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Ideal gas state thermodynamic functions for halogenated disiloxanes $(SiCl_3)_2O$ and $(SiF_3)_2O$

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Abstract

Thermodynamic functions (heat capacity, enthalpy, entropy and free energy) are calculated for hexachlorodisiloxane ($(SiCl_3)_2O$) and hexafluorodisiloxane ($(SiF_3)_2O$) in the ideal gas state from 298.15 to 1200 K at 1 atm pressure. The results obtained are critically compared with the available data.

INTRODUCTION

The availability of reliable spectroscopic and structural data [1–5] has prompted the estimation of the thermodynamic functions, heat capacity, enthalpy, entropy and free energy, for the two disiloxanes Si_2Cl_6O and Si_2F_6O in the ideal gas state from 298.15 to 1200 K at 1 atm pressure. The functions for each of these two compounds were calculated by the commonly used statistical methods, treating the internal rotational barrier contribution by the method developed by Pitzer [6]. The calculated results are listed in Table 1. The functions have been fitted to a five-constant polynomial of the form

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

where Λ 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, and are listed in Table 2. The molecular structural data needed for the calculation of the thermodynamic functions are given in Table 3. Table 4 shows the possible uncertainties in the calculated final function values, while Fig. 1 presents a comparison between computed values from this study and other works.

DISCUSSION

Hexachlorodisiloxane

The thermodynamic functions for hexachlorodisiloxane were calculated using the vibrational frequency assignments and the structural data given by Durig et al. [1] and Airey et al. [4], while the internal rotational barrier values were taken from the work of Durig et al. [2], Table 3. Considering the overall reliability of the spectroscopic and structural data used (Table 3), it is estimated that thermodynamic function values have up to ±3.0% accuracy; that is, the calculated values should be within the experimental error range. This is illustrated by Table 4 containing uncertainties in $C_p^{\ominus}$ and $S^{\ominus}$ values at 298.15 K if the five lowest valued frequencies are changed by ±10% and ±20%. These error estimates compare well with those found previously in the thermodynamic function calculations for various methylhalosilanes [7,8].

Hexafluorodisiloxane

The thermodynamic functions of hexafluorodisiloxane were calculated using the spectral and structural data suggested by Durig et al. [3] (Table 3). Figure 1 compares the calculated entropy and heat capacity values over the range 298.15–1200 K, between our work and the values obtained by Shinmei et al. [9]. The deviation [a] found between our work and the values of Shinmei et al. is explained by noting the differences made in the assumptions used to calculate the ideal gas state thermodynamic functions. Shinmei et al. [9] assumed that the hexafluorodisiloxane molecule may behave as a rigid rotor–harmonic oscillator for which the vibrational contributions may be estimated by further assuming that all 21 fundamentals available for the free $Si_2O_7^{6-}$ ion could also be used for the Si_2F_6O(gas) molecule; Shinmei et al. [9] used the values of all 21 fundamental frequencies as estimated by Lazarev [10,11]. Clearly this method of calculation does not include the contributions of the internal rotational barriers caused by the two rotating $-SiF_3$ tops. On the other hand, in our calculations we used fundamental frequency assignments made directly for the Si_2F_6O(gas) molecule including the internal rotational barrier contribution (Table 3). If we consider the overall reliability of the spectroscopic and structural data used (Table 3), we estimate the accuracy in the calculated thermodynamic functions to be within an interval of 2–3%; that is, within the experimental error range. This is corroborated by Table 4 presenting uncertainties in $C_p^{\ominus}$ and $S^{\ominus}$ values at 298.15 K for the hexafluorodisiloxane molecule if the five lowest valued frequencies are changed by ±10% and ±20%.

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[a] For $C_p^{\ominus}$ at 298.15 K, we calculated (Table 1) a value of 144.51 J mol^{-1} K^{-1} whereas Shinmei et al. [9] present a value of 140.5 J mol^{-1} K^{-1}; at 1200 K, we obtained 193.44 J mol^{-1} K^{-1}, whereas Shinmei et al. have a value of 200.6 J mol^{-1} K^{-1}. For $S^{\ominus}$ at 298.15 K, we obtained a value of 423.18 J mol^{-1} K^{-1}, whereas Shinmei et al. have a value 384.4 J mol^{-1} K^{-1}; at 1200 K, we have a value of 667.07 J mol^{-1} K^{-1}, whereas Shinmei et al. present a value of 632.7 J mol^{-1} K^{-1}.

TABLE 1

Thermodynamic functions calculated using the method of Pitzer [6]

Temperature (K)	Hexachlorodisiloxane				Hexafluorodisiloxane			
	$C_p^\ominus$ (J mol^{-1} K^{-1})	$(H^\ominus - H_0^\ominus)/T$ (J mol^{-1} K^{-1})	$-(F^\ominus - H_0^\ominus)/T$ (J mol^{-1} K^{-1})	$S^\ominus$ (J mol^{-1} K^{-1})	$C_p^\ominus$ (J mol^{-1} K^{-1})	$(H^\ominus - H_0^\ominus)/T$ (J mol^{-1} K^{-1})	$-(F^\ominus - H_0^\ominus)/T$ (J mol^{-1} K^{-1})	$S^\ominus$ (J mol^{-1} K^{-1})
298.15	164.09	114.96	374.36	489.30	144.51	96.92	326.26	423.18
300.00	164.39	115.26	375.06	490.32	144.88	97.21	326.87	424.07
350.00	171.04	122.74	393.44	516.19	153.87	104.68	342.43	447.11
400.00	176.12	129.11	410.26	539.38	161.10	111.32	356.83	468.14
450.00	180.03	134.54	425.81	560.35	166.86	117.13	370.32	487.45
500.00	183.09	139.31	440.20	579.51	171.57	122.39	382.91	505.30
550.00	185.52	143.34	453.71	597.05	175.39	126.99	394.83	521.82
600.00	187.47	146.91	466.36	613.26	178.53	131.15	406.07	537.22
650.00	189.04	150.09	478.25	628.33	181.14	134.94	416.69	551.63
700.00	190.32	152.94	489.46	642.40	183.33	138.31	426.83	565.13
750.00	191.37	155.51	500.08	655.59	185.17	141.33	436.50	577.82
800.00	192.28	157.77	510.19	667.97	186.72	144.09	445.73	589.82
850.00	193.05	159.82	519.82	679.64	188.04	146.64	454.54	601.18
900.00	193.70	161.69	529.01	690.70	189.16	148.98	462.98	611.96
950.00	194.25	163.40	537.79	701.19	190.12	151.15	471.08	622.23
1000.00	194.75	164.95	546.21	711.16	190.95	153.15	478.87	632.02
1050.00	195.18	166.37	554.30	720.67	191.70	154.96	486.39	641.35
1100.00	195.55	167.69	562.07	729.76	192.36	156.64	493.64	650.28
1150.00	195.87	168.91	569.55	738.46	192.93	158.21	500.63	658.84
1200.00	196.15	170.04	576.76	746.80	193.44	159.67	507.39	667.07

TABLE 2

Calculated constants *a*, *b*, *c*, *d* and *e* in eqn. (1) (J mol^{-1} K^{-1}) for the thermodynamic functions

Function	Compound	a	b	$c \times 10^3$	$d \times 10^6$	$e \times 10^{10}$
$C_p^{\ominus}$	$S_{i2}Cl_6O$	87.385	0.40724	−0.62260	0.44206	−1.19320
$C_p^{\ominus}$	Si_2F_6O	42.210	0.50440	−0.71769	0.48383	−1.25760
$S^{\ominus}$	Si_2Cl_6O	269.28	0.98175	−0.97593	0.57770	−1.41620
$S^{\ominus}$	Si_2F_6O	235.45	0.81067	−0.71573	0.39368	−0.92062
$-(F^{\ominus} - H_0^{\ominus})/T$	Si_2Cl_6O	227.30	0.62928	−0.53867	0.29942	−0.71110
$-(F^{\ominus} - H_0^{\ominus})/T$	Si_2F_6O	206.31	0.49962	−0.38170	0.20129	−0.46630
$(H^{\ominus} - H_0^{\ominus})/T$	Si_2Cl_6O	42.093	0.35173	−0.43559	0.27672	−0.69992
$(H^{\ominus} - H_0^{\ominus}/T$	Si_2F_6O	29.172	0.31091	−0.33378	0.19223	−0.45404

TABLE 3

Fundamental frequencies and molecular structural data used

Si_2Cl_6O	Si_2F_6O
Fundamental frequencies, ν (m^{-1}) [1,3]	
11.31, 7.30, 6.40, 6.40, 6.19, 6.19, 4.72, 4.19, 3.34, 3.36, 3.36, 2.47, 2.20, 2.20, 1.78, 1.78, 1.33, 1.33, 0.46	12.06, 9.89, 9.89, 9.49, 9.49, 8.38, 6.31, 6.01, 5.55, 4.61, 4.34, 4.02, 3.58, 3.41, 2.42, 2.25, 1.79, 1.57, 0.85
Product of principal moment of inertia, $I_{ABC} \times 10^{117}$ (g^3cm^6), this work	
8733564.0	670014.0
Moment of inertia of rotating top $\times 10^{40}$ (g cm^2), this work	
63.85976	20.43301
Reduced moment of inertia, $I_{red} \times 10^{40}$ (g cm^2), this work	
339.900	107.800
Symmetry number [1,3]	
2	2
Number of minima per revolution of top	
3	3
Internal rotational barrier (J mol^{-1} K^{-1}) [2,3]	
6276	8368
Bond lengths and structural angles	
Ref. 4	Refs. 3, 4
Molecular weight	
284.91	186.16

TABLE 4

Uncertainties in $C_p^\ominus$ and $S^\ominus$ values at 298.15 K if the five lowest valued frequencies (Table 3) are changed by ±10% and ±20%

Function	Compound	Uncertainty			
		+10%	+20%	−10%	−20%
$C_p^\ominus$	$(SiCl_3)_2O$	−0.20	−0.41	+0.18	+0.34
$C_p^\ominus$	$(SiF_3)_2O$	−0.37	−0.75	+0.33	+0.64
$S^\ominus$	$(SiCl_3)_2O$	−0.78	−1.49	+0.87	+1.85
$S^\ominus$	$(SiF_3)_2O$	−0.89	−1.65	+0.96	+2.07

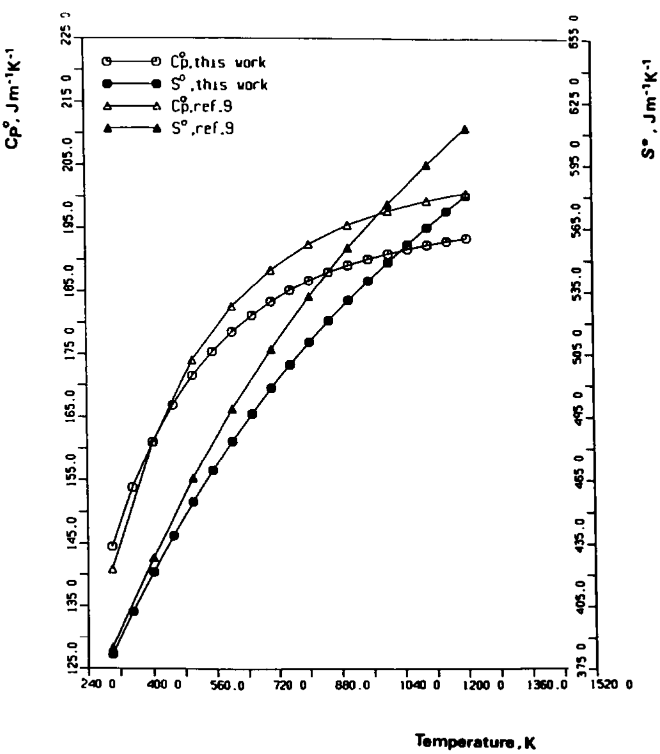

Fig. 1. Comparison of results between this work and Shinmei et al. [9] for Si_2F_6O as a function of temperature.

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