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THERMODYNAMIC FUNCTIONS FOR HALOGENATED NAPHTHALENES

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ABSTRACT

Thermodynamic functions (heat capacity, enthalpy, entropy and free energy) have been calculated for naphthalene and 11 halogenated naphthalenes in the ideal gas state from 273.15 to 1200 K at 1 atm pressure. All the functions were obtained by statistical–mechanical calculation methods. Agreement with experimental results, where such are available, is satisfactory.

INTRODUCTION

The published molecular structural and spectroscopic data have enabled the calculation of thermodynamic functions — heat capacity, enthalpy, entropy and free energy — for naphthalene[2, 5, 7, 8, 10–12, 14–26] and 11 halogenated naphthalenes [3, 5, 6, 9, 20, 27, 28] in the ideal gas state at 1 atm pressure.

The functions for each given compound were calculated by means of the well-

TABLE 1

COMPARISON OF EXPERIMENTAL AND CALCULATED THERMODYNAMIC FUNCTION VALUES FOR NAPHTHALENE

Ref.	*C_p^0 (cal/gmole K)*		*S^0 (e.u.)*	
	451.0 K	*522.7 K*	*451.0 K*	*522.7 K*
2 (Experimental work)	48.10 ±0.48	54.17 ±0.54	96.80 ±0.44	104.41 ±0.44
18	47.69	53.81	96.95	104.55
19	48.14	54.27	96.81	104.47
22	48.23	53.99	96.49	104.10
10	48.67	54.87	96.87	104.62
26	48.19	54.38	96.35	103.90
27	47.40	53.56	96.35	103.90
This work	48.73	54.92	96.98	104.63

TABLE 2

HEAT CAPACITY, ENTROPY, FREE ENERGY FUNCTION AND ENTHALPY FUNCTION

Temperature (K)	*Naphthalene*	*α-Fluoronaphthalene*	*α-Chloronaphthalene*	*α-Bromonaphthalene*	*α-Iodonaphthalene*	*β-Fluoronaphthalene*	*β-Chloronaphthalene*	*β-Bromonaphthalene*	*β-Iodonaphthalene*	*1,4-Dichloronaphthalene*	*1,4-Dibromonaphthalene*	*2,3-Dibromonaphthalene*
$C_p{}^0$ *(cal/mole K)*												
451.00	48.73	51.45	52.27	52.61	52.80	51.88	52.33	52.68	52.84	55.70	56.35	56.24
522.70	54.92	57.53	58.23	58.51	58.67	57.89	58.28	58.55	58.69	61.44	61.97	61.91
273.15	29.31	32.02	33.23	33.86	34.19	32.62	33.28	33.95	34.30	37.01	38.15	37.86
298.15	32.28	35.05	36.20	36.77	37.07	35.64	36.26	36.87	37.17	39.98	41.03	40.77
300.00	32.50	35.27	36.42	36.98	37.28	35.86	36.48	37.08	37.38	40.20	41.24	40.98
350.00	38.29	41.10	42.12	42.59	42.85	41.64	42.20	42.69	42.93	45.84	46.72	46.51
400.00	43.70	46.48	47.40	47.80	48.02	46.97	47.47	47.89	48.08	50.99	51.74	51.59
450.00	48.64	51.36	52.18	52.52	52.71	51.79	52.24	52.59	52.75	55.62	56.26	56.15
500.00	53.07	55.72	56.45	56.74	56.91	56.10	56.51	56.80	56.94	59.73	60.29	60.22
550.00	57.03	59.59	60.26	60.51	60.66	59.93	60.30	60.54	60.67	63.38	63.87	63.82
600.00	60.57	63.05	63.64	63.86	63.99	63.34	63.68	63.87	64.00	66.61	67.04	67.01
650.00	63.74	66.12	66.66	66.85	66.97	66.39	66.69	66.85	66.98	69.48	69.87	69.85
700.00	66.60	68.88	69.36	69.53	69.64	69.11	69.39	69.51	69.64	72.04	72.39	72.38
750.00	691.7	71.36	71.79	71.95	72.05	71.57	71.81	71.90	72.04	74.34	74.65	74.65
800.00	71.50	73.59	73.99	74.13	74.22	73.78	74.01	74.07	74.21	76.41	76.69	76.69
850.00	73.63	75.62	75.98	76.11	76.19	75.79	76.00	76.03	76.18	78.28	78.53	78.54
900.00	75.55	77.46	77.79	77.91	77.98	77.61	77.80	77.82	77.97	79.97	80.20	80.21
950.00	77.32	79.14	79.44	79.55	79.62	79.28	79.46	79.45	79.61	81.51	81.72	81.73
1000.00	78.94	80.68	80.95	81.05	81.11	80.80	80.96	80.94	81.10	82.92	83.11	83.12
1050.00	80.43	82.08	82.34	82.43	82.49	82.20	82.35	82.31	82.48	84.20	84.38	84.39
1100.00	81.80	83.37	83.61	83.69	83.75	83.48	83.62	83.57	83.74	85.38	85.54	85.55
1150.00	83.07	84.56	84.78	84.86	84.91	84.66	84.79	84.73	84.90	86.46	86.61	86.62
1200.00	84.23	85.66	85.86	85.93	85.98	85.75	85.87	85.80	85.97	87.45	87.59	87.60

S^0 (cal/mole K)

451.00	96.98	104.83	108.17	111.39	113.81	105.85	107.94	111.17	113.65	114.46	120.10	120.76
522.70	104.63	112.87	116.32	119.59	122.03	113.95	116.10	119.38	121.88	123.10	128.83	129.48
273.15	77.62	84.07	86.91	89.89	92.18	84.83	86.64	89.63	91.98	91.35	96.55	97.31
298.15	80.32	87.01	89.95	92.98	95.30	87.82	89.69	92.72	95.11	94.72	100.02	100.75
300.00	80.52	87.23	90.17	93.21	95.53	88.04	89.91	92.95	95.34	94.97	100.27	101.01
350.00	85.96	93.11	96.22	99.34	101.70	94.01	95.97	99.10	101.52	101.39	107.05	107.74
400.00	91.44	98.95	102.19	105.37	107.76	99.92	101.95	105.14	107.60	108.05	113.62	114.29
450.00	96.87	104.71	108.06	111.28	113.69	105.74	107.82	111.06	113.53	114.33	119.98	120.64
500.00	102.23	110.35	113.78	117.03	119.47	111.42	113.55	116.82	119.31	120.41	126.12	126.77
550.00	107.48	115.85	119.34	122.62	125.07	116.95	119.12	122.41	124.92	126.28	132.04	132.68
600.00	112.59	121.18	124.73	128.03	130.49	122.31	124.51	127.82	130.34	131.93	137.73	138.37
650.00	117.57	126.35	129.95	133.26	135.74	127.51	129.73	133.06	135.58	137.38	143.21	143.85
700.00	122.40	131.36	134.99	138.32	140.80	132.53	134.78	138.11	140.65	142.02	148.48	149.12
750.00	127.08	136.20	139.86	143.20	145.69	137.38	139.65	142.99	145.54	147.07	153.56	154.19
800.00	131.62	140.87	144.56	147.91	150.41	142.07	144.35	147.70	150.26	152.34	158.44	159.08
850.00	136.02	145.40	149.11	152.47	154.97	146.60	148.90	152.25	154.81	157.23	163.15	163.78
900.00	140.29	149.77	153.50	156.87	159.37	150.99	153.30	156.65	159.22	161.75	167.68	168.32
950.00	144.42	154.01	157.75	161.13	163.63	155.23	157.55	160.90	163.48	166.12	172.06	172.70
1000.00	148.43	158.10	161.87	165.25	167.76	159.34	161.66	165.01	167.60	170.33	176.29	176.93
1050.00	152.32	162.07	165.85	169.23	171.75	163.31	165.65	169.00	171.59	174.41	180.37	181.02
1100.00	156.09	165.92	169.71	173.10	175.62	167.17	169.51	172.85	175.46	178.36	184.33	184.97
1150.00	159.75	169.66	173.46	176.85	179.36	170.90	173.25	176.59	179.21	182.18	188.15	188.79
1200.00	163.31	173.28	177.09	180.48	183.00	174.53	176.88	180.22	182.84	185.88	191.86	192.50

TABLE 2 *(continued)*

Temperature (K)	*Naphthalene*	*α-Fluoronaphthalene*	*α-Chloronaphthalene*	*α-Bromonaphthalene*	*α-Iodonaphthalene*	*β-Fluoronaphthalene*	*β-Chloronaphthalene*	*β-Bromonaphthalene*	*β-Iodonaphthalene*	*1,4-Dichloronaphthalene*	*1,4-Dibromonaphthalene*	*2,3-Dibromonaphthalene*
$-(F^0 - H_0^0)/T$ *(cal/mole K)*												
451.00	71.87	77.73	80.09	82.71	84.74	78.31	79.90	82.51	84.58	83.57	88.15	89.01
522.70	75.84	82.00	84.51	87.21	89.30	82.65	84.31	87.01	89.14	88.40	93.14	93.97
273.15	61.82	66.81	68.68	70.97	72.78	67.18	68.53	70.79	72.63	70.87	74.88	75.84
298.15	63.26	68.38	70.34	72.68	74.54	68.78	70.17	72.50	74.39	72.72	76.84	77.78
300.00	63.37	68.49	70.46	72.81	74.66	68.90	70.29	72.63	74.52	72.86	76.98	77.93
350.00	66.21	71.59	73.71	76.16	78.09	72.06	73.53	75.97	77.93	76.49	80.80	81.71
400.00	69.02	74.65	76.89	79.44	81.42	75.18	76.71	79.24	81.26	80.04	84.49	85.37
450.00	71.81	77.67	80.03	82.65	84.68	78.25	79.84	82.45	84.52	83.50	88.08	88.94
500.00	74.59	80.65	83.12	85.80	87.87	81.28	82.93	85.60	87.71	86.89	91.58	92.42
550.00	77.34	83.61	86.16	88.90	91.00	84.28	85.97	88.69	90.84	90.20	94.99	95.81
600.00	80.06	86.52	89.15	91.93	94.06	87.22	88.95	91.73	93.91	93.45	98.32	99.12
650.00	82.76	89.38	92.09	94.91	97.07	90.12	91.89	94.71	96.91	96.62	101.56	102.35
700.00	85.42	92.20	94.98	97.83	100.01	92.97	94.78	97.63	99.86	99.72	104.73	105.51
750.00	88.04	94.98	97.81	100.70	102.90	95.77	97.61	100.49	102.74	102.75	107.81	108.59
800.00	90.62	97.70	100.58	103.50	105.72	98.52	100.38	103.30	105.56	105.71	110.83	111.59
850.00	93.17	100.37	103.30	106.25	108.48	101.22	103.10	106.04	108.33	108.60	113.77	114.52
900.00	95.67	103.00	105.97	108.94	111.19	103.86	105.77	108.73	111.03	111.43	116.64	117.39
950.00	98.12	105.57	108.59	111.57	113.84	106.45	108.38	111.37	113.68	114.19	119.44	120.18
1000.00	100.54	108.09	111.15	114.16	116.43	109.00	110.95	113.95	116.28	116.90	122.18	122.91
1050.00	102.91	110.57	113.66	116.68	118.97	111.49	113.46	116.47	118.82	119.54	124.85	125.58
1100.00	105.24	113.00	116.12	119.16	121.46	113.93	115.92	118.95	121.30	122.12	127.47	128.19
1150.00	107.54	115.38	118.53	121.59	123.89	116.33	118.33	121.37	123.74	124.65	130.02	130.75
1200.00	109.79	117.72	120.90	123.97	126.28	118.68	120.69	123.75	126.13	127.13	132.52	133.24

$(H^0 - H_0^0)/T$(*cal/mole K*)

451.00	25.11	27.10	28.08	28.68	29.07	27.54	28.04	28.66	29.07	30.89	31.95	31.75
522.70	28.79	30.87	31.82	32.38	32.74	31.30	31.79	32.37	32.74	34.70	35.69	35.51
273.15	15.80	17.26	18.23	18.92	19.40	17.65	18.11	18.83	19.35	20.48	21.68	21.47
298.15	17.05	18.63	19.61	20.30	20.76	19.03	19.51	20.22	20.73	21.99	23.18	22.97
300.00	17.15	18.73	19.17	20.40	20.87	19.14	19.62	20.32	20.83	22.10	23.29	23.08
350.00	19.76	21.51	22.51	23.17	23.61	21.94	22.44	23.12	23.59	25.10	26.25	26.04
400.00	22.42	24.30	25.30	25.93	26.34	24.74	25.24	25.90	26.33	28.02	29.13	28.92
450.00	25.06	27.04	28.02	28.63	29.02	27.49	27.98	28.61	29.01	30.83	31.90	31.70
500.00	27.64	29.70	30.66	31.23	31.60	30.14	30.63	31.22	31.60	33.52	34.54	34.35
550.00	30.14	32.24	33.18	33.73	34.07	32.67	33.15	33.72	34.08	36.07	37.05	36.87
600.00	32.53	34.67	35.58	36.10	36.43	35.09	35.56	36.10	36.43	38.49	39.42	39.25
650.00	34.81	36.97	37.86	38.35	38.67	37.38	37.84	38.35	38.67	40.76	41.65	41.50
700.00	36.98	39.15	40.01	40.49	40.79	39.55	40.00	40.48	40.79	42.91	43.76	43.61
750.00	39.04	41.22	42.05	42.50	42.79	41.61	42.04	42.50	42.80	44.93	45.74	45.61
800.00	41.00	43.17	43.98	44.41	44.69	43.55	43.97	44.40	44.69	46.83	47.61	47.49
850.00	42.86	45.02	45.80	46.22	46.49	45.39	45.80	46.21	46.49	48.63	49.38	49.26
900.00	44.62	46.78	47.53	47.93	48.19	47.13	47.53	47.91	48.19	50.32	51.05	50.94
950.00	46.30	48.44	49.17	49.55	49.80	48.78	49.16	49.53	49.80	51.92	52.62	52.52
1000.00	47.89	50.01	50.72	51.09	51.33	50.34	50.72	51.07	51.33	53.44	54.11	54.01
1050.00	49.40	51.50	52.19	52.55	52.78	51.83	52.19	52.52	52.78	54.87	55.52	55.43
1100.00	50.85	52.92	53.59	53.94	54.16	53.24	53.59	53.90	54.16	56.23	56.86	56.77
1150.00	52.22	54.27	54.92	55.26	55.47	54.58	54.92	55.22	55.47	57.52	58.13	58.05
1200.00	53.53	55.56	56.19	56.51	56.72	55.85	56.19	56.47	56.72	58.75	59.34	59.26

TABLE 3

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

C_p^0 *(cal/mole K)*

Compound	a	$b \times 10$	$c \times 10^3$	$d \times 10^7$	$e \times 10^{11}$
Naphthalene	−16.74295	0.21069	−0.17445	0.68870	−0.94559
α-fluoronaphthalene	−15.33987	0.22027	−0.19596	0.86066	−1.43878
α-chloronaphthalene	−13.16016	0.21574	−0.19187	0.84339	−1.41186
α-bromonaphthalene	−11.50632	0.21007	−0.18345	0.78441	−1.25384
α-iodonaphthalene	−10.66078	0.20718	−0.17893	0.75091	−1.11592
β-fluoronaphthalene	−14.50212	0 21981	−0.19804	0.88957	−1.54485
β-chloronaphthalene	−13.32027	0.21735	−0.19573	0.87888	−1.52528
β-bromonaphthalene	−11.59713	0.21161	−0.18735	0.81728	−1.34757
β-iodonaphthalene	−10.39375	0.20652	−0.17867	0.75432	−1.18073
1,4-dichloronaphthalene	− 9.86833	0.22173	−0.21117	1.01586	−1.93825
1,4-dibromonaphthalene	− 6.98409	0.21223	−0.19729	0.91926	−1.67961
2,3-dibromonaphthalene	− 7.93113	0.21566	−0.20184	0.94576	−1.73626

S^0 *(e.u.)*

Compound	a	$b \times 10$	$c \times 10^4$	$d \times 10^7$	$e \times 10^{10}$
Naphthalene	48.81033	0.96560	0.48684	−0.67110	0.21477
α-fluoronaphthalene	51.41003	1.15885	0.26144	−0.53474	0.18132
α-chloronaphthalene	52.42870	1.25940	0.11077	−0.42844	0.15261
α-bromonaphthalene	54.48724	1.31269	0.02463	−0.36452	0.13475
α-iodonaphthalene	56.30194	1.33949	−0.17380	−0.33386	0.12625
β-fluoronaphthalene	51.21547	1.21157	0.18254	−0.47953	0.16655
β-chloronaphthalene	52.03847	1.26611	0.10124	−0.42229	0.15111
β-bromonaphthalene	54.03839	1.32247	0.01119	−0.35730	0.13332
β-iodonaphthalene	55.90233	1.35151	−0.03865	−0.31756	0.12165
1,4-dichloronaphthalene	51.37451	1.54425	−0.25418	−0.19272	0.09219
1,4-dibromonaphthalene	54.88530	1.64102	−0.40848	−0.07917	0.06063
2,3-dibromonaphthalene	56.13467	1.61129	−0.35546	−0.12031	0.07238

$-(F^0 - H_0^0)/T$ *(cal/mole K)*

Compound	a	$b \times 10$	$c \times 10^5$	$d \times 10^8$	$e \times 10^{11}$
Naphthalene	46.36369	0.55894	0.50762	−0.190349	0.22420
α-fluoronaphthalene	49.53465	0.63701	0.03936	−0.76674	0.21337
α-chloronaphthalene	50.05797	0.70426	0.07342	−0.29725	0.09803
α-bromonaphthalene	51.33951	0.75714	−0.43484	0.16910	−0.02388
α-iodonaphthalene	52.46388	0.79360	−1.93483	0.51039	−0.11472
β-fluoronaphthalene	49.37041	0.66260	−0.21542	−0.63199	0.18403
β-chloronaphthalene	50.07210	0.69424	−0.55902	−0.43286	0.13688
β-bromonaphthalene	51.30887	0.74815	−1.26393	0.02922	0.01720
β-iodonaphthalene	52.39633	0.78871	−1.83800	0.42938	−0.09031
1,4-dichloronaphthalene	49.32930	0.83678	−1.80866	0.19555	−0.00226
1,4-dibromonaphthalene	51.62193	0.92635	−2.97298	0.96164	−0.19649
2,3-dibromonaphthalene	52.89310	0.91047	−2.77655	0.84185	−0.16768

TABLE 3 *(continued)*

$(H^0 - H_0^0)/T$ *(cal/mole K)*

Compound	*a*	*b* × *10*	*c* × *10*^{5}	*d* × *10*^{8}	*e* × *10*^{11}
Naphthalene	2.44651	0.40666	0.43607	−0.58075	1.92349
α-fluoronaphthalene	1.87515	0.52186	0.25747	−0.45803	1.59965
α-chloronaphthalene	2.37070	0.55514	0.18419	−0.39872	1.42808
α-bromonaphthalene	3.14751	0.55557	0.16807	−0.38139	1.37119
α-iodonaphthalene	3.83801	0.54590	0.17609	−0.38489	1.37719
β-fluoronaphthalene	1.84529	0.54896	0.20411	−0.41636	1.48159
β-chloronaphthalene	1.96621	0.57187	0.15711	−0.37897	1.37409
β-bromonaphthalene	2.72961	0.57432	0.13758	−0.36022	1.31604
β-iodonaphthalene	3.50601	0.56281	0.14515	−0.36051	1.30686
1,4-dichloronaphthalene	2.04539	0.70747	−0.07330	−0.21229	0.91978
1,4-dibromonaphthalene	3.26339	0.71467	−0.11118	−0.17533	0.80276
2,3-dibromonaphthalene	3.24172	0.70081	−0.07779	−0.20452	0.89159

known statistical–mechanical methods[1]. Agreement with experimental values, where such are found, is satisfactory (Table 1).

The results presented in Table 2 were fitted to five constant polynomials of the form

$$A = a + bT + cT^2 + dT^3 + eT^4 \qquad (1)$$

where A is the thermodynamic function at temperature T (K). The constants a, b, c, d and e (eqn. 1) were obtained using linear least squares curve fitting methods[29] and are found in Table 3. Table 4, however, presents the values of the molecular parameters used in thermodynamic function calculations. The accuracy and scope of this work is bound by its purpose to present a set of calculated thermodynamic function tables for use in chemical engineering problems.

DISCUSSION

Naphthalene

Although naphthalene is one of the simplest polycyclic compounds, there is no general agreement regarding the fundamental vibrational assignments for this molecule[2, 5, 7, 8, 10–12, 14–26]. For thermodynamic function calculations this problem is even more aggravated by the scarcity of calorimetric data. Indeed, the only direct calorimetric measurements for naphthalene are those of Barrow and McClellan[2] who obtained the C_p^0 and S^0 values at two temperatures (451.0 and 522.7 K) near the normal boiling point (491.15 K). As shown in Table 1, the experimental data accuracy is suggested to be ±1.0%.

The greatest uncertainty in naphthalene vibrational series is found in the lowest skeletal (A_u-mode) vibration which has been predicted by Scully and Whiffen[26] to be 207 cm^{-1}. However, other investigators[18, 19, 22, 27] have arbitrarily chosen this

ABLE 4

MOLECULAR PARAMETERS

Naphthalene^a	*α-Fluoronaphthalene*^{a}	*α-Chloronaphthalene*^{a}	*α-Bromonaphthalene*^{a}	*α-Iodonaphthalene*^{a}	*β-Fluoronaphthalene*^{a}	*β-Chloronaphthalene*^{a}	*β-Bromonaphthalene*^{a}	*β-Iodonaphthalene*^{a}	*1,4-Dichloronaphthalene*^{a}	*1,4-Dibromonaphthalene*^{a}	*2,3-Dibromonaphthalene*^{a}
Fundamental frequencies, ν (cm^{-1})											
176,213	530,158	180,135	180^c,125	180^c,125	191,147	191,138	191,135	191,122	188,150	185,140	174,139
285,361	270,361	240,355	235,362	226,362	310,355	280,352	274,355	253,355	224,371	215,371^b	249,357
388,476	417,475	408,474	406,473	405,478	422,480	410,478	395,478	386,477	411,494	409,470	406,481
508,512	512,570	513,534	512,528	510,524	519,522	510,517	502,514	498,515	517,530	517^b,527	574,593
575,619	620,710	603,663	580,651	568,640	620,708	605,644	580,630	568,627	597,676	560,662	607,635
724,747	770,750	768,746	766,745	767,745	747,750	749,746	749,745	737,745	755,745^g	753,745^g	758,745^g
762,783	877,1157	827,790^d	806,790^d	797,790^d	768,795	768,795	765,795	765,794	826,790	823,791	784,814
785,843	1231,1217	795,850	791,855	791,858	817,852	817,852	815,849	817,860	816,328	814,289	862,132
870,875	1264,1350	883,850	950,175	883,858	862,862	862,862	861,861	860,868	900,824	905,823	878,890
935,935	1385,1407	945,220	940,950	950,151	955,218	955,218	954,175	951,154	926,120	937,95	957,294
945,958	1442,1465	945,972	959,1024	945,945	943,967	943,967	937,964	937,965	956,987	956,963	890,947
979,1019	1514,1576	972,1023	272,884	967,1022	955,1025	955,1025	954,1020	951,1022	987,1023	963,1021	961,1019
1132,1139	1604,1624^b	353,1140	855,1136	226,1131	357,1134	357,1134	274,1132	230,1132	224,1146	174,1142	139,1136
1145,1167	790,795	1142,1162	1144,1167	1143,1160	1149,1160	1144,1155	1149,1156	1147,1159	1163,443	1161,377	1148,357
1212,1242	860,886	1205,1216	1204,1216	1203,1215	1215,1249	1195,1239	1196,1240	1196,1239	1205,1184	1207,1187	1192,1198
1270,1362	860,956	1250,1340	1252,1340	1249,1331	1267,1355	1267,1346	1273,1347	1272,1343	1260,1371	1256,1368	1262,1338
1379,1391	270,967	1373,1381	1368,1378	1365,1377	1383,1390	1382,1370	1377,1366	1377,1343	1363,1371	1352,1368	1301,1418
1442,1462	967,1037	1430,1459	1434,1455	1428,1450	1443,1469	1437,1453	1433,1450	1447,1457	1415,1450	1410,1450	1428,1476
1513,1574	461,1146	1503,1565	1501,1561	1499,1552	1517,1580	1504,1575	1503,1571	1500,1576	1502,1560	1494,1556	1576,1556
1599,1624^b	1146,180^c	1593,1624^b	1594,1624^b	1597,1624^b	1607,1624^b	1604,1624^b	1589,1624^b	1582,1624^b	1589,1624^b	1566,243	1383,1624^b
2978^b,2987^b	967,3076^b	394,299^b	3076^b,300	3076^b,250	3076^b,528	3076^b,399	3076^b,300^e	3076^b,250^f	3076^b,328	377,3027^b	3076^b,249
3027^b,3031^b	3027^b,3031^b	3027^b,3031^b	2987^b,3027^b	2987^b,3027^b	2987^b,3027^b	2987^b,3027^b	2987^b,3030^b	2987^b,3027^b	517,3027^b	3031^b,3060^b	357,3027^b
3060^b,3060^b	3060^b,3060^b	3060^b,3060^b	3031^b,3060^b	3031^b,3060^b	3031^b,3060^b	3031^b,3060^b	3031^b,3060^b	3031^b,3060^b	3031^b,3060^b	3060^b,3076^b	3031^b,3060^b
3076^b,3076^b	2987^b,3076^b	3076^b,3076^b	3076^b,3060^b	3060^b,3076^b	3060^b,3076^b	3060^b,3076^b	3090^b,3390^b	3060^b,3076^b	3060^b,3076^b	1624^b,3076^b	3060^b,3076^b

Product of the principal moments of inertia ($gm^3\ cm^6$)[i]											
166,916 $\times 10^{-117}$	371,534 $\times 10^{-117}$	722,355 $\times 10^{-117}$	1,566,599 $\times 10^{-117}$	2,598,055 $\times 10^{-117}$	394,367 $\times 10^{-117}$	772,005 $\times 10^{-117}$	1,726,077 $\times 10^{-117}$	2,860,927 $\times 10^{-117}$	2,398,517 $\times 10^{-117}$	10,377,640 $\times 10^{-117}$	9,213,850 $\times 10^{-117}$
Symmetry number											
4	1	1	1	1	1	1	1	1	2	2	1
Molecular weight											
128.19	146.17	162.62	207.08	254.07	146.17	162.62	207.08	254.07	197.07	285.97	285.97
Normal boiling point (K)											
491.15	488.15	531.95	554.15	575.15	490.15	529.15	554.15	581.15	563.15	560.00	560.00

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[a] These assignments are made by Michaelian and Ziegler[20] with exceptions indicated by separate footnotes.

[b] Assignments made by Sharma and Singh[27]

[c] This is assigned value (this work). It is assumed that α-fluoro-naphthalene B_{1u} vibrational mode is of the same frequency as those of α-chloro- and α-iodo-naphthalenes[20].

[d] Assigned, this work.

[e] Assigned, this work. Value taken in analogy with α-bromonaphthalenes[20].

[f] Assigned, this work. Value taken in analogy with α-iodonaphthalenes[20].

[g] Assigned, this work. Value was taken in accordance with monosubstituted naphthalenes[20].

[h] Assigned, this work, with the same value as the corresponding frequency in 1,4-dichloro-naphthalene[20].

[i] All moments of inertia have been calculated from the available structural data — see the pertinent discussions in the text of this work.

frequency as 400 cm^{-1} to match the experimentally obtained heat capacity and entropy values (Table 1). More recently, however, Michaelian and Ziegler[20] while evaluating their IR and Raman spectra work for a series of halogenated naphthalenes, have set this frequency as 213 cm^{-1}. The reassignment of this particular frequency to 213 cm^{-1} has been also recently confirmed by Bree and Kydd[3] and by Chantry et al.[6].

These differences in frequency assignment values have prompted us to re-evaluate the overall thermodynamic consistency of frequency assignments for naphthalene as found in the literature[2, 5, 7, 8, 10–12, 14–26]. The work of this re-evaluation is presently under way.

However, at this time we present calculated thermodynamic functions for naphthalene in the ideal gas state (Tables 2, 3 and 4) using the data of Michaelian and Ziegler[20], supplemented by the highest nine fundamental vibration values (which have not been assigned by Michaelian and Ziegler) of Sharma and Singh[27]. The moment of inertia product was recalculated using the bond distances of Cruikshank[7] and assuming that the naphthalene molecule is planar with all bond angles of 120° (Table 4).

Table 1 compares thermodynamic function values as obtained in this work (using Sharma and Singh[27] frequency assignments) with experimental values[2] and with calculated values using frequency assignments of other investigators[2, 10, 18, 19, 22, 26, 27]. Comparing (Table 1) we see that our work with the lower frequency values of Michaelian and Ziegler[20] contributes proportionately more and shows slightly higher thermodynamic function values than those obtained by other investigators[2, 10, 18, 19, 22, 26, 27]. While the calculated heat capacity deviation is at most 1.36% above the experimental value (this deviation is close to the experimental uncertainty in heat capacity, specified as ±1.0%), our calculated entropy values with maximum deviation of 0.22% above the experimental value are well within the specified entropy measurement error range of ±0.41% (Table 1).

If we accept the correctness of the values of newer low frequency skeletal frequencies[3, 6, 20], and if we note the somewhat diffuse character of the specified experimental uncertainty (±1.0%, measurements made close to the normal boiling point of naphthalene), it appears that the calculated thermodynamic functions (this work, Tables 2, 3 and 4) at high temperatures are more realistic than those obtained previously[2, 10, 18, 19, 22, 26, 27]. The fact that more recent studies[3, 6, 20] of naphthalene IR and Raman spectra for A_u-mode skeletal frequencies yield considerably lower frequency values than those assigned earlier[18, 19, 22, 27] from the "force-fit" adjustment of naphthalene vibrational frequencies with respect to the available experimental heat capacity and entropy data (ref. 2; see also Table 1, this work), assures us of the necessity of re-evaluating the overall thermodynamic consistency of frequency assignments for naphthalene as found in the literature.

α-Halonaphthalenes

To calculate the thermodynamic functions of α-halogenated naphthalenes (α-$C_{10}H_7X$, where X = F, Cl, Br and I) the available spectral data of Michaelian and Ziegler[20] were used. With lack of any direct evidence as to which naphthalene C–H stretching vibration is replaced by the substituent C–X stretching vibration, the lowest frequency naphthalene C–H stretch at 2978 cm^{-1} was selected for this exchange. The required C–X stretch frequency values were then taken from Michaelian and Ziegler[20] assignments. The other eight high frequency naphthalene C–H vibrations (used in this work, taken from ref. 27) were assumed to remain constant. The missing lowest B_{1u} frequency for α-fluoro- and α-bromo-naphthalene following Michaelian and Ziegler[20], by analogy with given α- chloro- and α-iodo-naphthalene assignment, was assigned the value of 180 cm^{-1}. Similarly, in accordance with the given value of 790 cm^{-1} for α-fluoronaphthalene[20]; the missing B_{3g} frequency for α-chloro-, α-bromo- and α-iodo-naphthalenes, was assigned the value of 790 cm^{-1}. Finally, and again in accordance with the given values of α-fluoro-, α-chloro- and α-bromo-naphthalenes[20], the following assignments were made for α-iodonaphthalene: 883 cm^{-1} for B_{3u}, 745 cm^{-1} for B_{2u}, 568 cm^{-1} for A_u, 362 cm^{-1} for B_{2u} and 950 cm^{-1} for B_{1g} modes of vibration.

Structural data needed for moment of inertia calculations were obtained in analogy with the halogenated benzenes following the work of Butler and Lielmezs[4]. Bond lengths of 1.30, 1.70, 1.88 and 2.08 Å were assumed for the C–F, C–Cl, C–Br and C–I bonds, respectively. C–C bonds were taken as 1.40 Å for the fluoro- and chloro-naphthalenes, and 1.405 Å for the bromo- and iodo-naphthalenes. Similar to the structural calculations of naphthalene, the α-halonaphthalenes were assumed to be regular and planar molecules.

β-Halonaphthalenes

The thermodynamic functions of β-halonaphthalenes (β-$C_{10}H_7X$, where X = F, Cl, Br and I) were calculated using the assignments of Michaelian and Ziegler[20]. This set is nearly complete, except for high frequency C–H vibrations and the missing C–X (X = F, Cl, Br, I) stretching fundamentals for β-bromo- and β-iodo-naphthalene. Advantage was taken of the similarity between the α- and β-halonaphthalenes, in assigning the two missing C–X stretching vibrations the values of 300 cm^{-1} and 250 cm^{-1} in accordance with the corresponding frequencies for α- bromo- and α-iodo-naphthalenes. The remaining eight high frequency C–H vibrations were assumed to remain the same as for naphthalene and α-halonaphthalenes. The moments of inertia for β-halonaphthalene series were calculated assuming the same bond lengths and bond angles as for the α-halonaphthalenes.

Disubstituted halonaphthalenes

The thermodynamic functions for disubstituted halonaphthalenes (1,4-dichloronaphthalene; 1,4-dibromonaphthalene and 2,3-dibromonaphdibromothalene) were calculated using chiefly the assignments as presented by Michaelian and Ziegler[20]. These compounds contain two C–X (X = F, Cl, Br, I) vibrations (replacing the 1132 cm^{-1} naphthalene fundamentals), two out-of-plane C–X vibrations (replacing a 935 cm^{-1} and a 843 cm^{-1} assignment) and two C–X stretching vibrations which appear instead of the high frequency 2978 cm^{-1} and the 2997 cm^{-1} naphthalene fundamentals. The missing B_{2u} fundamental was assumed to be of 745 cm^{-1} for all three dihalonaphthalenes in accordance with the monosubstituted naphthalenes. Finally, frequencies of 517 cm^{-1} (B_{1g}) and 371 cm^{-1} (B_{2u}) were assigned to 1,4-dibromo-naphthalene assuming it to be of the same value as that of the corresponding fundamental of 1,4-dichloronaphthalene. It is of interest to note that although skeletal vibrations differ little in this group, the lower moments product and higher C–X frequencies for 1,4-dichloronaphthalene cause it to have lower function values than for the heavier 1,4-dibromonaphthalene. Thermodynamic function values, however, are very nearly the same for 1,4-dibromonaphthalene and for 2,3-dibromonaphthalene and for 2,3-dibromonaphthalene indicating that at least for this exchange, the substituent position has only a small effect. The moments of inertia were calculated assuming the planarity of molecules, and the same bond lengths and bond angles as those used for α- and β-halonaphthalenes.

Accuracy and range of reliability

In this work, all values are in cal per gram mole K units and apply to the ideal gas state at 1 atm pressure. For internal consistency and precision, tabulated values are given to ±0.1 cal per gram mole K. However, probable errors may be larger than this.

The percentage errors ascribed below to the calculated thermodynamic functions are really estimates. These estimates were obtained considering the four general sources: mathematical errors due to the round-off in the computer; errors in bond lengths, bond angles and in geometrical asymmetry of the molecule; errors in frequency assignments such as improper analysis, liquid state frequency shifts; errors due to the inapplicability of the basic assumptions, for instance anharmonicity. Several tests were run to determine the extent of these errors. The possibility of mathematical round-off errors was quickly reduced by running the calculations in extended precision — no appreciable change in the calculated thermodynamic function values was detected. However, errors due to the estimation of structural properties are very real as bond lengths and angles are not known precisely for most of the molecules. Hence, assuming an uncertainty in bond lengths of ±0.01 Å, all bond lengths for α-fluoronaphthalene were increased by 0.02 Å. The resulting product of moments of inertia is about 10% higher (or about the difference in the products of the moments of inertia between β- and α-halonaphthalenes). This increased the thermodynamic function values for α-fluoronaphthalene by less than 0.1%. Very little error, therefore, is introduced in calculations due to the structural uncertainties. The most likely source of error, however, is the ever present uncertainty in the assignment values of the naphthalene fundamental vibrations. For instance ,calculation shows that, at 1000 cm^{-1}, a frequency shift of 200 cm^{-1} will cause a 0.7% difference in the thermodynamic function values at 522.7 K. Table 1 shows that for this temperature the experimental error for heat capacity is ±1.0% while for entropy ±0.41%. This effect increases at lower frequencies and temperatures. In addition, for some of the substituted naphthalenes (especially α-jodonaphthalene and the dihalonaphthalenes) several frequencies were estimated. Hence, while present assignments fit the observed behavior at temperatures near the normal boiling point (Table 1) there is possible deviation at somewhat higher temperatures. On the other hand, Hanson[11] has shown that for the napthalene system the inaccuracies in gaseous function values due to frequency shifts in passing from the gaseous to the liquid state (the used data, this work, were in the liquid state) are negligible. The neglected effect of anharmonicity will become significant only at elevated temperatures and should in any case be less than 1% for the stable, strongly bonded napthalene series.

This discussion indicates that, barring major errors in the frequency assignments, the expected overall error should be within ±0.5–2.0% range. This expectation is fully brought out by Table 1, which indicates that even if the frequency assignments are estimated, errors in the calculated thermodynamic functions are low. Indeed, it is thought that for this naphthalene series with the normal boiling point range from 480–600 K, the presented thermodynamic functions will be reliable from approximately 400 to 1000 K; the expected error range of ±0.5 to ±2.0% being well within the general experimental uncertainty of ±3.0% as specified by Whiffen[30].

NOMENCLATURE

Å	Angstrom
C_p^0	heat capacity, cal per mole K
e.u.	entropy unit, cal per mole K
$-(F^0 - H_0^0)/T$	free energy function, cal per mole K
$(H^0 - H_0^0)/T$	enthalpy function, where $H_0^0 = H^0$ at 0 K, cal per mole K
S^0	entropy, e.u.
σ	molecular symmetry number
ν	wave number, cm^{-1}
Superscript o	reference state, referring to the hypothetical state of an ideal gas at 1 atm
Subscript p	pressure, atm

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