Thermochimica Acta, 84 (1985) 57–70
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMODYNAMIC FUNCTIONS FOR METHYLDIHALOSILANES, METHYLTRIHALOSILANES AND TRIMETHYLHALOSILANES

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(Received 28 August 1984)

ABSTRACT

Thermodynamic functions (heat capacity, enthalpy, entropy and free energy) have been calculated for methyldihalosilanes, methyltrihalosilanes and trimethylhalosilanes in the ideal gas state from 298.15 to 1200 K at 1 atm pressure. Statistical thermodynamic methods have been used in the calculation, the functions being corrected for internal rotation by the method of Pitzer and Gwinn. Agreement with other literature data, where available, is satisfactory.

INTRODUCTION

The accessibility of spectroscopic and structural data [1–42] has made it possible to estimate the thermodynamic functions (heat capacity, enthalpy, entropy and free energy) for complete series of methyldihalosilanes, methyltrihalosilanes and trimethylhalosilanes in the ideal gas state from 298.15 to 1200 K at 1 atm pressure. The functions for each of these compounds were calculated by statistical mechanical methods treating, wherever needed, the internal rotational barrier contribution by the method developed by Pitzer [43]. The calculated results are found in Table 1. The functions have all been fitted to a five-constant polynomial of the form

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

where Λ is any thermodynamic function at temperature T (K). The constants a, b, c, d and e have been calculated by standard linear least-squares regression methods, and are listed in Table 2. The molecular structural data used to calculate thermodynamic functions are found in Tables 3–5. Table 6 compares values of this work with those of other investigators.

0040-6031/85/$03.30

TABLE 1

Heat capacity, entropy, free energy function and enthalpy function for methylhalosilanes

Temp. (K)	CH_3SiX_3				CH_3SiHX_2				$(CH_3)_3SiX$			
	X = F	Cl	Br	I	F	Cl	Br	I	F	Cl	Br	I
C_p (cal g^{-1} mol^{-1} K^{-1})												
298.15	21.50	24.17	25.74	26.36	19.36	21.62	22.44	22.92	29.87	31.99	32.77	32.67
300.00	21.57	24.23	25.79	26.41	19.43	21.69	22.51	22.98	29.98	32.10	32.79	32.79
350.00	23.39	25.83	27.12	27.63	21.29	23.43	24.16	24.63	32.92	35.01	35.89	35.89
400.00	25.02	27.21	28.30	28.72	22.98	24.93	25.59	26.04	35.70	37.65	38.55	38.63
450.00	26.47	28.42	29.34	29.70	24.49	26.25	26.83	27.27	38.29	40.06	40.95	41.08
500.00	27.75	29.47	30.26	30.57	25.85	27.42	27.93	28.34	40.68	42.27	43.13	43.27
550.00	28.88	30.41	31.09	31.35	27.06	28.46	28.91	29.30	42.88	44.30	45.09	45.28
600.00	29.88	31.24	31.84	32.07	28.15	29.40	29.80	30.17	44.89	46.17	46.92	47.09
650.00	30.78	31.99	32.52	32.72	29.14	30.26	30.61	30.95	46.76	47.91	48.60	48.77
700.00	31.59	32.67	33.14	33.32	30.04	31.04	31.36	31.68	48.50	49.53	50.17	50.35
750.00	32.33	33.30	33.72	33.88	30.86	31.77	32.05	32.35	50.13	51.05	51.65	51.81
800.00	33.00	33.87	34.25	34.39	31.62	32.44	32.69	32.97	51.64	52.49	53.03	53.18
850.00	33.61	34.40	34.75	34.88	32.32	33.06	33.29	33.54	53.07	53.83	54.34	54.47
900.00	34.18	34.90	35.21	35.33	32.96	33.64	33.85	34.08	54.40	55.09	55.57	55.69
950.00	34.70	35.35	35.64	35.75	33.56	34.17	34.37	34.58	55.65	56.27	56.72	56.83
1000.00	35.18	35.78	36.04	36.14	34.11	34.67	34.85	35.05	56.81	57.37	57.80	57.91
1050.00	35.62	36.17	36.42	36.51	34.61	35.13	35.30	35.49	57.90	58.41	58.82	58.91
1100.00	36.03	36.54	36.77	36.85	35.09	35.56	35.71	35.89	58.92	59.39	59.77	59.86
1150.00	36.41	36.88	37.09	37.17	35.52	35.96	36.10	36.27	59.87	60.30	60.65	60.74
1200.00	36.76	37.20	37.40	37.47	35.93	36.33	36.46	36.62	60.76	61.16	61.49	61.57
S (cal g^{-1} mol^{-1} K^{-1})												
298.15	75.33	84.12	92.93	98.74	73.28	78.57	84.03	87.73	84.47	86.26	88.71	89.75
300.00	75.46	84.27	93.09	98.91	73.40	78.70	84.17	87.88	84.66	86.46	88.91	89.95
350.00	78.92	88.13	97.16	103.07	76.53	82.18	87.76	91.54	89.50	91.62	94.20	95.24
400.00	82.15	91.67	100.86	106.83	79.49	85.41	91.08	94.93	94.08	96.47	99.17	100.21
450.00	85.19	94.95	104.26	110.27	82.28	88.42	94.17	98.07	98.44	101.05	103.85	104.91

500.00	88.04	98.00	107.40	113.45	84.93	91.25	97.05	101.00	102.59	105.39	108.28	109.35
550.00	90.74	100.85	110.32	116.40	87.45	93.91	99.76	103.74	106.57	109.51	112.48	113.57
600.00	93.30	103.53	113.06	119.16	89.86	96.43	102.32	106.33	110.40	113.44	116.49	117.59
650.00	95.73	106.06	115.64	121.75	92.15	98.82	104.73	108.78	114.07	117.21	120.31	121.42
700.00	98.04	108.46	118.07	124.20	94.35	101.09	107.03	111.10	117.60	120.83	123.97	125.10
750.00	100.24	110.74	120.38	126.52	96.45	103.26	109.22	113.30	121.00	124.29	127.48	128.62
800.00	102.35	112.90	122.57	128.72	98.46	105.33	111.31	115.41	124.28	127.62	130.86	132.00
850.00	104.37	114.97	124.66	130.82	100.40	107.31	113.30	117.47	127.46	130.85	134.11	135.27
900.00	106.31	116.95	126.66	132.83	102.27	109.22	115.22	119.36	130.53	133.96	137.25	138.42
950.00	108.17	118.85	128.57	134.75	104.06	111.05	117.07	121.22	133.50	136.97	140.28	141.46
1000.00	109.96	120.68	130.41	136.59	105.80	112.82	118.84	123.00	136.38	139.89	143.22	144.40
1050.00	111.69	122.43	132.18	138.36	107.48	114.52	120.55	124.72	139.18	142.72	146.06	147.25
1100.00	113.36	124.12	133.88	140.07	109.10	116.17	122.21	126.38	141.90	145.46	148.83	150.01
1150.00	114.97	125.75	135.53	141.72	110.67	117.76	123.80	127.99	144.54	148.12	151.51	152.69
1200.00	116.52	127.33	137.11	143.30	112.19	119.29	125.35	129.54	147.11	150.70	154.11	155.29
$-(F^0 - H_0^0)/T$ (cal g^{-1} mol^{-1} K^{-1})												
298.15	60.60	67.15	74.07	79.00	59.97	63.97	68.64	71.86	64.85	65.95	68.07	69.28
300.00	60.69	67.25	74.19	79.12	60.05	64.06	68.74	71.96	64.97	66.08	68.19	69.40
350.00	63.06	69.97	77.19	82.25	62.19	66.40	71.20	74.50	68.14	69.36	71.53	72.76
400.00	65.24	72.46	79.92	85.10	64.17	68.58	73.48	76.84	71.10	72.46	74.68	75.91
450.00	67.29	74.78	82.44	87.71	66.03	70.62	75.61	79.03	73.90	75.39	77.67	78.92
500.00	69.22	76.95	84.78	90.12	67.79	72.55	77.61	81.08	76.57	78.17	80.51	81.78
550.00	71.06	78.99	86.97	92.38	69.46	74.37	79.51	83.02	79.12	80.84	83.24	84.51
600.00	72.80	80.92	89.03	94.49	71.06	76.11	81.30	84.86	81.56	83.40	85.83	87.14
650.00	74.47	82.76	90.98	96.49	72.59	77.76	83.01	86.60	83.92	85.85	88.35	89.67
700.00	76.08	84.51	92.82	98.38	74.07	79.34	84.65	88.27	86.19	88.22	90.77	92.09
750.00	77.61	86.18	94.58	100.18	75.49	80.87	86.21	89.87	88.40	90.51	93.10	94.45
800.00	79.09	87.79	96.26	101.90	76.86	82.34	87.71	91.40	90.53	92.74	95.34	96.72
850.00	80.52	89.32	97.87	103.54	78.19	83.75	89.16	92.87	92.61	94.89	97.53	98.92
900.00	81.90	90.81	99.42	105.11	79.48	85.11	90.56	94.29	94.63	96.97	99.66	101.05
950.00	83.23	92.23	100.90	106.62	80.72	86.43	91.91	95.66	96.60	99.00	101.72	103.12
1000.00	84.52	93.61	102.33	108.07	81.93	87.70	93.21	96.98	98.52	100.96	103.73	105.14
1050.00	85.78	94.94	103.71	109.47	83.11	88.94	94.47	98.26	100.38	102.88	105.68	107.10
1100.00	86.99	96.23	105.04	110.82	84.25	90.14	95.70	99.51	102.21	104.75	107.57	109.02

TABLE 1 (continued)

Temp. (K)	CH_3SiX_3				CH_3SiHX_2				$(CH_3)_3SiX$			
	X = F	Cl	Br	I	F	Cl	Br	I	F	Cl	Br	I
1150.00	88.17	97.48	106.33	112.13	85.37	91.30	96.88	100.71	103.99	106.58	109.42	110.88
1200.00	89.32	98.69	107.58	113.39	86.45	92.44	98.03	101.88	105.73	108.36	111.23	112.70
$(H^0 - H_0^0)/T$ (cal g^{-1} mol^{-1} K^{-1})												
298.15	14.72	16.97	18.85	19.74	13.31	14.60	15.38	15.87	19.62	20.30	20.64	20.69
300.00	14.67	17.01	18.89	19.78	13.35	14.64	15.43	15.91	19.68	20.38	20.71	20.77
350.00	15.86	18.16	19.98	20.82	14.35	15.78	16.56	17.04	21.36	22.26	22.67	22.75
400.00	16.91	19.21	20.94	21.74	15.32	16.83	17.60	18.08	22.98	24.01	24.49	24.61
450.00	17.89	20.17	21.82	22.57	16.26	17.80	18.56	19.04	24.54	25.66	26.18	26.34
500.00	18.82	21.05	22.62	23.33	17.15	18.71	19.44	19.91	26.02	27.21	27.77	27.94
550.00	19.68	21.86	23.35	24.02	17.99	19.54	20.25	20.72	27.45	28.67	29.25	29.45
600.00	20.49	22.61	24.03	24.67	18.80	20.32	21.02	21.47	28.83	30.04	30.65	30.85
650.00	21.25	23.30	24.66	25.26	19.56	21.06	21.72	22.17	30.15	31.36	31.96	32.18
700.00	21.96	23.95	25.24	25.82	20.28	21.75	22.38	22.83	31.40	32.61	33.20	33.44
750.00	22.63	24.55	25.79	26.34	20.96	22.39	23.00	23.44	32.60	33.77	34.38	34.61
800.00	23.26	25.12	26.30	26.82	21.60	22.99	23.59	24.01	33.75	34.89	35.52	35.73
850.00	23.85	25.65	26.79	27.28	22.21	23.56	24.14	24.55	34.84	35.96	36.58	36.80
900.00	24.41	26.15	27.24	27.72	22.79	24.11	24.66	25.07	35.89	36.99	37.59	37.83
950.00	24.94	26.62	27.67	28.13	23.34	24.62	25.16	25.56	36.90	37.98	38.56	38.81
1000.00	25.44	27.07	28.08	28.52	23.87	25.12	25.63	26.02	37.87	38.93	39.49	39.73
1050.00	25.91	27.49	28.47	28.89	24.37	25.59	26.08	26.46	38.80	39.84	40.39	40.61
1100.00	26.36	27.89	28.84	29.25	24.84	26.03	26.51	26.88	39.69	40.70	41.25	41.47
1150.00	26.79	28.28	29.19	29.59	25.30	26.45	26.92	27.28	40.55	41.54	42.08	42.29
1200.00	27.20	28.64	29.53	29.91	25.73	26.86	27.31	27.66	41.37	42.34	42.88	43.08

TABLE 2

Calculated constants *a*, *b*, *c*, *d* and *e* in eqn. (1) (all values in cal g^{-1} mol^{-1} K^{-1})

Compound	a	$b \times 10^{-2}$	$c \times 10^{-5}$	$d \times 10^{-8}$	$e \times 10^{-11}$
(1) C_p^0					
CH_3SiX_3					
X = F	4.5879	7.8134	−8.5751	5.0160	−1.1955
Cl	8.9578	7.2511	−8.7505	5.6381	−1.1457
Br	13.5160	5.6906	−6.4433	4.0364	−1.0311
I	15.3620	5.0506	−5.4946	3.3799	−0.8580
CH_3SiHX_2					
X = F	2.7235	7.5155	−7.7021	4.3453	−1.0205
Cl	5.5347	7.5900	−8.9284	5.7598	−1.5077
Br	6.9814	7.3601	−8.8962	5.9042	−1.5811
I	7.3439	7.4646	−9.1780	6.1177	−1.6334
$(CH_3)_3SiX$					
X = F	5.9878	10.0310	−7.8114	3.6043	−0.7425
Cl	7.6200	10.7190	−10.1550	5.8867	−1.4760
Br	6.4156	12.0430	−13.0050	8.3069	−2.2058
I	4.8604	12.8600	−14.3810	9.2840	−2.4588
(2) S^0					
CH_3SiX_3					
X = F	48.9760	10.8290	−7.7705	3.9231	−0.8826
Cl	53.3590	13.1360	−11.1770	6.2792	−1.5059
Br	59.7110	14.4510	−13.2160	7.7317	−1.8964
I	64.4550	15.0410	−14.1890	8.4689	−2.1041
CH_3SiHX_2					
X = F	50.2410	9.2215	−5.7422	2.6292	−0.5525
Cl	51.6330	11.2480	−8.7153	4.6834	−1.0972
Br	55.8290	11.9000	−9.6451	5.2981	−1.2859
I	58.7290	12.3010	−10.1850	5.6574	−1.3457
$(CH_3)_3SiX$					
X = F	49.5910	13.7940	−8.0717	3.7903	−0.8335
Cl	47.6580	15.7120	−10.8410	5.6844	−1.3326
Br	49.0460	16.1490	−11.1070	5.6409	−1.2664
I	50.1770	16.0770	−10.9400	5.5409	−1.2550
(3) $(H^0 - H_0^0)/T$					
CH_3SiX_3					
X = F	6.4753	3.3756	−1.8719	0.5316	−0.0391
Cl	7.4684	4.1216	−3.6831	1.9682	−0.4467
Br	9.6695	4.0898	−4.0381	2.3677	−0.5782
I	10.8890	3.9713	−4.0211	2.4017	−0.5976
CH_3SiHX_2					
X = F	6.3677	2.5637	−0.7397	−0.2297	0.1558
Cl	5.5292	3.8337	−3.0885	1.5522	−0.3387
Br	6.1217	3.9879	−3.4733	1.8623	−0.4260
I	6.5600	4.0226	−3.5533	1.9171	−0.4405

TABLE 2 (continued)

Compound	a	$b \times 10^{-2}$	$c \times 10^{-5}$	$d \times 10^{-8}$	$e \times 10^{-11}$
$(CH_3)_3SiX$					
X = F	8.2160	4.2138	−1.2947	−0.0807	0.1269
Cl	5.9213	5.9214	−4.2713	2.1274	−0.4771
Br	5.4564	6.3134	−4.7471	2.3397	−0.5022
I	5.1986	6.3745	−4.7941	2.3775	−0.5220
(4) $-(F^0 - H_0^0)/T$					
CH_3SiX_3					
X = F	42.5700	7.5101	−5.8109	3.3184	−0.8221
Cl	45.8440	9.0415	−7.5523	4.3641	−1.0766
Br	49.8660	10.4750	−9.4327	5.5999	−1.3956
I	53.4400	11.1500	−10.3400	6.2126	−1.5585
CH_3SiHX_2					
X = F	43.7430	6.7471	−5.2061	3.0495	−0.7714
Cl	46.0820	7.4270	−5.6508	3.1486	−0.7627
Br	49.5670	8.0038	−6.3828	3.6364	−0.8930
I	52.1660	8.2774	−6.6307	3.7414	−0.9028
$(CH_3)_3SiX$					
X = F	41.2280	9.6797	−7.0112	4.0987	−1.0384
Cl	41.7440	9.7831	−6.5514	3.5424	−0.8519
Br	43.5070	9.8928	−6.5040	3.4551	−0.8220
I	44.9490	9.7178	−6.1787	3.1927	−0.7424

DISCUSSION

Methyldihalosilanes

The gas and few liquid frequency data used (Table 3) have been taken from the work of Clark [2]. In Clark's analysis, the measurements of the fundamental frequencies of methyldihalosilanes include experiments performed on the deuterated analogues, namely, CD_3SiHX_2 and CH_3SiDX_2 (X = F, Cl, Br, I) other than the compound CH_3SiX_2H itself. Table 4 lists the bond lengths and angles used to calculate principal moment of inertia products (Table 5). Table 5 also compares the calculated principal moment of inertia product values with the values found in the literature, and also lists the values of internal rotational barriers used. In the case of bromine and iodine derivatives, barriers were not available. For these cases, values of energy barriers were estimated by extrapolating from the known values of fluorine and chlorine derivative barriers [44]. Uncertainty for this type of estimation is expected to be as large as 20%, yet by calculation it was shown that it contributes less than 0.75% error to the predicted thermodynamic function values.

TABLE 3

Fundamental frequencies used (cm^{-1})

$(CH_3)_3SiX$				CH_3SiX_3				CH_3SiHX_2			
X = F	Cl	Br	I	F	Cl	Br	I	F	Cl	Br	I
[9]	[35]	[11]	[12]	[2]	[14]	[5]	[2]	[2]	[2]	[2]	[2]
2968	2978	2972^{a}	2973	2930^{a}	2923	2898	2896	2986	2986	2983	2987
2907	2908	2898^{a}	2913	1286	1271	1249	1247	2923	2920	2915	2919
1415	1421	1411^{a}	1462	701	764	746	721	2216	2212	2196	2232
1262	1264	1266	1261	894	458	314	252	1403	1401	1385	1410
912	485	371^{a}	333	391	229^{a}	153	116^{a}	1267	1265	1262	1275
760	857^{e}	834	763	—	—	—	—	889	880	884	858
619	638	631	628	2998	2990	2977	2975	759	746	731	775
259	228	210^{a}	198	1418	1417	1396	1390	683	674	668	677
2968	2977	2961	2973^{c}	791	804	800^{c}	790	504	380^{a}	316^{a}	931
1415	1415^{e}	1407^{b}	1404^{c}	983	577	453	388	257^{a}	222^{a}	196^{a}	293^{a}
858	857^{e}	732^{b}	761^{c}	332^{f}	229^{a}	186	171^{a}	187^{a}	122^{a}	89^{a}	350^{a}
—	—	—	—	235^{a}	163^{a}	98	76^{a}	2986	2985	2983	2987
2968	2978	2972^{b}	2973^{c}					1403	1422	1407	1397
2968	2971	2961^{a}	2973^{c}					853	832	810	858
2907	2908	2924	2902^{c}					744	738^{a}	720	734
1415	1421	1407^{b}	1415					569	457	394	960
1415	1421	1407^{b}	1415					199^{a}	181	170^{a}	243
1262	1258	1253	1255^{c}					—	—	—	208
858	853	855	852								
760	758	762	845^{a}								
695^{d}	696	699	703								
290	238	233^{a}	233								
206	186	170^{a}	163								

[a] R-liquid state. [b] Calculated by means of normal coordinate analysis (NCA). [c] Estimated, this work. [d] Ref. 12. [e] Ref. 10. [f] Ref. 3.

TABLE 4

Molecular structural data used

Compound and structural parameters	Substituent atoms and ref.							
	X = F	Ref.	X = Cl	Ref.	X = Br	Ref.	X = I	Ref.
CH_3SiX_3								
*r*CH	1.081	13	1.090	14	1.093	16	1.090	17
*r*CSi	1.812	13	1.880	15	1.900	16	1.913	17
*r*SiX	1.574	13	2.010	14	2.175	16	2.430	17
HCSi	111°1′	13	109.5°		109.5°		109.5°	
XSiC	112°20′	13	109.5°		109.5°		109.5°	
CH_3SiHX_2								
*r*SiC	1.840	18	1.878	7	1.895		1.900	
*r*SiX	1.580	18	2.042	7	2.210	7	2.384	
*r*SiH	1.471	18	1.485	7	1.495		1.500	
*r*CH	1.094	18	1.093	7	1.093		1.093	
XSiX	107°6′	18	108.8°	19	109.4°		109.4°	
CSiH	115°32′	18	110.9°	19	109.4°		109.4°	
CSiX	109°22′	18	109.8°	19	109.4°		109.4°	
HCX	108°32′	18	109.4°		109.4°		109.4°	
$(CH_3)_3SiX$								
*r*SiX	1.55	40	2.022	21	2.235	20	2.340	
*r*CH	1.10	39	1.095	21	1.095	20	1.095	
*r*SiC	1.88	39	1.857	21	1.856	20	1.856	
CSiX			110.5°	21	107.7°	20	107°	
HCH					109.5°	20	109.5°	
SiCH			110.15°	14				

Methyltrihalosilanes

For methyltrifluoro- and -iodosilanes the fundamental gas state vibrational frequencies supplemented by few liquid state assignments (Table 3) were taken from the work of Clark [2]. To obtain these fundamental assignment values, Clark had performed normal coordinate analysis (NCA), then compared his results with other researchers [3,4]. Less certain are the suggested (this work, Table 3) assignment values of methyltrichlorosilanes and methyltribromosilanes (Table 3). In the case of methyltrichlorosilanes, the gas state spectroscopic data supplemented by three liquid state assignments (Table 3) were taken from the work of Lee-Smith [14]; while for methyltribromosilanes the gas phase data of Murata and Hatashi [5] were supplemented by one estimated gas state frequency (this work, Table 3). Table 4 lists the bond lengths and angles needed to calculate principal and reduced moments of inertia while Table 5 compares the calculated moment

TABLE 5

Moment of inertia and internal rotational barrier value comparison

Compound	Worker	$I_{ABC} \times 10^{-117}$ g^3 cm^6	$I_A \times 10^{-39}$ g cm^2	$I_B \times 10^{-39}$ g cm^2	$I_C \times 10^{-39}$ g cm^2	$I_R \times 10^{-40}$ g cm^2	Internal rotational barrier (cal g^{-1} mol^{-1} K^{-1})
CH_3SiF_3	This work	10482	20.54741	22.58606	22.58606	5.158	930 [13]
	Others						
CH_3SiCl_3	This work	144473	47.5362	47.5362	63.9352	5.238	580 [22]
	Others	139202 [37]				5.26 [37]	
		138900 [14]	46.62 [14]	46.62 [14]	63.95 [14]		
CH_3SiBr_3	This work	1666593	100.6946	100.6466	164.4465	5.265	1000 [16]
	Others						
CH_3SiI_3	This work	11661688	187.5637	187.1416	332.233	5.274	1050 [a]
	Others						
CH_3SiHF_2	This work	3887	12.5199	13.6896	22.6788	5.066	1260 [27]
	Others	3758 [18]	12.2810 [18]	13.7364 [18]	22.3516 [18]		
CH_3SiHCl_2	This work	34027	19.4212	35.1136	49.8968	5.226	2090 [7]
	Others						
CH_3SiHBr_2	This work	242614	24.9321	89.2968	108.9739	5.256	2400 [a]
	Others						
CH_3SiHI_2	This work	870658	28.7317	162.8977	186.0251	5.267	2850 [a]
	Others						
$(CH_3)_3SiF$	This work	13725	24.1172	24.1173	23.5971	5.164	1270 [9]
	Others	15756 [9]				5.180 [9]	
$(CH_3)_3SiCl$	This work	34982	24.2203	37.9711	38.0371	5.208	2080 [21]
	Others	33290 [10]	26.1 [10]	37.2 [10]	37.2 [10]	5.3 [10]	
		39076 [37]	26.5 [37]	38.4 [37]	38.4 [37]	5.20 [37]	
$(CH_3)_3SiBr$	This work	85661	24.2201	59.4709	59.4709	5.234	2430 [a]
	Others						
$(CH_3)_3SiI$	This work	131641	24.2201	73.7238	73.7238	5.242	2777 [a]
	Others						

[a] Estimated (this work).

TABLE 6

Comparison of thermodynamic function values (cal g^{-1} mol^{-1} K^{-1}) at 298.15 K

Worker	CH_3SiF_3	CH_3SiCl_3	CH_3SiHCl_2	$(CH_3)_3SiF$	$(CH_3)_3SiCl$
C_p^0					
This work	21.50	24.17	21.62	29.87	31.99
Others	21.73 [3]	24.47 [37]		29.32 [9]	30.78 [37] 30.98 [10] 32.12 [32]
$(H^0-H_0^0)/T$					
This work	14.72	16.97	14.60	19.62	20.30
Others	11.75 [3]	17.12 [37]		19.27 [9]	19.90 [37] 19.79 [10] 19.92 [32]
$-(F^0-H_0^0)/T$					
This work	60.60	67.15	63.97	64.85	65.95
Others	60.39 [3]	66.79 [37]		64.54 [9] [a]	65.77 [10] [a] 65.99 [37] 67.61 [32]
S^0					
This work	75.33	84.12	78.57	84.47	86.26
Others	72.14 [3]	83.97 [37] 83.00 [34]	77.90 [33]	83.81 [9]	85.89 [32] 85.56 [10] 87.57 [32] 87.38 [36]

[a] Calculated from entropy and enthalpy functions.

of inertia values with the values available in the literature.

The values for internal rotational barriers of methyltrihalosilanes are listed in Table 5. In the case of methyltriiodosilane, the barrier used in this work has been obtained by extrapolation from the values of fluorine, chlorine and bromine derivatives (refs. 13, 22 and 16, respectively).

Trimethylhalosilanes

The vibrational frequency assignment sets for trimethylhalosilanes (Table 3) were obtained from varied sources. The frequency assignments for fluorinated silanes were taken from liquid state data of Spangenberg and Pfeiffer [9] supplemented by one gas state R-assignment [12]. For chlorinated silanes the vibrational assignments were taken from the gas state Raman spectra data of Durig and Jallilan [35] and supplemented by the liquid state assignments of Spangenberg [10]. The frequency assignments for trimethylbromosilanes (Table 3) were taken from the gas IR data, Raman liquid state measurements and normal coordinate analysis (NCA) results of Lazarev et al. [11]. For trimethyliodosilanes, frequency assignments (Table 3) were taken from the IR gas state, and one frequency from the Raman liquid state studies of Burger [12], while some frequencies were estimated (this work).

The bond lengths and angles needed to calculate principal and reduced moments of inertia (Table 5) are listed in Table 4. The results obtained are compared with literature values (Table 4). The barriers to internal rotation for trimethylhalosilanes are listed in Table 5. For trimethylhalosilanes there are three CH_3-torsional frequencies, which Ratcliffe and Waddington [34] have identified as $\nu_{24}(E)$ degenerate torsion and $\nu_{12}(A_2)$ torsion. Since it has been observed [9,10] that the deviation between an E and A_2 torsion is about 8% and since it has been calculated (this work) that this 8% deviation in barrier values may cause, at most, a 0.6% change in predicted thermodynamic function values, it appeared feasible in this work to use only the averaged barrier values.

Comparison with other work

Table 1 shows that for any constant temperature, for instance the 298.15 K isotherm, the function values for each compound listed increase with the mass of halogen substitute atom (X = F, Cl, Br, I) as expected. However, in terms of fixed substituent atom there appears to be no general trend between each kind of methylhalosilane. For instance, for the fluoro series, CH_3SiHF_2 has the smallest, while $(CH_3)_3SiF$ has the largest thermodynamic function value. The chloro and bromo series follow this trend to a certain extent, but not the iodo series.

In some cases (Table 1) the largest function value belongs either to CH_3SiX_3 or $(CH_3)_3SiX$. Table 6, on the other hand, compares the calculated thermodynamic function values (this work) with those selected from the literature. The largest deviations for $(CH_3)_3SiF$ and $(CH_3)_3SiCl$ found are between this work and Spangenberg and Pfeiffer [9] and Spangenberg [10], respectively. For $(CH_3)_3SiF$ a deviation of about 8% is found in the enthalpy function while for $(CH_3)_3SiCl$, both the heat capacity (about 3%) and the enthalpy function (about 12%) show the largest discrepancies. It is found, however, that Spangenberg and Pfeiffer's value for the free energy function (Table 6) is inconsistent and deviates greatly from the difference between the enthalpy function and entropy. If the free energy function values are corrected for the enthalpy function (entropy difference) the deviation is reduced to 0.5% for $(CH_3)_3SiF$ and to about 0.1% for $(CH_3)_3SiCl$.

Accuracy and range of reliability

In this work all values are in units of cal g^{-1} mol^{-1} K^{-1} and apply to the ideal gas state at 1 atm pressure (tabulated values given to ± 0.1 cal g^{-1} mol^{-1} K^{-1}). However, probable errors may be larger than this uncertainty. The percentage errors (uncertainties) assigned to the calculated thermodynamic function (as above) are really estimates. These estimates were obtained accounting for two main sources of uncertainties: the uncertainties in input parameters, and uncertainties in assumptions.

Input data uncertainties

The three main sources of input errors are found in the frequency assignments, moment of inertia calculations and in barrier height determinations [1]. In this work the overall error in the function values at 298.15 and 800 K was calculated. As a matter of fact, the accuracy of this work at 298.15 K has been estimated to be ±0.5, ±1.2 and ±1.4% for trihalomethylsilanes, methyldihalosilanes and trimethylhalosilanes, respectively. At 800 K, this accuracy is estimated to be ±0.4, ±0.5 and ±0.9%, respectively.

Table 5 shows that there is only one experimental value for entropy, S^0, at 298.15 K for trimethylchlorosilane, showing that the deviation between this entropy value and the calculated value is larger than the overall error of 1.4%. This deviation may be due to errors in determination of the experimental value of entropy, extrapolation of S^0 (value to 0 K), and calculation of S^0_{vap}. Table 5, in general, shows that the calculated values of other works compare well with values given in this study and the deviations lie very close to the overall error of this work. This enhances the credibility of this work, and indicates that the results of this study are both accurate and reliable, and that the calculated functions can be used to determine the properties of compounds of interest.

Calculation assumption errors

This work assumes that the molecules considered behave as harmonic oscillators and as ideal gases. At higher temperatures, however, the neglected anharmonicity effects may become important, and may introduce up to 1 or 2% errors in the function calculations, especially in structurally more complex molecules [1].

ACKNOWLEDGEMENT

The financial assistance of the Natural Sciences and Engineering Research Council of Canada (NSERC) is gratefully acknowledged.

NOMENCLATURE

Å	Ångstrom
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})
I_{ABC}	principal moment of inertia (g^3 cm^6)
I_R	reduced moment of inertia (g cm^2)
r	distance (Å)
S^0	entropy (e.u.)
ν	wavenumber (cm^{-1})

Superscript

0	reference state referring to the hypothetical state of an ideal gas at 1 atm

Subscript

p	pressure

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