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THERMODYNAMIC FUNCTIONS OF α-HALONAPHTHALENES FROM 0.25 TO 16 ATMOSPHERES

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ABSTRACT

Real gas thermodynamic functions, C_p, S, $(H - H_0)/T$, and $-(F - H_0)/T$, have been calculated for α-halonaphthalenes ($C_{10}H_7X$, where X = F, Cl, Br, I) from 0.25 to 16 atm within the temperature range of 273.15 to 1200 K correcting the thermodynamic property ideal gas values by means of the Berthelot equation of state.

INTRODUCTION

In previous work, McFee and Lielmezs[1] have calculated the thermodynamic functions of naphthalene and 11 halogenated naphthalenes in the ideal gas state from 273.15 to 1200 K at 1 atm pressure. In this work, using the ideal gas state thermodynamic property values of α-halonaphthalenes (α-$C_{10}H_7X$, X = F, Br, Cl, I) as obtained by McFee and Lielmezs[1], and correcting these values by means of the Berthelot equation of state, the real gas thermodynamic properties of the four α-halonaphthalenes have been calculated from 0.25 to 16 atm within the temperature range of 273.15 to 1200 K. (Table 1).

The results presented in Table 1 were fitted to five constant polynominal of the form:

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

where A is the real gas thermodynamic function at temperature T (K). The constants a, b, c, d and e (Equation 1) were obtained using linear least squares curve fitting methods[2] and are found in Table 2. The molecular structural data needed for thermodynamic function calculations are found in Table 3.

DISCUSSION

It is well known that at high pressures and low temperatures intermolecular force effects may contribute greatly to deviations from the ideal gas law:

$$PV = RT \quad (2)$$

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TABLE 1

HEAT CAPACITY, ENTHALPY AND FREE ENERGY FUNCTIONS AND ENTROPY

Temp.	*α-Fluoronaphthalene*				*α-Chloronaphthalene*			
(K)	C_p *(cal mol^{-1} K^{-1})*	$(H-H_0)/T$ *(cal mol^{-1} K^{-1})*	$-(F-H_0)/T$ *(cal mol^{-1} K^{-1})*	S *(cal mol^{-1} K^{-1})*	C_p *(cal mol^{-1} K^{-1})*	$(H-H_0)/T$ *(cal mol^{-1} K^{-1})*	$-(F-H_0)/T$ *(cal mol^{-1} K^{-1})*	S *(cal mol^{-1} K^{-1})*
P = 0.25 atm								
451.00	51.60	27.03	80.51	107.53	52.47	27.98	82.88	110.86
522.70	57.63	30.82	84.77	115.59	58.36	31.76	87.28	119.04
273.15	32.68	16.94	69.67	86.61	34.12	17.79	71.58	89.37
298.15	35.56	18.38	71.22	89.59	36.88	19.27	73.20	92.47
300.00	35.77	18.48	71.53	89.81	37.08	19.38	73.32	92.70
350.00	41.41	21.36	74.40	95.76	42.54	22.30	76.53	98.83
400.00	46.69	24.20	77.43	101.63	47.68	25.16	79.69	104.85
450.00	51.51	26.97	80.45	107.42	52.38	27.93	82.82	110.74
500.00	55.82	29.65	83.43	113.07	56.60	30.59	85.90	116.49
550.00	59.68	32.20	86.37	118.58	60.36	33.13	88.93	122.06
600.00	63.11	34.64	89.28	123.92	63.72	35.54	91.92	127.46
650.00	66.17	36.95	92.14	129.09	66.72	37.82	94.86	132.68
700.00	68.92	39.14	94.96	134.10	69.41	39.99	97.74	137.72
750.00	71.39	41.21	97.73	138.94	71.84	42.03	100.57	142.60
800.00	73.62	43.16	100.46	143.62	74.02	43.96	103.34	147.31
850.00	75.64	45.01	103.13	148.14	76.01	45.79	106.06	151.85
900.00	77.48	46.77	105.75	152.52	77.82	47.52	108.73	156.25
950.00	79.16	48.43	108.33	156.75	79.46	49.16	111.34	160.50
1000.00	80.69	50.00	110.85	160.85	80.97	50.71	113.91	164.62
1050.00	82.09	51.50	113.33	164.83	82.35	52.19	116.42	168.60
1100.00	83.38	52.92	115.76	168.68	83.62	53.59	118.88	172.46
1150.00	84.57	54.27	118.14	172.41	84.79	54.92	121.29	176.21
1200.00	85.66	55.56	120.48	176.03	85.87	56.19	123.65	179.84
P = 0.50 atm								
451.00	51.74	26.95	79.15	106.11	52.66	27.88	81.53	109.42
522.70	57.72	30.78	83.41	114.18	58.49	31.69	85.92	117.62
273.15	33.34	16.61	68.40	85.01	35.00	17.35	70.35	87.69
298.15	36.07	18.13	69.92	88.05	37.56	18.94	71.93	90.87
300.00	36.27	18.24	70.03	88.27	37.75	19.05	72.05	91.10
350.00	41.72	21.20	73.07	94.27	42.96	22.10	75.22	97.31
400.00	46.90	24.10	76.09	100.19	47.97	25.02	78.36	103.38
450.00	51.65	26.90	79.09	105.99	52 58	27.83	81.47	109.30
500.00	55.93	29.59	82.07	111.66	56.74	30.52	84.54	115.06
550.00	59.76	32.16	85.01	117.17	60.47	33.07	87.57	120.65
600.00	63.17	34.61	87.91	122.52	63.81	35.50	90.56	126.05
650.00	66.22	36.93	90.77	127.70	66.79	37.79	93.49	131.28
700.00	68.96	39.12	93.95	132.71	69.47	39.96	96.37	136.33
750.00	71.42	41.19	96.36	137.55	71.88	42.01	99.20	141.21
800.00	73.64	43.15	99.08	142.23	74.06	43.95	101.97	145.92
850.00	75.66	45.00	101.76	146.76	76.04	45.78	104.69	150.47
900.00	77.50	46.76	104.38	151.14	77.84	47.51	107.36	154.86
950.00	79.17	48.42	106.95	155.37	79.48	49.15	109.97	159.12
1000.00	80.70	50.00	109.47	159.47	80.99	50.70	112.53	163.23
1050.00	82.11	51.49	111.95	163.44	82.37	52.18	115.04	167.22
1100.00	83.39	52.91	114.38	167.29	83.64	53.58	117.50	171.08
1150.00	84.58	54.27	116.76	171.03	84.40	54.91	119.91	174.82
1200.00	85.67	55.55	119.10	174.65	85.88	56.18	122.28	178.46

α-Bromonaphthalene				*α-Iodonaphthalene*			
C_p (*cal mol*$^{-1}$ *K*$^{-1}$)	$(H-H_0)/T$ (*cal mol*$^{-1}$ *K*$^{-1}$)	$-(F-H_0)/T$ (*cal mol*$^{-1}$ *K*$^{-1}$)	S (*cal mol*$^{-1}$ *K*$^{-1}$)	C_p (*cal mol*$^{-1}$ *K*$^{-1}$)	$(H-H_0)/T$ (*cal mol*$^{-1}$ *K*$^{-1}$)	$-(F-H_0)/T$ (*cal mol*$^{-1}$ *K*$^{-1}$)	S (*cal mol*$^{-1}$ *K*$^{-1}$)
52.81	28.58	85.50	114.08	53.03	28.95	87.53	116.49
58.63	32.32	89.99	122.30	58.82	32.66	92.07	124.74
34.76	18.48	73.87	92.35	35.25	18.88	75.71	94.58
37.46	19.96	75.55	95.51	37.88	20.36	77.42	97.78
37.66	20.06	75.68	95.74	38.08	20.47	77.55	98.02
43.02	22.96	78.99	101.95	43.35	23.36	80.92	104.29
48.08	25.79	82.24	108.03	48.35	26.18	84.23	110.40
52.72	28.53	85.44	113.97	52.94	28.90	87.47	116.37
56.89	31.16	88.58	119.74	57.08	31.52	90.65	122.17
60.62	33.67	91.67	125.34	60.79	34.01	93.77	127.78
63.94	36.06	94.70	130.76	64.09	36.38	96.83	133.22
66.92	38.32	97.68	136.00	67.05	38.63	99.83	138.47
69.59	40.46	100.60	141.06	69.71	40.76	102.78	143.53
71.99	42.48	103.46	145.94	72.10	42.77	105.66	148.43
74.16	44.40	106.26	150.66	74.26	44.67	108.48	153.15
76.14	46.21	109.01	155.21	76.22	46.47	111.24	157.71
77.93	47.92	111.70	159.62	78.01	48.17	113.95	162.12
79.57	49.54	114.33	163.87	79.64	49.79	116.59	166.38
81.07	51.08	116.91	168.00	81.14	51.32	119.19	170.51
82.44	52.54	119.44	171.98	82.50	52.77	121.73	174.50
83.71	53.93	121.92	175.85	83.76	54.15	124.21	178.36
84.87	55.25	124.34	179.60	84.92	55.46	126.65	182.11
85.94	56.51	126.72	183.23	85.99	56.71	129.04	185.75
53.00	28.49	84.15	112.64	53.26	28.84	86.19	115.03
58.76	32.25	88.63	120.88	58.97	32.59	90.72	123.31
35.65	18.03	72.64	90.67	36.30	18.36	74.50	92.86
38.15	19.61	74.29	93.90	38.69	19.96	76.18	96.14
38.34	19.73	74.41	94.14	38.87	20.08	76.30	96.38
43.45	22.75	77.68	100.43	43.85	23.12	79.63	102.74
48.37	25.65	80.91	106.56	48.69	26.01	82.90	108.92
52.92	28.43	84.09	112.52	53.18	28.78	86.13	114.91
57.04	31.09	87.22	118.31	57.25	31.43	89.30	120.73
60.73	33.62	90.31	123.93	60.92	33.95	92.41	126.36
64.03	36.02	93.34	129.35	64.19	36.34	95.47	131.81
66.99	38.29	96.31	134.60	67.13	38.59	98.47	137.06
69.64	40.43	99.23	139.66	69.77	40.73	101.41	142.14
72.03	42.46	102.09	144.55	72.15	42.74	104.29	147.03
74.20	44.38	104.89	149.27	74.30	44.65	107.11	151.76
76.17	46.19	107.63	153.83	76.26	46.45	109.87	156.32
77.96	47.91	110.32	158.23	78.04	48.16	112.57	160.73
79.59	49.53	112.96	162.49	79.67	49.78	115.22	165.00
81.09	51.07	115.54	166.61	81.16	51.31	117.81	169.12
82.46	52.54	118.06	170.60	82.52	52.76	120.35	173.11
83.72	53.93	120.54	174.47	83.78	54.14	122.84	176.98
84.88	55.25	122.97	178.21	84.94	55.46	125.27	180.73
85.95	56.50	125.35	181.85	86.00	56.71	127.66	184.37

(Continued on p. 42)

TABLE 1 *(continued)*

Temp.	*α-Fluoronaphthalene*				*α-Chloronaphthalene*			
(K)	C_p *(cal mol^{-1} K^{-1})*	$(H-H_0)/T$ *(cal mol^{-1} K^{-1})*	$-(F-H_0)/T$ *(cal mol^{-1} K^{-1})*	S *(cal mol^{-1} K^{-1})*	C_p *(cal mol^{-1} K^{-1})*	$(H-H_0)/T$ *(cal mol^{-1} K^{-1})*	$-(F-H_0)/T$ *(cal mol^{-1} K^{-1})*	S *(cal mol^{-1} K^{-1})*
P = 1.00 atm								
451.00	52.04	26.81	77.82	104.63	53.06	27.69	80.22	107.91
522.70	57.91	30.68	82.06	112.74	58.74	31.57	84.59	116.16
273.15	34.67	15.95	67.24	83.19	36.77	16.47	69.26	85.73
298.15	37.08	17.62	68.71	86.33	38.92	18.26	70.78	89.04
300.00	37.27	17.74	68.82	86.56	39.09	18.39	70.89	89.28
350.00	42.35	20.89	71.79	92.69	43.80	21.68	73.98	95.66
400.00	47.33	23.89	74.78	98.67	48.53	24.74	77.07	101.82
450.00	51.95	26.75	77.76	104.51	52.97	27.64	80.16	107.79
500.00	56.15	29.49	80.72	110.21	57.03	30.38	83.21	113.59
550.00	59.92	32.09	83.65	115.74	60.69	32.97	86.23	119.20
600.00	63.30	34.55	86.55	121.10	63.97	35.42	89.20	124.62
650.00	66.32	36.88	89.41	126.29	66.92	37.73	92.13	129.86
700.00	69.04	39.08	92.23	131.30	69.57	39.91	95.01	134.92
750.00	71.48	41.16	94.99	136.15	71.96	41.97	97.83	139.80
800.00	73.70	43.13	97.71	140.84	74.13	43.91	100.60	144.52
850.00	75.71	44.98	100.38	145.37	76.10	45.75	103.32	149.07
900.00	77.53	46.74	103.00	149.75	77.89	47.49	105.99	153.47
950.00	79.20	48.41	105.58	153.98	79.53	49.13	108.60	157.73
1000.00	80.73	49.99	108.10	158.09	81.03	50.69	111.16	161.84
1050.00	82.13	51.48	110.58	162.06	82.40	52.17	113.67	165.83
1100.00	83.41	52.91	113.00	165.91	83.66	53.57	116.13	169.69
1150.00	84.60	54.26	115.39	169.64	84.83	54.90	118.54	173.44
1200.00	85.69	55.55	117.72	173.27	85.90	56.17	120.90	177.07
P = 2.00 atm								
451.00	52.62	26.52	76.53	103.06	53.84	27.31	78.96	106.27
522.70	58.29	30.50	80.74	111.24	59.24	31.32	83.29	114.61
273.15	37.31	14.64	66.29	80.93	40.31	14.71	68.46	83.17
298.15	39.12	16.61	67.66	84.28	41.64	16.91	69.84	86.75
300.00	39.26	16.75	67.76	84.52	41.76	17.06	69.95	87.01
350.00	43.61	20.27	70.62	90.89	45.49	20.85	72.87	93.72
400.00	48.17	23.48	73.54	97.01	49.66	24.19	75.88	100.06
450.00	52.54	26.47	76.47	102.94	53.76	27.25	78.90	106.15
500.00	56.58	29.28	79.41	108.69	57.61	30.09	81.92	112.02
550.00	60.24	31.93	82.33	114.25	61.12	32.76	84.92	117.67
600.00	63.54	34.43	85.21	119.64	64.31	35.26	87.88	123.13
650.00	66.52	36.78	88.06	124.85	67.18	37.60	90.79	128.39
700.00	69.19	39.01	90.87	129.88	69.78	39.81	93.66	133.47
750.00	71.61	41.10	93.63	134.73	72.14	41.89	96.48	138.37
800.00	73.80	43.08	96.35	139.43	74.27	43.85	99.25	143.09
850.00	75.79	44.94	99.02	143.96	76.21	45.69	101.96	147.65
900.00	77.61	46.71	101.64	148.34	77.99	47.44	104.62	152.06
950.00	79.27	48.38	104.21	152.59	79.61	49.09	107.23	156.32
1000.00	80.78	49.96	106.73	156.69	81.10	50.65	109.79	160.44
1050.00	82.18	51.46	109.20	160.67	82.46	52.14	112.30	164.43
1100.00	83.46	52.89	111.63	164.52	83.72	53.54	114.75	168.30
1150.00	84.63	54.24	114.01	168.26	84.88	54.88	117.16	172.05
1200.00	85.72	55.53	116.35	171.88	85.94	56.15	119.53	175.68

α-Bromonaphthalene				α-Iodonaphthalene			
C_p (cal mol^{-1} K^{-1})	$(H-H_0)/T$ (cal mol^{-1} K^{-1})	$-(F-H_0)/T$ (cal mol^{-1} K^{-1})	S (cal mol^{-1} K^{-1})	C_p (cal mol^{-1} K^{-1})	$(H-H_0)/T$ (cal mol^{-1} K^{-1})	$-(F-H_0)/T$ (cal mol^{-1} K^{-1})	S (cal mol^{-1} K^{-1})
53.40	28.29	82.84	111.13	53.73	28.61	84.89	113.50
59.02	32.13	87.29	119.42	59.27	32.44	89.39	121.83
37.45	17.14	71.56	88.70	38.40	17.31	73.47	90.78
39.53	18.93	73.13	92.06	40.31	19.16	75.06	94.22
39.69	19.06	73.25	92.31	40.46	19.29	75.18	94.47
44.30	22.33	76.44	98.77	44.85	22.62	78.41	101.03
48.94	25.37	79.62	104.99	49.36	25.68	81.63	107.31
53.32	28.23	82.78	111.01	53.65	28.55	84.83	113.38
57.33	30.95	85.89	116.84	57.60	31.26	87.98	119.24
60.95	33.51	88.96	122.47	61.17	33.82	91.08	124.90
64.20	35.94	91.98	127.92	64.39	36.24	94.12	130.36
67.12	38.22	94.95	133.18	67.29	38.52	97.12	135.63
69.75	40.38	97.86	138.25	69.89	40.67	100.05	140.72
72.12	42.42	100.72	143.14	72.25	42.70	102.92	145.62
74.27	44.35	103.52	147.87	74.39	44.61	105.74	150.35
76.23	46.16	106.26	152.43	76.33	46.42	108.50	154.92
78.01	47.88	108.95	156.84	78.10	48.13	111.20	159.34
79.63	49.51	111.58	161.10	79.72	49.75	113.85	163.60
81.12	51.06	114.16	165.22	81.20	51.29	116.44	167.73
82.49	52.52	116.69	169.21	82.56	52.74	118.98	171.72
83.75	53.91	119.17	173.08	83.81	54.13	121.46	175.59
84.90	55.24	121.59	176.83	84.96	55.44	123.90	179.35
85.97	56.49	123.97	180.47	86.03	56.70	126.29	182.98
54.20	27.90	81.59	109.49	54.67	28.15	83.66	111.81
59.53	31.88	85.99	117.87	59.87	32.15	88.11	120.26
41.04	15.36	70.77	86.12	42.62	15.21	72.78	87.99
42.29	17.56	72.21	89.77	43.55	17.55	74.22	91.76
42.40	17.71	72.32	90.03	43.64	17.71	74.33	92.03
46.00	21.49	75.34	96.82	46.85	21.63	77.36	98.99
50.08	24.80	78.43	103.23	50.70	25.02	80.47	105.49
54.12	27.84	81.53	109.37	54.59	28.09	83.60	111.69
57.91	30.66	84.61	115.27	58.28	30.93	86.71	117.63
61.39	33.30	87.65	120.95	61.69	33.57	89.78	123.35
64.54	35.77	90.66	126.43	64.79	36.04	92.81	128.85
67.39	38.10	93.61	131.71	67.60	38.37	95.78	134.15
69.96	40.28	96.52	136.80	70.15	40.55	98.71	139.26
72.29	42.34	99.37	141.71	72.45	42.60	101.58	144.18
74.41	44.28	102.16	146.44	74.55	44.53	104.39	148.92
76.34	46.11	104.90	151.01	76.47	46.35	107.14	153.50
78.11	47.84	107.59	155.43	78.22	48.08	109.84	157.92
79.72	49.47	110.22	159.69	79.82	49.71	112.49	162.19
81.20	51.02	112.80	163.82	81.29	51.25	115.07	166.32
82.55	52.49	115.32	167.82	82.63	52.71	117.61	170.32
83.80	53.89	117.80	171.68	83.88	54.10	120.10	174.20
84.95	55.21	120.22	175.44	85.02	55.42	122.53	177.95
86.01	56.48	122.60	179.07	86.08	56.68	124.91	181.59

(Continued on p. 44)

TABLE 1 *(continued)*

Temp.	*α-Fluoronaphthalene*				*α-Chloronaphthalene*			
(K)	C_p *(cal mol⁻¹ K⁻¹)*	$(H-H_0)/T$ *(cal mol⁻¹ K⁻¹)*	$-(F-H_0)/T$ *(cal mol⁻¹ K⁻¹)*	S *(cal mol⁻¹ K⁻¹)*	C_p *(cal mol⁻¹ K⁻¹)*	$(H-H_0)/T$ *(cal mol⁻¹ K⁻¹)*	$-(F-H_0)/T$ *(cal mol⁻¹ K⁻¹)*	S *(cal mol⁻¹ K⁻¹)*
P = 4.00 atm								
451.00	53.80	25.95	75.34	101.29	55.41	26.53	77.84	104.37
522.70	59.04	30.13	79.47	109.61	60.25	30.83	82.07	112.90
273.15	42.60	12.02	65.78	77.79	47.39	11.20	68.24	79.43
298.15	43.18	14.60	66.94	81.54	47.08	14.21	69.35	83.56
300.00	43.26	14.78	67.03	81.81	47.10	14.41	69.44	83.85
350.00	46.12	19.03	69.64	88.67	48.85	19.18	72.04	91.22
400.00	49.85	22.65	72.42	95.07	51.91	23.08	74.86	97.93
450.00	53.72	25.89	75.28	101.17	55.35	26.47	77.78	104.25
500.00	57.44	28.86	78.16	107.02	58.76	29.53	80.73	110.25
550.00	60.89	31.62	81.05	112.66	61.99	32.33	83.67	116.01
600.00	64.04	34.19	83.91	118.10	64.98	34.93	86.60	121.53
650.00	66.91	36.60	86.74	123.34	67.71	37.35	89.49	126.84
700.00	69.51	38.86	89.54	128.39	70.20	39.61	92.34	131.95
750.00	71.87	40.98	92.29	133.27	72.48	41.73	95.15	136.87
800.00	74.01	42.98	95.00	137.98	74.55	43.71	97.91	141.62
850.00	75.97	44.86	97.66	142.52	76.45	45.58	100.61	146.20
900.00	77.76	46.64	100.28	146.92	78.19	47.35	103.27	150.62
950.00	79.39	48.32	102.84	151.17	79.78	49.01	105.87	154.89
1000.00	80.89	49.91	105.36	155.28	81.24	50.59	108.43	158.02
1050.00	82.27	51.42	107.84	159.26	82.59	52.08	110.93	163.01
1100.00	83.54	52.85	110.26	163.11	83.83	53.50	113.39	166.89
1150.00	84.70	54.21	112.64	166.85	84.97	54.84	115.80	170.64
1200.00	85.78	55.51	114.98	170.48	86.03	56.12	118.16	174.28
P = 8.00 atm								
451.00	56.15	24.80	74.33	99.13	58.56	24.99	76.96	101.94
522.70	60.55	29.40	78.33	107.73	62.27	29.84	81.00	110.85
273.15	53.18	6.77	66.12	72.89	61.54	4.16	69.17	73.34
298.15	51.32	10.57	66.88	77.45	57.97	8.81	69.75	78.56
300.00	51.24	10.82	66.95	77.77	57.78	9.11	69.80	78.92
350.00	51.15	16.55	69.07	85.62	55.58	15.85	71.75	87.60
400.00	53.22	20.99	71.58	92.57	56.42	20.85	74.20	95.06
450.00	56.09	24.73	74.27	99.00	58.51	24.91	76.90	101.81
500.00	59.17	28.02	77.05	105.07	61.07	28.40	79.71	108.11
550.00	62.19	30.99	79.86	110.85	63.72	31.49	82.56	114.05
600.00	65.04	33.71	82.68	116.39	66.31	34.28	85.42	119.71
650.00	67.69	36.22	85.48	121.70	68.76	36.84	88.27	125.11
700.00	70.14	38.56	88.25	126.81	71.04	39.21	91.09	130.29
750.00	72.38	40.74	90.98	131.72	73.16	41.40	93.87	135.27
800.00	74.43	42.78	93.68	136.46	75.12	43.45	96.61	140.05
850.00	76.32	44.70	96.33	141.03	76.92	45.36	99.30	144.66
900.00	78.05	46.51	98.94	145.44	78.58	47.16	101.94	149.11
950.00	79.64	48.21	101.50	149.71	80.12	48.86	104.54	153.40
1000.00	81.11	49.82	104.01	153.83	81.53	50.46	107.09	157.54
1050.00	82.46	51.34	106.48	157.82	82.84	51.97	109.59	161.55
1100.00	83.70	52.78	108.90	161.68	84.04	53.40	112.04	165.44
1150.00	84.85	54.15	111.28	165.43	85.16	54.76	114.44	169.20
1200.00	85.91	55.45	113.61	169.06	86.19	56.04	116.80	172.84

α-Bromonaphthalene				*α-Iodonaphthalene*			
C_p (*cal mol*$^{-1}$ *K*$^{-1}$)	$(H-H_0)/T$ (*cal mol*$^{-1}$ *K*$^{-1}$)	$-(F-H_0)/T$ (*cal mol*$^{-1}$ *K*$^{-1}$)	S (*cal mol*$^{-1}$ *K*$^{-1}$)	C_p (*cal mol*$^{-1}$ *K*$^{-1}$)	$(H-H_0)/T$ (*cal mol*$^{-1}$ *K*$^{-1}$)	$-(F-H_0)/T$ (*cal mol*$^{-1}$ *K*$^{-1}$)	S (*cal mol*$^{-1}$ *K*$^{-1}$)
55.80	27.11	80.46	107.58	56.54	27.23	82.58	109.81
60.55	31.38	84.78	116.15	61.07	31.56	86.92	118.48
48.21	11.79	70.56	82.35	51.04	11.03	72.78	83.81
47.81	14.82	71.73	86.55	50.03	14.33	73.90	88.23
47.82	15.02	71.82	86.85	50.00	14.55	73.99	88.54
49.42	19.80	74.51	94.31	50.85	19.64	76.63	96.27
52.37	23.68	77.42	101.09	53.38	23.69	79.53	103.22
55.73	27.05	80.40	107.45	56.48	27.16	82.52	109.68
59.08	30.09	83.41	113.50	59.66	30.25	85.54	115.80
62.27	32.87	86.41	119.28	62.72	33.07	88.56	121.63
65.21	35.44	89.38	124.83	65.58	35.66	91.55	127.21
67.92	37.84	92.32	130.15	68.22	38.06	94.50	132.57
70.39	40.08	95.20	135.28	70.65	40.31	97.41	137.71
72.64	42.17	98.04	140.21	72.86	42.40	100.26	142.66
74.70	44.14	100.83	144.97	74.89	44.37	103.06	147.43
76.58	46.00	103.56	149.55	76.75	46.22	105.81	152.03
78.31	47.74	106.24	153.98	78.45	47.97	108.50	156.46
79.89	49.40	108.86	158.26	80.02	49.61	111.13	160.75
81.34	50.96	111.44	162.39	81.46	51.17	113.72	164.89
82.68	52.44	113.96	166.40	82.78	52.64	116.25	168.90
83.91	53.84	116.43	170.27	84.00	54.04	118.73	172.77
85.05	55.17	118.85	174.03	85.13	55.37	121.17	176.53
86.10	56.44	121.23	177.67	86.18	56.63	123.55	180.18
58.98	25.54	79.59	105.14	60.28	25.38	81.80	107.18
62.60	30.38	83.72	114.09	63.48	30.38	85.92	116.30
62.57	4.66	71.54	76.19	67.89	2.65	74.17	76.82
58.84	9.34	72.15	81.49	62.98	7.89	74.64	82.53
58.65	9.64	72.21	81.86	62.72	8.23	74.69	82.92
56.24	16.42	74.24	90.66	58.86	15.68	76.55	92.23
56.94	21.42	76.77	98.19	58.75	21.04	79.01	100.05
58.94	25.47	79.54	105.01	60.24	25.31	81.74	107.05
61.42	28.94	82.40	111.34	62.41	28.90	84.60	113.50
64.02	32.01	85.31	117.32	64.79	32.06	87.51	119.56
66.57	34.78	88.21	123.00	67.17	34.88	90.42	125.30
68.98	37.32	91.10	128.42	69.48	37.46	93.31	130.77
71.24	39.67	93.95	133.62	71.65	39.82	96.18	136.00
73.33	41.84	96.76	138.61	73.68	42.01	99.00	141.01
75.27	43.87	99.53	143.40	75.56	44.05	101.78	145.83
77.06	45.77	102.25	148.02	77.31	45.96	104.51	150.46
78.71	47.56	104.91	152.47	78.92	47.74	107.18	154.93
80.23	49.24	107.53	156.77	80.42	49.43	109.81	159.24
81.63	50.82	110.10	160.92	81.80	51.01	112.39	163.40
82.93	52.32	112.61	164.93	83.08	52.51	114.91	167.42
84.13	53.74	115.08	168.82	84.26	53.92	117.39	171.31
85.24	55.09	117.50	172.58	85.36	55.27	119.81	175.08
86.27	56.36	119.87	176.23	86.37	56.54	122.19	178.74

(Continued on p. 46)

TABLE 1 *(continued)*

Temp. (K)	α-Fluoronaphthalene				α-Chloronaphthalene			
	C_p (cal mol^{-1} K^{-1})	$(H-H_0)/T$ (cal mol^{-1} K^{-1})	$-(F-H_0)/T$ (cal mol^{-1} K^{-1})	S (cal mol^{-1} K^{-1})	C_p (cal mol^{-1} K^{-1})	$(H-H_0)/T$ (cal mol^{-1} K^{-1})	$-(F-H_0)/T$ (cal mol^{-1} K^{-1})	S (cal mol^{-1} K^{-1})
P = 16.00 atm								
451.00	60.85	22.50	73.68	96.18	64.85	21.90	76.57	98.47
522.70	63.57	27.93	77.41	105.34	66.31	27.87	80.25	108.12
273.15	74.33	−3.73	68.19	64.46	89.84	−9.90	72.43	62.53
298.15	67.58	2.51	68.14	70.65	79.73	−1.99	71.92	69.93
300.00	67.21	2.91	68.16	71.07	79.15	−1.49	71.91	70.42
350.00	61.21	11.59	69.30	80.89	69.03	9.20	72.54	81.74
400.00	59.96	17.68	71.27	88.95	65.43	16.41	74.27	90.67
450.00	60.82	22.41	73.63	96.05	64.84	21.80	76.52	98.33
500.00	62.61	26.34	76.20	102.54	65.68	26.14	79.05	105.19
550.00	64.78	29.73	78.88	108.61	67.19	29.80	81.72	111.52
600.00	67.04	32.75	81.60	114.34	68.98	32.99	84.45	117.44
650.00	69.26	35.47	84.33	119.80	70.86	35.83	87.21	123.04
700.00	71.39	37.96	87.05	125.01	72.73	38.40	89.96	128.36
750.00	73.40	40.26	89.75	130.00	74.53	40.75	92.69	133.44
800.00	75.28	42.39	92.41	134.80	76.24	42.91	95.39	138.30
850.00	77.02	44.38	95.04	139.42	77.86	44.92	98.05	142.97
900.00	78.64	46.23	97.63	143.87	79.37	46.79	100.67	147.47
950.00	80.15	47.98	100.18	148.16	80.79	48.55	103.25	151.80
1000.00	81.54	49.62	102.68	152.31	82.11	50.19	105.78	155.97
1050.00	82.83	51.17	105.14	156.32	83.34	51.74	108.27	160.01
1100.00	84.02	52.64	107.56	160.20	84.48	53.20	110.71	163.91
1150.00	85.13	54.03	109.93	163.96	85.54	54.59	113.11	167.69
1200.00	86.16	55.35	112.26	167.60	86.53	55.90	115.46	171.35

for one mole of gas. Indeed, it may well be assumed that the associating gas molecules may form dimers, trimers and higher order clusters. On association, the number of effective particles changes, and the rotational degrees of freedom of each individual molecule in an associated group are reduced, in turn reducing the entropy of the system. This then causes deviation from the ideal gas law (eqn (2)) and explains why the ideal gas thermodynamic property formulae derived, assuming that gas consists of individual non-interacting particles, do not suffice in case of the real gas.

Assuming that this molecular interaction is caused principally by the molecular Van der Waals forces; then, for low pressures it is possible to approximate this association — cluster formation by the second term virial expansion of eqn (2) as:

$$PV = RT + BT \tag{3}$$

where $B = B(T)$ and is the second virial coefficient. Due to the lack of input data for intermolecular potentials (such as Lennard-Jones; or Stockmayer) of halogenated naphthalenes, it is not possible to use eqn (3) directly to describe the real gas behaviour of α-halonaphthalenes. Noting the successful application of Berthelot state equation

α-Bromonaphthalene				*α-Iodonaphthalene*			
C_p (*cal mol*$^{-1}$ K^{-1})	$(H-H_0)/T$ (*cal mol*$^{-1}$ K^{-1})	$-(F-H_0)/T$ (*cal mol*$^{-1}$ K^{-1})	S (*cal mol*$^{-1}$ K^{-1})	C_p (*cal mol*$^{-1}$ K^{-1})	$(H-H_0)/T$ (*cal mol*$^{-1}$ K^{-1})	$-(F-H_0)/T$ (*cal mol*$^{-1}$ K^{-1})	S (*cal mol*$^{-1}$ K^{-1})
65.36	22.41	79.23	101.63	67.77	21.70	81.61	103.31
66.70	28.37	82.98	111.35	68.28	28.03	85.29	113.32
91.28	−9.61	74.86	65.24	101.58	−14.11	78.31	64.21
80.92	−1.62	74.38	72.76	88.89	−4.98	77.49	72.52
80.32	−1.11	74.37	73.26	88.15	−4.40	77.46	73.06
69.89	9.66	75.07	84.73	74.88	7.74	77.77	85.51
66.08	16.91	76.86	93.77	69.48	15.74	79.36	95.10
65.36	22.31	79.18	101.49	67.78	21.59	81.56	103.16
66.10	26.65	81.76	108.40	67.90	26.21	84.09	110.30
67.54	30.29	84.47	114.77	68.91	30.04	86.77	116.81
69.28	33.47	87.25	120.72	70.35	33.34	89.53	122.87
71.11	36.29	90.04	126.33	71.98	36.25	92.31	128.56
72.95	38.85	92.83	131.67	73.65	38.86	95.10	133.96
74.72	41.18	95.59	136.77	75.30	41.23	97.86	139.09
76.41	43.33	98.31	141.64	76.90	43.41	100.59	144.00
78.01	45.32	101.00	146.32	78.43	45.43	103.28	148.71
79.51	47.18	103.64	150.83	79.87	47.30	105.94	153.24
80.91	48.92	106.24	155.16	81.22	49.05	108.54	157.59
82.22	50.55	108.79	159.35	82.49	50.69	111.10	161.79
83.44	52.09	111.30	163.39	83.67	52.23	113.61	165.84
84.57	53.54	113.75	167.30	84.78	53.69	116.07	169.76
85.63	54.91	116.17	171.08	85.81	55.06	118.49	173.55
86.61	56.21	118.53	174.74	86.77	56.36	120.86	177.23

to fluorobenzene thermodynamic property calculation[3], this simple, two constant, state equation was used also for this work. As a matter of fact, the second virial coefficient (eqn (3)) may be expressed through Berthelot's equation of state as:

$$B = \frac{9}{128}\frac{RT_c}{p_c}\left[1 - 6\left(\frac{T_c}{T}\right)^2\right] \tag{4}$$

where the gas constant $R = 82.06$ cc atm K^{-1}, and the other quantities are in compatible units. The differences between the ideal gas thermodynamic functions (state equation $PV = RT$) and the real gas thermodynamic properties (state defined by eqn (3); valid for moderate pressures up to 16 atm) can be obtained through the application of the following equation set (5) which relates P–V–T properties of the gas to the desired thermodynamic functions:

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P;\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P;\left(\frac{\partial C_p}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P \tag{5}$$

TABLE 2

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

Pressure (atm)	*α-Fluoronaphthalene*									
	C_p					$(H - H_0^0)/T$				
	a	b	$c \times 10^3$	$d \times 10^7$	$e \times 10^{11}$	a	$b \times 10$	$c \times 10^1$	$d \times 10^7$	$e \times 10^{10}$
0.25	−12.2167	0.20501	−0.16796	0.63601	−0.77730	0.32017	0.59795	0.11784	−0.34599	0.12697
0.50	−9.09328	0.18974	−0.13995	0.41132	−0.11564	−1.23521	0.67406	−0.02185	−0.23389	0.09396
1.00	−2.84658	0.15921	−0.08395	−0.03804	1.20759	−4.34612	0.82631	−0.30124	−0.00967	0.02792
2.00	9.64575	0.09815	0.02805	−0.93661	3.85351	−10.56754	1.13078	−0.85999	0.43873	−0.10413
4.00	34.63226	−0.02397	0.25207	−2.73406	9.14647	−23.01054	1.73973	−1.97751	1.33556	−0.36825
8.00	84.60561	−0.26822	0.70012	−6.32893	19.73217	−47.89748	2.95770	−4.21269	3.12933	−0.89652
16.00	184.5500	−0.75670	1.59616	−13.51826	40.90237	−97.66557	5.39322	−8.68205	6.71593	−1.95276
	$-(F - H_0^0)/T$					S				
	a	$b \times 10$	$c \times 10^5$	$d \times 10^7$	$e \times 10^{11}$	a	b	$c \times 10^1$	$d \times 10^7$	$e \times 10^{10}$
0.25	52.80371	0.61178	0.50275	−0.11388	0.32295	53.12361	0.12097	0.16809	−0.45984	0.15926
0.50	51.94057	0.58655	0.96630	−0.15170	0.43261	50.70509	0.12606	0.07474	−0.38494	0.13720
1.00	51.59167	0.53608	1.89320	−0.22551	0.65181	47.24557	0.13624	−0.11192	−0.23517	0.09310
2.00	52.27155	0.43513	3.74742	−0.37438	1.09033	41.70387	0.15659	−0.48527	6.43765	0.00490
4.00	55.00800	0.23328	7.45465	−0.67200	1.96701	31.99820	0.19730	−1.23191	0.66342	−0.17150
8.00	61.85899	−0.17047	14.87031	−1.26736	3.72077	13.96399	0.27871	−2.72540	1.86173	−0.52436
16.00	76.93747	−0.97790	29.69981	−2.45789	7.22762	−20.72614	0.44152	−5.71168	4.25763	−1.22984
	α-Chloronapthalene									
	C_p					$(H - H_0^0)/T$				
	a	$b \times 10$	$c \times 10^3$	$d \times 10^7$	$e \times 10^{11}$	$a \times 10^{-1}$	$b \times 10$	$c \times 10^5$	$d \times 10^7$	$e \times 10^{11}$
0.25	−8.98073	1.95313	−0.15439	0.54270	−0.52636	0.02882	0.65703	−0.02778	−0.24868	0.98624
0.50	−4.80230	1.74891	−0.11694	0.24215	0.35861	−0.17943	0.75892	−1.89752	−0.09864	0.54436
1.00	3.55556	1.34041	−0.04200	−0.35908	2.12906	−0.59597	0.96272	−5.63732	0.20148	−0.33947
2.00	20.26974	0.52353	0.10784	−1.56128	5.66898	−1.42900	1.37030	−13.11163	0.80164	−2.10693
4.00	53.70180	−1.11051	0.40759	−3.96631	12.75112	−3.09506	2.18545	−28.07388	2.00193	−5.64160
8.00	120.56490	−4.37852	1.00707	−8.77629	26.91503	−6.42722	3.81579	−57.99099	4.40275	−12.71204
16.00	254.28270	−10.91393	2.20587	−18.39458	55.23710	−13.09142	7.07637	−117.82180	9.20399	−26.85132

Pressure (atm)	$-(F-H_0^0)/T$ a	$b\times10$	$c\times10^5$	$d\times10^8$	$e\times10^{11}$	S a	b	$c\times10^5$	$d\times10^7$	$e\times10^{10}$
0.25	53.50237	0.67046	−0.11348	−0.79553	0.24480	53.70057	0.13275	−0.14114	−0.32825	0.12311
0.50	52.81499	0.63661	0.50813	−1.29465	0.39184	51.02031	0.13956	−1.38994	−0.22805	0.09360
1.00	52.81667	0.56900	1.74963	−2.29121	0.68537	46.85686	0.15317	−3.88788	−0.02763	0.03458
2.00	54.19775	0.43375	4.23321	−4.28487	1.27260	39.90828	0.18040	−8.88217	−0.37306	−0.08340
4.00	58.33725	0.16325	9.20011	−8.27193	2.44698	27.38663	0.23487	−18.87402	1.17477	−0.31948
8.00	67.99376	−0.37775	19.13422	−16.24623	4.79577	3.72230	0.34380	−38.85548	2.77799	−0.79158
16.00	88.68539	1.45984	39.00435	−32.19720	9.49423	−42.23102	0.56167	−78.82107	5.98462	−1.73583

α-Bromonaphthalene

	C_p $a\times10^{-1}$	b	$c\times10^3$	$d\times10^7$	$e\times10^{11}$	$(H-H_0^0)/T$ a	$b\times10$	$c\times10^5$	$d\times10^7$	$e\times10^{11}$
0.25	−0.72677	0.18936	−0.14544	0.47949	−0.35588	1.03500	0.65891	−0.21569	−0.22922	0.92307
0.50	−0.30294	0.16864	−0.10744	0.17461	0.54187	−1.07779	0.76228	−2.11242	−0.07701	0.47484
1.00	0.54469	0.12722	−0.03145	−0.43510	2.33727	−5.30316	0.96900	−5.90576	0.22739	−0.42164
2.00	2.23998	0.04436	0.12054	−1.65455	5.92808	−13.75382	1.38244	−13.49205	0.83616	−2.21441
4.00	5.63066	−0.12136	0.42453	−4.09361	13.11026	−30.65539	2.20933	−28.66494	2.05374	−5.80007
8.00	12.41200	−0.45281	1.03252	−8.97177	27.47480	−64.45930	3.86319	−59.01330	4.48918	−12.97250
16.00	25.97439	−1.11567	2.24844	−18.72752	56.20195	−41.43932	5.73184	−80.81638	6.13945	−17.80446

	$-(F-H_0^0)/T$ a	$b\times10$	$c\times10^5$	$d\times10^8$	$e\times10^{11}$	S a	b	$c\times10^4$	$d\times10^7$	$e\times10^{10}$
0.25	54.79434	0.72282	−0.80468	−0.33676	0.12513	55.82906	0.13818	−0.10207	−0.26287	0.10481
0.50	54.11682	0.68851	−0.17471	−0.84245	0.27408	53.03896	0.14508	−0.22872	−0.16125	0.07489
1.00	54.13911	0.61990	1.08514	−1.85375	0.57195	48.83604	0.15889	−0.48204	−0.04200	0.01504
2.00	55.56126	0.48266	3.60509	−3.87661	1.16779	41.80766	0.18651	−0.98866	0.44848	−0.10465
4.00	59.78300	0.20818	8.64480	−7.92201	2.35933	29.12737	0.24175	−2.00210	1.26162	−0.34410
8.00	69.60385	−0.34077	18.72431	−16.01305	4.74254	5.14783	0.35222	−4.02830	2.88723	−0.82277
16.00	90.62196	−1.43860	38.88118	−32.19266	9.50795	−41.43932	0.57318	−8.08164	6.13945	−1.78045

TABLE 2 *(continued)*

Pressure (atm)	*α-Iodonaphthalene*									
	C_p					$(H - H_0^0)/T$				
	a	*b*	$c \times 10^3$	$d \times 10^7$	$e \times 10^{11}$	$a \times 10^{-1}$	$b \times 10$	$c \times 10^4$	$d \times 10^7$	$e \times 10^{11}$
0.25	−5.68559	0.18286	−0.13432	0.39298	−0.10516	0.13578	0.66723	−0.04655	−0.20622	0.85103
0.50	−0.71097	0.15855	−0.08972	0.03514	0.94855	−0.11221	0.78854	−0.26914	−0.02761	0.32505
1.00	9.23854	0.10992	−0.00051	−0.68057	3.05608	−0.60828	1.03123	−0.71444	0.32973	−0.72729
2.00	29.13673	0.01267	0.17788	−2.11186	7.27066	−1.60039	1.51657	−1.60500	1.04436	−2.83181
4.00	68.93523	−0.18185	0.53469	−4.97473	15.70074	−3.58465	2.48729	−3.38617	2.47367	−7.04091
8.00	148.53100	−0.57088	1.24832	−10.70047	32.56129	−7.55304	4.42865	−6.94816	5.33226	−15.45939
16.00	307.72070	−1.34893	2.67552	−22.15146	66.56129	−15.48975	8.31129	−14.07262	11.04904	−32.29450
	$-(F - H_0^0)/T$					S				
	a	$b \times 10$	$c \times 10^4$	$d \times 10^8$	$e \times 10^{12}$	*a*	$b \times 10$	$c \times 10^4$	$d \times 10^7$	$e \times 10^{11}$
0.25	56.04086	0.75330	−0.11950	−0.08351	0.60209	57.39859	1.42053	−0.16604	−0.21458	0.911275
0.50	55.48534	0.71302	−0.04555	−0.67708	2.35033	54.36279	1.50160	−0.31474	−0.09526	0.55990
1.00	55.75185	0.63245	0.10238	−1.86446	5.84766	49.66896	1.66368	−0.61207	0.14329	−0.14254
2.00	57.66237	0.47131	0.39824	−4.23931	12.84253	41.65858	1.98787	−1.20674	0.62042	−1.54751
4.00	62.86121	0.14900	0.99002	−8.98943	26.83358	27.01514	2.63625	−2.39610	1.56468	−4.35742
8.00	74.63637	−0.49564	2.17360	−18.49011	54.81765	−0.89277	3.93291	−4.77458	3.48300	−9.97671
16.00	99.56306	−1.78482	4.54048	−37.48830	110.7725	−55.33562	6.52655	−9.53234	7.30042	−21.21791

[a] To avoid large errors in applying eqn (1), all five constants (a, b, c, d, e) should be used.

TABLE 3

MOLECULAR PARAMETERS

α-Fluoronaphthalene	*α-Chloronaphthalene*	*α-Bromonaphthalene*	*α-Iodonaphthalene*
Fundamental frequencies[a], *ν* (cm^{-1})			
530, 158 270, 361 417	180, 135 240, 355 408	180, 125 235, 362 406	180, 115 226, 362 405
475, 512 570, 620 710	474, 513 534, 603 663	473, 512 528, 580 651	478, 510 524, 568 640
770, 750 877, 1157 1231	768, 746 827, 790 795	766, 745 806, 796 791	767, 745 797, 790 791
1217, 1264 1350, 1385 1407	850, 883 850, 945 220	855, 950 175, 940 950	858, 883 858, 950 151
1442, 1465 1514, 1576 1604	945, 972 972, 1023 353	959, 1024 272, 884 855	945, 945 967, 1022 226
1624, 790 795, 860 886	1140, 1142 1162, 1205 1216	1136, 1144 1167, 1204 1216	1131, 1143 1160, 1203 1215
860, 956 270, 967 967	1250, 1340 1373, 1381 1430	1252, 1340 1368, 1378 1434	1249, 1331 1365, 1377 1428
1037, 461 1146, 1146 180	1495, 1503 1565, 1593 1624	1455, 1501 1561, 1594 1624	1450, 1499 1552, 1597 1624
967, 3076 3027, 3031 3060	394, 2998 3027, 3031 3060	3076, 300 2987, 3027 3031	3076, 250 2987, 3027 3031
3060, 2987 3076,	3060, 3076 3076	3060, 3076 3060	3060, 3060 3076
Product of the principal moments of inertia[b] ($g^3\ cm^6$)			
$371{,}534 \times 10^{-117}$	$722,355 \times 10^{-117}$	$1{,}566{,}999 \times 10^{-117}$	$2{,}598{,}055 \times 10^{-117}$
Normal boiling point (K)			
488.15	531.95	554.15	575.15
Critical temperature[c] *(K)*			
728.60	807.50	834.50	864.20
Critical pressure[c] *(atm)*			
36.10	36.73	39.97	37.82
Symmetry number, σ			
1	1	1	1
Molecular weight			
146.17	162.62	207.08	254.07

[a] For frequency selection, see discussion by McFee and Lielmezs[1].

[b] For assumptions involving principal moment of inertia calculations, see McFee and Lielmezs[1].

[c] Estimated, this work. Note that any α-halonaphthalene gas is determined from its boiling point. Hence calculated thermodynamic property values (Tables 1 and 2) should be used with reference to the particular boiling point value. Any thermodynamic property value below the boiling point would refer to the α-halonaphthalene fictious vapor. This effect is especially noted at higher than 8 atm (Table 1).

Combining eqns (3)–(5), we arrive at eqns (6)–(8) which yield the real gas devivation from the ideal gas state at one atmosphere pressure:

$$(H - H_0^0)/T = \frac{9}{128}\frac{RT_c}{P_c}\left[1 - 18\left(\frac{T_c}{T}\right)^2\right]P \tag{6}$$

$$(C_p - C_p^0) = \frac{81}{32}\left(\frac{RT_c^3}{P_cT^3}\right)P \tag{7}$$

$$(S^0 - S)_T = \frac{27}{32}\left(\frac{RT_c^3}{P_cT^3}\right)P + R \ln P^* \tag{8}$$

These difference eqns (6)–(8) based on the Berthelot equation of state; have been used to calculate the presented (Table 1) thermodynamic functions.

As a matter of fact, in their use of Berthelot's equation of state for calculating the real gas thermodynamic functions for fluorobenzene, Butler and Lielmezs[3] noted very close agreement between the calculated real gas thermodynamic function values and the available experimental data. However, there are no available experimental data for α-halonaphthalenes and so the range of applicability of eqns (6)–(8) can only be inferred from the general limitations associated with the second virial coefficient expansion. Hence, it is suggested that eqns (6)–(8) will be more accurate in the lower pressure regions (approaching the ideal gas behaviour) and less accurate at the higher pressures and in the vicinity of the critical point which for the halonaphthalenes is at the pressure range of 36–40 atm and within 720–870 K temperature interval.

Indirectly, this observation has been brought out also by Butler and Lielmezs[3] who showed that for fluorobenzene the calculated heat capacities did fit the experimental data of Scott et al.[4] over a pressure range of 0.25 to 10 atm. Yet, studies by Waddington et al.[5] on normal hydrocarbons have indicated that corrections obtained by the use of Berthelot equation of state are too small at lower temperatures near the normal boiling point. Despite this aspect of caution, it is still felt that Butler's and Lielmezs'[3] work on fluorobenzene is sufficiently strong evidence to assume that Berthelot's equation of state in conjunction with the second virial coefficient expansion (eqns (3) and (4)) describes the P–V–T properties of α-halonaphthalenes reasonably well within the stated ranges of applicability (pressure range from 0.25 to 16 atm).

ACCURACY

McFee and Lielmezs[1] have already in detail discussed the accuracy and the range of reliability of the calculated thermodynamic functions for α-halonaphthalenes in the ideal gas state. They evaluated four types of errors: mathematical errors due

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* Term $R \ln P$ (eqn (8)) is correction which must be added to obtain the ideal gas entropy at pressure P; provided that this correction has not been already included in the ideal gas S^0-expression. It should be noted that for $P = 1$ atm, $R \ln P = 0$.

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; and errors due to the inapplicability of the basic assumptions, for instance the anharmonicity. McFee and Lielmezs[1] concluded that for α-halonaphthalenes the calculated ideal gas state thermodynamic functions should be reliable from approximately 400 to 1000°K; the expected error range of ± 2.0% being well within the general experimental uncertainty as specified by Whiffen[6].

The calculation of real gas thermodynamic functions additionally however involves (eqns (4), (6), (7) and (8) the knowledge of the critical point properties, the critical pressure P_c, and the critical temperature, T_c. For α-halonaphthalenes, these critical properties were obtained using the Lydersen incremental estimation method[7] (Table 3). For internal consistency, the estimated α-halonaphthalene critical properties were compared with the experimental critical property values of the correspondingly substituted halogenated benzene series[8]. Furthermore, the critical property uncertainty effect on the calculated real gas thermodynamic function values was investigated by calculating the thermodynamic functions for α-iodonaphthalene using critical temperature and critical pressure values 5% below the estimated critical property values for α-iodonaphthalene (Table 3). It was found that only at low temperatures and at high pressures the error was greater than 0.2–0.3%. Hence, the calculated real gas values (Table 1) should be accurate except at low temperatures where an error of less than 1% may be expected. In general, it was felt that barring major errors in the frequency assignments (McFee and Lielmezs[1]), the expected overall error should be at most 1–2%. This suggested error is expected to hold for all pressures between temperatures from about 400 to 1000°K.

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NOMENCLATURE

Å	=	angstrom unit
B	=	second virial coefficient, cc mol^{-1}
C_P^0	=	heat capacity, cal mol^{-1} K^{-1}
e.u.	=	entropy unit, cal mol^{-1} K^{-1}
$-(F^0 - H_0^0)/T$	=	free energy function, cal mol^{-1} K^{-1}
$(H^0 - H_0^0)/T$	=	enthalpy function, where $H_0^0 = H^0$ at 0 K, cal mol^{-1} K^{-1}
P	=	pressure, atm
R	=	universal gas constant
S^0	=	entropy, e.u.

T = temperature, K
V = volume, cc
σ = molecular symmetry number
ν = wave number, cm^{-1}

Superscript:
0 = reference state, referring to the hypothetical state of an ideal gas at 1 atm

Subscript:
c = critical state
p = pressure

REFERENCES

1 D. G. McFee and J. Lielmezs, unpublished manuscript, 1977.
2 J. Streal and L. C. Moore, *Curve Fitting Techniques*, The University of British Columbia, Computer Centre, B.C., 1976.
3 J. B. Butler and J. Lielmezs, *Thermochim. Acta*, 9 (1974) 359.
4 D. W. Scott, J. P. McCullough, D. W. Good, J. F. Messerly, R. E. Pennington, T. C. Kincheloe, I. A. Hossenlopp, D. R. Douslin and G. Waddington, *J. Am. Chem. Soc.*, 78 (1956) 5457.
5 G. Waddington, J. C. Smith, D. W. Scott and H. M. Huffman, *J. Am. Chem. Soc.*, 71 (1949) 3902.
6 D. H. Whiffen, *J. Chem. Soc.*, (1956) 1350.
7 R. C. Reid, J. M. Prausnitz and T. K. Sherwood, *The Properties of Gases and Liquids*, 3rd ed., McGraw-Hill, New York, 1977.
8 R. C. Weast (Editor), in *Handbook of Chemistry and Physics*, 56th ed., CRC Press, Cleveland, Ohio, 1975.