pitzer—Gwinn method [33—35].

The obtained results (calculated for C_1 and C_3, Table 2) were fitted to give a constant polynomial of the form

$$\Lambda_T^* = a + bT + cT^2 + dT^3 + eT^4 \tag{2}$$

where Λ_T^* is any thermodynamic function calculated from C_1 to C_3 at temperature T (K). The constants a, b, c, d and e [eqn. (2)] were obtained using linear least squares curve fitting methods and are found in Table 3. Comparison of computed and experimental values has been made in Table 4. As seen,

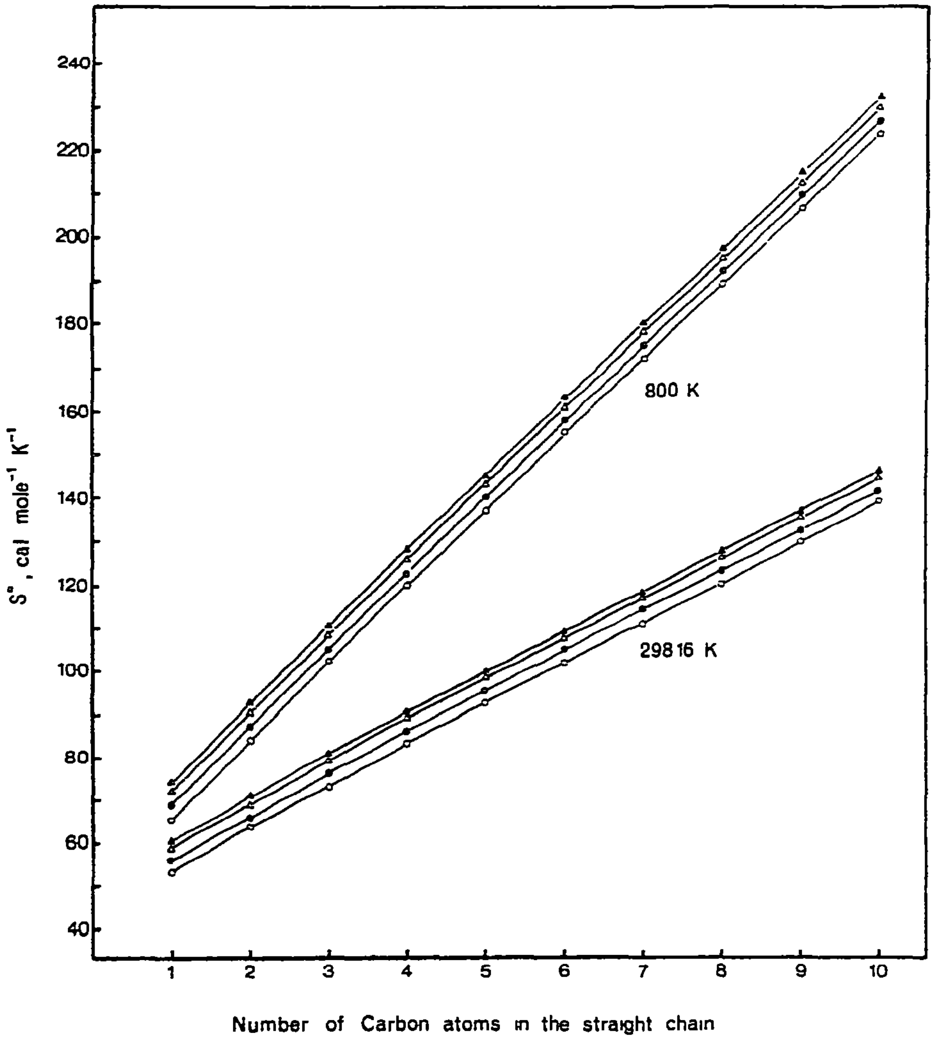

Fig. 1. Entropy of C_{1-10} *n*-alkyl halides. ○, *n*-Alkyl fluorides; ●, *n*-alkyl chlorides, △, *n*-alkyl bromides; ▲, *n*-alkyl iodides.

TABLE 2

Heat capacity, entropy, enthalpy function and free energy function for *n*-halogenated hydrocarbons, C_{1-3}

Temp (K)	*n*-Alkyl fluorides			*n*-Alkyl chlorides			*n*-Alkyl bromides			*n*-Alkyl iodides		
	Methyl	Ethyl	*n*-Propyl	Methyl	Ethyl	*n*-Propyl	Methyl	Ethyl	*n*-Propyl	Methyl	Ethyl	*n*-Propyl
C_p^o (cal g mole^{-1} K^{-1})												
298.16	8.96	14.21	19.43	9.74	14.97	20.11	10.14	15.36	20.52	10.54	15.62	20.83
300.00	8.99	14.27	19.53	9.77	15.03	20.20	10.18	15.42	20.61	10.57	15.69	20.92
350.00	9.73	16.00	22.04	10.63	16.80	22.77	11.06	17.17	23.12	11.46	17.41	23.45
400.00	10.56	17.71	24.50	11.51	18.54	25.27	11.94	18.87	25.56	12.33	19.08	25.90
450.00	11.41	19.34	26.81	12.37	20.16	27.61	12.78	20.46	27.87	13.15	20.66	28.21
500.00	12.26	20.86	28.97	13.19	21.65	29.78	13.56	21.93	30.00	13.92	22.10	30.35
550.00	13.07	22.27	30.95	13.95	23.02	31.76	14.30	23.27	31.96	14.62	23.42	32.30
600.00	13.84	23.56	32.77	14.66	24.28	33.58	14.98	24.50	33.75	15.28	24.64	34.09
650.00	14.56	24.75	34.45	15.32	25.43	35.24	15.61	25.63	35.39	15.89	25.74	35.73
700.00	15.23	25.85	36.00	15.94	26.49	36.78	16.20	26.67	36.90	16.45	26.77	37.23
750.00	15.87	26.87	37.44	16.51	27.47	38.19	16.75	27.64	38.30	16.98	27.72	38.62
800.00	16.46	27.82	38.78	17.05	28.38	39.49	17.27	28.53	39.60	17.48	28.60	39.90
850.00	17.01	28.70	40.02	17.55	29.23	40.71	17.75	29.36	40.79	17.94	29.42	41.09
900.00	17.53	29.52	41.17	18.02	30.02	41.83	18.20	30.13	41.91	18.38	30.18	42.20
950.00	18.01	30.29	42.24	18.46	30.75	42.88	18.63	30.86	42.95	18.79	30.90	43.22
1000.00	18.45	31.00	43.25	18.87	31.43	43.85	19.02	31.53	43.91	19.17	31.56	44.17
1050.00	18.87	31.66	44.18	19.26	32.07	44.76	19.39	32.16	44.81	19.53	32.18	45.06
1100.00	19.26	32.28	45.05	19.62	32.66	45.60	19.74	32.74	45.64	19.87	32.76	45.88
1150.00	19.62	32.86	45.85	19.95	33.21	46.38	20.07	33.29	46.42	20.18	33.30	46.64
1200.00	19.96	33.39	46.61	20.27	33.73	47.11	20.37	33.80	47.14	20.48	33.81	47.35
S^o (cal g mole^{-1} K^{-1})												
298.16	53.25	63.34	73.46	55.97	65.92	76.13	58.70	68.71	79.04	60.64	70.68	80.86
300.00	53.50	63.43	73.58	56.03	66.01	76.25	58.76	68.81	79.16	60.70	70.77	80.98
350.00	54.74	65.76	76.84	57.60	68.92	79.57	60.39	71.90	82.52	62.40	73.32	84.38
400.00	56.10	68.00	80.01	59.08	71.11	82.79	61.93	73.95	85.75	63.98	75.75	87.65
450.00	57.39	70.19	83.08	60.49	73.10	85.90	63.38	76.04	88.89	65.49	78.10	90.32
500.00	58.63	72.30	86.05	61.83	75.30	88.93	64.77	78.27	91.94	66.91	80.35	93.90
550.00	59.84	74.36	88.95	63.13	77.43	91.87	66.10	80.43	94.89	68.27	82.52	96.88
600.00	61.01	76.35	91.75	64.37	79.49	94.72	67.37	82.50	97.75	69.57	84.61	99.77
650.00	62.15	78.28	94.47	65.57	81.48	97.49	68.60	84.51	100.52	70.82	86.62	102.56

700 00	63.25	80.16	97 10	66 73	83 40	100 16	69 77	86 45	103.20	72.02	88.57	106.27
750.00	64 32	81.98	99 65	67 85	85.26	102 75	70 91	88 32	105.80	73 17	90.45	107.88
800 00	65.37	83 74	102 13	68 93	87 07	105 26	72 01	90 13	108 32	74.28	92.27	110.42
850 00	66.38	85.46	104 53	69 98	88 81	107 70	73 07	91.89	110.76	75.36	94.02	112.87
900.00	67.37	87.12	106 87	71 00	90.51	110.06	74.10	93.59	113 12	76.39	95.73	115.26
950.00	68 33	88 73	109.13	71.98	92 15	112 36	75.09	95.24	115 42	77.40	97.38	117.57
1000.00	69.27	90.31	111 34	72.94	93 74	114 59	76.06	96.84	117 65	78.37	98.98	119.81
1050.00	70.18	91.84	113 48	73.87	95.29	116.75	77 00	98.39	119.81	79.32	100.53	121 99
1100.00	71.06	93.32	115.56	74 78	96 79	118 85	77.91	99.90	121.92	80.23	102.05	124.10
1150.00	71.93	94 77	117.59	75.66	98.26	120 90	78.79	101 37	123.97	81.12	103.51	126.16
1200.00	72.77	96 18	119 56	76 51	99 69	122.89	79.65	102.80	125.96	81.99	104.94	128.16
$(H^\circ - H_0^\circ)/T$ (cal g mole^{-1} K^{-1})												
298 16	8.12	10.29	13 05	8 35	10.63	13.40	8.51	10 90	13 76	8 67	11.11	13.93
300.00	8 13	10.31	13 09	8 36	10.66	13.45	8 52	10.93	13.80	8.68	11.14	13.98
350.00	8.30	11 00	14.19	8 62	11 41	14 59	8.82	11 70	14 95	9 02	11.91	15.14
400.00	8.53	11 73	15 33	8 93	12.19	15 78	9.15	12 49	16.12	9.38	12.70	16.33
450.00	8.81	12.49	16.49	9.26	12 99	16.96	9.51	13.29	17.30	9.75	13.50	17.52
500.00	9.11	13.25	17.63	9.61	13.78	18.14	9.87	14.08	18.46	10.13	14.29	18.70
550.00	9.43	14 01	18 76	9 97	14.56	19 29	10 24	14.85	19.60	10.51	15.06	19.85
600.00	9.77	14.75	19.85	10 34	15 32	20.41	10.61	15.61	20.71	10.88	15.81	20.96
650.00	10.11	15 47	20.91	10.69	16.05	21 48	10.97	16.33	21.77	11.24	16.53	22.03
700.00	10.45	16.17	21 93	11 05	16.76	22 52	11.32	17.04	22.80	11.59	17.23	23.07
750.00	10.79	16.85	22.92	11.39	17 45	23 52	11.67	17.71	23.79	11.93	17.90	24.06
800.00	11.13	17 51	23 86	11.73	18.10	24 47	12.00	18 36	24.74	12.26	18.53	25.01
850.00	11.46	18.14	24 78	12.06	18 73	25.39	12.33	18.98	25.64	12.58	19.15	25 92
900.00	11 78	18 75	25.66	12.38	19.33	26.27	12 64	19 58	26.52	12.89	19.74	26.79
950 00	12.09	19 34	26.50	12 68	19 92	27 12	12 94	20 15	27.35	13 19	20.31	27.63
1000 00	12 40	19 90	27 31	12.98	20.47	27 93	13.24	20 70	28 15	13 48	20 85	28.43
1050 00	12 70	20.45	28 09	13.27	21.01	28 71	13 52	21.23	28.92	13.76	21.38	29.20
1100.00	12 99	20.97	28 84	13 55	21.52	29 46	13 80	21 74	29.66	14.03	21.88	29.94
1150.00	13 27	21 48	29 56	13.83	22 02	30.17	14 06	22 23	30.38	14.29	22.37	30.64
1200.00	13.54	21 96	30 26	14.09	22 50	30 86	14.32	22.71	31 07	14.55	22 84	31.33
$-(F^\circ - H_0^\circ)/T$ (cal g mole^{-1} K^{-1})												
298 16	45 12	53 05	60 41	47.62	55.29	62 72	50 19	57 81	65 28	51.97	59.56	66 92
300.00	45.17	53.11	60 49	47.68	55.35	62.81	50.24	57.88	65.36	52 02	59.63	67.01
350 00	46 44	54 75	62 65	48 98	57 05	64 97	51 58	59 62	67 57	53 38	61.41	69.23
400 00	47 56	56 27	64.67	50 15	58 63	67 01	52.78	61 24	69 63	54.61	63.05	71 32
450.00	48 58	57 69	66 59	51 22	60 11	68 94	53 87	62 75	71 60	55 73	64.59	73.30

TABLE 2 (continued)

Temp.	*n*-Alkyl fluorides			*n*-Alkyl chlorides			*n*-Alkyl bromides			*n*-Alkyl iodides		
	Methyl	Ethyl	*n*-Propyl	Methyl	Ethyl	*n*-Propyl	Methyl	Ethyl	*n*-Propyl	Methyl	Ethyl	*n*-Propyl
500.00	49.53	59.05	68.42	52.22	61 52	70.79	54.90	64.19	73.48	56.78	66.06	75.20
550.00	50 41	60.35	70.19	53.15	62.87	72.59	55.85	65.57	75.29	57.76	67.45	77.03
600.00	51.24	61.60	71.90	54.04	64.17	74.32	56.76	66.90	77.05	58.69	68.80	78.81
650.00	52.04	62.81	73.56	54.88	65.42	76.01	57 62	68.18	78.75	59.58	70.09	80.53
700.00	52.80	63.98	75.17	55.68	66.64	77.64	58.45	69.41	80.40	60.43	71.34	82.20
750.00	53.53	65.12	76 74	56.46	67 82	79.23	59.24	70.61	82.01	61.24	72.55	83.83
800.00	54.24	66.23	78.27	57.20	68.97	80.79	60.01	71.78	83.58	62.02	73.73	85.41
850.00	54.93	67.31	79 75	57.92	70.09	82.31	60.74	72.91	85.11	62.77	74.87	86.96
900.00	55.59	68.37	81.21	58.62	71.17	83.79	61.46	74.01	86.60	63.50	75.98	88.46
950.00	56.24	69.40	82.63	59.30	72.23	85.24	62.15	75.08	88.06	64.20	77.07	89.94
1000.00	56.86	70.40	84.02	59.96	73.27	86.65	62.82	76.13	89.49	64.89	78.13	91.38
1050.00	57.48	71.39	85.39	60.60	74.28	88.04	63.47	77.16	90.89	65.55	79.16	92.78
1100.00	58.07	72.35	86.72	61.22	75.27	89.40	64.11	78.16	92.25	66.20	80.16	94.17
1150.00	58.66	73.29	88.03	61.83	76.24	90.72	64.73	79.13	93.59	66.83	81.15	95.51
1200.00	59.23	74.22	89.31	62.42	77.19	92.03	65.33	80.09	94.89	67.44	82.11	96.83

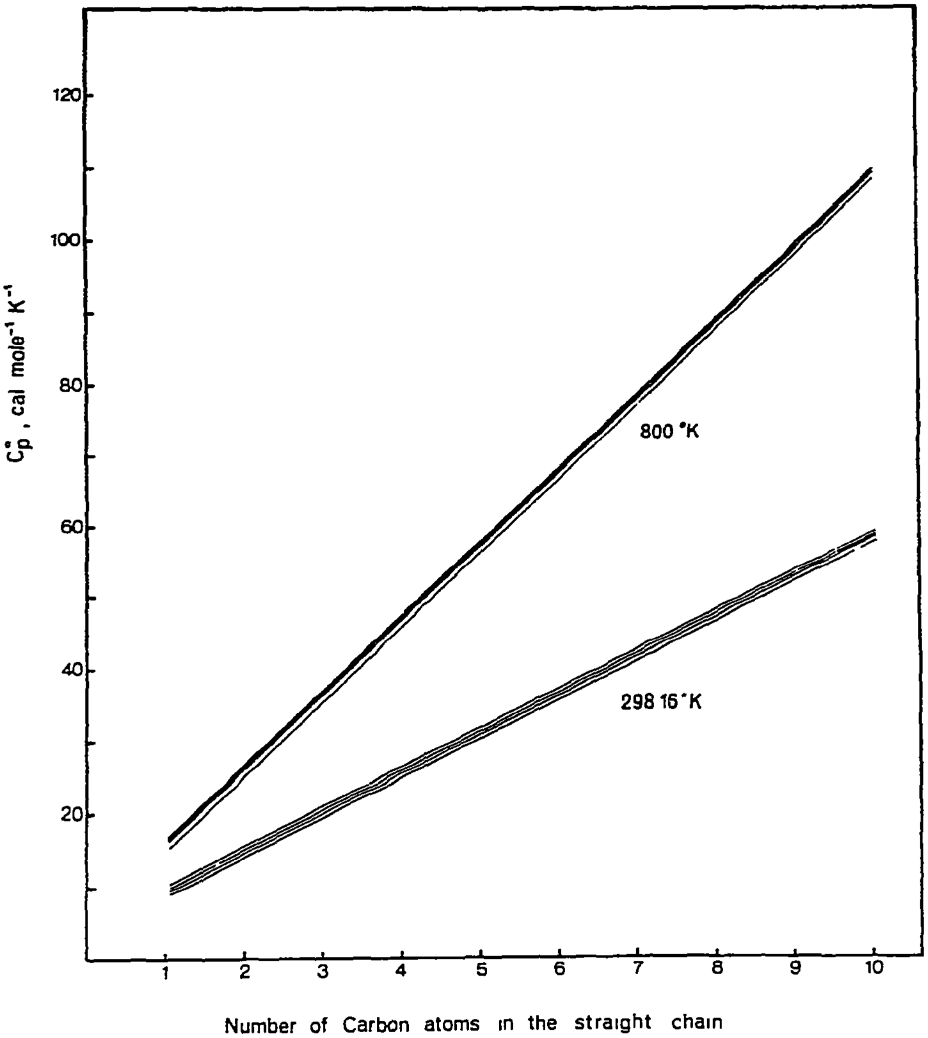

Fig 2. Heat capacity of C_{1-10} *n*-alkyl halides. Compounds identified in Fig. 1.

the calculated values check closely with the available experimental and calculated values. Tables 5 and 6 present the values of the molecular parameters used to calculate thermodynamic functions.

CALCULATED THERMODYNAMIC FUNCTIONS

Methyl halides

Earlier calculations are summarized by Morgan and Lielmezs [3] and Rodgers et al. [6]. Their values are in excellent agreement with the measured quantities (Table 4) and the values of the complete tabulated thermodynamic functions given in this work (Table 2).

Ethyl halides

The agreement between the results presented (Table 2) and the values obtained either by experiment or by comparative calculations (Table 4) is quite satisfactory.

TABLE 3

Calculated constants a, b, c, d and e in eqn. (2)

(all values in cal g mole^{-1} K^{-1})

Compound	a	$b \times 10^{-1}$	$c \times 10^{-3}$	$d \times 10^{-6}$	$e \times 10^{-10}$
	C_p°				
Fluoromethane	17.0532	−0.72936	0.21148	−0.20580	0.68438
Chloromethane	15.3945	−0.57348	0.17964	−0.17999	0.60961
Bromomethane	15.2635	−0.53478	0.17066	−0.17231	0.58666
Iodomethane	15.2090	−0.50165	0.16276	−0.16544	0.56588
Fluoroethane	1.187537	0.4987770	−0.02059188	−0.002754048	0.03271143
Chloroethane	0.7981608	0.5740156	−0.03633131	0.009935297	−0.003790807
Bromoethane	1.284856	0.5744455	−0.03808707	0.01193172	−0.01050440
Iodoethane	1.70321	0.569216	−0.038183	0.0122862	−0.0117390
n-Fluoropropane	11.55458	−0.007615089	0.1372143	−0.1633543	0.5836946
n-Chloropropane	11.36479	0.04020452	0.1295581	−0.1586420	0.5732860
n-Bromopropane	12.42056	0.007776432	0.1339901	−0.1615813	0.5808061
n-Iodopropane	12.46555	0.02227305	0.1317055	−0.1602511	0.5780222
	$(H^\circ - H_0^\circ)/T$				
Fluoromethane	8.67196	−0.08399	0.27889	−0.21637	0.58752
Chloromethane	7.84871	−0.03131	0.20879	−0.17628	0.50151
Bromomethane	7.51583	−0.00474	0.16698	−0.14795	0.42921
Iodomethane	7.22827	0.01998	0.12740	−0.12071	0.35877
Fluoroethane	7.183535	0.05205376	0.2359418	−0.2289460	0.6812940
Chloroethane	6.830003	0.08701352	0.1900651	−0.2037848	0.6309140
Bromoethane	6.835320	0.1029329	0.1602114	−0.1814993	0.5701419
Iodoethane	6.92958	0.110683	0.144434	−0.169608	0.538086
n-Fluoropropane	7.168521	0.1507775	0.2205453	−0.2453040	0.7541024
n-Chloropropane	7.167343	0.1656818	0.2110863	−0.2460529	0.7691513
n-Bromopropane	7.476758	0.1698225	0.2001294	−0.2385566	0.7535551
n-Iodopropane	7.460487	0.1794872	0.1869847	−0.2293550	0.7256200

n-*Propyl halides*

The agreement between the presently computed results (Table 2) and the available calculated literature values (Table 4) is satisfactory. Table 6 presents the molecular parameters used in calculations.

Proposed linear relationship

Figures 1 and 2 indicate the general validity eqn. (1) for *n*-alkyl halide series. In this work we have assumed that the various steric and electronic interaction effects of the substituent halogen atoms become negligible for $n > 7$, when

$$(\mathrm{d}\Delta_T/\mathrm{d}n)_{n>7} = 0 \qquad (3)$$

The use of eqn. (1) subject to the restrain of eqn. (3) reflects this [2—4, 28—32,49,50] and so we tacitly assume that the slope is merely the thermo-

a	$b \times 10^{-1}$	$c \times 10^{-4}$	$d \times 10^{-7}$	$e \times 10^{-11}$
S°				
43.1853	0.39475	−0.22499	0.12371	−0 32652
44.7241	0.44602	−0.26769	0.13679	−0.32938
46.7894	0.47759	−0.30573	0.15876	−0.37910
48.0919	0.50843	−0.34394	0 18157	−0.43250
47.90629	0.5658684	−0.1699914	0.02852108	−0.003850687
49.36250	0.6166984	−0.2210476	0.05299568	−0.04858181
51.52282	0.6491122	−0.2667166	0.08342156	−0.1267479
53 06179	0.670977	−0.29803	0.104243	−0.180020
51.84741	0 7884640	−0.2206871	0.02140197	0 05712388
54 25912	0.7942075	−0.2060806	0.003840408	0 1128569
56 79680	0.8136261	−0.2343692	0 02272479	0 06512881
58.30811	0.8267987	−0.2453127	0 02857433	0 04942982
$-(F^\circ - H^\circ_0)/T$				
34.5132	0.47875	−0.50392	0 34012	−0 91420
36.8755	0 47735	−0 47647	0.31307	−0.83090
39 2738	0.48231	−0.47268	0 30669	−0.80823
40.8635	−0 48847	−0.47138	0.30232	−0 79141
40.72070	0 5139156	−0.4061777	0.2577147	−0.6860257
42 52806	0.5299368	−0.4116635	0.2572755	−0 6810716
44 68201	0.5464970	−0.4276128	0.2655273	−0.6987924
46 12625	0.560542	−0.44313	0.274521	−0 720215
44.67899	0 6376803	−0.4412144	0.2666861	−0 6969039
47 09183	0 628519	−0.4171442	0.2498656	−0.6561865
49 31972	0.6438237	−0.4345372	0.2613127	−0.6885150
50 84714	0.6473446	−0.4323736	0.2580034	−0.6764460

dynamic function per CH_2-group increment for the given substituent atom [3,4]. It is of interest to note, however, that although statistical-mechanical justification for the use of this type of universal linear increment has already been made by Pitzer [51] (see also refs. 49 and 50), recently it has been asked [31,32,52] whether the incremental enthalpy of formation for the addition of a CH_2-group to an existing alkyl carbon framework is independent of a terminal substituent atom. Indeed, Montgomery and Rossini [52] have found experimentally that the differences between the observed and extrapolated values of incremental enthalpy of formation for alkyl type carbon series can be related to the electronegativities of the constituent atoms of the terminal group. To what extent our proposed relations [eqn. (1), Table 2] are subject to this type of interaction, is a question worthy of further study.

TABLE 4

Comparison of computed and experimental values

(All values in cal g mole^{-1} K^{-1})

Compound	Temp. (K)	Experimental		Computed	
		C_p^o	S^o	C_p^o	S^o
Methyl fluoride	298.16			8.96 [6], 8.94 [3], 8.96 (this work)	53.25 [6], 53.24 [3], 53.25 (this work)
	400.00			10.56 [6], 10.56 [3], 10.56 [5], 10.56 (this work)	56.09 [6], 56.08 [3], 56.10 [5], 56.10 (this work)
	1000.00			18.45 [6], 18.43 [3], 18.44 [5], 18.45 (this work)	69.26 [6], 69.21 [3], 69.26 [5], 69.27 (this work)
Methyl chloride	248.96		54.27 [36]		54.29 [6], 54.29 (this work)
	298.16		55.94 [36]	9.74 [6,3], 9.73 [5], 9.74 (this work)	55.81 [3], 55.99 [5], 55.97 (this work)
	400.00			11.51 [6], 11.51 [3], 11.50 [5], 11.51 (this work)	59.08 [6], 58.92 [3], 59.09 [5], 59.08 (this work)
	1000.00			18.87 [6], 18.86 [3], 18.86 [5], 18.87 (this work)	72.94 [6], 70.83 [3], 72.93 [5], 72.94 (this work)
Methyl bromide	276.71		57.90 [37]		58.02 [9], 57.95 (this work)
	298.16		58.61 [37]	10.14 [1], 10.15 [3], 10.14 (this work)	58.82 [1], 58.82 [3], 58.70 (this work)
	400.00			11.92 [1], 11.94 [3], 11.94 (this work)	62.04 [1], 62.05 [3], 61.93 (this work)
	1000.00			19.01 [1], 19.01 [3], 19.02 (this work)	76.16 [1], 76.18 [3], 76.06 (this work)
Methyl iodide	298.16			10.55 [1], 10.55 [3], 10.54 (this work)	60.47 [1], 60.47 [3], 60.64 (this work)
	400.00			12.36 [1], 12.36 [3], 12.33 (this work)	63.84 [3], 63.83 [1], 63.98 (this work)
	1000.00			19.20 [1], 19.19 [3], 19.17 (this work)	78.24 [1], 78.24 [3], 78.37 (this work)
Ethyl fluoride	298.16			13.73 [3], 14.21 [10], 14.21 (this work)	62.78 [3], 63.34 [10], 63.35 (this work)
	400.00			17.23 [3], 17.71 [10], 17.71 (this work)	67.30 [3], 68.00 [10], 68.01 (this work)
	1000.00			31.43 [3], 31.00 [10], 31.00 (this work)	89.54 [3], 90.31 [10], 90.31 (this work)

Ethyl chloride	200.00	11.82 [38]		11.75 [7], 11.69 [4], 11.75 (this work)	
	280.00	14.02 [38]		14.33 [7], 14.14 [4], 14.33 (this work)	
	285.37		65.31 [39]		65.27 [7], 65.27 (this work)
	298.16		65.91 [39]	14.97 [7], 14.72 [3], 15.01 [2], 14.97 (this work)	65.91 [7], 65.93 [3], 65.99 [2], 65.92 (this work)
	315.15	15.7 [40]		15.50 [7], 15.50 (this work)	
	500.00		74.7 [41] 76.8 [42]	21.66 [7], 21.44 [3], 21.65 (this work)	75.30 [7], 75.17 [3], 75.35 [2], 75.30 (this work)
	1000.00			31.85 [3], 31.45 [2], 31.43 [7], 31.43 (this work)	93.67 [3], 93.83 [2], 93.74 [7], 93.74 (this work)
Ethyl bromide	298.16			15.42 [2], 15.19 [3], 15.36 (this work)	68.80 [2], 68.94 [3], 68.71 (this work)
	400.00			18.89 [11], 18.93 [2], 18.64 [3], 18.87 (this work)	73.67 [11], 74.04 [2], 73.89 [3], 73.72 (this work)
	1000.00			31.53 [11], 31.56 [2], 31.96 [3], 31.53 (this work)	96.81 [11], 96.70 [2], 97.04 [3], 96.84 (this work)
Ethyl iodide	298.16			15.47 [3], 15.62 (this work)	70.65 [13], 70.68 (this work)
	400.00			19.08 [11], 18.92 [3], 19.08 (this work)	75.71 [11], 75.68 [3], 75.75 (this work)
	1000.00			31.56 [11], 32.07 [3], 31.56 (this work)	98.93 [11], 98.99 [3], 98.98 (this work)
n-Propyl fluoride	298.16			19.02 [3], 19.43 (this work)	71.81 [3], 73.46 (this work)
	400.00			24.06 [3], 24.50 (this work)	78.10 [3], 80.01 (this work)
	1000.00			44.62 [3], 43.25 (this work)	110.95 [3], 111.34 (this work)
n-Propyl chloride	298.16			20.24 [2], 19.69 [3], 20.11 (this work)	76.27 [2], 75.90 [3], 76.13 (this work)
	400.00			25.36 [2], 24.84 [3], 25.27 (this work)	82.93 [2], 82.36 [3], 82.79 (this work)
	1000.00			43.59 [2], 44.76 [3], 43.85 (this work)	114.55 [2], 114.18 [3], 114.59 (this work)
n-Propyl bromide	298.16			20.66 [2], 20.11 [3], 20.52 (this work)	79.08 [2], 79.29 [3], 79.04 (this work)
	400.00			25.70 [2], 25.21 [3], 25.56 (this work)	85.85 [2], 85.94 [3], 85.75 (this work)
	1000.00			43.70 [2], 44.30 [3], 43.91 (this work)	118.11 [2], 117.94 [3], 117.65 (this work)
n-Propyl iodide	298.16			20.60 [3], 20.83 (this work)	79.43 [3], 80.86 (this work)
	400.00			25.68 [3] 25.90 (this work)	86.20 [3], 87.65 (this work)
	1000.00			44.33 [3], 44.17 (this work)	119.17 [3], 119.81 (this work)

TABLE 5

Molecular parameters for methyl and ethyl halides

Methyl fluoride [a]	Methyl chloride	Methyl bromide [a]	Methyl iodide [a]
Fundamental frequencies, ν (cm^{-1})			
1049, 1182, 1182, 1462, 1467, 1467, 2930, 3006, 3006	732, 1017, 1017, 1355, 1452, 1452, 2937, 3039, 3039	611, 955, 955, 1306, 1443, 1443, 2935, 3056, 3056	533, 882, 882, 1251, 1436, 1436, 2933, 3060, 3060
Principal moment of inertia product (g^3 cm^6)			
5.9373×10^{-117} [6]	21.155×10^{-117} [6]	39.5675×10^{-117} [43]	65.9376×10^{-117} [14]
Reduced moment of inertia of CH_3-group (g cm^2)			
Barrier to internal rotation, CH_3-group (cal g $mole^{-1}$)			
Symmetry number, σ			
3 [3]	3 [12]	3 [12]	1 [12]
Molecular weight			
34 0334	50.488	94 944	141 939

[a] The gas phase assignments were taken from Shimanouchi [12].

[b] In general the frequency values adopted were taken from Dürig et al. [23] Other changes or additions made are noted in separate footnotes.

Accuracy

Generally, the calculated thermodynamic functions for methyl and ethyl halides are expected to be highly accurate [6,7,11] (Tables 4 and 5) because of the availability of reliable vibrational frequencies and molecular parameters (Table 5).

The calculated thermodynamic functions for *n*-propyl halides, especially *n*-propyl fluoride, are expected to be less accurate than their ethyl halide counterparts because of the corrections required for two internal rotations and the uncertainties in the frequency assignments (Table 6). However, the availability of recent and reliable vibrational data and molecular parameters permits us to suggest (even if experimental data are not available to substantiate these estimates) that the uncertainties in the calculated thermodynamic function values of *n*-propyl halides are roughly ±1.5% for *n*-fluoropropane and most ±1.0 for chloro-, bromo, and iodo-propane at low to moderate temperatures. At temperatures in excess of 1000 K, the total errors could be as high as ±3%, especially due to the neglected anharmonicity

Ethyl fluoride [a]	Ethyl chloride [a]	Ethyl bromide [a]	Ethyl iodide [b]
243, 415, 810, 880, 1048, 1048, 1108, 1277, 1365, 1395, 1449, 1449, 1479, 2915, 2941, 3003, 3003, 3003	251, 336, 677, 786, 974, 974, 1081, 1251, 1289, 1385, 1448, 1448, 1463, 2881, 2946, 2967, 2986, 3014	247, 290, 583, 770, 964, 964, 1061, 1248, 1252, 1386, 1451, 1451, 1451, 2880, 2937, 2988, 2988, 3018	230 [c], 258, 511 [d], 741, 954 [d], 1049, 1054, 1201, 1207 [d], 1382 [d], 1429, 1447, 1462, 2931 [d], 2973, 2986, 2989, 3025
212.72×10^{-117} [20]	699.66×10^{-117} [7]	1492×10^{-117} [44]	2456.83×10^{-117} [3]
4.333×10^{-40} [20]	4.615×10^{-40} [7]	4.917×10^{-40} [2]	5.03×10^{-40} [3]
3306 [8]	3691 [7]	3684 [16]	3660 [22]
1 [12]	1 [12]	1 [12]	1 [3]
48 060	64.515	101.971	155.966

[c] The torsional frequency value taken from Morgan and Lielmezs [3].
[d] Proposed values, this work.

effects [53]. In view of our corrected input data *, it is felt that the overall accuracy of the presented thermodynamic function values [eqn. (1), Table 2] for the higher order (C_4 and higher) alkyl halides may well be within the range of the experimental certainty.

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* In order to obtain the proposed linear relation [eqn. (1)] we first used the calculated alkyl halide (C_1—C_3) values, Table 1, while the higher order (C_4—C_7) alkyl halide methylene group increment values (Table 2) were obtained taking into account the possible halogen atom electrostatic and steric substitution effects.

TABLE 6

Molecular parameters for *n*-propyl halides

n-Propyl fluoride [a]	*n*-Propyl chloride [b]	*n*-Propyl bromide [c]	*n*-Propyl iodide [d]
Fundamental frequencies, ν (cm⁻¹)			
Trans-form			
98, 211, 266, 374, 747, 856, 923, 1006, 1055, 1077, 1157, 1187, 1926, 1375, 1395, 1410, 1450, 1455, 1465, 1470, 2950, 2950, 2950, 2950, 2950, 2950, 2950	130, 212 [e], 242, 364, 743 [f], 745 [g], 861, 903, 1032, 1079, 1108, 1212, 1258, 1300 [h], 1335, 1389, 1441, 1450, 1457, 1464, 2870 [i], 2870 [i], 2870 [i], 2950 [i], 2950 [i], 2950 [i], 2950 [i]	122, 217, 223 [j], 311, 660, 752, 848, 895, 1033 [k], 1033 [k], 1099 [l], 1213 [l], 1217, 1296, 1340, 1383, 1443, 1451, 1451, 1464, 2900 [i], 2900 [i], 2900 [i], 2960 [i], 2960 [i], 2960 [i], 2960 [i]	116, 197, 203 [o], 285, 602, 726 [p], 823, 895, 1013, 1024, 1089, 1185, 1185, 1291, 1332, 1383, 1428 [q], 1443, 1458, 1460 [q], 2900 [r], 2900 [r], 2900 [r], 2960 [r], 2960 [r], 2960 [r], 2960 [r]
Gauche-form			
161, 302, 323, 478, 802, 856, 923, 970, 1003, 1007, 1157, 1187, 1296, 1375, 1395, 1410, 1450, 1455, 1465, 1470, 2950, 2950, 2950, 2950, 2950, 2950, 2950	130, 207, 288, 422, 663, 793, 857, 898, 1042, 1067, 1108, 1212, 1258, 1307, 1352, 1389, 1431, 1450, 1457, 1464, 2870 [i], 2870 [i], 2870 [i], 2950 [i], 2950 [i], 2950 [i], 2950 [i]	127 [m], 298, 268, 401, 572, 780, 836, 883, 1033 [n], 1033 [n], 1085 [n], 1200, 1235, 1288, 1348, 1393, 1443, 1451, 1451, 1464, 2900 [i], 2900 [i], 2900 [i], 2960 [i], 2960 [i], 2960 [i], 2960 [i]	90 [s], 189, 256, 388, 518, 765, 812. 880, 1013, 1035, 1076, 1195 [t], 1195 [t], 1279, 1343, 1383, 1435, 1438, 1443, 1460 [u], 2900 [r], 2900 [r], 2900 [r], 2960 [r], 2960 [r], 2960 [r], 2960 [r]
Principal moment of inertia product (g^3 cm^6)			
Trans-form			
1665.240 x 10^{-117} [18]	4223.172 x 10^{-117} [17]	8983.941 x 10^{-117} [17]	14843.570 x 10^{-117} [117]
Gauche-form			
1866 100 x 10^{-117} [18]	5271 770 x 10^{-117} [17]	11143.801 x 10^{-117} [17]	19007.012 x 10^{-117} [17]
Energy of isomerization, ΔE_{iso} (cal g mole⁻¹)			
–470.0 [18]	–50.0 [17]	190 0 [15]	290 0 [17]
Internal rotational barrier (methyl rotating group) (cal g mole⁻¹)			
Trans-form			
2690 0 [18]	2780.0 [17]	2360.0 [17]	2470.0 [17]
Gauche-form			
2870 0 [18]	2960 0 [17]	2650 0 [17]	2770 0 [17]
Reduced moments of inertia (methyl rotating group) (g cm²)			
Trans-form			
5.303 x 10^{-40} [18]	4 591 x 10^{-40} [17]	4 594 x 10^{-40} [17]	4 602 x 10^{-40} [17]
Gauche-form			
5 303 x 10^{-40} [18]	5 198 x 10^{-40} [17]	5 248 x 10^{-40} [17]	5 275 x 10^{-40} [17]

Internal rotational barrier (ethyl rotating group) (cal g mole^{-1})			
Trans-form			
2910.0[v]	3610.0 [17]	3680.0 [17]	4070.0 [17]
Gauche-form			
3360.0 [17]	4240.0 [17]	4650.0 [17]	5200.0 [17]
Reduced moments of inertia (ethyl rotating group) (g cm^2)			
Trans-form			
15.291×10^{-40} [w]	21.670×10^{-40} [17]	$24\ 410 \times 10^{-40}$ [17]	$26\ 650 \times 10^{-40}$ [17]
Gauche-form			
$15\ 291 \times 10^{-40}$ [17]	21.380×10^{-40} [17]	25.390×10^{-40} [17]	28.320×10^{-40} [17]
Symmetry number, σ			
1	1	1	1
Number of minima per revolution of rotating top			
3	3	3	3
Molecular weight			
62.807	78.543	123.000	169.993

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[a] Liquid state assignments used by Morgan and Lielmezs [3] were adopted for this work.

[b] In general, frequency values for both the *trans*- and *gauche*-forms of *n*-propylchloride were taken from the gas state assignments of Ogawa et al. [13]. Frequencies added or changes made in assignments are noted in separate footnotes.

[c] Again, in general, frequency values for *trans*- and *gauche*-forms of *n*-propyl bromide were taken from the gas state assignments of Ogawa et al. [13]. In separate footnotes we note changes or additions made.

[d] In general, the frequencies of both isomers, *trans*- and *gauche*-, of *n*-propyl iodide were taken from Ogawa et al [13]. Since no CH-stretch assignment is available for *n*-iodopropane, the corresponding assignments for 1-bromopropane were used. Other changes or additions made are noted in separate footnotes.

[e] This value was adopted from the liquid state assignment of Brown and Sheppard [5].

[f] This value has been adopted, this work Compare with gas state assignments made by Komaki et al [46].

[g] This value has been adopted, this work.

[h] This is liquid state assignment, see Ogawa et al. [13].

[i] The CH-stretch assignment was taken from Komaki et al. [46] work.

[j] This value was adopted (liquid state) from Brown and Sheppard's work [45].

[k] This corresponding gas state assignment was taken from Komaki et al. work [46].

[l] This is liquid state assignment.

[m] This C_2H_5 torsion for *gauche*-1-bromo-propane was adopted from Radcliffe and Wood [17].

[n] These gas state assignments were taken from Komaki et al. [46].

[o] This value taken from Brown and Sheppard [45] liquid state assignments.

[p] Liquid phase assigment

[q] Liquid phase assigments

[r] Values taken from the corresponding assignments for *trans*-1-bromo-propane.

[s] This C_2H_5 torsion value adopted from Morgan and Lielmezs' [3] work.

[t] This value taken from the liquid state assignments of Brown and Sheppard [45].

[u] Liquid phase assignment.

[v] Estimated, this work. Compare also with findings by Lielmezs and Morgan [47] and Lielmezs [48].

[w] Assumed to be the same as that for the *gauche*-form.

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