ond virial coefficient. Thus, the following relationship has been derived[17]

$$\alpha^5 - \alpha^3 = 2C_M\psi_1(1 - \Theta/T)M^{1/2} \qquad (10)$$

where C_M is defined according to equation 6. ψ_1 may therefore be computed from the intrinsic viscosity measurements yielding α^3, provided C_M (at the temperature T; see above), Θ, and M are known. If Θ is not known, viscosity measurements at two temperatures suffice for resolution of the quantity $\psi_1(1 - \Theta/T)$. As shown in Table II, the ψ_1 value obtained in this manner for the polyisobutylene–benzene system is about half that obtained from the second virial coefficient. Application of the intrinsic viscosity method to other systems yields similar or smaller ψ_1 values; hence, the result for polyisobutylene–benzene is not exceptional.

It is too much to expect that the present treatments of the second virial coefficient and of the expansion factor α should be quantitatively exact. Experimental measurements[18] of intrinsic viscosities over very wide ranges in molecular weight show equation 10 to be only approximately of the correct form. The ψ_1 value calculated from intrinsic viscosity for this particular system could be brought into agreement with that obtained by one of the other methods by a numerical revision of the right hand member in equation 6; however, in view of the above-noted deficiency in the form of the ($\alpha^5 - \alpha^3$) relation, an improved treatment of intramolecular interactions may be required to remove these discrepancies.

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Thermodynamic Functions of the Halogenated Methanes[1]

BY EDWARD GELLES AND KENNETH S. PITZER

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The heat capacity C_p^0, heat content ($H^0 - H_0^0$), free energy function $-(F^0 - H_0^0)/T$ and entropy S^0 of 39 halogenated methanes have been calculated for 18 temperatures in the range 100–1500°K. to the rigid rotator-harmonic oscillator approximation employing recently revised vibration frequency assignments. The available thermodynamic data on the halogenated methanes are discussed in the light of these calculations.

The vibrational frequency assignments for the halogenated methanes have been examined recently by the authors with the aid of the Substitution Product Rule.[2]

Previous assignments for a number of halogenated methanes have been revised, and the confirmation of other assignments together with recent accurate infrared measurements on the vapors of a number of these compounds has provided a secure basis for the calculation of the vibrational contributions to the thermodynamic functions of the halogenated methanes.

TABLE I

PRODUCTS OF PRINCIPAL MOMENTS OF INERTIA OF HALOGENATED METHANES

$10^{117} \times I_1I_2I_3$ (g.^{3} cm.^{6})

Compound		Compound	
CF_4	3.24×10^3	CH_2I_2	5.69×10^4
CCl_4	1.14×10^5	CF_2Cl_2	2.50×10^4
CBr_4	2.35×10^6	CF_2Br_2	1.60×10^5
CH_3F	5.92	CCl_2Br_2	5.44×10^5
CH_3Cl	17.9	CH_2FCl	4.72×10^2
CH_3Br	44.6	CH_2FBr	1.06×10^3
CH_3I	55.1	CH_2ClBr	4.54×10^3
CHF_3	9.73×10^2	CH_2ClI	8.82×10^3
CF_3Cl	1.03×10^4	CH_2BrI	3.11×10^4
CF_3Br	2.38×10^4	CF_2HCl	3.44×10^3
CF_3I	4.50×10^4	CF_2HBr	8.22×10^3
$CHCl_3$	3.30×10^4	CF_2ClBr	6.08×10^4
CCl_3F	6.22×10^4	CCl_2HF	1.09×10^4
CCl_3Br	2.56×10^5	CCl_2HBr	7.50×10^4
$CHBr_3$	6.10×10^5	CCl_2FBr	1.30×10^5
$CFBr_3$	8.30×10^5	CBr_2HF	8.00×10^4
$CClBr_3$	1.24×10^6	CBr_2HCl	2.11×10^5
CH_2F_2	1.17×10^2	CBr_2FCl	3.22×10^5
CH_2Cl_2	1.87×10^3	$CHFClBr$	2.68×10^4
CH_2Br_2	1.41×10^4		

TABLE II

COMPARISON OF CALCULATED AND EXPERIMENTAL ENTROPY VALUES

(All at 298.16° K. in units of cal./deg. mole.)

Substance	$S_{calc.}$	$S_{expl.}$
CF_4	62.48	62.43[3]
CCl_4	73.94	73.7[4]
CH_3Cl	55.80	55.94[5]
CH_3Br	58.82	58.61[6]
$CFCl_3$	73.96	74.07[7]

(1) This work was assisted by the American Petroleum Institute through Research Project 50.

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TABLE III

THE HEAT CAPACITY AT CONSTANT PRESSURE, C_p°, OF THE HALOGENATED METHANES

Compound	100°K.	150°K.	200°K.	250°K.	298.16°K.	300°K.	400°K.	500°K.	600°K
CF_4	8.30	9.61	11.32	13.07	14.61	14.67	17.33	19.32	20.77
CCl_4	11.24	14.31	16.69	18.54	19.92	19.97	21.92	23.09	23.83
CBr_4	15.17	17.72	19.46	20.80	21.80	21.83	23.21	24.02	24.52
CH_3F	7.95	7.96	8.08	8.41	8.94	8.96	10.52	12.22	13.80
CH_3Cl	7.96	8.06	8.40	8.99	9.73	9.76	11.50	13.28	14.64
CH_3Br	7.97	8.18	8.75	9.06	10.14	10.17	11.92	13.55	14.97
CH_3I	8.01	8.34	8.94	9.71	10.55	10.58	12.36	13.95	15.31
CHF_3	8.10	8.81	9.84	11.03	12.20	12.24	14.88	16.55	18.13
CF_3Cl	8.77	10.63	12.64	14.45	15.97	16.22	18.53	20.32	21.60
CF_3Br	9.35	11.47	13.44	15.13	16.54	16.59	18.93	20.62	21.82
CF_3I	9.86	12.04	13.93	15.55	16.90	16.95	19.20	20.83	21.98
$CHCl_3$	9.62	11.13	13.02	14.47	15.71	15.76	17.83	19.34	20.44
CCl_3F	10.27	13.03	15.33	17.18	18.61	18.67	20.81	22.20	23.11
CCl_3Br	12.23	15.25	17.46	18.40	20.42	20.47	22.25	23.40	24.00
$CHBr_3$	11.61	13.23	14.63	15.90	16.99	17.03	18.83	20.12	21.05
$CFBr_3$	12.80	15.57	17.53	19.03	20.18	20.21	21.91	23.00	23.72
$CClBr_3$	14.08	16.87	18.79	20.26	21.35	21.38	22.90	23.79	24.35
CH_2F_2	8.01	8.29	8.78	9.46	10.28	10.32	12.27	14.14	15.76
CH_2Cl_2	8.53	9.27	10.15	11.17	12.22	12.26	14.69	15.87	17.36
CH_2Br_2	9.21	10.14	10.96	12.55	13.09	13.13	15.36	16.67	17.91
CH_2I_2	9.65	10.52	11.62	12.76	13.83	13.86	15.90	17.89	19.03
CF_2Cl_2	9.46	11.78	13.95	15.79	17.28	17.33	19.68	21.28	22.37
CF_2Br_2	10.87	13.49	15.54	17.16	18.45	18.49	20.51	21.90	22.84
CCl_2Br_2	13.11	16.05	18.12	19.70	20.88	20.92	22.57	23.56	24.17
CH_2FCl	8.20	8.75	9.46	10.32	11.25	11.29	13.29	15.08	16.57
CH_2FBr	8.42	8.96	9.93	10.82	11.76	11.79	13.75	15.46	16.88
CH_2ClBr	8.86	9.65	10.57	11.54	12.67	12.69	14.71	16.34	17.60
CH_2ClI	9.10	9.94	11.06	11.98	13.02	13.06	15.02	16.60	17.85
CH_2BrI	9.45	10.27	11.30	12.42	13.47	13.51	15.43	16.95	18.15
CF_2HCl	8.44	9.60	10.89	12.16	13.35	13.40	15.63	17.69	18.57
CF_2HBr	8.97	9.97	11.32	11.75	13.78	13.83	16.01	17.77	19.13
CF_2ClBr	10.12	12.58	14.70	16.43	17.82	17.89	20.61	21.55	22.58
CCl_2HF	8.97	10.49	11.66	13.34	14.57	14.61	16.75	18.45	19.71
CCl_2HBr	10.24	12.04	13.59	14.97	16.16	16.20	18.17	19.61	20.65
CCl_2FBr	11.11	13.94	16.15	17.89	19.22	19.27	21.26	22.53	23.37
CBr_2HF	10.05	11.72	13.16	14.45	15.57	15.61	17.87	19.07	20.20
CBr_2HCl	10.89	12.65	14.13	15.46	16.60	16.64	18.52	19.87	20.86
CBr_2FCl	11.95	14.78	16.87	18.49	19.73	19.77	21.61	22.79	23.56
$CHFClBr$	9.50	11.13	12.59	13.93	15.11	15.20	17.22	18.80	19.98

Statistical mechanical calculations of the thermodynamic functions have been carried out previously for a few halogenated methanes. Yost and Blair obtained an approximate value for the entropy of CCl_4 at 25°.[8] Vold calculated the heat capacities and heat contents of the chloromethanes from 0–500°.[9] Stevenson and Beach computed the standard entropy at 298.1°K., and the standard free energy functions and heat contents in the temperature range 298.1–1200°K. for the chloro- and bromomethanes, as well as the heat capacities of the bromomethanes over a smaller temperature range.[10] Glockler and Edgell obtained the heat capacities from 250–650°K. for CHF_3, CF_2HCl and CCl_2HF,[11] and the entropies at 298.1°K. and heat capacities from 298.1 to 600°K. for CH_3F, CH_3I and CH_2Br_2.[12]

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(12) W. F. Edgell and G. Glockler, *ibid.*, **9**, 484 (1941).

(TABLE III *Continued*)

Compound	700°K.	800°K.	900°K.	1000°K.	1100°K.	1200°K.	1300°K.	1400°K.	1500°K.
CF_4	21.82	22.63	23.18	23.63	23.97	24.25	24.46	24.64	24.79
CCl_4	24.31	24.64	24.88	25.05	25.18	25.28	25.36	25.42	25.48
CBr_4	24.84	25.06	25.21	25.33	25.41	25.48	25.53	25.57	25.60
CH_3F	15.20	16.43	17.50	18.43	19.24	19.95	20.56	21.10	21.56
CH_3Cl	15.92	17.03	17.76	18.86	19.60	20.26	20.82	21.32	21.75
CH_3Br	16.19	17.25	18.19	19.01	19.73	20.36	20.92	21.40	21.82
CH_3I	16.48	17.51	18.40	19.20	19.89	20.50	21.04	21.50	21.92
CHF_3	19.36	20.33	20.99	21.74	22.26	22.70	23.06	23.37	23.63
CF_3Cl	22.50	23.17	23.66	24.03	24.31	24.54	24.72	24.86	24.98
CF_3Br	22.68	23.30	23.77	24.12	24.39	24.60	24.78	24.91	25.03
CF_3I	22.81	23.41	23.86	24.19	24.45	24.66	24.82	24.95	25.06
$CHCl_3$	21.27	21.91	22.43	22.88	23.21	23.51	23.77	23.99	24.17
CCl_3F	23.74	24.18	24.50	24.73	24.91	25.05	25.16	25.25	25.32
CCl_3Br	24.44	24.74	24.96	25.12	25.24	25.33	25.40	25.46	25.51
$CHBr_3$	21.76	22.31	22.76	23.13	23.44	23.71	23.94	24.13	24.30
$CFBr_3$	24.21	24.55	24.80	24.98	25.12	25.23	25.31	25.38	25.44
$CClBr_3$	24.71	24.96	25.13	25.26	25.36	25.43	25.49	25.53	25.57
CH_2F_2	17.12	18.25	19.20	20.00	20.68	21.25	21.76	22.18	22.55
CH_2Cl_2	18.47	19.38	20.15	20.80	21.36	21.84	22.26	22.65	22.94
CH_2Br_2	18.91	19.74	20.45	21.06	21.58	22.03	22.42	22.76	23.06
CH_2I_2	19.30	20.08	20.73	21.30	21.79	22.21	22.58	22.90	23.18
CF_2Cl_2	23.14	23.69	24.09	24.39	24.62	24.81	24.95	25.07	25.16
CF_2Br_2	23.51	23.98	24.33	24.59	24.79	24.95	25.07	25.17	25.25
CCl_2Br_2	24.58	24.85	25.05	25.19	25.30	25.38	25.45	25.50	25.54
CH_2FCl	17.79	18.81	19.67	20.39	21.01	21.55	22.00	22.39	22.73
CH_2FBr	18.05	19.02	19.84	20.54	21.14	21.65	22.09	22.45	22.80
CH_2ClBr	18.69	19.57	20.30	20.93	21.47	21.94	22.34	22.69	23.00
CH_2ClI	18.87	19.71	20.42	21.04	21.56	22.02	22.41	22.76	23.06
CH_2BrI	19.11	19.91	20.62	21.18	21.68	22.12	22.51	22.83	23.12
CF_2HCl	19.97	20.84	21.54	22.11	22.57	22.96	23.29	23.57	23.81
CF_2HBr	20.19	21.02	21.69	22.24	22.69	23.06	23.38	23.65	23.87
CF_2ClBr	23.30	23.82	24.19	24.48	24.70	24.87	25.00	25.10	25.20
CCl_2HF	20.67	21.42	22.02	22.52	22.92	23.26	23.55	23.80	24.01
CCl_2HBr	21.43	22.05	22.54	22.95	23.29	23.58	23.83	24.04	24.22
CCl_2FBr	23.94	24.34	24.62	24.84	25.00	25.13	25.23	25.31	25.37
CBr_2HF	21.06	21.74	22.29	22.74	23.11	23.43	23.69	23.92	24.12
CBr_2HCl	21.60	22.19	22.66	23.05	23.37	23.66	23.89	24.09	24.26
CBr_2FCl	24.09	24.45	24.72	24.92	25.07	25.18	25.28	25.35	25.41
$CHFClBr$	20.89	21.60	22.17	22.64	23.03	23.35	23.63	23.87	24.07

They have also computed the heat capacities from 250–600°K. for CH_2F_2, CH_2Cl_2, CH_2I_2, CH_2FCl, CCl_3Br, CCl_2Br_2 and CBr_3Cl.[13] Justi and Langer calculated the thermodynamic properties of CF_2Cl_2 and CH_2Cl_2 and of CCl_3F and CF_3Cl over a limited temperature range.[14] Thompson and Temple have calculated the heat capacity, heat content function, free energy function and entropy from 250–600°K. for CF_3Cl, CCl_3F and CF_2Cl_2.[15] Masi has also reported calculations for CF_2Cl_2.[16] As these scattered data cover only limited ranges of temperature and as in some cases reassignments have been made, and more accurate values for fundamental frequencies are now available, it has been thought

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TABLE IV

THE HEAT CONTENT, $(H^0 - H_0^0)$, OF THE HALOGENATED METHANES

Compound	100°K.	150°K.	200°K.	250°K.	298.16°K.	300°K.	400°K.	500°K.	600°K.
CF_4	0.800	1.244	1.766	2.376	3.043	3.071	4.676	6.513	8.522
CCl_4	0.882	1.679	2.301	3.183	4.111	4.147	6.250	8.505	10.85
CBr_4	1.078	1.906	2.839	3.845	4.872	4.912	7.171	9.535	11.96
CH_3F	0.795	1.192	1.593	2.004	2.421	2.437	3.408	4.545	5.847
CH_3Cl	.795	1.195	1.605	2.039	2.489	2.507	3.569	4.821	6.196
CH_3Br	.795	1.198	1.618	2.041	2.536	2.555	3.660	4.935	6.362
CH_3I	.796	1.203	1.634	2.100	2.587	2.607	3.754	5.072	6.537
CHF_3	.797	1.217	1.683	2.205	2.764	2.787	4.130	5.690	7.427
CF_3Cl	.810	1.293	1.875	2.553	3.287	3.316	5.050	6.997	9.097
CF_3Br	.825	1.345	1.968	2.684	3.447	3.478	5.260	7.241	9.367
CF_3I	.841	1.389	2.040	2.777	3.558	3.590	5.403	7.410	9.553
$CHCl_3$	.836	1.363	1.975	2.663	3.390	3.419	5.104	6.967	8.959
CCl_3F	.851	1.434	2.145	2.959	3.823	3.857	5.838	7.993	10.26
CCl_3Br	.922	1.614	2.434	3.189	4.305	4.343	6.486	8.769	11.14
$CHBr_3$	.931	1.554	2.251	3.015	3.807	3.838	5.636	7.586	9.647
$CFBr_3$	.961	1.674	2.504	3.419	4.364	4.402	6.514	8.764	11.10
$CClBr_3$	1.014	1.792	2.687	3.664	4.667	4.707	6.928	9.265	11.67
CH_2F_2	0.796	1.202	1.628	2.083	2.558	2.577	3.705	5.027	6.524
CH_2Cl_2	.809	1.253	1.738	2.270	2.834	2.857	4.235	5.651	7.377
CH_2Br_2	.840	1.317	1.843	2.494	3.023	3.047	4.504	6.051	7.783
CH_2I_2	.871	1.374	1.927	2,536	3.177	3.202	4.710	6.572	8.386
CF_2Cl_2	.828	1.358	2.003	2.748	3.545	3.577	5.435	7.487	9.673
CF_2Br_2	.879	1.490	2.218	3.037	3.895	3.929	5.886	8.020	10.25
CCl_2Br_2	.963	1.697	2.553	3.500	4.479	4.517	6.700	9.010	11.40
CH_2FCl	.799	1.222	1.677	2.171	2.690	2.710	3.940	5.360	6.945
CH_2FBr	.805	1.239	1.724	2.238	2.781	2.803	4.080	5.543	7.163
CH_2ClBr	.821	1.284	1.789	2.340	2.928	2.950	4.325	5.880	7.582
CH_2ClI	.832	1.307	1.822	2.400	3.002	3.026	4.432	6.016	7.741
CH_2BrI	.856	1.347	1.886	2.479	3.103	3.127	4.578	6.200	7.957
CF_2HCl	.804	1.253	1.765	2.342	2.956	2.981	4.435	6.155	7.912
CF_2HBr	.809	1.274	1.807	2.405	3.040	3.066	4.561	6.253	8.101
CF_2ClBr	.851	1.419	2.098	2.883	3.708	3.741	5.746	7.729	9.939
CCl_2HF	.817	1.304	1.841	2.499	3.171	3.198	4.768	6.539	8.449
CCl_2HBr	.861	1.419	2.061	2.775	3.525	3.555	5.278	7.171	9.187
CCl_2FBr	.882	1.510	2.265	3.117	4.015	4.048	6.081	8.275	10.57
CBr_2HF	.859	1.404	2.027	2.717	3.441	3.470	5.185	6.968	8.935
CBr_2HCl	.891	1.481	2.152	2.892	3.664	3.695	5.458	7.381	9.419
CBr_2FCl	.919	1.590	2.384	3.269	4.191	4.227	6.303	8.526	10.85
$CHFClBr$	.836	1.352	1.945	2.609	3.308	3.336	4.959	6.763	8.705

worthwhile to include the above compounds in the present calculations.

We are accordingly presenting in Tables III to VI the standard thermodynamic functions of the 39 halogenated methanes for which vibration frequency assignments are considered reasonably certain. These functions, the heat capacity at constant pressure C_p^0, the heat content $(H^0 - H_0^0)$, the free energy function $-(F^0 - H_0^0)/T$ and the entropy S^0 are for standard conditions of the ideal gas at 1 atmosphere pressure and are in cal./deg. mole or kcal./mole units. They have been calculated for 18 temperatures in the range 100–1500°K. The compounds are arranged in these tables in groups of decreasing molecular symmetry.

The translational and rotational contributions were calculated from the usual statistical mechanical equations employing the most recent values for the fundamental constants.[17] Moments of inertia obtained from spectroscopic measurements were

(17) F. D. Rossini, F. T. Gucker, H. L. Johnston, L. Pauling and G. W. Vinal, THIS JOURNAL, **74**, 2699 (1952).

TABLE IV (*Continued*)

Compound	700°K.	800°K.	900°K.	1000°K.	1100°K.	1200°K.	1300°K.	1400°K.	1500°K.
CF_4	10.65	12.88	15.17	17.51	19.89	22.30	24.74	27.19	29.66
CCl_4	13.26	15.71	18.19	20.68	23.19	25.72	28.25	30.79	33.33
CBr_4	14.43	16.93	19.44	21.97	24.51	27.05	29.60	32.16	34.71
CH_3F	7.298	8.881	10.58	12.38	14.26	16.22	18.25	20.33	22.46
CH_3Cl	7.725	9.374	10.89	12.97	14.89	16.89	18.94	21.05	23.21
CH_3Br	7.921	9.594	11.37	13.23	15.17	17.17	19.24	21.35	23.51
CH_3I	8.128	9.828	11.63	13.51	15.46	17.48	19.56	21.69	23.86
CHF_3	9.304	11.29	13.36	15.51	17.71	19.96	22.24	24.57	28.42
CF_3Cl	11.30	13.59	15.93	18.32	20.73	23.18	25.64	28.12	30.61
CF_3Br	11.59	13.89	16.25	18.64	21.07	23.52	25.99	28.47	30.97
CF_3I	11.79	14.11	16.47	18.88	21.31	23.76	26.24	28.73	31.23
$CHCl_3$	11.04	13.21	15.42	17.69	19.99	22.33	24.69	27.08	29.49
CCl_3F	12.67	15.00	17.44	19.90	22.38	24.88	27.39	29.91	32.44
CCl_3Br	13.56	16.02	18.51	21.01	23.53	26.06	28.59	31.14	33.69
$CHBr_3$	11.79	13.99	16.25	18.54	20.87	23.23	25.61	28.02	30.44
$CFBr_3$	13.50	15.94	18.41	20.90	23.40	25.92	28.44	30.98	33.52
$CClBr_3$	14.13	16.61	19.12	21.64	24.17	26.71	29.25	31.80	34.36
CH_2F_2	8.171	9.941	11.81	13.78	15.81	17.91	20.06	22.26	24.49
CH_2Cl_2	9.171	11.06	13.04	15.09	17.20	19.36	21.56	23.82	26.09
CH_2Br_2	9.625	11.56	13.57	15.65	17.78	19.96	22.18	24.44	26.73
CH_2I_2	10.15	11.98	14.02	16.12	18.28	20.48	22.72	24.99	27.30
CF_2Cl_2	11.95	14.29	16.68	19.11	21.56	24.03	26.52	29.02	31.53
CF_2Br_2	12.57	14.95	17.36	19.81	22.28	24.76	27.26	29.78	32.30
CCl_2Br_2	13.84	16.31	18.80	21.32	23.84	26.37	28.92	31.46	34.02
CH_2FCl	8.665	10.50	12.42	14.43	16.50	18.62	20.80	23.03	25.26
CH_2FBr	8.911	10.77	12.71	14.73	16.82	18.95	21.14	23.33	25.64
CH_2ClBr	9.401	11.32	13.31	15.37	17.49	19.66	21.88	24.13	26.42
CH_2ClI	9.577	11.51	13.52	15.59	17.72	19.90	22.12	24.38	26.67
CH_2BrI	9.822	11.77	13.83	15.89	18.03	20.22	22.47	24.72	27.02
CF_2HCl	9.856	11.90	14.02	16.20	18.44	20.71	23.03	25.37	27.74
CF_2HBr	10.07	12.13	14.27	16.47	18.71	21.00	23.32	25.67	28.05
CF_2ClBr	12.23	14.59	16.99	19.43	21.89	24.36	26.86	29.34	31.88
CCl_2HF	10.47	12.57	14.74	16.98	19.25	21.56	23.90	26.27	28.66
CCl_2FBr	11.29	13.47	15.70	17.97	20.29	22.63	25.00	27.40	29.81
CCl_2HBr	12.94	15.35	17.80	20.28	22.77	25.28	27.78	30.32	32.85
CBr_2HF	11.00	13.14	15.33	17.59	19.89	22.21	24.57	26.95	29.35
CBr_2HCl	11.54	13.73	15.98	18.26	20.58	22.94	25.35	27.71	30.13
CBr_2FCl	13.23	15.66	18.12	20.60	23.10	25.61	28.13	30.67	33.20
$CHFClBr$	10.75	12.88	15.07	17.31	19.59	21.91	24.26	26.63	29.03

employed where available. For other compounds they were calculated using experimental interatomic distances and angles, and in the absence of structural information a tetrahedral model was employed with interatomic distances for the C–H, C–F, C–Cl, C–Br and C–I bonds of 1.10, 1.34, 1.75, 1.91 and 2.10 Å. The products of the principal moments of inertia are listed in Table I.

The vibrational contributions to the thermodynamic functions were calculated with the aid of tables prepared by H. L. Johnston, L. Savedoff and J. Belzer.[18]

The vibrational frequency assignments were presented by the authors previously.[2] The numerical values of the fundamental frequencies for CF_4, CCl_4, CBr_4, CH_3F, CF_3Cl, CCl_3F, CCl_3Br, CBr_3Cl, CHF_3, $CHCl_3$, $CHBr_3$, CH_2F_2, CH_2Cl_2, CH_2Br_2, CF_2Cl_2,

(18) "Contributions to the Thermodynamic Functions by a Planck-Einstein Oscillator in One Degree of Freedom," Office of Naval Research, Department of the Navy, Washington, D. C., 1949.

TABLE V

THE FREE ENERGY FUNCTION, $-(F^0 - H_0^0)/T$, OF THE HALOGENATED METHANES

Compound	100°K.	150°K.	200°K.	250°K.	298.16°K.	300°K.	400°K.	500°K.	600°K.
CF_4	42.76	46.05	48.50	50.54	52.27	52.34	55.48	58.24	60.72
CCl_4	48.19	52.01	55.12	57.82	60.15	60.24	64.48	68.12	71.32
CBr_4	54.48	59.23	63.10	66.39	69.19	69.29	74.23	78.35	81.91
CH_3F	36.40	39.63	41.91	43.70	45.12	45.17	47.55	49.52	51.23
CH_3Cl	38.68	41.90	44.20	46.00	47.45	47.51	49.99	52.06	53.86
CH_3Br	41.47	44.70	47.01	48.80	50.31	50.37	52.89	55.02	56.88
CH_3I	42.88	46.11	48.44	50.29	51.79	51.84	54.44	56.61	58.44
CHF_3	43.62	46.88	49.25	51.18	52.77	52.83	55.63	58.06	60.22
CF_3Cl	47.20	50.56	53.15	55.32	57.19	57.26	60.66	63.63	66.29
CF_3Br	49.11	52.59	55.28	57.58	59.54	59.60	63.16	66.24	68.98
CF_3I	50.61	54.15	56.97	59.34	61.37	61.44	65.10	68.27	70.97
$CHCl_3$	48.82	52.34	55.07	57.35	59.29	59.36	62.83	65.81	68.44
CCl_3F	49.91	53.55	56.46	58.97	61.14	61.22	65.16	68.58	71.60
CCl_3Br	50.38	54.41	57.71	60.07	63.01	63.10	67.51	71.28	74.57
$CHBr_3$	54.39	58.37	61.48	64.07	66.26	66.34	70.21	73.47	76.32
$CFBr_3$	54.99	59.18	62.59	65.51	68.00	68.09	72.55	76.33	79.60
$CClBr_3$	55.79	60.25	63.90	67.03	69.70	69.80	74.56	78.55	82.01
CH_2F_2	41.46	44.69	47.02	48.85	50.34	50.39	52.95	55.10	57.01
CH_2Cl_2	45.69	49.02	51.46	53.44	55.08	55.14	58.03	60.36	62.60
CH_2Br_2	49.97	53.45	56.04	58.30	59.88	59.95	63.05	65.56	67.88
CH_2I_2	52.86	56.49	59.18	61.39	63.22	63.29	66.52	69.52	71.89
CF_2Cl_2	49.36	52.86	55.59	57.93	59.95	60.02	63.68	66.87	69.71
CF_2Br_2	53.04	56.82	59.84	62.43	64.65	64.73	68.72	72.20	75.18
CCl_2Br_2	55.01	59.25	62.70	65.69	68.25	68.34	72.91	76.79	80.17
CH_2FCl	45.02	48.30	50.67	52.58	54.14	54.19	56.89	59.19	61.22
CH_2FBr	47.34	50.65	53.07	55.04	56.65	56.69	59.50	61.88	63.98
CH_2ClBr	49.25	52.65	55.16	57.20	58.89	58.95	61.91	64.43	66.66
CH_2ClI	50.89	54.33	56.90	58.98	60.72	60.78	63.82	66.39	68.66
CH_2BrI	52.95	56.50	59.14	61.30	63.08	63.15	66.29	68.95	71.30
CF_2HCl	47.72	51.02	53.49	55.52	57.21	57.27	60.29	62.94	65.20
CF_2HBr	49.83	53.17	55.69	57.77	59.51	59.58	62.69	65.34	67.71
CF_2ClBr	52.64	56.27	59.13	61.59	63.70	63.78	67.70	70.90	73.82
CCl_2HF	49.41	52.81	55.36	57.55	59.37	59.43	62.68	65.46	67.94
CCl_2HBr	52.86	56.51	59.34	61.74	63.75	63.83	67.42	70.50	73.20
CCl_2FBr	53.77	57.58	60.65	63.30	65.58	65.67	69.79	73.34	76.45
CBr_2HF	53.42	57.04	59.85	62.18	64.16	64.23	67.79	70.72	73.34
CBr_2HCl	54.75	58.54	61.51	63.99	66.09	66.17	69.90	73.07	75.85
CBr_2FCl	55.49	59.49	62.71	65.31	67.90	67.98	72.27	75.94	79.14
$CHFClBr$	51.44	54.95	57.64	59.88	61.78	61.85	65.23	68.12	70.67

CCl_2Br_2, CH_2FCl, CH_2ClBr, CF_2HCl, CCl_2HF, CCl_2HBr and CBr_2HCl are taken from the recent infrared vapor phase studies of Plyler and Benedict.[19]

Those for CF_2HBr and CF_2ClBr[20] and for $CHFClBr$[21] are also based on the work of Plyler and co-workers.

The fundamentals for CH_3Cl and CH_3Br are as given by Decius.[22]

The fundamentals for CF_3Br and CF_3I are taken from the paper by Edgell and May,[23] the assignment of the two lowest frequencies of CF_3I being reversed.[2]

The source of the fundamental frequencies of the remaining compounds is the Landolt–Börnstein

(19) E. K. Plyler and W. S. Benedict, *J. Research Natl. Bur. Standards*, **47**, 202 (1951).

(20) E. K. Plyler and N. Acquista, *ibid.*, **48**, 92 (1952).

(21) E. K. Plyler and M. A. Lamb, *ibid.*, **46**, 382 (1951).

(22) J. C. Decius, *J. Chem. Phys.*, **16**, 214 (1948).

(23) W. F. Edgell and C. E. May, *ibid.*, **20**, 1822 (1952).

TABLE V (*Continued*)

Compound	700°K.	800°K.	900°K.	1000°K.	1100°K.	1200°K.	1300°K.	1400°K.	1500°K.
CF_4	62.98	65.07	67.02	68.83	70.53	72.12	73.62	75.05	76.40
CCl_4	74.18	76.75	79.09	81.41	82.48	84.40	86.82	88.43	89.96
CBr_4	85.03	87.83	90.32	92.64	94.75	96.70	98.51	100.20	101.80
CH_3F	52.78	54.22	55.56	56.84	58.04	59.20	60.29	61.35	62.37
CH_3Cl	55.51	57.03	58.21	59.78	61.04	62.24	63.39	64.48	65.54
CH_3Br	58.57	60.12	61.58	62.94	64.22	65.44	66.61	67.72	68.79
CH_3I	60.27	61.95	63.34	64.73	66.05	67.29	68.48	69.61	70.69
CHF_3	62.19	64.02	65.73	67.33	68.83	70.26	71.61	72.89	74.12
CF_3Cl	68.71	70.92	72.95	74.85	76.63	78.29	79.85	81.32	82.72
CF_3Br	71.47	73.73	75.82	77.75	79.55	81.24	82.82	84.32	85.73
CF_3I	73.59	75.89	78.01	79.97	81.79	83.49	85.10	86.61	88.03
$CHCl_3$	70.80	72.96	74.94	76.78	78.49	80.09	81.59	83.01	84.36
CCl_3F	74.34	76.75	79.00	81.07	82.99	84.78	86.45	88.02	89.50
CCl_3Br	77.49	80.13	82.51	84.71	86.73	88.61	90.35	92.99	93.53
$CHBr_3$	78.85	81.15	83.24	85.17	86.96	88.62	90.18	91.65	93.04
$CFBr_3$	82.52	85.14	87.52	89.69	91.70	93.56	95.31	96.94	98.48
$CClBr_3$	85.07	87.80	90.28	92.54	94.62	96.54	98.33	100.01	101.58
CH_2F_2	58.74	60.36	61.85	63.27	64.62	65.89	67.10	68.26	69.37
CH_2Cl_2	64.56	66.35	68.03	69.58	71.05	72.43	73.73	74.99	76.17
CH_2Br_2	69.94	71.82	73.56	75.18	76.70	78.12	79.47	80.75	81.96
CH_2I_2	73.75	75.70	77.51	79.18	80.73	82.20	83.58	84.89	86.14
CF_2Cl_2	72.26	74.59	76.74	78.73	80.57	81.29	83.91	85.43	86.87
CF_2Br_2	77.87	80.32	82.56	84.62	86.52	88.30	89.97	91.54	93.01
CCl_2Br_2	83.15	85.84	88.27	90.50	92.54	94.44	96.21	97.87	99.42
CH_2FCl	63.06	64.76	66.35	67.82	69.24	70.57	71.82	73.03	74.18
CH_2FBr	65.87	67.62	69.25	70.77	72.19	73.54	74.83	76.05	77.22
CH_2ClBr	68.66	70.50	72.31	73.90	75.38	76.68	78.02	79.28	80.48
CH_2ClI	70.70	72.59	74.31	75.93	77.44	78.87	80.22	81.48	82.70
CH_2BrI	73.39	75.31	77.11	78.72	80.26	81.71	83.09	84.37	85.59
CF_2HCl	67.30	69.23	71.02	72.70	74.27	75.75	77.14	78.47	79.74
CF_2HBr	69.87	71.84	73.66	75.36	76.96	78.46	79.88	81.23	82.50
CF_2ClBr	76.44	78.82	81.01	83.03	84.90	86.66	88.29	89.81	91.29
CCl_2HF	70.18	72.23	74.11	75.87	77.52	79.06	80.52	81.90	83.20
CCl_2HBr	75.62	77.82	79.84	81.71	83.45	85.07	86.59	88.02	89.39
CCl_2FBr	79.24	81.75	84.05	86.15	88.12	89.93	91.63	93.22	93.72
CBr_2HF	75.71	77.85	79.82	81.64	83.35	84.94	86.44	87.85	89.18
CBr_2HCl	78.62	81.58	82.63	84.53	86.29	87.94	89.48	90.93	92.31
CBr_2FCl	81.99	84.55	86.90	89.04	91.02	92.87	94.58	96.20	97.72
CHFClBr	72.97	75.07	77.00	78.80	80.48	82.04	83.52	84.91	86.24

Tabellen,[24] with assignments as given by the present authors.[2]

The rigid rotator-harmonic oscillator approximation, the uncertainty of several wave numbers in the fundamental frequencies and a possible error of a few per cent. in the product of the principal moments of inertia places a limit on the accuracy of the calculated thermodynamic functions of ±0.1 cal./deg. mole. At the higher temperatures the effect of anharmonicity may be substantial but the data are not available for its inclusion. Consequently, the error in these functions may well exceed ±0.1 cal./deg. mole at the higher temperatures.

The calculated thermodynamic properties presented in this paper are in good agreement with the available experimental data. Table II gives the comparison for the entropy values. The error in the experimental entropy values is of the order of ±0.2 cal. deg./mole.

(24) Landolt-Börnstein "Tabellen," Sixth edition, Vol. I, parts 2 and 3, Springer-Verlag, Berlin, 1951.

TABLE VI

THE ENTROPY, S^0, OF THE HALOGENATED METHANES

Compound	100°K.	150°K.	200°K.	250°K.	298.16°K.	300°K.	400°K.	500°K.	600°K.
CF_4	50.76	54.34	57.33	60.05	62.48	62.57	67.18	71.27	74.93
CCl_4	57.01	62.16	66.63	70.55	73.94	74.07	80.10	85.13	89.41
CBr_4	65.26	71.94	77.29	81.78	85.53	85.66	92.16	97.43	101.85
CH_3F	44.35	47.58	49.88	51.72	53.24	53.30	56.07	58.61	60.98
CH_3Cl	46.63	49.87	52.23	54.16	55.80	55.86	58.91	61.70	64.19
CH_3Br	49.42	52.69	55.10	56.97	58.82	58.89	62.04	64.90	67.48
CH_3I	50.84	54.14	56.62	58.69	60.47	60.53	63.83	66.76	69.42
CHF_3	51.60	55.00	57.67	60.00	62.04	62.12	65.96	69.44	72.60
CF_3Cl	55.30	59.18	62.52	65.54	68.23	68.32	73.29	77.63	81.45
CF_3Br	57.36	61.55	65.12	68.31	71.09	71.20	76.31	80.73	84.59
CF_3I	59.02	63.44	67.17	70.46	73.32	73.41	78.61	83.08	86.98
$CHCl_3$	57.19	61.43	64.94	68.00	70.66	70.76	75.58	79.74	83.37
CCl_3F	58.42	63.11	67.18	70.81	73.96	74.08	79.77	84.57	88.70
CCl_3Br	59.61	65.17	69.88	72.83	77.45	77.57	83.73	88.82	93.13
$CHBr_3$	63.70	68.73	72.73	76.13	79.03	79.14	84.30	88.64	92.39
$CFBr_3$	64.60	70.36	75.11	79.20	82.65	82.76	88.83	93.85	98.11
$CClBr_3$	65.93	72.20	77.34	81.69	85.36	85.49	91.88	97.08	101.47
CH_2F_2	49.41	52.71	55.16	57.18	58.92	58.98	62.22	65.16	67.88
CH_2Cl_2	53.77	57.37	60.15	62.52	64.59	64.66	68.62	71.67	74.90
CH_2Br_2	58.37	62.28	65.25	68.28	70.02	70.10	74.31	77.70	80.85
CH_2I_2	61.57	65.65	68.81	71.54	73.88	73.96	78.29	82.67	85.88
CF_2Cl_2	57.65	61.91	65.60	68.93	71.84	71.95	77.27	81.85	85.83
CF_2Br_2	61.83	66.76	70.93	74.58	77.72	77.83	83.44	88.24	92.25
CCl_2Br_2	64.64	70.56	75.46	79.69	83.27	83.40	89.66	94.82	99.17
CH_2FCl	53.02	56.45	59.06	61.26	63.16	63.23	66.74	69.91	72.80
CH_2FBr	55.39	58.91	61.67	63.99	65.97	66.05	69.70	72.97	75.91
CH_2ClBr	57.46	61.21	64.10	66.56	68.71	68.79	72.72	76.19	79.29
CH_2ClI	59.21	63.05	66.70	68.59	70.78	70.87	74.90	78.43	81.57
CH_2BrI	61.50	65.48	68.58	71.21	73.49	73.58	77.74	81.35	84.55
CF_2HCl	55.75	59.38	62.32	64.88	67.13	67.21	71.38	75.26	78.38
CF_2HBr	57.92	61.67	64.73	67.39	69.71	69.80	74.09	77.85	81.22
CF_2ClBr	61.15	65.74	69.65	73.13	76.14	76.25	81.71	86.36	90.38
CCl_2HF	57.58	61.50	64.56	67.55	70.00	70.09	74.60	78.54	82.02
CCl_2HBr	61.47	65.97	69.65	72.84	75.58	75.68	80.62	84.84	88.51
CCl_2FBr	62.59	67.66	71.98	75.78	79.05	79.16	85.00	89.88	94.07
CBr_2HF	62.01	66.40	69.99	72.79	75.70	75.79	80.75	84.65	88.18
CBr_2HCl	63.66	68.42	72.27	75.56	78.39	78.49	83.55	87.80	91.54
CBr_2FCl	64.67	70.09	74.63	78.59	81.95	82.08	88.03	92.99	97.22
$CHFClBr$	59.80	63.96	67.37	70.32	72.88	72.97	77.63	81.64	85.18

In addition heat capacity measurements have been made on a number of halogenated methanes. CF_2Cl_2 was investigated by Masi[25] whose results are about 0.1 cal./deg. mole higher than the calculated values. Masi accounts for the difference by a shift of one frequency and anharmonicity. We do not believe that frequency change is justifiable on the basis of the spectroscopic data, and would be inclined to ascribe the entire difference to anharmonicity. Masi's calculated functions are consistent with his experimental data and are to be preferred for some purposes. However, we have preferred to give values consistent with the remainder of our tables, *i.e.*, omitting anharmonicity.

(25) J. G. Masi, *ibid.*, **74**, 4738 (1952); see also R. M. Buffington and J. Fleischer, *Ind. Eng. Chem.*, **23**, 1291 (1931); A. Eucken and A. Bertram, *Z. physik. Chem.*, **B31**, 361 (1936).

TABLE VI (*Continued*)

Compound	700°K.	800°K.	900°K.	1000°K.	1100°K.	1200°K.	1300°K.	1400°K.	1500°K.
CF_4	78.20	81.17	83.87	86.32	88.61	90.71	92.65	94.47	96.18
CCl_4	93.12	96.39	99.30	101.93	104.33	106.52	108.55	110.44	112.19
CBr_4	105.65	108.98	111.91	114.61	117.03	119.25	121.28	123.17	124.94
CH_3F	63.21	65.32	67.31	69.21	71.00	72.71	74.33	75.88	77.15
CH_3Cl	66.55	68.75	70.30	71.75	74.58	76.32	77.97	79.52	81.01
CH_3Br	69.88	72.12	74.21	76.16	78.01	79.75	81.41	82.98	84.47
CH_3I	71.88	74.15	76.26	78.24	80.10	81.86	83.53	85.10	86.60
CHF_3	75.48	78.13	80.58	82.84	84.94	86.89	88.72	90.44	92.06
CF_3Cl	84.85	87.90	90.66	93.17	95.48	97.60	99.58	101.40	103.13
CF_3Br	88.03	91.10	93.88	96.39	98.71	100.83	102.82	104.66	106.38
CF_3I	90.44	93.53	96.32	98.84	101.16	103.30	105.28	107.13	108.85
$CHCl_3$	86.59	89.47	92.08	94.47	96.67	98.70	100.59	102.35	104.02
CCl_3F	92.31	95.51	98.38	100.97	103.34	105.51	107.52	109.39	111.01
CCl_3Br	96.88	100.16	103.08	105.72	108.12	110.33	112.35	114.23	115.99
$CHBr_3$	95.69	98.63	101.29	103.71	105.93	107.98	109.88	111.66	113.34
$CFBr_3$	101.81	105.06	107.97	110.59	112.98	115.16	117.19	119.07	120.83
$CClBr_3$	105.26	108.57	111.53	114.17	116.57	118.80	120.84	122.73	124.48
CH_2F_2	70.42	72.78	74.98	77.05	78.99	80.81	82.54	84.16	85.70
CH_2Cl_2	77.66	80.18	82.52	84.67	86.68	88.56	90.32	92.00	93.66
CH_2Br_2	83.69	86.27	88.64	90.82	92.86	94.75	96.54	98.21	99.79
CH_2I_2	88.05	90.68	93.09	95.30	97.35	99.28	101.06	102.74	104.34
CF_2Cl_2	89.34	92.46	95.28	97.84	100.18	102.32	104.31	106.16	107.90
CF_2Br_2	95.83	99.00	101.85	104.42	106.78	108.94	110.94	112.81	114.55
CCl_2Br_2	102.92	106.23	109.16	111.81	114.21	116.42	118.46	120.34	122.09
CH_2FCl	75.44	77.89	80.16	82.25	85.23	86.08	87.83	89.47	91.03
CH_2FBr	78.60	81.08	83.37	85.50	87.46	89.34	91.10	92.75	94.31
CH_2ClBr	82.09	84.64	86.99	89.17	91.18	93.08	94.85	96.52	98.09
CH_2ClI	84.40	86.98	89.34	91.52	93.55	95.45	97.23	98.86	100.48
CH_2BrI	87.43	90.03	92.47	94.61	96.66	98.56	100.38	102.03	103.62
CF_2HCl	81.39	84.11	86.60	88.90	91.03	93.01	94.86	96.59	98.23
CF_2HBr	84.25	87.00	89.51	91.83	93.98	95.96	97.83	99.56	101.20
CF_2ClBr	93.91	97.06	99.89	102.46	104.80	106.96	108.95	110.77	112.55
CCl_2HF	85.30	87.95	90.51	92.85	95.02	97.03	98.90	100.66	102.31
CCl_2HBr	91.75	94.65	97.28	99.68	101.89	103.93	105.82	107.59	109.25
CCl_2FBr	97.72	100.95	103.83	106.43	108.82	110.99	113.01	114.88	116.63
CBr_2HF	91.42	94.28	96.86	99.24	101.43	103.45	105.34	107.09	108.75
CBr_2HCl	94.82	97.75	100.38	102.79	105.01	107.05	108.95	110.73	112.40
CBr_2FCl	100.89	104.13	107.03	109.64	112.02	114.23	116.22	118.10	119.85
$CHFClBr$	88.33	91.16	93.74	96.11	98.29	100.30	102.18	103.94	105.59

Heat capacity measurements on CF_2HCl, CCl_2HF and CCl_3F[26,27] have yielded data in fair agreement with the present calculations. For example, the experimental heat capacities at constant pressure C_p° at 407.5°K. are 15.77, 16.99 and 21.04 cal./deg. mole for CF_2HCl, CCl_2HF and CCl_3F, respectively, compared with calculated values of 15.79, 16.91 and 20.98. At lower temperatures the agreement is not as good.

More recently, the increasing technical importance of the halogenated methanes has led to the study and tabulation of thermodynamic properties of halogenated methanes used particularly in refrigeration.[28]

There are at present relatively few reliable data on the heat of formation of these substances. Consequently we have not attempted at this time to discuss either heat or free energy of formation data. The tables presented herewith should find a variety of applications.

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