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Note

Thermodynamic functions for perfluorotoluene

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The availability of molecular structural and spectroscopic data[1] has made it possible to estimate the thermodynamic functions, C_p^0, S^0, $(H^0-H_0^0)/T$, $-(F^0-H_0^0)/T$, for the perfluorotoluene in the ideal gas state at 1 atm pressure. Table I presents the thermodynamic functions obtained by means of statistical mechanical calculations using the harmonic oscillator approximation, while at the same time the internal rotational contribution is treated by means of the Pitzer–Gwinn method[4]. The results presented in Table I are fitted to Eqn. 1:

$$A = a+bT+cT^2 \tag{1}$$

TABLE I

THERMODYNAMIC FUNCTIONS FOR PERFLUOROTOLUENE

Temp. (°K)	C_p^0 (cal·mole^{-1}·°K^{-1})	$(H^0-H_0^0)T$ (cal·mole^{-1}·°K^{-1})	$-(F^0-H_0^0)/T$ (cal·mole^{-1}·°K^{-1})	S^0 (e.u.)
273.15	44.13	26.28	78.62	104.90
298.15	46.54	27.88	80.99	108.87
350	51.08	30.99	85.71	116.70
377.15	53.23	32.51	88.08	120.59
400	54.92	33.78	89.99	123.77
450	58.30	36.29	94.15	130.44
500	61.24	38.64	98.10	136.74
550	63.81	40.82	101.88	142.70
600	66.03	42.83	105.52	148.35
650	67.96	44.69	109.02	153.71
700	69.64	46.41	112.40	158.81
750	71.09	48.01	115.66	163.67
800	72.37	49.50	118.80	168.30
850	73.48	50.88	121.84	172.72
900	74.45	52.15	124.79	176.94
950	75.31	53.35	127.64	180.99
1000	76.07	54.47	130.41	184.88

where A is the thermodynamic function in question and T is the temperature (°K). The constants a, b, c (Eqn. 1) were evaluated using common least square curve

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fitting methods[5] and are given in Table II. The use of the temperature dependent Eqn. 1 may cause deviations in the calculated thermodynamic function values (Table II) from those shown in Table I. The values of the molecular parameters used in the calculation of thermodynamic functions (Table I) are given in Table III.

TABLE II

CALCULATED CONSTANTS FOR PERFLUOROTOLUENE (EQUATION 1)

Function	*a*	$b \times 10^2$	$c \times 10^5$	*Standard*[a] *deviation* ($cal \cdot mole^{-1} \cdot {}^{\circ}K^{-1}$)
C_p^0	18.129	11.34	−5.616	±0.471
$(H^0 - H_0^0)/T$	8.213	7.51	−2.910	±0.164
$-(F^0 - H_0^0)/T$	52.138	10.52	−2.717	±0.134
S^0	60.351	18.03	−5.628	±0.297

[a]Standard deviation of residuals, S

$$S = \sqrt{\frac{\sum_{i=1}^{n} (y_i - \hat{y}_i)^2}{n - m - 1}}$$

where n is the number of observations, m is the number of independent variables, y_i is the ith observed value of Y (Table I), and $\hat{y}_i$ is the ith predicted value of Y (Eqn. 1).

Although there are no available experimental data, the overall reliability of the frequency assignments[1], even if they were mostly made for the liquid state, suggests that the error should be within the limits of the experimental accuracy.

TABLE III

MOLECULAR PARAMETERS FOR PERFLUOROTOLUENE

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

1657	1657	1525	1510	1434	1350	1237	1237
1192	1154	1154	1090	994	875	744	714
694	667	609	584	548	498	462	442
382	364	342	306	305	300[b]	282	276
200	200	174	167	88	85		

Moment of inertia product[c]	$I_{ABC} = 4{,}459{,}251 \times 10^{-117}\ g^3 \cdot cm^6$
Molecular shape factor[d]	$\sigma = 6$
Molecular weight	$M = 236.07$
Reduced moment of inertia[e]	$I_{red} = 114.15 \times 10^{-40}\ g \cdot cm^{-2}$
Internal rotational barrier[f]	$V = 13.0\ cal \cdot mole^{-1}$
Physical constants[g]	

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[a]Most of the frequencies are in the liquid state[1]; however, the overall change in the value of thermodynamic functions due to vapour–liquid shift is expected to be within ±1% (Ref. 3). [b]Wagging mode —internal vibrations of CF_3 group of b_1 class, expected to occur in range $\nu = 200$ to 400. See Ref. 1. In this work we have used the average value of 300 cm⁻¹. [c]Calculated this work using suggested (Ref. 1) bond lengths and angles. [d]See Ref. 1. [e]Calculated this work. Bond lengths and angles chosen as suggested by Ref. 1. [f]See Ref. 1. [g]See Ref. 2.

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