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THERMODYNAMIC FUNCTIONS OF FLUOROBENZENE FROM 0.25 TO 10 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 fluorobenzene from 0.25 to 10 atm within the temperature range of 273.15 to 1000 K correcting the thermodynamic property ideal gas values by means of the Berthelot equation of state. The agreement with experimental data wherever available, is excellent.

INTRODUCTION

In previous work, Butler and Lielmezs[1] have calculated the thermodynamic functions of 38 halogenated benzenes, including fluorobenzene, in the ideal gas state. In this work, using the thermodynamic property values of fluorobenzene as obtained by Butler and Lielmezs[1] and correcting these values by means of the Berthelot equation of state, the real gas thermodynamic properties of fluorobenzene have been calculated (Table 1) from 0.25 to 10 atm within the temperature range of 273.15 to 1000 K.

DISCUSSION

If the state equation is present as the virial expansion at the second virial coefficient, i.e.:

$$PV = RT + BT \tag{1}$$

where $B = B(T)$, and is the second virial coefficient; one may use Berthelot's equation of state to calculate the second virial coefficient B† as:

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

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†For fluorobenzene the following B-values have been obtained. At 318.4 K: $B = -1460$ cc/g-mole (experimental, ref. 2); -1272 cc/g-mole [calculated, eqn (2)]; at 382.4 K: $B = -916$ cc/g-mole (experimental, ref. 2); -861 cc/g-mole [calculated, eqn (2)]. As seen, the calculated results [this work, eqn (2)] compare very well with the experimental measurements.

TABLE 1

FLUOROBENZENE THERMODYNAMIC FUNCTIONS

Temperature (K)	*Heat capacity, C_p (cal mol^{-1} K^{-1})*					*Entropy, S (cal mol^{-1} K^{-1})*				
	0.25 atm	*1 atm*	*2 atm*	*5 atm*	*10 atm*	*0.25 atm*	*1 atm*	*2 atm*	*5 atm*	*10 atm*
273.15	20.86	21.59	22.56	25.48	30.34	73.11	70.11	68.41	65.61	62.61
298.15	22.73	23.29	24.04	26.28	30.02	75.01	72.07	70.44	67.88	65.25
300.00	22.87	23.42	24.15	26.36	30.03	75.15	72.22	70.59	68.04	65.44
350.00	26.55	26.90	27.36	28.75	31.06	78.96	76.09	74.56	72.27	70.13
400.00	30.01	30.25	30.56	31.48	33.03	82.73	79.90	78.42	76.29	74.40
450.00	33.17	33.33	33.55	34.20	35.29	86.45	83.64	82.19	80.16	78.42
500.00	36.00	36.12	36.28	36.75	37.54	90.10	87.30	85.87	83.89	82.25
550.00	38.52	38.61	38.73	39.09	39.68	93.65	90.86	89.45	87.51	85.93
600.00	40.77	40.84	40.93	41.21	41.67	97.10	94.32	92.91	91.00	89.47
650.00	42.78	42.84	42.91	43.13	43.49	100.44	97.67	96.27	94.38	92.88
700.00	44.59	44.63	44.69	44.86	45.15	103.68	100.91	99.52	97.64	96.16
750.00	46.22	46.25	46.30	46.44	46.68	106.81	104.05	102.65	100.79	99.33
800.00	47.69	47.72	47.76	47.87	48.07	109.84	107.08	105.69	103.83	102.39
850.00	49.03	49.06	49.09	49.18	49.35	112.78	110.01	108.63	106.77	105.34
900.00	50.25	50.27	50.30	50.38	50.52	115.61	112.85	111.47	109.62	108.20
950.00	51.37	51.39	51.41	51.48	51.60	118.36	115.60	114.22	112.37	110.96
1000.00	52.40	52.41	52.43	52.49	52.59	121.02	118.26	116.88	115.04	113.63

in which the gas constant $R = 82.06$ cc atm K^{-1} and the other quantities are in compatible units. By calculating [eqn (2)] and subsequent comparison with the experimental data[2], it can be shown that among considered two constant state equations (Van der Waals, Dieterici and Berthelot), the Berthelot equation of state yields the best second virial coefficient B values.

The differences between the ideal gas thermodynamic functions (state equation: $PV = RT$) and the real gas thermodynamic properties (state defined as: $PV = RT + BT$; valid for moderate pressures up to 15 atm) can be obtained through the application of the following equation set (3) which relate P–V–T properties of the gas to the desired thermodynamic functions:

$$\left[\frac{\partial H}{\partial P}\right]_T = V - T\left[\frac{\partial V}{\partial T}\right]_P; \qquad \left[\frac{\partial S}{\partial V}\right]_T = \left[\frac{\partial P}{\partial T}\right]_V$$
$$\left[\frac{\partial S}{\partial P}\right]_T = -\left[\frac{\partial V}{\partial T}\right]_P; \qquad \left[\frac{\partial C_p}{\partial P}\right]_T = -T\left[\frac{\partial^2 V}{\partial T^2}\right]_P \tag{3}$$

Combining eqns (1)–(3), we arrive at eqns (4)–(6):

$$(H - H^\circ)/T = \frac{9}{128}\frac{RT_c}{P_c}\left\{1 - 18\left[\frac{T_c}{T}\right]^2 P\right\} \tag{4}$$

Enthalpy function, $(H-H_0^\circ)/T$ (cal mol^{-1} K^{-1})					*Free energy function, $-(F-H_0^\circ)/T$ (cal mol^{-1} K^{-1})*				
0.25 atm	*1 atm*	*2 atm*	*5 atm*	*10 atm*	*0.25 atm*	*1 atm*	*2 atm*	*5 atm*	*10 atm*
12.06	11.70	11.22	9.78	7.38	61.05	58.41	57.19	55.83	55.23
12.88	12.60	12.23	11.13	9.29	62.14	59.47	58.21	56.75	55.96
12.94	12.67	12.30	11.22	9.42	62.22	59.55	58.29	56.82	56.02
14.62	14.45	14.22	13.55	12.42	64.34	61.64	60.33	58.73	57.71
16.33	16.22	16.07	15.62	14.86	66.40	63.68	62.35	60.67	59.53
18.03	17.95	17.85	17.53	17.01	68.42	65.69	64.35	62.62	61.41
19.69	19.63	19.56	19.33	18.95	70.41	67.67	66.32	64.57	63.30
21.29	21.25	21.19	21.02	20.74	72.36	69.62	68.26	66.49	65.19
22.82	22.79	22.74	22.62	22.40	74.28	71.53	70.17	68.39	67.07
24.28	24.25	24.22	24.12	23.95	76.16	73.42	72.05	70.26	68.92
25.67	25.65	25.62	25.54	25.41	78.01	75.27	73.90	72.10	70.75
26.98	26.97	26.95	26.88	26.78	79.83	77.08	75.71	73.90	72.55
28.23	28.22	28.20	28.15	28.06	81.61	78.86	77.49	75.68	74.32
29.42	29.41	29.39	29.35	29.28	83.36	80.61	79.23	77.42	76.06
30.54	30.53	30.52	30.49	30.43	85.07	82.32	80.95	79.13	77.77
31.61	31.60	31.59	31.56	31.51	86.75	84.00	82.62	80.81	79.44
32.62	32.62	32.61	32.58	32.54	88.40	85.65	84.27	82.46	81.09

$$(C_p - C_p^\circ) = \frac{81}{32}\frac{RT_c^3}{P_c T^3}P \tag{5}$$

$$(S^\circ - S)_T = \frac{27}{32}\frac{RT_c^3}{P_c T^3}P + R\ln P^* \tag{6}$$

These difference equations which are based on the Berthelot equation of state, have been used to calculate the thermodynamic functions presented in Table 1. The free energy function (Table 1) is found by subtracting eqns (6) and (4). The molecular structural data needed for thermodynamic function calculations are found in Table 2.

ACCURACY

Scott et al.[2] have found experimentally that for fluorobenzene the second virial coefficient can be related to temperature as follows:

$$B = 212 - 158.6\exp(750/T) \tag{7}$$

valid for $318\ \text{K} \leq T \leq 500\ \text{K}$

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*The $R \ln P$ term is a correction which must be included to obtain the ideal gas entropy at pressure P before the non-ideality correction [the first term in eqn (6)] is applied.

TABLE 2

SUMMARY OF USED MOLECULAR PARAMETERS

Frequencies in wave numbers[1], ν (cm^{-1})

519	808	1008	1022	1157
1220	1449	1596	3044	3067
3101	405	614	1066	1157
1236	1323	1460	1603	3058
3091	405	826	970	242
500	685	754	894	997

Principal moments of inertia[1] ($g\text{-}cm^2 \times 10^{39}$)

$I_A = 89.230$
$I_B = 196.642$
$I_C = 285.949$

Critical data for fluorobenzene[5]

$T_c = 560.1$ K; $P_c = 44.6$ atm

Molecular Weight, 96.100

Patrick and Prosser[3], again calculating the second virial coefficient of fluorobenzene, observed that the Berthelot equation compares very satisfactorily with the experimental measurements. However, the upper limit of applicability for pressure of the Berthelot state equation is found to be below the critical point[4].

On the other hand Scott et al.[2] have shown by experiment that the Berthelot equation of state will describe with high accuracy the P–V–T behavior at least up to and below 0.25 atm.

The heat capacities calculated (Table 1) fit the experimental data of Scott et al.[2] over the proposed range (0.25 to 10 atm) of the applicability of the Berthelot equation. The deviation between the experimental data and the calculated values (Table 1) range from −0.28% at 500.20 K and 0.25 atm, to −1.90% at 389.20 K and 2.0 atm. The deviation in the real vapor entropy of fluorobenzene varies from +0.03% at 382.20 K and 2.0 atm to a deviation of −0.14% at 318.40 K and 0.20 atm. As expected, at 1 atm the real gas effects are small, since the intermolecular force effects are small. Furthermore, at this pressure, as the temperature increases, the thermodynamic functions for the real gas approach those of the ideal gas more closely. As a matter of fact, for fluorobenzene (Table 1) at 1 atm the real gas contributions to the entropy are 0.25 e.u. and 0.01 e.u. at 298.15 K and 1000 K, respectively. The contributions to the heat capacity are 0.75 cal/g-mole K and 0.02 cal/g-mole K at 298.15 K and 1000 K, respectively, again at 1 atm pressure.

The real gas convection method using the Berthelot equation of state has yielded results (Table 1) which compare excellently with the experimental data available[2,3] for fluorobenzene over the specified temperature and pressure range.

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