Ideal Gas Thermodynamic Properties of $CH_{4-(a+b+c+d)}F_aCl_bBr_cI_d$ Halomethanes

Shanti A. Kudchadker and Arvind P. Kudchadker

Kanpur Critical Data Center, Department of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur, India 20 80 16

The available molecular parameters, fundamental frequencies, and enthalpies of formation at 298.15K ($\Delta Hf°(298)$) for halomethanes of the type $CH_{4-(a+b+c+d)}F_aCl_bBr_cI_d$ have been critically evaluated and recommended values selected. Molecular parameters and $\Delta Hf°(298)$ for some halomethanes have been estimated as the experimental values for these compounds are not available. This information has been utilized to calculate the ideal gas thermodynamic properties C_p°, S°, $H^\circ - H_0^\circ$, $-(G^\circ - H_0^\circ)/T$, ΔHf°, ΔGf°, and $\log Kf$ from 0 to 1500 K and at a pressure of one atmosphere using the rigid rotor-harmonic oscillator approximation for the following compounds: CH_2FBr, CH_2ClBr, CH_2ClI, CH_2BrI, CHF_2Br, $CHFClBr$, $CHFBr_2$, $CHCl_2Br$, $CHClBr_2$, CF_3Br, CF_3I, CF_2ClBr, CF_2Br_2, CF_2I_2, $CFCl_2Br$, $CFClBr_2$, $CFBr_3$, CCl_3Br, CCl_3I, CCl_2Br_2, $CClBr_3$.

Key words: Critically evaluated data; estimated enthalpies of formation; estimated molecular parameters, ideal gas thermodynamic properties; mixed halomethanes.

Contents

List of Tables

0047-2689/78/4127-1285 $04.00

List of Tables—Continued

1. Introduction

1.1. Scope and Objectives

This work is the continuation of calculations of the thermodynamic properties of bromo- and iodomethanes [1].[1] For this purpose, a systematic literature survey complete up to 1976 was carried out on vibrational frequencies, structural parameters and enthalpies of formation of mixed halomethanes, $CX_{4-a-b}Br_aI_b$(X=H, F, Cl). Out of forty seven compounds of this type the vibrational frequencies were available for only twenty one compounds. The structural data and gaseous enthalpies of formation at 298.15 K were available for very few compounds. Hence we had to estimate them for most of the compounds in order to calculate their thermodynamic properties. These estimation procedures are discussed in sections 1.2 and 1.4.

The thermodynamic properties were calculated assuming rigid rotator-harmonic oscillator approximations from 0–1500 K and at pressure of one atmosphere. The properties tabulated are heat capacity, C°_p; entropy, S°; relative enthalpy, $H^\circ-H^\circ_0$; Gibbs energy function, $-(G^\circ-H^\circ_0)/T$; enthalpy of formation, ΔHf°; Gibbs energy of formation, ΔGf°; and the equilibrium constant of formation, log Kf. The values are reported at 100 degree temperature intervals and at 273.15 and 298.15 K (henceforth referred to as 298). The reader is referred to references [1] and [2] (chloro- and fluoromethanes and bromo- and iodomethanes, respectively) for the values of the thermodynamic properties of the elements, atomic masses, uncertainties, etc. The compounds are arranged according to decreasing number of atoms in the following order of atoms: H, F, Cl, Br, and I. Thermodynamic properties are given in units of cal mol^{-1}. For conversion to SI units, 1 cal=4.184 J, and 1 atm.=101325 Pa.

1.2. Structural Data

Out of twenty one halomethanes complete experimental structural data are available for only six compounds, CF_3Br, CF_3I, $CFBr_3$, CCl_3Br [3], CHFClBr [3a], CH_2FBr [3b], and partial data for two compounds, CH_2ClBr and CCl_2Br_2 [3]. Experimental values of moments of inertia were used when available. In most cases, however, the moments had to be calculated from estimated structural parameters. As the thermal functions are not very sensitive to the molecular parameters, their calculations using the predicted values of the structural parameters should not be far from the true values. The estimated uncertainties in the predicted bond distances are ±0.05 Å and those in the bond angles are ±2.0 deg. The estimated uncertainties in S° and $(G^\circ-H^\circ_0)/T$ due to the uncertainties in the molecular parameters are ±0.2 cal K^{-1} mol^{-1}.

The bond distances C–H, C–Cl, C–Br, and C–I and bond angles HCH, FCF, ClCCl, BrCBr, and ICI were predicted by averaging the known values of the above parameters in all halomethanes for which experimental data are available [1, 2, 3]. This was done as no particular trend of these parameters in various compounds was observed. The exception is the C–F bond distance, where it was found that the presence of one, two, or three fluorine atoms in a compound shows a certain trend in the magnitude of the C–F distance. Hence three different values of C–F were obtained by averaging the values of C–F in the particular type of fluoromethanes. In the case of CX_2YZ type molecules the angles YCZ and XCZ were required to calculate the moments of inertia. They were estimated as follows: (1) Bond angle YCZ: If the values for angle YCY in CY_2W_2 and angle ZCZ in CZ_2W_2 are available, then $\angle YCZ = 1/2(\angle YCY + \angle ZCZ)$. (2) Bond angle XCZ: Very few values are available for $\angle XCZ$ in halomethanes having two X atoms. Hence values of $\angle XCZ$ angles

---

[1] Figures in brackets indicate literature references at the end of this paper.

were obtained from molecules having three X atoms, viz. CX_3Z. It was found that whatever the atom Z (H, F, Cl, Br, I) the angle XCZ is almost the same (table 1). Hence the average value for this angle in various CX_3Z molecules was taken as angle XCZ.

The estimated values for various structural parameters for halomethanes are given in table 2 and those adopted for twenty CX_3Y and CX_2YZ type mixed halomethanes are given in table 3 and 4, respectively. For CHFClBr see section 7.

1.3. Vibrational Frequencies

The infrared and Raman spectra of most of these mixed halomethanes were studied in the early days of spectroscopy. Only for a few molecules (CHFClBr, CF_2I_2, CCl_3I, etc.) have the spectra been studied with newer instruments with higher resolution. The adopted vibrational frequencies are reported in table 5. The uncertainties in the vibrational frequencies due to the instrumental limitations and liquid-phase shift are the sources of the major uncertainties in the derived thermodynamic properties. These uncertainties reported in table 5a have been computed assigning the uncertainties in the vibrational frequencies which are given in table 5a.

1.4. Enthalpy of Formation

Out of twenty-one halomethanes mentioned above the gaseous enthalpies of formation at 298 K are available for only the following three compounds: CF_3Br, CF_3I, and CCl_3Br [4]. Hence we had to estimate ΔHf° (298) for rest of the compounds. The usual method for the estimation of enthalpies of formation is the application of the bond additivity scheme corrected for near neighbor bond interactions between two bonds [5] or two and three bonds (trigonal) [6] taken at a time. It is shown [7, 8, 9] that this method can be successfully applied to the halomethanes. Recently, Somayajulu and Zwolinski [10] applied the triatomic additivity method very satisfactorily to estimate the enthalpies of formation of a large number of substituted alkanes. As the experimental ΔHf° (298) data on mixed halomethanes are very scanty, it is impossible to obtain the basic interaction terms in the triatomic additivity method. Hence we are restricted to the usual bond additivity scheme containing interactions of two or three bonds. Only a few trigonal interaction terms could be determined. The rest of the terms were assumed to be negligible.

For this purpose, the most recently recommended values of ΔHf° (298) [1, 2, 11] were used to obtain the bond and bond interaction contributions. The Cl–I and Br–I contributions could not be obtained as ΔHf° (298) were not available for any of the compounds which contained these terms. Hence they were estimated by analyzing all the interaction terms. The bond and bond interaction contributions are given in table 6. It may be noticed that the magnitude of the interactions are appreciable only in compounds which contain CH bonds and hence the estimated ΔHf° (298) would not differ much from the true values by neglecting the trigonal interactions in other compounds. Comparison of our calculated values of ΔHf° (298) for CH_2FCl, CHF_2Cl, $CHFCl_2$ with the literature values suggests that the neglect of trigonal interactions of type H–X–Y, when there is only one CH bond in the compound, would not cause serious error in the estimated ΔHf° (298) values. The experimental and estimated values of ΔHf° (298) for all halomethanes are given in table 7. The estimated error in most of the compounds is less than ±2 kcal mol^{-1}. In the compounds containing ClI and BrI terms it may be as high as ±5 kcal mol^{-1}.

TABLE 1. ∠XCZ in various CX_3Z compounds (degrees)

Compound	HCZ	Compound	FCZ	Compound	ClCZ	Compound	BrCZ	Compound	ICZ
CH_3F	108. 94	CF_3H	110. 13	CCl_3H	107. 34	CBr_3H	107. 83	CI_3H	105. 65
CH_3Cl	108. 0	CF_3Cl	110. 17	CCl_3F	107. 15	CBr_3F	104. 27	CI_3F	104. 38
CH_3Br	107. 23	CF_3Br	109. 43	CCl_3Br	107. 38	CBr_3Cl	106. 03	CI_3Cl	
CH_3I	107. 63	CF_3I	110. 41	CCl_3I	107. 15	CBr_3I		CI_3Br	
Average	107. 95	Average	110. 04	Average	107. 26	Average	106. 04	Average	105. 02

TABLE 2. Structural parameters for halomethanes

Bond	Distance (Å)	XCX (deg)		XCZ [a] (deg)		YCZ [b] (deg)		YCZ [b] (deg)	
C–H	1. 09	HCH	111. 35	HCZ	107. 95	HCF	109. 84	FCBr	110. 48
C–F(CF)	1. 40	FCF	108. 36	FCZ	110. 04	HCCl	111. 51	FCI	111. 09
C–F(CF_2)	1. 35	ClCCl	111. 57	ClCZ	107. 26	HCBr	111. 99	ClCBr	112. 15
C–F(CF_3)	1. 33	BrCBr	112. 63	BrCZ	106. 04	HCI	112. 60	ClCI	112. 75
C–Cl	1. 76	ICI	113. 85	ICZ	105. 02	FCCl	109. 99	BrCI	113. 24
C–Br	1. 93								
C–I	2. 13								

[a] Z=H, F, Cl, Br, I (X≠Z).

[b] For CX_2YZ and CXYZW type molecules.

TABLE 3. Structural parameters and moments of inertia for CX_3Y[b] and CX_2Y_2[c] type mixed halomethanes

Compound	C–X(Å)	C–Y(Å)	X–C–X(deg)	Y–C–Y(deg)	I_A	I_B	I_C
					amu Å²		
CF_3Br	1. 330	1. 908	108. 0		87. 971	242. 098	242. 098
CF_3I	1. 332	2. 134	108. 0		88. 247	331. 710	331. 710
CF_2Br_2[a]	1. 35	1. 93	108. 36	112. 63	157. 513	452. 115	518. 510
CF_2I_2[a]	1. 35	2. 13	108. 36	113. 85	180. 994	853. 346	943. 221
CBr_3F	1. 91	1. 44	114.		475. 993	475. 993	820. 121
CCl_3Br	1. 764	1. 936	111. 2		300. 426	432. 080	432. 080
CCl_3I[a]	1. 76	2. 13	111. 57		300. 386	567. 080	567. 080
CCl_2Br_2	1. 75	1. 93	111. 57[a]	112. 63[a]	357. 811	555. 019	615. 902
CBr_3Cl[a]	1. 93	1. 76	112. 63		575. 476	575. 476	824. 315

[a] Estimated values.

[b] Symmetry number=3.

[c] Symmetry number=2.

TABLE 4. Structural data[a] and moments of inertia for CX_2YZ[b] type mixed halomethanes

Compound	C–X (A°)	C–Y (A°)	C–Z (A°)	XCX (deg)	XCZ (deg)	YCZ (deg)	I_A	I_B	I_C
							amu Å²		
CH_2FBr[c]	1. 09	1. 38	1. 92	112. 00	108. 50	111. 00	12. 683	134. 415	143. 875
CH_2ClBr	1. 09	1. 76	1. 93	111. 35	107. 95	112. 15	17. 420	238. 511	252. 663
CH_2ClI	1. 09	1. 76	2. 13	111. 35	107. 95	112. 75	18. 466	311. 349	326. 547
CH_2BrI	1. 09	1. 93	1. 76	111. 35	107. 95	113. 24	21. 143	569. 293	587. 169
CF_2HBr	1. 35	1. 09	1. 93	108. 36	110. 04	111. 99	50. 168	177. 613	218. 507
CBr_2HF	1. 93	1. 09	1. 40	112. 63	106. 04	109. 84	90. 292	418. 614	495. 996
CCl_2HBr	1. 76	1. 09	1. 93	111. 57	107. 26	111. 99	157. 263	263. 659	406. 783
CBr_2HCl	1. 93	1. 09	1. 76	112. 63	106. 04	111. 51	187. 331	419. 960	591. 688
CF_2ClBr	1. 35	1. 76	1. 93	108. 36	110. 04	112. 15	132. 268	306. 258	347. 465
CCl_2FBr	1. 76	1. 40	1. 93	111. 57	107. 26	110. 48	218. 283	333. 358	415. 462
CBr_2FCl	1. 93	1. 40	1. 76	112. 63	106. 04	109. 99	258. 427	485. 320	597. 424

[a] Estimated values.

[b] Symmetry number=1.

[c] Experimental values.

TABLE 5. Vibrational frequencies [a] (cm^{-1}) of mixed halomethanes [b]

Compound	1	2	3	4	5	6	7	8	9
1 CH_2FBr	2993	1461	1313	1050	637	314	3053	1227	940
2 CH_2ClBr	2987	1421	1235	737	618	228	3060	1139	854
3 CH_2ClI	2978	1392	1183	718	527	194	3048	1126	801
4 CH_2BrI	2978	1374	1130	616	517	144	3053	1065	754
5 CHF_2Br	3003	1280	1135	718	577	240	1344	1108	323
6 $CHFClBr$	3026	1311	1205	1078	788	664	427	315	226
7 $CHFBr_2$	3015	1295	1063	620	358	171	1170	704	295
8 $CHCl_2Br$	3028	1177	734	597	330	220	1270	773	215
9 $CHClBr_2$	3034	1191	756	576	279	168	1149	669	201
10 CF_3Br	1089	760	349	1210(2)	547(2)	306(2)			
11 CF_3I	1080	742	286	1187(2)	537(2)	260(2)			
12 CF_2ClBr	1102	872	648	440	337	220	1150	425	290
13 CF_2Br_2	1090	623	340	168	281	1153	369	831	325
14 CF_2I_2	1064	605	270	112	208	1110	304	740	250
15 $CFCl_2Br$	1080	796	502	339	306	218	838	392	204
16 $CFClBr_2$	1075	806	460	341	268	162	754	308	196
17 $CFBr_3$	1069	398	218	743(2)	306(2)	150(2)			
18 CCl_3Br	716	422	247	775(2)	295(2)	193(2)			
19 CCl_3I	684	390	224	755(2)	284(2)	188(2)			
20 CCl_2Br_2	746	380	242	154	175	771	262	698	229
21 $CClBr_3$	745	327	211	677(2)	211(2)	140(2)			

[a] Frequencies are given in the traditional equivalent wavenumber (cm^{-1}).

[b] Numbers in parentheses are degeneracies.

TABLE 5a. Maximum uncertainties Δ in the vibrational frequencies and derived thermodynamic properties at 100–1500 K

Compound	State [a]	Δ	$C_p°$	$S°$	$-(G°-H_0°)/T$	$H°-H_0°$
		cm^{-1}	$cal\ K^{-1}\ mol^{-1}$			$kcal\ mol^{-1}$
CH_2FBr	l	10	0.06	0.18	0.13	0.08
CH_2ClBr	g,l	5	0.03	0.12	0.08	0.04
CH_2ClI	l	10	0.07	0.24	0.19	0.08
CH_2BrI	l	10	0.08	0.29	0.23	0.08
CHF_2Br	g	5	0.05	0.13	0.10	0.04
$CHFClBr$	g	2	0.02	0.06	0.05	0.02
$CHFBr_2$	l	10	0.14	0.35	0.28	0.09
$CHCl_2Br$	g	5	0.08	0.18	0.15	0.05
$CHClBr_2$	g	5	0.09	0.20	0.17	0.05
CF_3Br	g	5	0.06	0.16	0.13	0.05
CF_3I	g	5	0.08	0.18	0.15	0.05
CF_2ClBr	g	5	0.08	0.20	0.16	0.05
CF_2Br_2	g	5	0.10	0.23	0.19	0.05
CF_2I_2	g	5	0.13	0.29	0.25	0.05
$CFCl_2Br$	g	5	0.11	0.23	0.20	0.05
$CFClBr_2$	g,l	5	0.13	0.26	0.23	0.05
$CFBr_3$	l	7	0.21	0.42	0.37	0.08
CCl_3Br	l	7	0.20	0.38	0.33	0.08
CCl_3I	l	5	0.15	0.28	0.25	0.06
CCl_2Br_2	g	5	0.16	0.31	0.27	0.06
$CClBr_3$	l	7	0.25	0.50	0.44	0.08

[a] State in which spectra studied.

TABLE 6. Contributions to ΔHf° (g, 298) in kcal mol^{-1}

Bond		Bond-bond interaction				Trigonal interaction			
CH	−4. 470	HF	3. 065	FBr	2. 405	HHF	1. 356	HBrBr	−0. 903
CF	−55. 755	HCl	−0. 576	FI	3. 452	HFF	−1. 352	HHI	−1. 025
CCl	−5. 725	HBr	−1. 023	ClBr	1. 042	HHCl	0. 457	HII	1. 025
CBr	4. 750	HI	1. 255	ClI	1. 1	HClCl	−0. 409	FFCl	−0. 095
CI	16. 010	FCl	1. 356	BrI	1. 5	HHBr	0. 903	FClCl	0. 254

TABLE 7. ΔHf° (g, 298) of halomethanes (kcal/mol)

Compound	Obs.	This work	Ref. 74	Ref. 7
1. CH_4	−17. 88	−17. 88	−17. 80	−17. 9
2. CH_3F	−55. 90[a]	−55. 90	−67. 92	−54. 8
3. CH_2F_2	−108. 2	−108. 18	−117. 92	−105. 5
4. CHF_3	−166. 6	−166. 60	−169. 92	−162. 6
5. CF_4	−223. 02	−223. 02	−219. 92	−218. 6
6. CH_3Cl	−19. 59	−19. 49	−20. 54	−19. 5
7. CH_2Cl_2	−22. 8	−22. 60	−22. 42	−21. 5
8. $CHCl_3$	−24. 6	−24. 60	−24. 81	−23. 4
9. CCl_4	−22. 9	−22. 90	−24. 61	−25. 2
10. CH_3Br	−9. 02	−9. 02	−8. 49	−8. 9
11. CH_2Br_2	−3. 53[a]	−3. 53	1. 14	3.
12. $CHBr_3$	4. 0	4. 00	10. 16	19.
13. CBr_4	19. 0	19. 00	20. 19	38.
14. CH_3I	3. 29	3. 29	4. 20	
15. CH_2I_2	28. 10	28. 10	27. 11	
16. CHI_3	50. 40	50. 40	51. 13	
17. CI_4	64. 04[a]	64. 04		
18. CH_2FCl	−63. 2[a]	−62. 27	−71. 92	−63.
19. CH_2FBr		−51. 20	−59. 89	−50.
20. CH_2FI		−36. 26	−47. 40	
21. CH_2ClBr		−10. 71	−11. 89	−9.
22. CH_2ClI		3. 24	2. 10	
23. CH_2BrI		13. 66	12. 12	
24. CHF_2Cl	−115. 6	−114. 89	−120. 92	−112.
25. CHF_2Br		−102. 66	−109. 89	−98.
26. CHF_2I		−87. 03	−95. 90	
27. $CHFCl_2$	−68. 1[c]	−67. 20	−72. 91	−66.
28. $CHFClBr$		−54. 93	−61. 89	−52.
29. $CHFClI$		−40. 29		
30. $CHFBr_2$		−45. 80	−49. 86	−38.
31. $CHFBrI$		−28. 81		
32. $CHFI_2$		−14. 70		
33. $CHCl_2Br$		−11. 67	−12. 89	−9.
34. $CHCl_2I$		1. 98		
35. $CHClBr_2$		−2. 14	−1. 86	5.
36. $CHClBrI$		13. 86		
37. $CHClI_2$		26. 98		
38. $CHBr_2I$		22. 35		
39. $CHBrI_2$		37. 81		
40. CF_3Cl	−169. 2	−169. 21	−171. 21	−167. 7
41. CF_3Br	−155. 3	−155. 30	−157. 89	−150.
42. CF_3I	−140. 9	−140. 90	−143. 90	
43. CF_2Cl_2	−117. 0	−117. 22	−119. 01	−116. 7
44. CF_2ClBr		−104. 02	−110. 89	−100.
45. CF_2ClI		−90. 60	−97. 90	
46. CF_2Br_2		−92. 39	−98. 86	−85.
47. CF_2BrI		−77. 50	−86. 88	
48. CF_2I_2		−65. 68	−72. 89	
49. $CFCl_3$	−68. 1	−68. 18	−70. 81	−68. 3
50. $CFCl_2Br$		−55. 00	−62. 89	−53.

TABLE 7. Δ*Hf*° (g, 298) of halomethanes (kcal mol^{-1})—Continued

Compound	Obs.	This work	Ref. 74	Ref. 7
51. $CFCl_2I$		−42.58		
52. $CFClBr_2$		−43.73	−51.86	−38.
53. $CFClBrI$		−29.86		
54. $CFClI_2$		−19.00		
55. $CFBr_3$		−34.29	−40.84	−22.
56. $CFBr_2I$		−18.98		
57. $CFBrI_2$		−6.68		
58. CFI_3		2.63		
59. CCl_3Br	−9.3	−9.30	−10.23	−9.4
60. CCl_3I		2.14		
61. CCl_2Br_2		2.22	−0.86	6.
62. CCl_2BrI		15.09		
63. CCl_2I_2		24.97		
64. $CClBr_3$		11.65	10.17	22.
65. $CClBr_2I$		25.97		
66. $CClBrI_2$		37.29		
67. $CClI_3$		45.60		
68. CBr_3I		34.76		
69. CBr_2I_2		47.52		
70. $CBrI_3$		57.28		

[a] Calculated values in references 1, 2, or 11.

2. Eluorobromomethane (CH_2FBr)

Curnuck and Sheridan [3b] studied this molecule in the microwave region and obtained the rotational constants for ^{79}Br and ^{81}Br isotopic species. We have used the average values of the moments of inertia obtained from their rotational constants. They are presented in table 4.

The vibrational frequencies available are the ones from Raman spectral measurements by Delwaulle and Francois [12] reported as early as 1946. Pitzer and Gelles [13] from the Teller-Redlich product rule and El-Sabban et al. [14] from the normal coordinate analysis confirmed these assignments. We have adopted these frequencies in this work and they are given in table 5.

No experimental Δ*Hf*°$_{298}$ is available and hence the predicted value discussed in section 1.4 was adopted.

The ideal gas thermal functions were calculated using the data given in table 4 and 5 and are presented in table 8.

3. Chlorobromomethane (CH_2ClBr)

Plyler and Benedict [15] determined the bond length C–Br from their infrared measurements. They assumed certain values for other structural parameters. We have adopted here our estimated values which are given in table 4.

Shimanouchi [16] has critically reviewed the infrared and Raman spectral data and selected the assignments for the gaseous state except for two frequencies (852, 229 cm^{-1}) which are observed in the liquid state. The same values were adopted here and are given in table 5. The other references for infrared and Raman work are [17, 18, 19].

No experimental Δ*Hf*°$_{298}$ is available and hence the predicted value discussed in section 1.4 was used.

The ideal gas thermal functions were calculated using the data given in tables 4 and 5 and are presented in table 9.

4. Chloroiodomethane (CH_2ClI)

No experimental structural parameters are available for CH_2ClI. Hence the predicted values obtained by the procedures discussed in section 1.2 were used. The adopted values are given in table 4.

Bacher and Wagner [20] and Wagner [21] reported the vibrational frequencies from their Raman spectral measurements in the liquid state in 1939. Pitzer and Gelles from the Teller-Redlich product rule [13] and El-Sabban et al. [14] from a normal coordinate analysis confirmed the assignments. These were adopted here and are given in table 5.

No experimental Δ*Hf*°$_{298}$ is available and hence the predicted value discussed in section 1.4 was used.

The ideal gas thermal functions were calculated using the data given in tables 4 and 5 and are presented in table 10.

TABLE 8. Ideal gas thermodynamic properties of fluorobromomethane (CH_2FBr)

Temp K	$C_p°$	$S°$	$-(G°-H_0°)/T$	$H°-H_0°$	$\Delta Hf°$	$\Delta Gf°$	log Kf
	cal deg^{-1} mol^{-1}			kcal mol^{-1}			
0	0.000	0.000	0.000	0.000	−47.720	−47.720	Infinite
50.00	7.968	49.817	41.866	0.398	−48.101	−48.490	211.948
100.00	8.419	55.447	47.398	0.805	−48.369	−48.775	106.596
150.00	9.127	58.992	50.703	1.243	−48.699	−48.908	71.258
200.00	9.913	61.723	53.129	1.719	−49.072	−48.924	53.462
273.15	11.247	65.005	55.883	2.492	−50.946	−48.733	38.991
298.15	11.739	66.011	56.691	2.779	−51.200	−48.481	35.537
300.00	11.776	66.084	56.748	2.801	−51.218	−48.505	35.335
400.00	13.731	69.742	59.550	4.077	−55.338	−46.771	25.554
500.00	15.453	72.997	61.919	5.539	−55.788	−44.566	19.480
600.00	16.875	75.944	64.015	7.158	−56.107	−42.291	15.404
700.00	18.044	78.636	65.914	8.905	−56.357	−39.966	12.478
800.00	19.017	81.111	67.661	10.760	−56.549	−37.621	10.277
900.00	19.837	83.400	69.285	12.704	−56.691	−35.234	8.556
1000.00	20.535	85.527	70.804	14.723	−56.788	−32.842	7.177
1100.00	21.132	87.513	72.233	16.807	−56.849	−30.454	6.051
1200.00	21.645	89.374	73.585	18.947	−56.885	−28.055	5.110
1300.00	22.087	91.125	74.863	21.134	−56.900	−25.644	4.311
1400.00	22.470	92.776	76.088	23.362	−56.897	−23.223	3.625
1500.00	22.801	94.338	77.253	25.626	−56.881	−20.827	3.034

TABLE 9. Ideal gas thermodynamic properties of chlorobromomethane (CH_2ClBr)

Temp K	$C_p°$	$S°$	$-(G°-H_0°)/T$	$H°-H_0°$	$\Delta Hf°$	$\Delta Gf°$	log Kf
	cal deg^{-1} mol^{-1}			kcal mol^{-1}			
0	0.000	0.000	0.000	0.000	−7.327	−7.327	Infinite
50.00	8.070	51.686	43.719	0.398	−7.708	−8.079	35.313
100.00	8.846	57.509	49.302	0.821	−7.962	−8.350	18.249
150.00	9.618	61.240	52.693	1.282	−8.272	−8.479	12.354
200.00	10.525	64.127	55.202	1.785	−8.626	−8.498	9.286
273.15	12.060	67.631	58.075	2.610	−10.469	−8.318	6.656
298.15	12.597	68.710	58.922	2.918	−10.710	−8.114	5.947
300.00	12.636	68.788	58.982	2.942	−10.727	−8.097	5.899
400.00	14.634	72.704	61.935	4.308	−14.787	−6.400	3.497
500.00	16.274	76.153	64.440	5.856	−15.175	−4.247	1.857
600.00	17.580	79.240	66.654	7.551	−15.435	−2.037	0.742
700.00	18.639	82.032	68.655	9.364	−15.634	0.214	−0.067
800.00	19.517	84.580	70.489	11.273	−15.780	2.484	−0.678
900.00	20.260	86.923	72.186	13.263	−15.882	4.779	−1.160
1000.00	20.895	89.091	73.770	15.322	−15.944	7.081	−1.548
1100.00	21.440	91.109	75.255	17.439	−15.973	9.375	−1.863
1200.00	21.911	92.995	76.656	19.607	−15.980	11.678	−2.127
1300.00	22.319	94.765	77.981	21.819	−15.967	13.990	−2.352
1400.00	22.673	96.433	79.240	24.069	−15.939	16.310	−2.546
1500.00	22.981	98.008	80.440	26.352	−15.897	18.604	−2.711

TABLE 10. Ideal gas thermodynamic properties of chloroiodomethane (CH_2ClI)

Temp K	$C_p°$	$S°$	$-(G°-H_0°)/T$	$H°-H_0°$	$\Delta Hf°$	$\Delta Gf°$	log Kf
	cal deg⁻¹ mol⁻¹			kcal mol⁻¹			
0	0.000	0 000	0.000	0.000	5.187	5.187	Infinite
50.00	8.184	53.125	45.225	0.400	4.792	4.376	−19.127
100.00	9.094	59.174	50.854	0.832	4.533	4.064	−8.881
150.00	9.936	63.018	54.302	1.307	4.228	3.894	−5.673
200.00	10.910	66.006	56.866	1.828	3.897	3.829	−4.184
273.15	12.479	69.637	59.814	2.683	3.404	3.893	−3.115
298.15	13.015	70.753	60.685	3.002	3.240	3.942	−2.889
300.00	13.054	70.834	60.747	3.026	3.228	3.946	−2.875
400.00	15.014	74.866	63.785	4.432	0.692	4.345	−2.374
500.00	16.598	78.393	66.361	6.016	−4.930	5.803	−2.537
600.00	17.852	81.535	68.633	7.741	−5.165	7.733	−2.817
700.00	18.866	84.365	70.682	9.578	−5.342	10.178	−3.178
800.00	19.709	86.941	72.556	11.508	−5.470	12.400	−3.387
900.00	20.423	89.305	74.287	13.516	−5.557	14.644	−3.556
1000.00	21.035	91.489	75.900	15.589	−5.606	16.895	−3.692
1100.00	21.562	93.519	77.410	17.720	−5.625	19.136	−3.802
1200.00	22.018	95.415	78.832	19.899	−5.623	21.386	−3.895
1300.00	22.413	97.194	80.177	22.121	−5.603	23.644	−3.975
1400.00	22.756	98.867	81.453	24.380	−5.568	25.908	−4.044
1500.00	23.055	100.448	82.667	26.671	−5.521	28.147	−4.101

5. Bromoiodomethane (CH_2BrI)

No experimental molecular parameters are available for CH_2BrI. They were estimated by the procedures given in section 1.2 and are presented in table 4.

Bacher and Wagner [20] and Wagner [21] reported the vibrational frequencies from their Raman spectral measurements in liquid state as early as 1939. Pitzer and Gelles [13] from the Teller-Redlich product rule and El-Sabban et al. [14] from the normal coordinate analysis confirmed the assignments. These are adopted here and are given in table 5.

No experimental $\Delta H\overset{\circ}{f}_{298}$ is available and hence the predicted value discussed in section 1.4 was used.

The ideal gas thermal functions were calculated using the data given in tables 4 and 5 and are presented in table 11.

6. Difluorobromomethane (CHF_2Br)

No experimental molecular parameters are available for CHF_2Br. They were estimated by the procedure given in section 1.2 and are presented in table 4.

Plyler and Aquista [22] and Palm et al. [23] reported the vibrational frequencies from their infrared measurement in gaseous state. Holzer [24] reported seven frequencies from Raman spectral measurement in the gaseous state for the first time and they agree well with those reported from infrared measurements. We have adopted Palm et al.'s assignments as they have been confirmed by their normal coordinate analysis and are presented in table 5.

No experimental $\Delta H\overset{\circ}{f}_{298}$ is available and hence the predicted value discussed in section 1.4 was adopted.

The ideal gas thermal functions were calculated using the data given in tables 4 and 5 and are presented in table 12.

7. Fluorochlorobromomethane (CHFClBr)

Very recently for the first time complete structural parameters have been reported by Diem and Burow [3a] obtained from the gas phase electron diffraction measurements by Jacob. These structural parameters are adopted here and they are: CH=1.132, CF=1.348, CCl=1.753 and CBr=1.927 Å; ∠HCF=108.5, ∠HCCl=108.0, ∠HCBr=109.95, ∠FCCl=109.56, ∠FCBr=109.23, and ∠ClCBr=111.54 deg. The calculated moments of inertia for CHFClBr are: $I_A=72.275$; $I_B=264.66$; and $I_C=326.00$ amu. Å².

The Raman spectral measurements were made by Glockler and Leader [25] and Delwaulle [26]. The infrared measurements were reported by Plyler and Lamb [27] in the liquid state. El-Sabban and Zwolinski [28] checked these assignments by normal coordinate analysis. Very recently Diem and Burow [3a] reported the vibrational assignments from their Raman spectral measurements of the gaseous, liquid and solid phases and the infrared spectral measurements in the gaseous phase of four isotopic species of CHFClBr. We have adopted these frequencies, which are presented in table 5.

No experimental $\Delta H\overset{\circ}{f}_{298}$ is available and hence the estimated value discussed in section 1.4 was adopted.

The ideal gas thermal functions were calculated using the above moments of inertia and the vibrational frequencies (table 5) and are presented in table 13.

TABLE 11. Ideal gas thermodynamic properties of bromoiodomethane (CH_2BrI)

Temp K	$C_p°$	$S°$	$-(G°-H_0°)/T$	$H°-H_0°$	$\Delta Hf°$	$\Delta Gf°$	log Kf
	cal deg^{-1} mol^{-1}			kcal mol^{-1}			
0	0. 000	0. 000	0. 000	0. 000	17. 338	17. 338	Infinite
50. 00	8. 508	55. 318	47. 236	0. 404	17. 020	15. 650	−68. 407
100. 00	9. 446	61. 537	52. 983	0. 855	16. 721	14. 402	−31. 475
150. 00	10. 273	65. 516	56. 533	1. 347	16. 333	13. 324	−19. 412
200. 00	11. 307	68. 609	59. 178	1. 886	15. 897	12. 383	−13. 531
273. 15	12. 938	72. 375	62. 222	2. 773	13. 940	11. 250	−9. 001
298. 15	13. 480	73. 531	63. 123	3. 103	13. 660	11. 013	−8. 072
300. 00	13. 520	73. 615	63. 187	3. 128	13. 640	10. 996	−8. 011
400. 00	15. 453	77. 779	66. 328	4. 580	7. 494	11. 027	−6. 025
500. 00	16. 976	81. 398	68. 988	6. 205	1. 849	12. 465	−5. 448
600. 00	18. 167	84. 602	71. 328	7. 964	1. 639	14. 369	−5. 234
700. 00	19. 126	87. 477	73. 433	9. 831	1. 483	16. 785	−5. 240
800. 00	19. 924	90. 085	75. 354	11. 784	1. 373	18. 974	−5. 183
900. 00	20. 603	92. 472	77. 125	13. 812	1. 301	21. 184	−5. 144
1000. 00	21. 186	94. 673	78. 772	15. 902	1. 265	23. 399	−5. 114
1100. 00	21. 691	96. 717	80. 311	18. 046	1. 258	25. 602	−5. 087
1200. 00	22. 128	98. 623	81. 759	20. 238	1. 271	27. 813	−5. 065
1300. 00	22. 509	100. 410	83. 125	22. 470	1. 300	30. 031	−5. 049
1400. 00	22. 840	102. 090	84. 421	24. 738	1. 343	32. 256	−5. 035
1500. 00	23. 129	103. 676	85. 652	27. 037	1. 397	34. 455	−5. 020

TABLE 12. Ideal gas thermodynamic properties of difluorobromomethane (CHF_2Br)

Temp K	$C_p°$	$S°$	$-(G°-H_0°)/T$	$H°-H_0°$	$\Delta Hf°$	$\Delta Gf°$	log Kf
	cal deg^{-1} mol^{-1}			kcal mol^{-1}			
0	0. 000	0. 000	0. 000	0. 000	−99. 505	−99. 505	Infinite
50. 00	8. 060	52. 331	44. 367	0. 398	−99. 808	−99. 947	436. 864
100. 00	9. 209	58. 225	49. 958	0. 827	−100. 101	−99. 969	218. 479
150. 00	10. 545	62. 216	53. 409	1. 321	−100. 406	−99. 837	145. 460
200. 00	11. 772	65. 419	56. 023	1. 879	−100. 714	−99. 602	108. 839
273. 15	13. 479	69. 343	59. 080	2. 803	−102. 456	−99. 080	79. 274
298. 15	14. 044	70. 548	59. 991	3. 147	−102. 660	−98. 684	72. 337
300. 00	14. 086	70. 635	60. 057	3. 173	−102. 675	−98. 740	71. 931
400. 00	16. 169	74. 980	63. 258	4. 689	−106. 593	−96. 630	52. 796
500. 00	17. 874	78. 779	65. 990	6. 394	−106. 853	−94. 099	41. 130
600. 00	19. 205	82. 160	68. 408	8. 251	−107. 000	−91. 533	33. 341
700. 00	20. 243	85. 202	70. 594	10. 226	−107. 098	−88. 946	27. 770
800. 00	21. 064	87. 960	72. 595	12. 292	−107. 158	−86. 361	23. 593
900. 00	21. 724	90. 481	74. 444	14. 433	−107. 186	−83. 745	20. 336
1000. 00	22. 262	92. 798	76. 165	16. 633	−107. 186	−81. 135	17. 732
1100. 00	22. 708	94. 942	77. 776	18. 882	−107. 166	−78. 543	15. 605
1200. 00	23. 080	96. 934	79. 291	21. 172	−107. 135	−75. 939	13. 830
1300. 00	23. 393	98. 794	80. 720	23. 496	−107. 094	−73. 338	12. 329
1400. 00	23. 659	100. 538	82. 074	25. 849	−107. 046	−70. 729	11. 041
1500. 00	23. 886	102. 178	83. 360	28. 227	−106. 992	−68. 143	9. 928

TABLE 13. Ideal gas thermodynamic properties of fluorochlorobromomethane (CHFClBr)

Temp K	$C_p°$	$S°$	$-(G°-H_0°)/T$	$H°-H_0°$	$\Delta Hf°$	$\Delta Gf°$	log Kf
	cal deg⁻¹ mol⁻¹			kcal mol⁻¹			
0	0. 000	0. 000	0. 000	0. 000	−51. 878	−51. 878	Infinite
50. 00	8. 095	53. 848	45. 878	0. 399	−52. 182	−52. 285	228. 536
100. 00	9. 455	59. 823	51. 488	0. 833	−52. 468	−52. 273	114. 241
150. 00	11. 070	63. 967	54. 986	1. 347	−52. 757	−52. 112	75. 927
200. 00	12. 525	67. 355	57. 666	1. 938	−53. 042	−51. 856	56. 665
273. 15	14. 426	71. 546	60. 838	2. 925	−54. 742	−51. 313	41. 056
298. 15	15. 021	72. 835	61. 790	3. 293	−54. 930	−50. 954	37. 350
300. 00	15. 064	72. 928	61. 858	3. 321	−54. 943	−50. 969	37. 131
400. 00	17. 131	77. 557	65. 220	4. 935	−58. 793	−48. 856	26. 693
500. 00	18. 717	81. 558	68. 096	6. 731	−58. 987	−46. 339	20. 254
600. 00	19. 914	85. 081	70. 639	8. 665	−59. 074	−43. 801	15. 954
700. 00	20. 830	88. 223	72. 931	10. 704	−59. 121	−41. 250	12. 879
800. 00	21. 550	91. 053	75. 022	12. 825	−59. 136	−38. 703	10. 573
900. 00	22. 129	93. 626	76. 949	15. 010	−59. 126	−36. 140	8. 776
1000. 00	22. 603	95. 983	78. 736	17. 247	−59. 093	−33. 583	7. 340
1100. 00	22. 997	98. 156	80. 404	19. 528	−59. 043	−31. 047	6. 168
1200. 00	23. 327	100. 172	81. 968	21. 844	−58. 984	−28. 500	5. 191
1300. 00	23. 607	102. 050	83. 442	24. 191	−58. 917	−25. 960	4. 364
1400. 00	23. 845	103. 809	84. 834	26. 564	−58. 845	−23. 413	3. 655
1500. 00	24. 049	105. 461	86. 155	28. 959	−58. 768	−20. 892	3. 044

8. Fluorodibromomethane ($CHFBr_2$)

No experimental molecular parameters are available for $CHFBr_2$. They were estimated by the procedure given in section 1.2 and are presented in table 4.

No infrared spectral measurements are reported for $CHFBr_2$. Pitzer and Gelles [13] confirmed the assignments obtained from Raman spectral measurements [25, 26] by Teller-Redlich product rule which are adopted here (table 5).

No experimental $\Delta H\mathring{f}_{298}$ is available and hence the estimated value discussed in section 1.4 was adopted.

The ideal gas thermal functions were calculated using the data given in tables 4 and 5 and are presented in table 14.

9. Dichlorobromomethane ($CHCl_2Br$)

No experimental molecular parameters are available for $CHCl_2Br$. They were estimated by the procedure given in section 1.2 and are presented in table 4.

Infrared [15, 29] and Raman [12, 25] spectral measurements in the liquid state have been reported. Polo et al. [29] have reported the vibrational frequencies from their infrared spectral measurements in the gaseous state which are adopted here and are given in table 5.

No experimental $\Delta H\mathring{f}_{298}$ is available and hence the estimated value discussed in section 1.4 was adopted.

The ideal gas thermal functions were calculated using the data given in tables 4 and 5 and are presented in table 15.

10. Chlorodibromomethane ($CHClBr_2$)

No experimental molecular parameters are available for $CHClBr_2$. They were estimated by the procedure given in section 1.2 and are presented in table 4.

Infrared [15, 30] and Raman [12, 25, 31, 32] spectral measurements in the liquid state have been reported. Pontarelli et al. [30] have reported the vibrational frequencies from their infrared measurements in the gaseous state which were adopted here and are given in table 5.

No experimental $\Delta H\mathring{f}_{298}$ is available and hence the estimated value discussed in section 1.4 was adopted.

The ideal gas thermal functions were calculated using the data given in tables 4 and 5 and are presented in table 16.

TABLE 14. Ideal gas thermodynamic properties of fluorodibromomethane ($CHFBr_2$)

Temp K	$C_p°$	$S°$	$-(G°-H_0°)/T$	$H°-H_0°$	$\Delta Hf°$	$\Delta Gf°$	log Kf
	cal deg⁻¹ mol⁻¹			kcal mol⁻¹			
0	0.000	0.000	0.000	0.000	−41.064	−41.064	Infinite
50.00	8.341	55.794	47.769	0.401	−41.292	−42.341	185.070
100.00	10.044	62.072	53.481	0.859	−41.614	−43.257	94.538
150.00	11.716	66.470	57.109	1.404	−41.971	−44.002	64.110
200.00	13.158	70.042	59.908	2.027	−42.347	−44.624	48.762
273.15	15.000	74.423	63.226	3.058	−45.499	−45.287	36.234
298.15	15.569	75.761	64.222	3.440	−45.800	−45.217	33.144
300.00	15.610	75.857	64.293	3.469	−45.821	−45.253	32.967
400.00	17.572	80.629	67.797	5.133	−53.277	−43.524	23.780
500.00	19.068	84.718	70.782	6.968	−53.496	−41.043	17.940
600.00	20.194	88.299	73.410	8.934	−53.561	−38.546	14.040
700.00	21.056	91.480	75.768	10.998	−53.591	−36.039	11.252
800.00	21.736	94.337	77.914	13.139	−53.591	−33.539	9.162
900.00	22.284	96.930	79.885	15.341	−53.569	−31.025	7.534
1000.00	22.734	99.302	81.710	17.592	−53.524	−28.518	6.232
1100.00	23.109	101.487	83.410	19.885	−53.465	−26.032	5.172
1200.00	23.424	103.512	85.001	22.212	−53.397	−23.537	4.287
1300.00	23.691	105.397	86.499	24.568	−53.322	−21.050	3.539
1400.00	23.919	107.162	87.912	26.949	−53.242	−18.555	2.897
1500.00	24.115	108.819	89.251	29.351	−53.159	−16.087	2.344

TABLE 15. Ideal gas thermodynamic properties of dichlorobromomethane ($CHCl_2Br$)

Temp K	$C_p°$	$S°$	$-(G°-H_0°)/T$	$H°-H_0°$	$\Delta Hf°$	$\Delta Gf°$	log Kf
	cal deg⁻¹ mol⁻¹			kcal mol⁻¹			
0	0.000	0.000	0.000	0.000	−8.802	−8.802	Infinite
50.00	8.262	55.184	47.186	0.400	−9.104	−9.163	40.051
100.00	10.243	61.488	52.884	0.860	−9.365	−9.114	19.918
150.00	12.035	65.993	56.553	1.419	−9.613	−8.934	13.016
200.00	13.555	69.668	59.371	2.060	−9.857	−8.672	9.476
273.15	15.491	74.188	62.751	3.124	−11.501	−8.139	6.512
298.15	16.077	75.570	63.769	3.519	−11.670	−7.827	5.737
300.00	16.119	75.570	63.842	3.548	−11.682	−7.803	5.684
400.00	18.072	80.588	67.431	5.263	−15.461	−5.732	3.132
500.00	19.502	84.783	70.493	7.145	−15.592	−3.274	1.431
600.00	20.554	88.436	73.185	9.151	−15.626	−0.807	0.294
700.00	21.352	91.667	75.599	11.248	−15.629	1.665	−0.520
800.00	21.979	94.561	77.792	13.415	−15.606	4.132	−1.129
900.00	22.485	97.180	79.803	15.639	−15.563	6.599	−1.602
1000.00	22.903	99.571	81.662	17.910	−15.501	9.063	−1.981
1100.00	23.251	101.771	83.391	20.218	−15.425	11.504	−2.286
1200.00	23.545	103.807	85.009	22.558	−15.342	13.953	−2.541
1300.00	23.796	105.702	86.529	24.925	−15.252	16.393	−2.756
1400.00	24.010	107.473	87.962	27.316	−15.158	18.838	−2.941
1500.00	24.194	109.136	89.319	29.726	−15.059	21.255	−3.097

TABLE 16. Ideal gas thermodynamic properties of chlorodibromomethane ($CHClBr_2$)

Temp K	C_p°	S°	$-(G^\circ-H_0^\circ)/T$	$H^\circ-H_0^\circ$	ΔHf°	ΔGf°	log Kf
	cal deg^{-1} mol^{-1}			kcal mol^{-1}			
0	0.000	0.000	0.000	0.000	2.424	2.424	Infinite
50.00	8.572	56.992	48.925	0.403	2.198	1.200	−5.244
100.00	10.881	63.657	54.748	0.891	1.905	0.326	−0.712
150.00	12.616	68.413	58.544	1.480	1.588	−0.396	0.576
200.00	14.080	72.246	61.505	2.148	1.249	−1.008	1.101
273.15	15.962	76.921	65.027	3.249	−1.855	−1.671	1.337
298.15	16.532	78.344	66.084	3.655	−2.140	−1.644	1.205
300.00	16.572	78.446	66.160	3.686	−2.160	−1.641	1.195
400.00	18.461	83.487	69.881	5.442	−9.552	0.063	−0.034
500.00	19.826	87.761	73.040	7.361	−9.712	2.502	−1.094
600.00	20.821	91.468	75.809	9.395	−9.727	4.946	−1.802
700.00	21.572	94.737	78.285	11.517	−9.712	7.392	−2.308
800.00	22.160	97.657	80.527	13.704	−9.676	9.831	−2.686
900.00	22.636	100.296	82.579	15.945	−9.621	12.269	−2.979
1000.00	23.030	102.702	84.473	18.229	−9.548	14.703	−3.213
1100.00	23.359	104.913	86.232	20.549	−9.462	17.111	−3.400
1200.00	23.638	106.957	87.875	22.899	−9.370	19.528	−3.556
1300.00	23.876	108.859	89.417	25.275	−9.273	21.933	−3.687
1400.00	24.080	110.636	90.870	27.673	−9.172	24.345	−3.800
1500.00	24.256	112.304	92.244	30.090	−9.067	26.728	−3.894

11. Trifluorobromomethane (CF_3Br)

The structural parameters from the microwave measurements are reported by Sheridan and Gordy [33] and Sharbaugh et al. [34]. Anderson [35] and Bowen [36] have reported the structural parameters from their electron diffraction measurements. We have adopted the values obtained from microwave measurements [33], which are given in table 3.

The infrared and Raman measurements have been reported by many workers [22, 24, 37–42] and their assignments are in very good agreement. Nagai and Mann [43] carried out a normal coordinate analysis of mixed halomethanes using UBFF and confirmed these assignments. Recently, Shimanouchi [44] has critically reviewed the available data and recommended the assignments which are adopted here (table 5).

Wagman et al. [45] reported the enthalpy of formation, ΔHf° (g, 298) = −153.6 kcal mol^{-1}. Corbett et al. [46] studied the thermal bromination of CF_3H (1)

$$CF_3H\ (g) + Br_2(g) \rightarrow CF_3Br\ (g) + HBr\ (g) \qquad (1)$$

and obtained ΔHr° (g, 298) = −3.3 ± 0.6 kcal mol^{-1}. Combining Corbett et al.'s ΔHr° (g, 298) with ΔHf° (CF_3H, g, 298) = −166.6 ± 0.8 kcal mol^{-1} [11], ΔHf° (Br_2, g, 298) = 7.387 and ΔHf° (HBr, g, 298) = −8.70 kcal mol^{-1} [45] we have calculated ΔHf° (CF_3Br, g, 298) = −153.8 ± 1.0 kcal mol^{-1}.

Coomber and Whittle [47] studied reaction (1) and obtained ΔHr° (1, 298) = −4.59 ± 0.28 kcal mol^{-1}. Using the same values of ΔHf° (g, 298) as above for the species involved in reaction (1), ΔHf° (CF_3Br, g, 298) = −155.1 ± 0.8 kcal mol^{-1} is obtained.

Lord et al. [48] studied the gaseous equilibrium (2) and obtained ΔHr° (2, 298) = 9.55 ± 0.06 kcal mol^{-1}.

$$CF_3Br\ (g) + I_2\ (g) \rightarrow CF_3I\ (g) + IBr\ (g). \qquad (2)$$

Combining Lord et al's ΔHr° with ΔHf° (I_2, g, 298) = 14.923, ΔHf° (IBr, g, 298) = 9.76 [45], and ΔHf° (CF_3I, g, 298) = 140.9 ± 0.8 kcal mol^{-1} (this work), we have obtained ΔHf° (CF_3Br, g, 298) = −155.6 ± .8 kcal mol^{-1}. In this work we have adopted the average value of ΔHf° (CF_3Br, g, 298) = −155.3 ± 0.8 kcal mol^{-1} obtained from last two calculations.

The ideal gas thermal functions were calculated using the data given in tables 3 and 5 and are presented in table 17.

12. Trifluoroiodomethane (CF_3I)

Sheridan and Gordy [33] reported the structural parameters from their microwave measurements. The structural parameters reported from electron diffraction measurements [35, 36, 49, 49a] are in very good agreement with each other. We have adopted the values obtained from microwave measurements, which are given in table 3.

The infrared and Raman measurements have been reported by many workers [22, 37–41] and their assignments are in good agreement. They are confirmed by Nagai and Mann [43] from their normal coordinate analysis of mixed halomethanes by UBFF. Recently, Shimanouchi [44] critically reviewed the available data and recommended the vibrational frequencies for CF_3I which are given in table 5.

Goy et al. [50] studied the gaseous equilibrium (3) and obtained $\Delta Hr°$ (3, 298) = 17.10 ± 0.17 kcal mol^{-1}.

$$CF_3H\ (g) + I_2\ (g) \rightarrow CF_3I\ (g) + HI\ (g) \qquad (3)$$

Combining their $\Delta Hr°$ with $\Delta Hf°$ (I_2, g, 298) = 14.923, $\Delta Hf°$ (HI, g, 298) = 6.33 [45], and $\Delta Hf°$ (CF_3H, g, 298) = −166.6 ± 0.8 kcal mol^{-1} [11], we obtained $\Delta Hf°$ (CF_3I, g, 298) = −140.9 ± 0.8 kcal mol^{-1}. We have adopted this value in our work.

The ideal gas thermal functions were calculated using the data given in tables 3 and 5 and are presented in table 18.

13. Difluorochlorobromomethane (CF_2ClBr)

No experimental molecular parameters are available for CF_2ClBr. They were estimated by the procedure given in section 1.2 and are presented in table 4.

The only available spectral data for CF_2ClBr is the infrared spectrum of the gas state by Plyler and Acquista [22]. El-Sabban and Zwolinski [51] reexamined their assignments and recommended new assignments applying Rayleigh's rule and were confirmed by normal coordinate analysis. Recently Nagai and Mann [43] have rechecked these assignments from their normal coordinate analysis of mixed halomethanes using UBFF. The vibrational frequencies are given in table 5.

No experimental ΔHf_{298}° is available and hence the estimated value obtained by the procedure discussed in section 1.4 was adopted here.

The ideal gas thermal functions were calculated using the data given in tables 4 and 5 and are presented in table 19.

14. Difluorodibromomethane (CF_2Br_2)

No experimental molecular parameters are available for CF_2Br_2. They were estimated by the procedure given in section 1.2 and are presented in table 3.

Decker et al. [52] reported the vibrational frequencies for CF_2Br_2 from their infrared spectral measurements in the gaseous state and Raman spectral measurements in the liquid state. These assignments were recently checked by Nagai and Mann [43] from their normal coordinate analysis of mixed halomethanes using UBFF. Recently, Shimanouchi [44] critically reviewed the data and recommended the vibrational frequencies which are given in table 5. The other references for infrared and Raman work are refs. [22, 31, 53, 54].

No experimental ΔHf_{298}° is available and hence the predicted value discussed in section 1.4 was adopted.

The ideal gas thermal functions were calculated using the data given in tables 3 and 5 and are presented in table 20.

TABLE 17. Ideal gas thermodynamic properties of trifluorobromomethane (CF_3Br)

Temp K	$C_p°$	$S°$	$-(G°-H_0°)/T$	$H°-H_0°$	$\Delta Hf°$	$\Delta Gf°$	log Kf
	cal deg^{-1} mol^{-1}			kcal mol^{-1}			
0	0. 000	0. 000	0. 000	0. 000	−152. 404	−152. 404	Infinite
50. 00	8. 004	51. 489	43. 534	0. 398	−152. 630	−152. 351	665. 919
100. 00	9. 349	57. 351	49. 105	0. 824	−152. 970	−151. 935	332. 050
150. 00	11. 484	61. 543	52. 576	1. 345	−153. 279	−151. 348	220. 512
200. 00	13. 451	65. 123	55. 275	1. 970	−153. 539	−150. 665	164. 637
273. 15	15. 843	69. 683	58. 538	3. 044	−155. 150	−149. 520	119. 631
298. 15	16. 548	71. 101	59. 532	3. 449	−155. 300	−148. 880	109. 130
300. 00	16. 598	71. 204	59. 604	3. 480	−155. 310	−148. 961	108. 517
400. 00	18. 928	76. 315	63. 159	5. 262	−159. 000	−146. 080	79. 814
500. 00	20. 611	80. 730	66. 242	7. 244	−159. 038	−142. 835	62. 433
600. 00	21. 810	84. 600	68. 986	9. 368	−158. 983	−139. 600	50. 848
700. 00	22. 670	88. 030	71. 466	11. 595	−158. 904	−136. 374	42. 577
800. 00	23. 296	91. 100	73. 732	13. 894	−158. 811	−133. 178	36. 382
900. 00	23. 761	93. 872	75. 818	16. 248	−158. 709	−129. 961	31. 559
1000. 00	24. 114	96. 395	77. 752	18. 643	−158. 599	−126. 767	27. 705
1100. 00	24. 386	98. 706	79. 553	21. 069	−158. 486	−123. 603	24. 557
1200. 00	24. 600	100. 838	81. 239	23. 518	−158. 377	−120. 428	21. 933
1300. 00	24. 770	102. 814	82. 824	25. 987	−158. 273	−117. 271	19. 715
1400. 00	24. 909	104. 655	84. 318	28. 471	−158. 173	−114. 110	17. 813
1500. 00	25. 022	106. 377	85. 732	30. 968	−158. 077	−110. 971	16. 168

TABLE 18. Ideal gas thermodynamic properties of trifluoroiodomethane (CF_3I)

Temp K	C_p°	S°	$-(G^\circ-H_0^\circ)/T$	$H^\circ-H_0^\circ$	ΔHf°	ΔGf°	log Kf
	cal deg^{-1} mol^{-1}			kcal mol^{-1}			
0	0. 000	0. 000	0. 000	0. 000	−139. 494	−139. 494	Infinite
50. 00	8. 110	52. 952	44. 982	0. 398	−139. 734	−139. 497	609. 734
100. 00	10. 011	59. 079	50. 619	0. 846	−140. 069	−139. 121	304. 045
150. 00	12. 186	63. 560	54. 212	1. 402	−140. 351	−138. 583	201. 913
200. 00	14. 037	67. 326	57. 031	2. 059	−140. 573	−137. 960	150. 754
273. 15	16. 283	72. 046	60. 437	3. 171	−140. 827	−136. 956	109. 578
298. 15	16. 952	73. 501	61. 472	3. 586	−140. 900	−136. 481	100. 042
300. 00	17. 000	73. 606	61. 547	3. 618	−140. 905	−136. 575	99. 493
400. 00	19. 223	78. 817	65. 231	5. 435	−143. 077	−135. 028	73. 775
500. 00	20. 837	83. 290	68. 406	7. 442	−148. 358	−132. 510	57. 919
600. 00	21. 988	87. 197	71. 219	9. 587	−148. 287	−129. 586	47. 201
700. 00	22. 812	90. 652	73. 753	11. 829	−148. 196	−126. 196	39. 400
800. 00	23. 412	93. 739	76. 062	14. 142	−148. 092	−123. 076	33. 622
900. 00	23. 857	96. 523	78. 183	16. 506	−147. 983	−119. 937	29. 124
1000. 00	24. 193	99. 055	80. 146	18. 909	−147. 866	−116. 821	25. 531
1100. 00	24. 453	101. 374	81. 972	21. 342	−147. 749	−113. 735	22. 597
1200. 00	24. 658	103. 511	83. 679	23. 798	−147. 637	−110. 639	20. 150
1300. 00	24. 821	105. 491	85. 281	26. 272	−147. 529	−107. 562	18. 083
1400. 00	24. 952	107. 335	86. 792	28. 761	−147. 428	−104. 481	16. 310
1500. 00	25. 061	109. 061	88. 219	31. 262	−147. 330	−101. 421	14. 777

TABLE 19. Ideal gas thermodynamic properties of difluorochlorobromomethane (CF_2ClBr)

Temp K	C_p°	S°	$-(G^\circ-H_0^\circ)/T$	$H^\circ-H_0^\circ$	ΔHf°	ΔGf°	log Kf
	cal deg^{-1} mol^{-1}			kcal mol^{-1}			
0	0. 000	0. 000	0. 000	0. 000	−101. 344	−101. 344	Infinite
50. 00	8. 138	55. 007	47. 031	0. 399	−101. 569	−101. 355	443. 017
100. 00	10. 111	61. 159	52. 676	0. 848	−101. 887	−101. 010	220. 754
150. 00	12. 619	65. 741	56. 291	1. 418	−102. 151	−100. 511	146. 443
200. 00	14. 734	69. 672	59. 156	2. 103	−102. 358	−99. 933	109. 200
273. 15	17. 155	74. 640	62. 655	3. 274	−103. 895	−98. 964	79. 181
298. 15	17. 841	76. 172	63. 725	3. 711	−104. 020	−98. 429	72. 150
300. 00	17. 890	76. 283	63. 802	3. 744	−104. 029	−98. 475	71. 738
400. 00	20. 067	81. 747	67. 625	5. 649	−107. 626	−95. 874	52. 382
500. 00	21. 559	86. 395	70. 926	7. 735	−107. 583	−92. 931	40. 619
600. 00	22. 585	90. 422	73. 847	9. 945	−107. 460	−90. 011	32. 786
700. 00	23. 303	93. 961	76. 473	12. 242	−107. 324	−87. 113	27. 198
800. 00	23. 817	97. 108	78. 859	14. 599	−107. 183	−84. 246	23. 015
900. 00	24. 195	99. 936	81. 047	17. 001	−107. 040	−81. 375	19. 760
1000. 00	24. 479	102. 501	83. 066	19. 435	−106. 894	−78. 525	17. 161
1100. 00	24. 696	104. 845	84. 941	21. 894	−106. 749	−75. 709	15. 042
1200. 00	24. 866	107. 001	86. 691	24. 373	−106. 611	−72. 884	13. 274
1300. 00	25. 002	108. 997	88. 331	26. 866	−106. 479	−70. 081	11. 782
1400. 00	25. 111	110. 854	89. 874	29. 372	−106. 353	−67. 275	10. 502
1500. 00	25. 200	112. 590	91. 331	31. 888	−106. 232	−64. 493	9. 396

TABLE 20. Ideal gas thermodynamic properties of difluorodibromomethane (CF_2Br_2)

Temp K	$C_p°$	$S°$	$-(G°-H_0°)/T$	$H°-H_0°$	$\Delta Hf°$	$\Delta Gf°$	log Kf
	cal deg^{-1} mol^{-1}			kcal mol^{-1}			
0	0. 000	0. 000	0. 000	0. 000	−88. 061	−88. 061	Infinite
50. 00	8. 395	55. 368	47. 334	0. 402	−88. 211	−88. 863	388. 417
100. 00	10. 864	61. 870	53. 091	0. 878	−88. 561	−89. 369	195. 312
150. 00	13. 491	66. 791	56. 863	1. 489	−88. 883	−89. 700	130. 691
200. 00	15. 524	70. 963	59. 879	2. 217	−89. 171	−89. 929	98. 269
273. 15	17. 773	76. 151	63. 563	3. 439	−92. 152	−90. 065	72. 061
298. 15	18. 407	77. 735	64. 685	3. 891	−92. 390	−89. 786	65. 814
300. 00	18. 452	77. 849	64. 766	3. 925	−92. 407	−89. 850	65. 455
400. 00	20. 463	83. 451	68. 758	5. 877	−99. 612	−87. 496	47. 805
500. 00	21. 847	88. 175	72. 182	7. 997	−99. 600	−84. 452	36. 914
600. 00	22. 801	92. 248	75. 195	10. 232	−99. 462	−81. 435	29. 662
700. 00	23. 470	95. 816	77. 891	12. 548	−99. 314	−78. 442	24. 490
800. 00	23. 949	98. 983	80. 333	14. 920	−99. 164	−75. 481	20. 620
900. 00	24. 302	101. 825	82. 566	17. 333	−99. 013	−72. 517	17. 609
1000. 00	24. 566	104. 400	84. 623	19. 777	−98. 860	−69. 575	15. 205
1100. 00	24. 770	106. 751	86. 529	22. 244	−98. 710	−66. 668	13. 245
1200. 00	24. 929	108. 914	88. 306	24. 730	−98. 567	−63. 751	11. 611
1300. 00	25. 055	110. 914	89. 969	27. 229	−98. 430	−60. 859	10. 231
1400. 00	25. 157	112. 775	91. 532	29. 740	−98. 299	−57. 961	9. 048
1500. 00	25. 241	114. 514	93. 007	32. 260	−98. 174	−55. 090	8. 026

15. Difluorodiiodomethane (CF_2I_2)

No experimental molecular parameters are available for CF_2I_2. They were estimated by the procedure given in section 1.2 and are presented in table 3.

Only available spectral data for CF_2I_2 are from the infrared spectrum in the gaseous state by McAlpine and Sutcliff [55]. In their assignment the five low lying fundamental frequencies were obtained from overtones and combination bonds. Recently, Nagai and Mann [43] reassigned the frequencies on the basis of their normal coordinate analysis using UBFF. We adopted these frequencies and are given in table 5.

No experimental $\Delta Hf°_{298}$ is available and hence the estimated value discussed in section 1.4 was adopted.

The ideal gas thermal functions were calculated using the data given in tables 3 and 5 and are presented in table 21.

16. Fluorodichlorobromomethane ($CFCl_2Br$)

No experimental molecular parameters are available for $CFCl_2Br$. They were estimated by the procedure given in section 1.2 and are presented in table 4.

Delwaulle and Francois [53] reported the vibrational frequencies for $CFCl_2Br$ from their Raman spectral measurements in the liquid state. These were checked by Pitzer and Gelles [13] by Teller-Redlich product rule. Gilbert et al. [56] reported the vibrational assignments and infrared spectral measurements in gaseous and liquid state and Raman spectral measurements in liquid state. These were recently checked by Nagai and Mann [43] by the normal coordinate analysis of the mixed halomethanes using UBFF. Recently, Shimanuouchi [44] critically reviewed the data and recommended the vibrational frequencies which are adopted here (table 5).

No experimental ΔHf°_{298} is available and hence the estimated value discussed in section 1.4 was adopted.

The ideal gas thermal functions were calculated using the data given in tables 4 and 5 and are presented in table 22.

17. Fluorochlorodibromomethane ($CFClBr_2$)

No experimental molecular parameters are available for $CFClBr_2$. They were estimated by the procedure given in section 1.2 and are presented in table 4.

Delwaulle and Francois [53] reported the vibrational frequencies for $CFClBr_2$ from their Raman spectral measurements in the liquid state. These were checked by Pitzer and Gelles [13] by Teller-Redlich product rule. Gilbert et al. [56] reported the vibrational assignments from their infrared spectral measurements in gaseous state (only three frequencies) and liquid state and Raman spectral measurements in liquid state. These were recently checked by Nagai and Mann [43] by the normal coordinate analysis of mixed halomethanes using UBFF. Recently, Shimanouchi [44] critically reviewed the data and recommended the vibrational frequencies which are adopted here and are given in table 5.

No experimental ΔHf°_{298} is available and hence the estimated value discussed in section 1.4 was adopted.

The ideal gas thermal functions were calculated using the data given in tables 4 and 5 and are presented in table 23.

TABLE 21. Ideal gas thermodynamic properties of difluorodiiodomethane (CF_2I_2)

Temp K	$C_p°$	$S°$	$-(G°-H_0°)/T$	$H°-H_0°$	$\Delta Hf°$	$\Delta Gf°$	log Kf
	cal deg^{-1} mol^{-1}			kcal mol^{-1}			
0	0.000	0.000	0.000	0.000	−64.373	−64.373	Infinite
50.00	9.173	58.137	49.873	0.413	−64.541	−65.269	285.288
100.00	12.455	65.500	55.961	0.954	−64.857	−65.857	143.929
150.00	14.944	71.054	60.101	1.643	−65.118	−66.298	96.594
200.00	16.706	75.606	63.425	2.436	−65.331	−66.658	72.840
273.15	18.672	81.118	67.450	3.734	−65.596	−67.094	53.682
298.15	19.233	82.778	68.666	4.207	−65.680	−67.151	49.222
300.00	19.273	82.897	68.753	4.243	−65.686	−67.240	48.984
400.00	21.067	88.703	73.039	6.266	−69.853	−67.578	36.922
500.00	22.304	93.545	76.669	8.438	−80.328	−66.013	28.854
600.00	23.154	97.692	79.836	10.713	−80.159	−63.645	23.183
700.00	23.748	101.308	82.651	13.060	−79.986	−60.347	18.841
800.00	24.173	104.508	85.187	15.457	−79.810	−57.504	15.725
900.00	24.485	107.375	87.496	17.891	−79.651	−54.779	13.302
1000.00	24.718	109.967	89.615	20.352	−79.486	−52.019	11.369
1100.00	24.898	112.332	91.574	22.833	−79.327	−49.293	9.794
1200.00	25.038	114.504	93.395	25.330	−79.178	−46.560	8.480
1300.00	25.149	116.513	95.098	27.840	−79.035	−43.849	7.372
1400.00	25.239	118.380	96.695	30.359	−78.901	−41.138	6.422
1500.00	25.313	120.124	98.199	32.887	−78.774	−38.449	5.602

TABLE 22. Ideal gas thermodynamic properties of fluorodichlorobromomethane ($CFCl_2Br$)

Temp K	$C_p°$	$S°$	$-(G°-H_0°)/T$	$H°-H_0°$	$\Delta Hf°$	$\Delta Gf°$	log Kf
	cal deg^{-1} mol^{-1}			kcal mol^{-1}			
0	0.000	0.000	0.000	0.000	−52.564	−52.564	Infinite
50.00	8.329	56.088	48.079	0.400	−52.788	−52.517	229.549
100.00	11.046	62.610	53.823	0.879	−53.077	−52.123	113.913
150.00	13.869	67.649	57.618	1.505	−53.288	−51.597	75.175
200.00	16.069	71.954	60.676	2.255	−53.440	−51.009	55.739
273.15	18.476	77.339	64.438	3.524	−54.899	−50.051	40.046
298.15	19.134	78.986	65.590	3.994	−55.000	−49.565	36.332
300.00	19.180	79.105	65.673	4.030	−55.007	−49.572	36.113
400.00	21.176	84.917	69.780	6.055	−58.513	−47.024	25.692
500.00	22.465	89.791	73.308	8.241	−58.394	−44.156	19.300
600.00	23.315	93.967	76.412	10.533	−58.207	−41.326	15.053
700.00	23.893	97.607	79.185	12.895	−58.019	−38.527	12.028
800.00	24.300	100.826	81.693	15.306	−57.834	−35.760	9.769
900.00	24.594	103.706	83.982	17.752	−57.653	−33.005	8.015
1000.00	24.813	106.309	86.036	20.222	−57.474	−30.270	6.615
1100.00	24.979	108.682	88.034	22.712	−57.300	−27.571	5.478
1200.00	25.109	110.861	89.847	25.217	−57.135	−24.867	4.529
1300.00	25.211	112.875	91.542	27.733	−56.978	−22.187	3.730
1400.00	25.294	114.746	93.133	30.259	−56.828	−19.505	3.045
1500.00	25.361	116.494	94.633	32.791	−56.683	−16.849	2.455

TABLE 23. Ideal gas thermodynamic properties of fluorochlorodibromomethane ($CFClBr_2$)

Temp K	$C_p°$	$S°$	$-(G°-H_0°)/T$	$H°-H_0°$	$\Delta Hf°$	$\Delta Gf°$	log Kf
	cal deg^{-1} mol^{-1}			kcal mol^{-1}			
0	0.000	0.000	0.000	0.000	−39.648	−39.648	Infinite
50.00	8.677	57.737	49.650	0.404	−39.796	−40.455	176.829
100.00	11.912	64.707	55.541	0.917	−40.110	−40.979	89.558
150.00	14.744	70.102	59.524	1.587	−40.376	−41.352	60.250
200.00	16.830	74.643	62.751	2.378	−40.610	−41.643	45.504
273.15	19.069	80.240	66.708	3.696	−43.516	−41.891	33.517
298.15	19.678	81.936	67.915	4.181	−43.730	−41.696	30.563
300.00	19.721	82.058	68.002	4.217	−43.745	−41.723	30.395
400.00	21.561	88.003	72.283	6.288	−50.861	−39.561	21.615
500.00	22.746	92.951	75.936	8.508	−50.773	−36.730	16.055
600.00	23.526	97.172	79.133	10.824	−50.572	−33.941	12.363
700.00	24.057	100.841	81.977	13.205	−50.373	−31.184	9.736
800.00	24.429	104.079	84.542	15.630	−50.179	−28.461	7.775
900.00	24.699	106.973	86.876	18.087	−49.990	−25.751	6.253
1000.00	24.899	109.586	89.019	20.567	−49.805	−23.062	5.040
1100.00	25.052	111.967	90.998	23.065	−49.625	−20.410	4.055
1200.00	25.170	114.152	92.838	25.576	−49.455	−17.752	3.233
1300.00	25.264	116.170	94.556	28.098	−49.293	−15.120	2.542
1400.00	25.340	118.045	96.168	30.629	−49.139	−12.485	1.949
1500.00	25.401	119.796	97.685	33.166	−48.990	−9.877	1.439

18. Fluorotribromomethane ($CFBr_3$)

The structural parameters are reported by Wouters and deHemptinne [57] from their electron diffraction measurements, which are adopted here and are given in table 3.

The only available spectral data are from the Raman measurements in liquid state by Delwaulle and Francois [53]. Their assignments were checked by Meister et al. [58] by normal coordinate analysis using VFF, and recently by Nagai and Mann [43] using UBFF. Recently, Shimanouchi [44] recommended the same values of vibrational frequencies and are given in table 5.

No experimental $\Delta Hf°_{298}$ is available and hence the estimated value discussed in section 1.4 is adopted here.

The ideal gas thermal functions were calculated using the data given in tables 3 and 5 and are presented in table 24.

19. Trichlorobromomethane (CCl_3Br)

The structural parameters reported from electron diffraction measurements [59, 60] are in good agreement. Bowen [3] has recalculated these parameters which are used in this work and are given in table 3.

Shimanouchi [16] has critically reviewed the infrared and Raman spectral data for CCl_3Br. He selected values of the vibrational frequencies for the liquid state. These were checked by Mattes and Becher [61] and Nagai and Mann [43] by normal coordinate analysis. These frequencies were adopted in this work and are presented in table 5. Other references on infrared and Raman work are [62–65].

Sullivan and Davidson [66] studied the thermal bromination of chloroform (4)

$$CHCl_3\ (g)+Br_2\ (g)\rightarrow CCl_3Br\ (g)+HBr\ (g) \quad (4)$$

and reported $\Delta Hr°$ (4, 298) = −1.4 kcal mol^{-1}. Benson [67] using experimental data of Sullivan and Davidson and more accurate values of $C_p°$ and $S°$ of species involved in reaction (4) obtained $\Delta Hr°$ (4, 298) = −0.80±0.13 kcal mol^{-1}. Combining this value with $\Delta Hf°$ ($CHCl_3$, g, 298) = −24.6±0.2 [1], $\Delta Hf°$ (Br_2, g, 298) = 7.387 and $\Delta Hf°$ (HBr, g, 298) = −8.70 [45], we obtained $\Delta Hf°$ (CCl_3Br, g, 298) = −9.3±0.3 kcal mol^{-1}. This value is adopted here.

The ideal gas thermal functions were calculated using the data given in tables 3 and 5 and are presented in table 25.

TABLE 24. Ideal gas thermodynamic properties of fluorotribromomethane ($CFBr_3$)

Temp K	$C_p°$	$S°$	$-(G°-H_0°)/T$	$H°-H_0°$	$\Delta Hf°$	$\Delta Gf°$	log *Kf*
	cal deg⁻¹ mol⁻¹			kcal mol⁻¹			
0	0. 000	0. 000	0. 000	0. 000	−28. 559	−28. 559	Infinite
50. 00	9. 161	57. 144	48. 934	0. 410	−28. 629	−30. 107	131. 595
100. 00	12. 802	64. 625	55. 018	0. 961	−28. 963	−31. 437	68. 705
150. 00	15. 565	70. 373	59. 212	1. 674	−29. 286	−32. 603	47. 501
200. 00	17. 526	75. 133	62. 614	2. 504	−29. 604	−33. 661	36. 782
273. 15	19. 609	80. 923	66. 768	3. 867	−33. 962	−34. 955	27. 967
298. 15	20. 173	82. 665	68. 028	4. 364	−34. 290	−34. 993	25. 651
300. 00	20. 212	82. 790	68. 119	4. 401	−34. 313	−35. 038	25. 525
400. 00	21. 911	88. 855	72. 571	6. 514	−45. 042	−33. 038	18. 051
500. 00	23. 002	93. 871	76. 344	8. 763	−44. 989	−30. 021	13. 122
600. 00	23. 719	98. 132	79. 629	11. 102	−44. 776	−27. 048	9. 852
700. 00	24. 205	101. 827	82. 542	13. 500	−44. 567	−24. 109	7. 527
800. 00	24. 547	105. 083	85. 161	15. 938	−44. 366	−21. 205	5. 793
900. 00	24. 794	107. 989	87. 539	18. 406	−44. 171	−18. 315	4. 447
1000. 00	24. 978	110. 612	89. 717	20. 895	−43. 980	−15. 447	3. 376
1100. 00	25. 117	112. 999	91. 727	23. 400	−43. 796	−12. 617	2. 507
1200. 00	25. 226	115. 189	93. 592	25. 917	−43. 621	−9. 779	1. 781
1300. 00	25. 312	117. 212	95. 332	28. 444	−43. 455	−6. 970	1. 172
1400. 00	25. 381	119. 091	96. 963	30. 979	−43. 296	−4. 157	0. 649
1500. 00	25. 438	120. 844	98. 497	33. 520	−43. 145	−1. 372	0. 200

TABLE 25. Ideal gas thermodynamic properties of trichlorobromomethane (CCl_3Br)

Temp K	$C_p°$	$S°$	$-(G°-H_0°)/T$	$H°-H_0°$	$\Delta Hf°$	$\Delta Gf°$	log *Kf*
	cal deg⁻¹ mol⁻¹			kcal mol⁻¹			
0	0. 000	0. 000	0. 000	0. 000	−7. 114	−7. 114	Infinite
50. 00	8. 570	54. 829	46. 776	0. 403	−7. 336	−6. 891	30. 119
100. 00	12. 120	61. 807	52. 643	0. 916	−7. 590	−6. 332	13. 839
150. 00	15. 167	67. 332	56. 646	1. 603	−7. 744	−5. 666	8. 256
200. 00	17. 308	72. 015	59. 918	2. 420	−7. 840	−4. 959	5. 419
273. 15	19. 765	77. 811	63. 957	3. 784	−9. 223	−3. 849	3. 080
298. 15	20. 389	79. 570	65. 193	4. 286	−9. 300	−3. 357	2. 460
300. 00	20. 432	79. 696	65. 282	4. 324	−9. 305	−3. 320	2. 418
400. 00	22. 231	85. 843	69. 680	6. 465	−12. 725	−0. 602	0. 329
500. 00	23. 312	90. 929	73. 436	8. 747	−12. 535	2. 416	−1. 056
600. 00	23. 989	95. 244	76. 720	11. 114	−12. 291	5. 383	−1. 961
700. 00	24. 433	98. 977	79. 639	13. 537	−12. 056	8. 311	−2. 595
800. 00	24. 738	102. 261	82. 266	15. 996	−11. 831	11. 205	−3. 061
900. 00	24. 955	105. 188	84. 653	18. 481	−11. 617	14. 072	−3. 417
1000. 00	25. 114	107. 826	86. 841	20. 985	−11. 408	16. 922	−3. 698
1100. 00	25. 234	110. 225	88. 859	23. 503	−11. 208	19. 732	−3. 920
1200. 00	25. 327	112. 425	90. 733	26. 031	−10. 839	22. 545	−4. 106
1300. 00	25. 399	114. 455	92. 480	28. 567	−10. 839	25. 332	−4. 259
1400. 00	25. 458	116. 340	94. 118	31. 110	−10. 667	28. 119	−4. 390
1500. 00	25. 505	118. 098	95. 659	33. 659	−10. 501	30. 879	−4. 499

20. Trichloroiodomethane (CCl_3I)

No experimental molecular parameters are available for CCl_3I. They were estimated by the procedure given in section 1.2 and are presented in table 3.

Very recently, for the first time Mann and Mani [68] reported the vibrational frequencies for CCl_3I from their far infrared, infrared, and Raman spectral measurements in the liquid state. They were checked by their normal coordinate analysis using UBFF. Recently, Shimanouchi [44] recommended these values. We have adopted these frequencies and they are given in table 5.

No experimental ΔHf_{298}° is available. We adopted the value obtained by the procedure given in section 1.4 (table 7).

The ideal gas thermal functions were calculated using the data given in tables 3 and 5 and are presented in table 26.

21. Dichlorodibromomethane (CCl_2Br_2)

Capron and Perlinghi [69] reported the molecular parameters from their electron diffraction measurements assuming all angles to be tetrahedral. The values being not very reliable we have adopted estimated values obtained from the procedure given in section 1.2 and are given in table 3.

Shimanouchi [16] has recommended the vibrational frequencies from the infrared and Raman spectral measurements [64, 70] in the liquid state. Mattes and Becher [61] and Nagai and Mann [43] checked Davis et al.'s [70] assignments which were obtained by infrared (gas) and Raman (liquid) spectral measurements by normal coordinate analysis. We have adopted these frequencies and are given in table 5.

No experimental ΔHf°_{298} is available and hence the estimated value discussed in section 1.4 was adopted.

The ideal gas thermal functions were calculated using the data given in tables 3 and 5 and are presented in table 27.

22. Chlorotribromomethane ($CClBr_3$)

No experimental molecular parameters are available for $CClBr_3$. They were estimated by the procedure given in section 1.2 and are presented in table 3.

Shimanouchi [16] critically reviewed the infrared and Raman spectral data for $CClBr_3$. He selected the vibrational frequencies for the liquid state. These assignments were checked by Mattes and Becher [61] and Nagai and Mann [43] by their normal coordinate analysis using VFF and UBFF, respectively. These frequencies were adopted here and are given in table 5. The other references on infrared and Raman work are refs. [17, 58, 71, 72].

No experimental ΔHf°_{298} is available and hence the estimated value discussed in section 1.4 was adopted.

The ideal gas thermal functions were obtained using the data in tables 3 and 5 and are presented in table 28.

TABLE 26. Ideal gas thermodynamic properties of trichloroiodomethane (CCl_3I)

Temp K	C_p°	S°	$-(G^\circ-H_0^\circ)/T$	$H^\circ-H_0^\circ$	ΔHf°	ΔGf°	log Kf
	cal deg⁻¹ mol⁻¹			kcal mol⁻¹			
0	0. 000	0. 000	0. 000	0. 000	2. 889	2. 889	Infinite
50. 00	8. 683	56. 030	47. 954	0. 404	2. 653	3. 070	−13. 419
100. 00	12. 477	63. 178	53. 873	0. 931	2. 397	3. 603	−7. 874
150. 00	15. 552	68. 856	57. 950	1. 636	2. 253	4. 241	−6. 179
200. 00	17. 761	73. 648	61. 291	2. 471	2. 182	4. 915	−5. 371
273. 15	20. 076	79. 550	65. 415	3. 861	2. 143	5. 928	−4. 743
298. 15	20. 680	81. 335	66. 676	4. 370	2. 140	6. 271	−4. 597
300. 00	20. 721	81. 463	66. 767	4. 409	2. 140	6. 297	−4. 587
400. 00	22. 447	87. 682	71. 245	6. 475	0. 229	7. 747	−4. 233
500. 00	23. 473	92. 811	75. 061	8. 875	−4. 832	10. 104	−4. 417
600. 00	24. 111	97. 151	78. 390	11. 257	−4. 579	12. 828	−4. 672
700. 00	24. 528	100. 901	81. 344	13. 690	−4. 335	15. 990	−4. 992
800. 00	24. 813	104. 196	83. 999	16. 158	−4. 105	18. 878	−5. 157
900. 00	25. 016	107. 131	86. 409	18. 650	−3. 887	21. 738	−5. 279
1000. 00	25. 164	109. 775	88. 616	21. 159	−3. 675	24. 580	−5. 372
1100. 00	25. 276	112. 179	90. 650	23. 682	−3. 473	27. 383	−5. 440
1200. 00	25. 362	114. 382	92. 537	26. 214	−3. 283	30. 189	−5. 498
1300. 00	25. 430	116. 415	94. 297	28. 753	−3. 102	32. 968	−5. 542
1400. 00	25. 484	118. 302	95. 945	31. 299	−2. 929	35. 746	−5. 580
1500. 00	25. 529	120. 061	97. 495	33. 850	−2. 764	38. 499	−5. 609

TABLE 27. Ideal gas thermodynamic properties of dichlorodibromomethane (CCl_2Br_2)

Temp K	$C_p°$	$S°$	$-(G°-H_0°)/T$	$H°-H_0°$	$\Delta Hf°$	$\Delta Gf°$	log Kf
	cal deg^{-1} mol^{-1}			kcal mol^{-1}			
0	0.000	0.000	0.000	0.000	6.054	6.054	Infinite
50.00	9.031	57.144	48.984	0.408	5.910	5.391	−23.565
100.00	13.095	64.663	55.040	0.962	5.638	4.996	−10.919
150.00	16.020	70.567	59.265	1.695	5.431	4.723	−6.882
200.00	18.074	75.471	62.720	2.550	5.251	4.514	−4.933
273.15	20.250	81.447	66.962	3.957	2.412	4.362	−3.490
298.15	20.825	83.246	68.252	4.470	2.220	4.547	−3.333
300.00	20.864	83.375	68.345	4.509	2.207	4.561	−3.323
400.00	22.522	89.625	72.911	6.685	−4.833	6.823	−3.728
500.00	23.518	94.766	76.784	8.991	−4.683	9.735	−4.255
600.00	24.141	99.113	80.152	11.377	−4.431	12.595	−4.588
700.00	24.549	102.868	83.135	13.812	−4.190	15.414	−4.812
800.00	24.829	106.165	85.812	16.282	−3.961	18.199	−4.972
900.00	25.028	109.102	88.240	18.776	−3.742	20.956	−5.089
1000.00	25.174	111.746	90.460	21.286	−3.531	23.695	−5.178
1100.00	25.284	114.151	92.506	23.809	−3.327	26.394	−5.244
1200.00	25.369	116.355	94.403	26.342	−3.135	29.097	−5.299
1300.00	25.436	118.388	96.171	28.882	−2.952	31.772	−5.341
1400.00	25.489	120.275	97.826	31.429	−2.777	34.449	−5.378
1500.00	25.533	122.035	99.382	33.980	−2.609	37.097	−5.405

TABLE 28. Ideal gas thermodynamic properties of chlorotribromomethane ($CClBr_3$)

Temp K	$C_p°$	$S°$	$-(G°-H_0°)/T$	$H°-H_0°$	$\Delta Hf°$	$\Delta Gf°$	log Kf
	cal deg^{-1} mol^{-1}			kcal mol^{-1}			
0	0.000	0.000	0.000	0.000	17.107	17.107	Infinite
50.00	9.663	57.844	49.520	0.416	17.043	15.642	−68.369
100.00	14.159	66.008	55.825	1.018	16.761	14.371	−31.407
150.00	16.923	72.316	60.311	1.801	16.503	13.233	−19.281
200.00	18.824	77.458	63.974	2.697	16.242	12.182	−13.312
273.15	20.835	83.642	68.442	4.152	11.956	10.875	−8.701
298.15	21.362	85.490	69.795	4.680	11.650	10.787	−7.907
300.00	21.399	85.622	69.892	4.719	11.629	10.782	−7.854
400.00	22.904	92.004	74.651	6.941	0.979	12.729	−6.954
500.00	23.796	97.219	78.660	9.280	1.097	15.674	−6.851
600.00	24.349	101.610	82.128	11.689	1.363	18.564	−6.762
700.00	24.710	105.393	85.188	14.143	1.615	21.411	−6.685
800.00	24.956	108.709	87.925	16.627	1.853	24.224	−6.518
900.00	25.131	111.659	90.401	19.132	2.079	27.007	−6.558
1000.00	25.259	114.314	92.662	21.652	2.297	29.771	−6.506
1100.00	25.355	116.726	94.742	24.183	2.505	32.494	−6.456
1200.00	25.429	118.936	96.667	26.722	2.703	35.222	−6.415
1300.00	25.487	120.973	08.460	20.268	2.800	37.920	−6.375
1400.00	25.534	122.864	100.136	31.819	3.069	40.620	−6.341
1500.00	25.572	124.627	101.711	34.375	3.241	43.291	−6.307

23. Comparison

No experimental data on gaseous heat capacity or entropy are available for any of the compounds. The agreement of our values of $C_p°$ and $S°$ with those of Gelles and Pitzer [73] is satisfactory except for $S°$ of CCl_3Br and CHF_2Br. They are 2.1 and 0.8 cal deg^{-1} mol^{-1}, respectively, lower than our values at 298.15 K. Our values agree very well with those of Gurvich, et al. [74] for all compounds. The values for CCl_3I are reported for the first time in this work.

$\Delta Hf°$ (g, 298) adopted in this work are compared with those reported by other workers in table 7. We feel our estimated values are more reliable as we have used the most recent recommended values of $\Delta Hf°$ (g, 298) in our calculations.

Acknowledgements

The authors thank IIT-Kanpur Computer Center for providing the computer facilities, the Office of Standard Reference Data of the U.S. National Bureau of Standards for financial assistance, A. Kumar, L. Srivastava, and R. K. Srivastava for the literature survey, and S. Chen for calculation of the moments of inertia of CHFClBr.

References

[1] Rodgers, A. S., Chao, J., Wilhoit, R. C., and Zwolinski, B. J., J. Phys. Chem. Ref. Data **3**, 117 (1974).

[2] Kudchadker, S. A., and Kudchadker, A. P., J. Phys. Chem. Ref. Data **4**, 457 (1975); **5**, 529 (1976).

[3] Tables of Interatomic Distances and Configuration in Molecules and Ions, Special Publication no. 16, The Chemical Society (London) (1958), supplement (1965).

[3a] Diem, M., and Burow, D. F., J. Chem. Phys. **64**, 5179 (1976).

[3b] Curnuck, P. A., and Sheridan, J., Nature **202**, 591 (1964).

[4] Cox, J. D., and Pilcher, G., *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, London and New York (1970).

[5] Zahn, C. T., J. Chem. Phys. **2**, 671 (1934).

[6] Allen, T. L., J. Chem. Phys. **31**, 1039 (1959).

[7] Bernstein, H. J., J. Phys. Chem. **69**, 1550 (1965).

[8] Rodgers, A. S., J. Phys. Chem. **71**, 1996 (1967).

[9] Lacher, J. R., and Skinner, H. A., J. Chem. Soc. (A), 1034 (1968).

[10] Somayajulu, G. R., and Zwolinski, B. J., J. Chem. Soc. Faraday Trans. II **70**, 973 (1974).

[11] Chen, S. S., Wilhoit, R. C., and Zwolinski, B. J., J. Phys. Chem. Ref. Data **5**, 571 (1976).

[12] Delwaulle, M. L., and Francois, F., J. Phys. Radium **7**, 15 (1946).

[13] Pitzer, K. S., and Gelles, E., J. Chem. Phys. **21**, 855 (1953).

[14] El-Sabban, M. Z., Danti, A., and Zwolinski, B. J., J. Chem. Phys. **44**, 1770 (1966).

[15] Plyler, E. K., and Benedict, W. S., J. Res. Natl. Bur. Stand. **49**, 1 (1952).

[16] Shimanouchi, T., Tables of Molecular Vibrational Frequencies Part 2. National Standard Reference Data Series, National Bureau of Standards (1968).

[17] Plyler, E. K., Smith, W. H., and Aquista, N., J. Res. Natl. Bur. Stand. **44**, 503 (1950).

[18] Weber, A., Meister, A. G., and Cleveland, F. F., J. Chem. Phys. **21**, 930 (1953).

[19] Tanaka, A. N., Narasimhan, K. V., Meister, A. G., Cleveland, F. F., Sundaram, S., Piotrowski, F. A., Bernstein, R. B., and Miller, S. I., J. Mol. Spectrosc. **15**, 319 (1965).

[20] Bacher, W., and Wagner, J., Z. Phys. Chem. **B43**, 191 (1939).

[21] Wagner, J., Z. Phys. Chem. **B45**, 69 (1939).

[22] Plyler, E. K., and Aquista, N., J. Res. Natl. Bur. Stand. **48**, 92 (1952).

[23] Palm, A., Voelz, F. L., and Meister, A. G., J. Chem. Phys. **23**, 726 (1955).

[24] Holzer, W., J. Mol. Spectrosc. **25**, 123 (1968).

[25] Glockler, G., and Leader, G. R., J. Chem. Phys. **8**, 125 (1940).

[26] Delwaulle, M. L., c. r. Acad. Sci. **216**, 735 (1943).

[27] Plyler, E. K., and Lamb, A. M., J. Res. Natl. Bur. Stand. **46**, 382 (1951).

[28] El-Sabban, M. Z., and Zwolinski, B. J., J. Mol. Spectrosc. **19**, 231 (1966).

[29] Polo, S. R., Palm, A., Voelz, F. L., Cleveland, F. F., Meister, A. G., Bernstein, R. B., and Sherman, R. H., J. Chem. Phys. **23**, 833 (1955).

[30] Pontarelli, D. A., Meister, A. G., Cleveland, F. F., and Voelz, F. L., J. Chem. Phys. **20**, 1949 (1952).

[31] Glockler, G., and Leader, G. R., J. Chem. Phys. **7**, 553 (1939).

[32] Emschwiller, G., and Lecomte, J., J. Phys. radium 8, 130 (1947).

[33] Sheridan, J., and Gordy, W., J. Chem. Phys. **20**, 591 (1952).

[34] Sharbaugh, A. H., Pritchard, B. S., and Madison, T. C., Phys. Rev. **77**, 302 (1950).

[35] Anderson, R. E., Diss. Abstr. **19**, 50 (1958).

[36] Bowen, H. J. M., Trans. Far. Soc. **50**, **444** (1954).

[37] Edgell, W. F., and May, C. E., J. Chem. Phys. **20**, 1822 (1952).

[38] Polo, S. R., and Wilson, M. K., J. Chem. Phys. **20**, 1183 (1952).

[39] McGee, P. R., Cleveland, F. F., Meister, A. G., and Decker, C. E., J. Chem. Phys. **21**, 242 (1953).

[40] Edgell, W. F., and May, C. E., J. Chem. Phys. **22**, 1808 (1954).

[41] Taylor, R. C., J. Chem. Phys. **22**, 714 (1954).

[42] Person, W. B., and Polo, S. R., Spectrochim. Acta. **17**, 101 (1961).

[43] Nagai, L. H., and Mann, R. H., J. Mol. Spectrosc. **38**, 322 (1971).

[44] Shimanouchi, T., "Tables of Molecular Vibrational Frequencies Part 8," J. Chem. Phys. Ref. Data **3**, 269 (1974).

[45] Wagman, D. D., Evans, W. H., Parker, V. B., Halow, I., Bailey, S. M., and Schumm, R. H., "Selected Values of Chemical Thermodynamic Properties", National Bureau of Standards, Technical Note 270–3 (1968).

[46] Corbett, P., Tass, A. M., and Whittle, E., Trans. Faraday Soc. **59**, 1609 (1963).

[47] Coomber, J. W., and Whittle, E., Trans. Faraday Soc. **63**, 608 (1967).

[48] Lord, A., Goy, C. A., and Pritchard, H. O., J. Phys. Chem. **71**, 2705 (1967).

[49] Wong, C., and Schomaker, V., J. Chem. Phys. **28**, 1010 (1958).

[49a] Andreasen, A. L., and Bauer, S. H., J. Chem. Phys. **56**, 3802 (1972).

[50] Goy, C. A., Lord, A., and Pritchard, H. O., J. Phys. Chem. **71**, 1086 (1967).

[51] El-Sabban, M. Z., and Zwolinski, B. J., J. Mol. Spectrosc. **22**, 23 (1967).

[52] Decker, C. E., Cleveland, F. F., and Bernstein, R. B., J. Chem. Phys. **21**, 189 (1953).

[53] Delwaulle, M. L., and Francois, F., c. r. Acad. Sci. **214**, 828 (1942).

[54] Cleveland, F. F., J. Chem. Phys. **11**, 1 (1943).

[55] McAlpine, I., and Sutcliffe, H., Spectrochim. Acta. **25**, 1723 (1969).

[56] Glbert, R. L., Piotrowski, E. A., Dowling, J. M., and Cleveland, F. F., J. Chem. Phys. **31**, 1633 (1959).

[57] Wouters, J., and deHemptinne, M., Nature **141**, 412 (1938).

[58] Meister, A. G., Rosser, S. E., and Cleveland, F. F., J. Chem. Phys. **18**, 346 (1950).

[59] Capron, P., and deHemptinne, M., Am. Soc., Sci. Brux. **56B**, 342 (1936).

[60] Kimura, M., and Marino, Y., J. Chem. Soc., Japan **68**, 77 (1947).

[61] Mattes, R., and Becher, H. J., Z. Phys. Chem. **61**, 177 (1968).

[62] Zietlow, J. P., Cleveland, F. F., and Meister, A. G., J. Chem. Phys. 18, 1076 (1950).

[63] Madigan, J. R., and F. F. Cleveland, J. Chem. Phys. **19**, 115 (1951).

[64] Plyler, E. K., and Benedict, W. S., J. Res. Natl. Bur. Stand. **47**, 202 (1951).

[65] Long, D. A., and Miller, G., Trans. Faraday Soc. **54**, 330 (1958).

[66] Sullivan, J. H., and Davidson, N., J. Chem. Phys. **19**, 143 (1951).

[67] Benson, S. W., J. Chem. Phys. **43**, 2044 (1965).

[68] Mann, R. H., and Mani, P. M., J. Mol. Spectrosc. **45**, 65 (1973).

[69] Capron, P., and Perlinghi, L. T., Bull. Soc. Chim. Belg. **45**, 730 (1936).

[70] Davis, A., Cleveland, F. F., and Meister, A. G., J. Chem. Phys. **20**, 454 (1952).

[71] Delwaulle, M. L., Buisset, M. B., and Delhaye, M., J. Am. Chem. Soc. **74**, 5768 (1952).

[72] Krupp, R. H., Ferigle, S. M., and Weber, A., J. Chem. Phys. **24**, 355 (1956).

[73] Gelles, E., and Pitzer, K. S., J. Am. Chem. Soc. **75**, 5259 (1953).

[74] Gurvich, L. V., et al., Thermodynamic Properties of Industrial Substances, Vol. 2. Academy of Science, U.S.S.R. (1962).