Thermochimica Acta, 44 (1981) 43—57
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

THERMODYNAMIC FUNCTIONS FOR METHYLHALOSILANES

F. BENNETT, JR. * and J. LIELMEZS

The University of British Columbia, Department of Chemical Engineering, Vancouver, B.C. V6T 1W5 (Canada)

(Received 30 July 1980)

ABSTRACT

Thermodynamic functions (heat capacity, enthalpy, entropy and free energy) are calculated for methylhalosilanes, dimethylhalosilanes, and dimethyldihalosilanes in the ideal gas state from 298.16 to 1200 K at 1 atm pressure. Statistical thermodynamic methods have been used in the calculations, with functions corrected for internal rotation by the method of Pitzer. Agreement with other literature data, where available, is satisfactory.

INTRODUCTION

The recent availability of spectroscopic and structural data [1—17] has made it possible to estimate the thermodynamic functions — heat capacity, enthalpy, entropy and free energy — for a series of methylmonohalosilanes, dimethylhalosilanes and dimethyldihalosilanes in the ideal gas state from 298.16 to 1200 K at 1 atm pressure. The functions for each of these compounds were calculated by statistical mechanical methods treating, whereever needed, the internal rotational barrier contribution by the method developed by Pitzer [18]. The calculated results are found in Table 1. The functions have all been fitted to a five constant polynomial of the form

$$\Lambda = a + bT + cT^2 + dT^3 + eT^4$$

where Λ is any thermodynamic function at temperature T(K). The constants a, b, c, d and e [eqn. (1)] have been obtained using linear least squares curve fitting methods [19], and are found in Table 2. The molecular structural data needed for the calculation of thermodynamic functions are found in Tables 3 and 4. Table 5 presents a comparison of computed values between this and other work, while Tables 6 and 7 give the possible uncertainties in the calculated final function values.

---

* Present address: Texaco Canada Resources Ltd., Willesdan Green, Alta., Canada.

TABLE 1

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

Temp.	$(CH_3)SiH_2X$				$(CH_3)_2SiHX$				$(CH_3)_2SiX_2$			
(K)	X=F	X=Cl	X=Br	X=I	X=F	X=Cl	X=Br	X=I	X=F	X=Cl	X=Br	X=I
C_p^0 (cal g^{-1} $mole^{-1}$ K^{-1})												
298.16	17.39	18.39	18.81	19.10	24.46	25.36	25.55	25.83	25.95	28.04	29.11	29.84
300.00	17.46	18.46	18.88	19.17	24.56	25.46	25.64	25.92	26.03	28.12	29.19	29.92
350.00	19.32	20.28	20.63	20.89	27.10	27.97	27.97	28.25	28.37	30.31	31.24	31.92
400.00	21.03	21.91	22.21	22.44	29.39	30.19	30.08	30.35	30.52	32.28	33.09	33.74
450.00	22.59	23.38	23.63	23.84	31.42	32.17	31.98	32.25	32.50	34.09	34.78	35.36
500.00	24.00	24.71	24.92	25.11	33.26	33.95	33.72	33.96	34.31	35.72	36.32	36.85
550.00	25.28	25.91	26.10	26.26	34.93	35.54	35.31	35.54	35.95	37.20	37.73	38.21
600.00	26.45	27.01	27.17	27.32	36.46	37.01	36.77	36.98	37.45	38.56	39.03	39.45
650.00	27.53	28.03	28.17	28.30	37.86	38.36	38.13	38.31	38.82	39.82	40.23	40.61
700.00	28.51	28.96	29.09	29.21	39.16	39.61	39.39	39.56	40.09	40.98	41.35	41.69
750.00	29.42	29.83	29.94	30.05	40.37	40.78	40.57	40.72	41.26	42.07	42.39	42.71
800.00	30.26	30.63	30.73	30.83	41.50	41.87	41.67	41.82	42.34	43.07	43.36	43.66
850.00	31.04	31.37	31.46	31.55	42.56	42.89	42.71	42.84	43.35	44.01	44.27	44.54
900.00	31.76	32.06	32.14	32.23	43.54	43.84	43.67	43.79	44.30	44.89	45.13	45.38
950.00	32.43	32.70	32.78	32.86	44.46	44.74	44.57	44.69	45.18	45.72	45.93	46.16
1000.00	33.05	33.30	33.37	33.44	45.32	45.58	45.42	45.52	46.00	46.49	46.69	46.89
1050.00	33.62	33.85	33.91	33.98	46.12	46.36	46.20	46.30	46.76	47.21	47.39	47.58
1100.00	34.16	34.37	34.42	34.48	46.86	47.09	46.94	47.03	47.47	47.89	48.05	48.23
1150.00	34.65	34.84	34.89	34.95	47.56	47.77	47.64	47.72	48.14	48.52	48.67	48.84
1200.00	35.10	35.28	35.33	35.39	48.21	48.40	48.28	48.36	48.76	49.12	49.25	49.41
S^0 (cal g^{-1} $mole^{-1}$ K^{-1})												
298.16	68.52	71.29	74.15	76.16	76.73	79.41	82.68	84.59	80.21	85.92	91.81	96.42
300.00	68.63	71.41	74.26	76.28	76.88	79.56	82.84	84.75	80.37	86.09	91.99	96.61
350.00	71.46	74.39	77.30	79.36	80.86	83.68	86.97	88.92	84.55	90.58	96.63	101.37
400.00	74.16	77.20	80.16	82.25	84.63	87.56	90.84	92.83	88.49	94.76	100.93	105.75
450.00	76.72	79.87	82.87	84.98	88.21	91.23	94.49	96.51	92.20	98.67	104.93	109.82
500.00	79.18	82.41	85.42	87.56	91.61	94.72	97.96	100.00	95.72	102.35	108.67	113.63
550.00	81.53	84.82	87.85	90.01	94.86	98.03	101.24	103.32	99.07	105.83	112.20	117.20
600.00	83.78	87.12	90.17	92.34	97.97	101.18	104.38	106.47	102.26	109.12	115.55	120.58
650.00	85.94	89.32	92.39	94.56	100.94	104.20	107.38	109.48	105.31	112.26	118.71	123.78

700.00	88.01	91.43	94.51	96.69	103.80	107.09	110.25	112.37	108.23	115.25	121.73	126.83
750.00	90.01	93.46	96.54	98.74	106.54	109.86	113.01	115.14	111.04	118.11	124.62	129.74
800.00	91.94	95.41	98.50	100.70	109.19	112.53	115.66	117.80	113.74	120.86	127.39	132.53
850.00	93.80	97.29	100.39	102.59	111.73	115.10	118.21	120.36	116.34	123.51	103.05	135.20
900.00	95.59	99.11	102.21	104.42	114.19	117.58	120.68	122.84	118.84	126.05	132.61	137.77
950.00	97.33	100.86	103.96	106.18	116.56	119.97	123.07	125.23	121.26	128.50	135.07	140.25
1000.00	99.01	102.55	105.66	107.88	118.87	122.28	125.38	127.55	123.60	130.86	137.44	142.64
1050.00	100.63	104.19	107.30	109.52	121.10	124.52	127.62	129.79	125.86	133.15	139.74	144.19
1100.00	102.21	105.78	108.89	111.12	123.26	126.70	129.79	131.96	128.05	135.36	141.96	147.17
1150.00	103.74	107.32	110.43	112.66	125.37	128.81	131.89	134.07	130.18	137.50	144.11	149.33
1200.00	105.22	108.81	111.92	114.15	127.41	130.86	133.93	136.11	132.24	139.58	146.19	151.42
$-(F^0 - H_0^0)/T$ (cal g^{-1} mole^{-1} K^{-1})												
298.16	56.54	58.81	61.31	63.07	61.20	63.30	66.03	67.72	63.10	67.24	72.02	75.86
300.00	56.61	58.89	61.38	63.15	61.29	63.40	66.14	67.82	63.20	67.36	72.14	75.99
350.00	58.53	60.89	63.44	65.25	63.80	66.00	68.82	70.54	65.96	70.36	75.31	79.28
400.00	60.32	62.76	65.36	67.20	66.17	68.46	71.34	73.09	68.53	73.16	78.26	82.31
450.00	62.00	64.51	67.15	69.03	68.43	70.78	73.71	75.49	70.96	75.78	81.00	85.15
500.00	63.60	66.18	68.86	70.76	70.58	73.00	75.96	77.77	73.27	78.26	83.59	87.81
550.00	65.12	67.77	70.48	72.40	72.64	75.13	78.12	79.94	75.46	80.61	86.03	90.33
600.00	66.59	69.28	72.02	73.96	74.62	77.18	80.18	82.03	77.56	82.85	88.35	92.71
650.00	67.99	70.74	73.50	75.46	76.54	79.13	82.16	84.03	79.58	84.99	90.57	94.97
700.00	69.35	72.15	74.93	76.90	78.39	81.04	84.06	85.94	81.53	87.05	92.69	97.14
750.00	70.66	73.50	76.30	78.29	80.17	82.87	85.90	87.80	83.40	89.03	94.72	99.22
800.00	71.93	74.81	77.63	79.63	81.90	84.64	87.68	89.59	85.21	90.93	96.68	101.22
850.00	73.16	76.08	78.91	80.93	83.58	86.35	89.40	91.33	86.96	92.77	98.56	103.14
900.00	74.35	77.30	80.16	82.18	85.22	88.02	91.07	93.02	88.66	94.54	100.38	105.00
950.00	75.52	78.50	81.36	83.40	86.81	89.64	92.69	94.65	90.31	96.26	102.14	106.78
1000.00	76.65	79.66	82.53	84.58	88.35	91.22	94.27	96.23	91.92	97.93	103.84	108.51
1050.00	77.75	80.79	83.67	85.72	89.86	92.75	95.80	97.78	93.48	99.55	105.50	110.19
1100.00	78.83	81.89	84.78	86.84	91.33	94.25	97.30	99.28	95.00	101.13	107.10	111.82
1150.00	79.88	82.96	85.86	87.93	92.76	95.70	98.75	100.74	96.48	102.66	108.66	113.40
1200.00	80.90	84.00	86.92	88.99	94.16	97.12	100.18	102.18	97.93	104.16	110.18	114.94
$(H^0 - H_0^0)/T$ (cal g^{-1} mole^{-1} K^{-1})												
298.16	11.98	12.48	12.84	13.08	15.53	16.11	16.65	16.87	17.11	18.67	19.79	20.56
300.00	12.02	12.52	12.88	13.12	15.59	16.17	16.70	16.92	17.17	18.73	19.85	20.62
350.00	12.93	13.50	13.86	14.11	17.05	17.68	18.15	18.38	18.60	20.22	21.32	22.09
400.00	13.84	14.45	14.80	15.05	18.46	19.11	19.50	19.74	19.95	21.60	22.67	23.44

TABLE 1 (continued)

Temp.	$(CH_3)SiH_2X$				$(CH_3)_2SiHX$				$(CH_3)_2SiX_2$			
(K)	X=F	X=Cl	X=Br	X=I	X=F	X=Cl	X=Br	X=I	X=F	X=Cl	X=Br	X=I
450.00	14.72	15.36	15.71	15.96	19.78	20.45	20.78	21.03	21.24	22.90	23.93	24.67
500.00	15.58	16.23	16.56	16.80	21.04	21.71	21.99	22.23	22.45	24.09	25.09	25.82
550.00	16.40	17.05	17.38	17.61	22.22	22.89	23.13	23.38	23.61	25.22	26.17	26.87
600.00	17.19	17.84	18.15	18.38	23.35	24.01	24.20	24.44	24.70	36.38	27.20	27.87
650.00	17.94	18.58	18.88	19.10	24.40	25.07	25.22	25.45	25.72	27.26	28.15	28.81
700.00	18.66	19.29	19.57	19.79	25.41	26.05	26.20	26.42	26.70	28.19	29.04	29.69
750.00	19.35	19.96	20.24	20.44	26.37	26.99	27.10	27.34	27.63	29.08	20.89	30.52
800.00	20.01	20.60	20.87	21.07	27.29	27.89	27.97	28.20	28.53	29.93	30.71	31.30
850.00	20.64	21.22	21.47	21.67	28.15	28.75	28.81	29.03	29.39	30.74	31.84	32.05
900.00	21.24	21.80	22.05	22.24	28.97	29.56	29.61	29.82	30.18	31.50	32.23	32.77
950.00	21.81	22.36	22.60	22.78	29.75	30.32	30.38	30.58	30.95	32.23	32.93	33.46
1000.00	22.36	22.89	23.12	23.30	30.51	31.06	31.11	31.31	31.68	32.92	33.60	34.12
1050.00	22.88	23.40	23.62	23.80	31.24	31.77	31.82	32.01	32.38	33.59	34.24	34.75
1100.00	23.38	23.89	24.11	24.27	31.93	32.45	32.68	33.05	34.23	34.23	34.85	35.35
1150.00	23.86	24.36	24.56	24.73	32.60	33.10	33.13	33.32	33.69	34.84	35.44	35.92
1200.00	24.32	24.80	25.00	25.16	33.25	33.73	33.75	33.93	34.31	35.42	36.01	36.47

TABLE 2

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

Compound	C_p^0					S^0				
	a	$b \times 10^{-2}$	$c \times 10^{-4}$	$d \times 10^{-8}$	$e \times 10^{-12}$	a	$b \times 10^{-2}$	$c \times 10^{-4}$	$d \times 10^{-8}$	$e \times 10^{-12}$
CH_3SiH_2X										
X=F	1.62265	6.89022	−0.62861	3.27613	−7.37647	48.25054	7.93826	−0.43401	1.86089	−3.83257
X=Cl	2.67735	7.04278	−0.70761	4.11299	−10.17328	49.32819	8.81209	−0.55985	2.71416	−6.05389
X=Br	3.86189	6.65534	−0.65324	3.75349	−9.25828	51.47282	9.19683	−0.62132	3.16472	−7.29925
X=I	4.41535	6.54257	−0.64401	3.72515	−9.25155	53.00749	9.44707	−0.65859	3.42580	−7.99849
$(CH_3)_2SiHX$										
X=F	2.00941	10.21895	−1.08461	6.67701	−17.18942	47.73797	11.51556	−0.68893	3.14793	−6.61275
X=Cl	2.77178	10.44768	−1.16729	7.47844	−19.72659	48.91497	12.28033	−0.79600	3.86499	−8.47878
X=Br	5.74238	8.80875	−0.86604	5.11219	−12.93059	51.78864	12.58139	−0.86963	4.53139	−10.57182
X=I	5.76315	9.00532	−0.91452	5.53956	−14.23833	53.26907	12.78561	−0.89374	4.66425	−10.84746
$(CH_3)_2SiX_2$										
X=F	6.28405	8.52301	−0.75458	3.82300	−8.29541	49.11545	12.58883	−0.84199	4.25694	−9.77264
X=Cl	9.27369	8.34444	−0.81784	4.70454	−11.49004	51.34031	14.39518	−1.10518	6.05985	−14.50999
X=Br	11.77032	7.66762	−0.73800	4.25342	−10.49647	55.44539	15.34789	−1.25241	7.11231	−17.36268
X=I	12.59325	7.73435	−0.78390	4.75427	−12.19268	58.85623	15.96599	−1.33997	7.69923	−18.87380

Compound	$(H^0 - H_0^0)/T$					$-(F^0 - H_0^0)/T$				
	a	$b \times 10^{-2}$	$c \times 10^{-4}$	$d \times 10^{-8}$	$e \times 10^{-12}$	a	$b \times 10^{-2}$	$c \times 10^{-4}$	$d \times 10^{-8}$	$e \times 10^{-12}$
CH_3SiH_2X										
X=F	6.12421	1.99284	0.00956	−0.74015	2.74895	42.12017	5.94961	−0.44449	2.60878	−6.60431
X=Cl	5.56895	2.61079	−0.10175	0.09320	0.45919	43.75162	6.20568	−0.45895	2.62774	−6.53212
X=Br	5.76256	2.73629	−0.13212	0.35287	−0.31975	45.70218	6.46527	−0.49013	2.81946	−7.00133
X=I	5.88103	2.82140	−0.15067	0.50196	−0.74792	47.11862	6.63026	−0.50884	2.93128	−7.27201

TABLE 2 (continued)

Compound	C_p^0					S^0				
	a	$b \times 10^{-2}$	$c \times 10^{-4}$	$d \times 10^{-8}$	$e \times 10^{-12}$	a	$b \times 10^{-2}$	$c \times 10^{-4}$	$d \times 10^{-8}$	$e \times 10^{-12}$
$(CH_3)_2SiHX$										
X=F	4.83672	4.18350	−0.21824	0.60960	−0.43188	42.90301	7.32965	−0.47002	2.53121	−6.15498
X=Cl	4.68239	4.61775	−0.29788	1.21109	−2.12014	44.23426	7.66042	−0.49763	2.64826	−6.33878
X=Br	5.73356	4.43188	−0.29721	1.36421	−2.86346	46.04931	8.15193	−0.57276	3.16872	−7.70911
X=I	5.80776	4.51383	−0.31001	1.43541	−2.98916	47.45856	8.27229	−0.58368	3.22708	−7.84905
$(CH_3)_2SiX_2$										
X=F	6.59570	4.16786	−0.24084	0.91204	−1.63045	42.50534	8.42993	−0.60303	3.36056	−8.18852
X=Cl	6.88257	4.96917	−0.39955	2.13494	−5.04190	44.44254	9.43517	−0.70750	3.94047	−9.51384
X=Br	7.88425	5.11328	−0.44573	2.53888	−6.23528	47.54644	10.24316	−0.80839	4.58737	−11.16773
X=I	8.55896	5.20665	−0.47083	2.73083	−6.73284	50.28990	10.76290	−0.86976	4.97249	−12.15015

TABLE 3

Fundamental frequencies (cm^{-1})

CH_3SiH_2X [a]

Assignment	X=F	X=Cl	X=Br	X=I
CH_3 d-stretch	2987	2988	2989	2984
CH_3 d-stretch	2978	2978	2978	2977
CH_3 s-stretch	2922	2920	2919	2916
SiH_2 a-stretch	2202	2198	2182	2180
SiH_2 s-stretch	2188	2192	2193	2189
CH_3 d-deform	1416	1409	1419	1413
CH_3 d-deform	1416	1420 [b]	1423	1416
CH_3 s-deform	1266	1264	1262	1262
CH_3 rock	974	968	962	948
CH_3 rock	872	873	871	856
CSi stretch	859	913	899	884
SiH_2 scissors	759	750	744	736
SiH_2 twist	734	686	659	640
SiH_2 wag	685	699	701 [b]	696 [b]
SiH_2 rock	525	521	498	485
SiX stretch	954	530	408	355
CSiX deform.	263	213 [b]	192	176
CH_3 torsion		225		

$(CH_3)_2SiHX$ [c]

Assignment	X=F	X=Cl	X=Br	X=I
CH_3 a-stretch [2]	2981	2983	2980	2987
CH_3 a-stretch [2]	2974	2974	2974	2974
CH_3 s-stretch [2]	2917	2916	2914	2913
SiH stretch	2169	2176	2176	2172
CH_3 a-deform [2]	1436	1435	1432	1430
CH_3 a-deform [2]	1422	1420	1417	1401
CH_3 s-deform [2]	1266	1264	1264	1262
CH_3 rock	921	909	908	904
CH_3 rock	844	855	880	872
SiH bend	742	726	711	711
CSi stretch	703 [d]	698 [d]	707 [e]	697
CSi stretch	651	671	665	656
CH_3 rock	825	845	846	846
CH_3 rock	777	777	775	772
SiH bend	638	636	637	637
SiX stretch	929	507	402	350
SiX bend	270	207 [d]	186 [d]	167 [d]
CSiX bend	218 [d]	209 [d]	194 [d]	185 [d]
SiC_2 deform	287	258 [d]	244 [d]	237 [d]
SiC torsion [2]				

$(CH_3)_2SiX_2$

Assignment	X=F [f]	X=Cl [g]	X=Br [h]	X=I [i]
CH_3 a-stretch [2]	2980	2984	2986	2988
CH_3 a-stretch [2]	2980	2984	2986	2973
CH_3-s-stretch [2]	2920	2918	2917	2916
CH_3 a-deform. [2]	1415	1412	1410	1407

TABLE 3 (continued)

$(CH_3)_2SiX_2$

Assignment	X=F	X=Cl	X=Br	X=I
CH_3 a-deform. [2]	1415	1412	1410	1399
CH_3 s-deform. [2]	1278	1261	1258	1254
CH_3 s rock	828	847	846	845
CH_3 a rock	860	823	815	810
CH_3 s rock	828	847	750	704
CH_3 a rock	823	823	800	750
SiC a-stretch	760	805	797	788
SiC s-stretch	646	688	682	672
SiX a-stretch	1042	553	426	385
SiX s-stretch	952	473	355	306
SiC_2 s-deform.	330	232	196	192
$SiMe_2$ rock	330	241	212	154
SiX_2 rock	271	241	186	185
SiX_2 twist	213	177	167	111
SiX_2 s-deform.	213	168	119	90
SiC torsion [2]	156			

[a] All frequencies taken from IR spectrum of gas unless otherwise noted. All assignments from Clark [1].

[b] Frequencies taken from Raman spectrum of liquid.

[c] Frequency assignments from IR spectrum of gas unless indicated otherwise. All assignments from Clark [1].

[d] Raman liquid assignment.

[e] Normal coordinate analysis calculation, Clark [1].

[f] Frequencies taken from liquid state data of Spangenburg and Pfeiffer [5].

[g] Frequencies taken from liquid state data of Shimuzu and Murata [6].

[h] Frequencies from liquid state data of Murata and Hayashi [7], and Durig and Hawley [3]. C—H frequencies estimated, this work.

[i] Frequencies from Durig and Hawley [3].

TABLE 4

Molecular structural data used for methylhalosilanes

Bond lengths

Methylmonohalosilanes (CH_3SiH_2X) and dimethylhalosilanes [$(CH_3)_2SiHX$], lengths in Å

	X=F [a]	X=Cl [b]	X=Br [c]	X=I [d]
r_{CH}	1.090	1.090	1.090	1.090
r_C	1.848	1.889 [e]	1.889 [e]	1.889 [e]
r_{SiH}	1.473	1.485	1.57	1.487
r_{SiX}	1.600	2.050	2.209	2.437

Dimethyldihalosilanes [$(CH_3)_2SiX_2$]

	X=F [f]	X=Cl [g]
r_{CH}	1.09	1.093
r_{CSi}	1.833	1.850
r_{SiH}	1.474	1.467
r_{SiH}	1.583	2.040

	Methyl mono halosilanes	Dimethyl halosilanes	Dimethyl dihalosilanes
Product of principal moments of inertia, $I_{ABC} \times 10^{-117}$ gm^3 cm^{-6}			
X=F	787.7	4917.1	13 510.6
X=Cl	2 962.0	14 078.0	79 074.4
X=Br	7 043.8	32 802.8	455 700.3
X=I	12 547.2	57 783.2	1 693 783.0
Reduced moments of inertia, $I_R \times 10^{-40}$ gm cm^{-2}			
X=F	4.6813	5.1403	5.1884
X=Cl	4.9886	5.1881	5.2509
X=Br	5.0843	5.2189	5.2791
X=I	5.1673	5.2369	5.2898
Internal rotational barrier, V (kcal g^{-1} mole^{-1} K^{-1})			
X=F	1.559 [h]	2.39 [k]	1.70 [k]
X=Cl	1.84 [i]	2.56 [k]	1.75 [j]
X=Br	1.80 [j]	2.07 [k]	1.81 [k]
X=I	1.80 [j]	2.18 [k]	2.02 [k]
Molecular weight [l]			
X=F	64.135	78.162	96.153
X=Cl	80.590	94.617	129.062
X=Br	125.046	139.073	217.974
X=I	172.041	186.068	311.964

[a] Data from CH_3SiH_2F [11].

[b] Assumed from SiH_3Cl [13].

[c] Assumed from SiH_3Br [13].

[d] Assumed from SiH_3I [12].

[e] Assumed from CH_3SiH_3 [14].

[f] Assumed from CH_3SiHF_2 [14].

[g] Assumed from CH_3SiHCl_2 [15].

[h] Pierce [11].

[i] Durig and Hawley [3,4].

[j] Estimated this work.

[k] Durig and Hawley [3].

[l] Molecular weights taken from ref. 23.

TABLE 5

Comparison of computed values between this[a] and other work (all values in cal g^{-1} $mole^{-1}$ K^{-1})

Compound	Temp. (K)	C_p^0		S^0	
CH_3SiH_2Cl	298.16	18.39		71.29	69.4 [2]
	1000.00	33.00		102.55	
$(CH_3)_2SiHCl$	298.16	25.36		79.41	77.9 [2]
	1000.00	45.58		122.28	
$(CH_3)_2SiF_2$	298.16	25.95	25.17 [5]	80.21	80.21 [5]
	1000.00	46.00	45.87 [5]	123.60	123.18 [5]
$(CH_3)_2SiCl_2$	298.16	28.04		85.92	85.5 [2]
	1000.00	46.69		130.86	

[a] If reference not indicated, this work.

TABLE 6

Percent errors assumed in parameters for calculation of overall function error

Compound	ν_1, ν_2, ν_3 [a]	I_{ABC}	V_0
$(CH_3)SiH_2F$	0.5	5	5
$(CH_3)SiH_2Cl$	0.5	5	5
$(CH_3)SiH_2Br$	0.5	5	20
$(CH_3)SiH_2I$	0.5	5	20
$(CH_3)_2SiHF$	1	5	5
$(CH_3)_2SiHCl$	2	5	5
$(CH_3)_2SiHBr$	2	5	5
$(CH_3)_2SiHI$	2	5	5
$(CH_3)_2SiF_2$	2	5	5
$(CH_3)_2SiCl_2$	4	5	10
$(CH_3)_2SiBr_2$	4	10	5
$(CH_3)_2SiI_2$	4	10	5

[a] $\nu_{i=1,2,3}$ are the three lowest valued frequencies in cm^{-1} in each of the given compounds.

TABLE 7

Uncertainties in final function values at 298.16 K (% error) [a]

Function	Compound	X=F	C=Cl	X=Br	X=I
C_p^0	$(CH_3)SiH_2X$	0.1	0.1	0.4	0.4
	$(CH_3)_2SiHX$	0.2	0.3	0.2	0.2
	$(CH_3)_2SiX_2$	0.3	0.3	0.2	0.2
$(H-H_0^0)/T$	$(CH_3)SiH_2X$	0.2	0.2	0.4	0.4
	$(CH_3)_2SiHX$	0.2	0.4	0.4	0.4
	$(CH_3)_2SiX_2$	0.6	0.6	0.5	0.4
$-(F-H_0^0)/T$	$(CH_3)SiH_2X$	0.1	0.1	0.3	0.3
	$(CH_3)_2SiHX$	0.2	0.3	0.3	0.3
	$(CH_3)_2SiX_2$	0.3	0.4	0.4	0.4
S^0	$(CH_3)SiH_2X$	0.1	0.1	0.2	0.1
	$(CH_3)_2SiHX$	0.2	0.2	0.2	0.2
	$(CH_3)_2SiX_2$	0.3	0.4	0.4	0.4

[a] All errors obtained by using % error values in parameters as suggested in Table 6.

DISCUSSION

Methylmonohalosilanes

The carefully documented gas state frequency data of Clark [1] have been used to calculate the thermodynamic functions of methylmonohalosilanes. The analysis of Clark [1] involved spectroscopic measurements of the frequencies of deuterated analogues of each compound in addition to spectroscopic measurements on the compound itself. In the frequency evaluation process, normal coordinate analysis has been used [1], and the frequencies of each compound were compared with those of previous researches [3,4,8–10].

The value of the principal moment of inertia product for methylfluorosilane was taken from the published microwave measurements [11], while the values for other monohalosilanes were calculated using bond lengths of SiH_3X [12,13] and CH_3SiH_3 [14] (Table 4). All angles were assumed to be tetrahedral, and the symmetry numbers were found by inspection to be 1. Table 4 shows that changes in bond lengths with replacement of a hydrogen by a methyl group are at most 1.7% for the Si—H bond length and 0.25% for the Si—X bond length (see refs. 11, 12, 16 and 17). Assuming that electronegativity effects are primarily responsible for such changes (the methyl group serving as a source of electrons to a strongly electronegative substituent), we may expect that the other monohalogenated compounds, being less negative and neglecting all steric effects, will show less of a change in bond length. If the angles are tetrahedral, the error in the calculated value for the principal moment of inertia will be at most 1%. The effect of bond length errors on error of the values of the reduced moments of inertia was found to be very small; that is, maximum deviation of 0.04% for 0.25% error in bond lengths, with decrease in the direction of the increasing molecular weight. The values of internal rotational barriers are listed in Table 4. For the methylmonohalosilanes internal rotational barrier values were available only for fluorinated and chlorinated compounds [11,4]. The barriers of the bromine and iodine derivatives were estimated by comparison with changes in barrier height with substituent atom for the dimethylhalosilanes, for which complete data were available. The errors anticipated by these estimations are probably at most 20% which by calculation will contribute 0.5% error in the final function value — compare with analysis of Tables 6 and 7.

Dimethylhalosilanes

The gas state frequency data (Table 3) are taken from the work by Clark [1]. The bond length values used to calculate principal and reduced moments of inertia (Table 4) have been taken from refs. 12–14. The error in the value of the principal moment of inertia product is estimated to be at most 5%. All the internal rotational barriers used (Table 4) were those of Durig and Hawley [3].

Dimethyldihalosilanes

For the dimethyldihalosilanes, liquid state frequencies (Table 3) of a number of researchers were adopted [3,5—7]. The C—H frequencies of the brominated compounds, for which data were not available, are estimated in this work by comparison with the corresponding frequencies of the fluorine, chlorine and iodine derivatives. For the dimethyldifluoro and dimethyldichlorosilanes, bond data from the corresponding monomethyldihalosilanes [15,16] were adopted. For the dimethyldibromo and dimethyldiiodosilanes the analogous dihalogenated silanes have not been previously studied. The bond lengths that were therefore used were those of the methylmonohalosilanes. Comparison of the corresponding bond lengths for the monohalogenated and dihalogenated compounds (Table 4) shows that the bond lengths for the chlorinated compounds differ by less than 2%. Assuming that the percent difference is the same for the brominated and iodinated compounds, the errors in the principal moments of inertia are found by calculation to be less than 9%. In case of the reduced moment of inertia, for the dibrominated and diiodinated compounds, for which an error of 2% in the bond lengths was assumed, the error was less than 0.02%.

The internal rotational barriers used (Table 4) were those determined by Durig and Hawley [3]. However, because of a coincidental degeneracy of the torsional mode with one of the bending modes for the chlorinated compounds, Durig and Hawley [3] were unable to determine its exact frequency and hence were not able to calculate the barrier height.

In view of Lielmezs and Morgan's [20] and Lielmezs' [21] findings regarding the relation between the internal rotational barrier and the ionization energy of substituent atoms in ethyl halides and allyl halides, the internal rotational barrier for the chlorinated compound was chosen as an intermediate value between the values of the fluorinated and brominated compounds. The symmetry number for $(CH_3)_2SiHX$ and $(CH_3)SiH_2X$ is $\sigma = 1$; but for $(CH_3)_2SiX_2$ it is assumed to be $\sigma = 2$.

Comparison with other work

In Table 5 we compare our calculated thermodynamic function values with those available from the literature. Agreement is quite satisfactory, especially for the $(CH_3)_2SiF_2$. For chlorinated methylsilanes, however, our values are higher than those obtained by Hajiev and Agarunov [2]. This discrepancy may well be due to the fact that their values were obtained by means of a bond contribution method [15].

ACCURACY AND RANGE OF RELIABILITY

In this work all values are in cal g^{-1} $mole^{-1}$ K^{-1} units and apply to the ideal gas state at 1 atm pressure, tabulated values are given to ±0.1 cal g^{-1} $mole^{-1}$ K^{-1}. However, probable errors may be larger than this.

The percentage errors assigned to the calculated thermodynamic functions are really estimates. These estimates were obtained considering two main sources of errors: the errors in the input parameters and errors in the assumptions.

Input data errors

One of the input parameter errors that can significantly affect the final results is the overall frequency measurement accuracy.

In this work the assignments for the methylmonohalosilanes, because they are all gas phase values, should be considered the least uncertain. The frequency measurements of dihalogenated compounds, on the other hand, were all liquid phase measurements. By comparing the frequency differences in gas and liquid state measurements of Clark [1], it is found that those frequency phase shifts rarely exceed 2.5% and that the frequencies in general tend to be within 1% of each other. Table 6 (first column) considers this, showing the uncertainties that could be expected in the three lowest frequency assignments of each of the given compounds, this work.

The assignment of possible errors of the principal moment of inertia product variations (Table 6, second column) was guided by the contributions of errors in bond length estimates to errors in the calculated values for the principal moment of inertia — see previous discussion on the principal moment of inertia calculation.

The errors in the values of internal rotational barrier (Table 4) are estimates, as no uncertainty has been assigned to them originally. Table 7 shows the calculated probable uncertainties on the basis of the suggested error magnitudes (Table 6) in final thermodynamic function values (Table 1) at 298.16 K. The thermodynamic functions which can be expected to be the most accurate at 298.16 K (Table 7) are those for methylmonofluorosilane and methylmonochlorosilanes which have maximum uncertainties of 0.2%. The least accurate are likely to be the dimethylhalosilanes, with a maximum function error of 0.6%. If error analysis for higher temperatures is considered it can be shown that errors increase with temperature for some parameters and decrease for others. The net result of these changes would then determine the overall error effect with temperature.

There are other errors, however, which do increase with temperature and which are the errors in calculation assumptions.

Calculation assumption errors

There are four sources of error in the assumptions made that may significantly contribute to the function error at higher temperatures. These are generally collected under the term anharmonicity, and they affect deviations of vibrations from the harmonic oscillator, as well as effects of rotational and vibrational motion on moments of inertia and contributions to the functions by electronic transitions. On the basis of previous research [22] it is expected that these effects may contribute about 1—2% to the error in the functions at the top end of the temperature range and less than 0.5% at the lower end.

This discussion indicates that, barring major errors in frequency assignments, the expected overall error should be within the 0.3—1.0% range. This expectation is brought out by Table 7, which implies that even if frequency assignments are estimated (Table 3), errors in the calculated thermodynamic function values will be low.

ACKNOWLEDGEMENT

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

NOMENCLATURE

Å	Angstrom
C_p°	heat capacity, cal mole^{-1} K^{-1}
e.u.	entropy unit, cal mole^{-1} K^{-1}
$-(F^\circ - H_0^\circ)/T$	free energy function, cal mole^{-1} K^{-1}
$(H^\circ - H_0^\circ)/T$	enthalpy function, where $H_0^\circ = H^\circ$ at 0 K, cal mole^{-1} K^{-1}
I_{ABC}	principal moment of inertia, g^3 cm^{-6}
I_R	reduced moment of inertia, g cm^{-2}
r	distance, in Å
S°	entropy, e.u.
V, V_0	internal rotational barrier, cal mole^{-1} K^{-1}
ν	wave number, cm^{-1}

Superscript

$^\circ$	reference state referring to the hypotherical state of an ideal gas at 1 atm

Subscript

p	pressure

REFERENCES

1 A.J.F. Clark, Ph.D. Dissertation, University of Windsor, 1979.
2 S.N. Hajiev and M.J. Agarunov, J. Organomet. Chem., 22 (1970) 305.
3 J.R. Durig and C.W. Hawley, J. Chem. Phys., 58(1) (1973) 237.
4 J.R. Durig and C.W. Hawley, J. Chem. Phys., 59(1) (1973) 1.
5 H.J. Spangenburg and M. Pfeiffer, Z. Phys. Chem., 232 (1966) 343.
6 K. Shimuzu and H. Murata, J. Mol. Spectrosc., 4 (1960) 214.
7 H. Murata and S. Hayashi, J. Chem. Phys., 19 (1951) 1217.
8 Z. Meic, A. Braun, H. Knehr and W. Zeil, Ber., 78 (1974) 1249.
9 H. Kriegsmann and G. Englehardt, Z. Anorg. Allg. Chem., 310 (1961) 321.
10 E.A.V. Ebsworth, M. Onyszchuk and N. Sheppard, J. Chem. Soc., (1958) 1453.
11 L. Pierce, J. Chem. Phys., 29(2) (1958) 383.
12 R. Kewley, P.M. McKinney and A.G. Robiette, J. Mol. Spectrosc., 34 (1970) 390.
13 J.M. Mays and B.P. Dailey, J. Chem. Phys., 20(11) (1952) 1695.

14 R.W. Kilb and L. Pierce, J. Chem. Phys., 27(1) (1957) 108.
15 K. Endo, H. Takeo and C. Matsumura, Bull. Chem. Soc. Jpn., 50(3) (1977) 626.
16 J.D. Swalen and B.P. Stoicheff, J. Chem. Phys., 28(4) (1958) 671.
17 V.W. Laurie, J. Chem. Phys., 26(6) (1957) 1359.
18 K.S. Pitzer, Quantum Chemistry, Prentice-Hall, Englewood Cliffs, NJ, 1953.
19 Computer Programmes, The University of British Columbia, Computer Centre, B.C., Canada, 1980.
20 J. Lielmezs and J.P. Morgan, Nature (London), 202 (1964) 1106.
21 J. Lielmezs, Thermochim. Acta, 12 (1975) 1.
22 R.E. Pennington and K.A. Kobe, J. Chem. Phys., 22 (1954) 1442.
23 R.C. Weast (Ed.), Handbook of Chemistry and Physics, CRC Press, Cleveland, OH, 1974, 55th edn.