Ideal Gas Thermodynamic Properties of the Eight Bromo- and Iodomethanes

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The available molecular parameters, fundamental frequencies, and enthalpy of formation for eight bromo- and iodomethanes have been critically evaluated and recommended values selected. 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 using the rigid rotor-harmonic oscillator approximation.

Key words: Bromomethanes; critically evaluated data; ideal gas thermodynamic properties; iodomethanes.

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1. Introduction

1.1. Scope and Objectives

This report involves the calculation of the ideal gas thermodynamic properties of eight bromine and iodine derivatives of methane. For this purpose, a systematic literature survey complete up to December 1972 was carried out and the pertinent information was compiled. The available data on vibrational frequencies, structural parameters, and enthalpies of formation have been critically examined and the recommended values have been selected. The properties tabulated are heat capacity, C_p°; entropy, S°; relative enthalpy, $H^\circ - H_0^\circ$; Gibbs energy function, $(G^\circ - H_0^\circ)/T$, enthalpy of formation, ΔHf°; Gibbs energy of formation, ΔGf°; and the equilibrium constant of formation, log *Kf*. Values are reported at temperatures from 0 to 1500 K at 100 deg. intervals and at 273.15 and 298.15 K (henceforth referred to as 298). The first four properties have been calculated from the partition function based on the rigid-rotor harmonic oscillator approximations. The $\Delta Hf°(298)$ and the calculated thermal functions have been used to calculate $\Delta Hf°$, $\Delta Gf°$ and log *Kf* at various temperatures by the usual thermodynamic formulae.

The ideal gas thermodynamic properties are useful (1) in calculating values of the real gas properties required in design calculations, and (2) for testing correlation procedures for predicting properties of more complex halogenated compounds. When *P–V–T* data are not available to compute the difference between the real gas and the ideal gas property, the ideal gas thermodynamic properties serve as useful approximations for the real gas properties.

For each compound the discussion is centered around the following topics:

a) Molecular parameters
b) Fundamental frequencies
c) Enthalpy of formation
d) Thermal properties
e) Comparison with literature data

Important literature sources are cited and their experimental data are discussed in detail resulting in systematic evaluation and proper selection of recommended values. All references for a particular property are also given. In many cases, Shimanouchi's assignments of the fundamental frequencies [1, 2, 3][1] have been adopted. The selection of the $\Delta Hf°(298)$ is based partly upon the compilations of Wagman et al. [4], Stull et al., [5] and Cox and Pilcher [6]. In some cases the ΔH_v values (enthalpy of vaporization values) are required. These were taken from the literature, or calculated using the Clapeyron equation:

$$(dP/dT) = \Delta H_v/T\Delta V \cong \Delta H_v P/RT^2. \quad (1)$$

The ideal gas correction to ΔH_v has been calculated using the standard procedures.

The thermal properties computed in the present investigation are compared with the reliable literature values in tables 16 to 19.

1.2. Physical Constants

Values of the physical constants used in this work are given below [7].

Constant	Symbol	Value	Units
Speed of light in vacuum	c	2.9979250×10^8	m s^{-1}
Avogadro number	N	6.022169×10^{23}	molecules mol^{-1}
Planck constant	h	6.626186×10^{-34}	J s
Boltzmann constant	k	1.380621×10^{-23}	J K^{-1}
Gas constant	R	1.98717	cal K^{-1} mol^{-1}

The currently approved atomic weights used in these calculations are: carbon 12.011; hydrogen, 1.008; bromine, 79.904; iodine, 126.9045 [8]. Following the practice of related compilations [4–6], thermodynamic properties are given in units of cal/mol. For conversion to SI units, 1 cal = 4.184 J.

1.3. Uncertainties

The uncertainties in the derived thermal properties are a result of the uncertainties in the measured quantities, i.e., molecular parameters, fundamental frequencies, and $\Delta Hf°$ values, etc. and of the neglect of the effect of anharmonicity, rotational stretching, etc. In some cases authors' reported uncertainties were available. When they were not available, the uncertainties were estimated based upon our past experience. If an average of two or more values is the selected value, then the uncertainty in this value is taken to be the largest uncertainty from among the averaged values. The uncertainties in the thermal properties were computed using the principle of the propagation of errors. For this purpose, the maximum uncertainty in the measured properties were used, and the estimated maximum uncertainties for each of the derived quantities for each compound are given in the respective thermal functions table.

1.4. Auxiliary Data

The enthalpies of formation of various compounds at 298 K used in these calculations were taken from Wagman [4] and are given in table 1.

TABLE 1. Enthalpy of formation of key compounds

Compound	$\Delta Hf°(298)$ kcal mol^{-1}
$CH_4(g)$	−17.88
$Br_2(g)$	+7.387
$I_2(g)$	14.923
HCl(g)	−22.062
HBr(g)	−8.70
HI(g)	+6.33
$Br_2(l)$	0.00

The thermodynamic properties of the elements in their reference states used in the calculation of $\Delta Hf°$, $\Delta Gf°$, and log *Kf* for the compounds studied are given in table 2 and are taken from the following references.

1. Graphite—National Bureau of Standards report 6928, Table B–39 by W. Evans for the range 0 to 1200 K (1960); West and Ishihara, "Advances in Thermophysical Properties at Extreme Temperatures and Pressures", A.S.T.M. (1965).
2. Hydrogen—TRC Tables [9].
3. Bromine—JANAF Tables [10], Hildenbrand, et al. [11].
4. Iodine—JANAF Tables [10], Hultgren, et al. [12].

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

TABLE 2. Thermodynamic properties of elements

T,K	Carbon, graphite C		Hydrogen, gas, H_2^a		Bromine, Br_2^b		Iodine, I_2^c	
	$H^\circ - H_0^\circ$ cal mol^{-1}	$(G^\circ - H_0^\circ)/T$ cal K^{-1} mol^{-1}	$H^\circ - H_0^\circ$ cal mol^{-1}	$(G^\circ - H_0^\circ)/T$ cal K^{-1} mol^{-1}	$H^\circ - H_0^\circ$ cal mol^{-1}	$(G^\circ - H_0^\circ)/T$ cal K^{-1} mol^{-1}	$H^\circ - H_0^\circ$ cal mol^{-1}	$(G^\circ - H_0^\circ)/T$ cal K^{-1} mol^{-1}
100	14.7	−0.081	759.9	−16.798	668.0	−6.190	729.0	−7.290
150	43.5	−0.166	1046.0	−19.733	1223.9	−9.206	1302.2	−10.537
200	92.5	−0.276	1361.6	−21.712	1839.0	−11.703	1907.0	−13.160
273.15	202.8	−0.469	1853.3	−23.801	5403.0	−15.007	2830.3	−16.267
298.15	251.2	−0.530	2023.7	−24.418	5859.0	−16.733	3154.0	−17.179
300	255.0	−0.536	2036.4	−24.462	5892.0	−16.854	3178.0	−17.245
400	502.0	−0.837	2730.9	−26.422	14032.0	−25.873	8350.0	−20.727
500	821.0	−1.157	3429.4	−27.948	15015.0	−33.142	19873.0	−27.130
600	1198.0	−1.488	4129.4	−29.201	15903.0	−38.286	20770.0	−33.895
700	1622.0	−1.821	4831.5	−30.264	16796.0	−42.173	21669.0	−38.941
800	2082.0	−2.150	5537.1	−31.187	17692.0	−45.249	22570.0	−42.888
900	2569.0	−2.472	6248.1	−32.002	18590.0	−47.766	23474.0	−46.083
1000	3074.0	−2.790	6966.2	−32.734	19490.0	−49.880	24379.0	−48.740
1100	3595.0	−3.080	7692.5	−33.400	20392.0	−51.691	25286.0	−50.996
1200	4132.0	−3.380	8428.0	−34.010	21295.0	−53.270	26195.0	−52.945
1300	4682.0	−3.660	9173.7	−34.574	22200.0	−54.662	27104.0	−54.653
1400	5242.0	−3.940	9929.9	−35.099	23106.0	−55.907	28016.0	−56.166
1500	5810.0	−4.200	10696.9	−35.589	24014.0	−57.028	28929.0	−57.521

[a] Normal.

[b] Reference state: 0 K–265.90 K (crystal); 265.90 K–332.62 K (liquid); 332.62 K onwards (gas).

[c] Reference state: 0 K–386.75 K (crystal); 386.75 K–458.38 K (liquid); 458.38 K onwards (gas).

2. Bromomethane (Methyl Bromide)

Miller et al. [13] made microwave measurements on seven isotopic species from which they calculated the structural parameters. Costain [14] used the data of Miller et al. and recalculated the structural parameters, taking into account the changes in the average bond distances with isotopic substitution. These values of Costain being most reliable, are adopted in this work and are presented in table 3. Earlier studies on structural parameters have been summarized in ref. [15].

Shimanouchi [2] has critically reviewed the infrared and Raman spectral data for CH_3Br. His selected values for the vibrational frequencies for the gaseous state are adopted in this work and are presented in table 4. Other references on infrared and Raman work are refs. [16 to 24].

The enthalpy of formation of CH_3Br reported in NBS Circular 500 [25] is −8.5 kcal mol^{-1} at 298 K and was based on very early measurements of Thomsen [26] and of Berthelot [27]. The more recent NBS compilation [4] recommends $\Delta Hf^\circ = -8.4$ kcal mol^{-1}. Equilibrium studies of Bak [28] for reaction (2) result in $\Delta H_r^\circ(2{,}298) = -2.4 \pm 0.10$ kcal mol^{-1}.

$$CH_3Cl(g) + HBr(g) \rightleftharpoons CH_3Br(g) + HCl(g) \qquad (2)$$

Combining Bak's ΔH_r° value with $\Delta Hf^\circ(CH_3Cl, g, 298) = -19.59$ [29], ΔHf° for HCl, and HBr (table 1), we have calculated $\Delta Hf^\circ(CH_3Br, g, 298) = -8.64 \pm 0.14$ kcal mol^{-1}.

Carson et al. [30] obtained ΔHf° $(CH_3Br, g, 298) = 8.6$ kcal mol^{-1} based upon a complex thermochemical reaction which involves both the heat of combustion

TABLE 3. Structural data and principal moments of inertia for bromo- and iodomethanes [a]

Compound	C—H	C—X [b]	∠ HCH	∠ HCX	∠ XCX	I_A	I_B	I_C
CH_3Br	1.0954	1.9388	111.63	107.23	–	3.311	52.727	52.727
CH_2Br_2	1.097	1.925	110.9	–	112.9	19.466	412.956	429.131
$CHBr_3$	1.068	1.930	–	107.89	111.0	410.996	410.996	808.594
CBr_4	–	1.942	–	–	109.47	803.592	803.592	803.592
CH_3I	1.084	2.132	111.2	107.63	–	3.226	66.831	66.831
CH_2I_2	1.09 [c]	2.12	111.3 [c]	–	114.7	22.758	805.025	824.538
CHI_3	1.09 [c]	2.12	–	105.65	113.0	799.743	799.743	1586.434
CI_4	–	2.135	–	–	109.47	1542.588	1542.588	1542.588

[a] Units: Bond length—angstrom (10^{-8} cm); Bond angle—degrees; Moments of inertia—amu Å^2.

[b] x = Br or I.

[c] Estimated values.

TABLE 4. Vibrational frequencies for bromo- and iodomethanes[a,b]

Compound	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9
CH_3Br	2935	1305	611	3075(2)	1443(2)	954(2)	—	—	—
CH_2Br_2	3009	1382	588	174	1096	3076	812	1195	653
$CHBr_3$	3050	543	223	1149(2)	669(2)	155(2)	—	—	—
CBr_4	267	123(2)	672(3)	183(3)	—	—	—	—	—
CH_3I	2933	1252	533	3060(2)	1437(2)	882(2)	—	—	—
CH_2I_2	2967	1350	484	127	1031	3047	716	1108	570
CHI_3	2974	427	153	1065(2)	573(2)	111(2)	—	—	—
CI_4	178	90(2)	555(3)	123(3)	—	—	—	—	—

[a] Numbers in parenthesis are degeneracies.
[b] Distribution of vibrational frequencies in various species:

$CX_3Y : 3A+3E$
$CX_2Y_2: 4A_1+1A_2+2B_1+2B_2$
$CX_4 \; : 1A_1+1E+2F$

of mercury dimethyl and its reaction with alcoholic solution of bromine. This ΔHf° value is subject to more error than the other values mentioned.

The enthalpy of hydrogenation of CH_3Br for reaction (3) has been measured by Fowell et al. [31] at 523.15 K. They obtained ΔH_r° (3, 523.15) $=-18.06\pm0.325$ kcal mol^{-1}.

$$CH_3Br\,(g)+H_2\,(g)=CH_4\,(g)+HBr\,(g) \qquad (3)$$

The enthalpy change for this reaction has been corrected to 298 K with Kirchoff equation (4) using C_p° data for CH_4 [32], H_2 [9], HCl [10] and CH_3Br (this work),

$$\Delta H_r^\circ, T_2-\Delta H_r^\circ, T_1=\int_{T_1}^{T_2}\Delta C_p^\circ dT, \qquad (4)$$

yield ΔH_r° (298) $=-17.57\pm0.33$ kcal mol^{-1}. This value combined with ΔHf° (298) for CH_4 and HBr (table (1)) yields ΔHf° (CH_3Br, g, 298) $=-9.01\pm0.36$ kcal mol^{-1}.

Adams et al. [33] have measured the enthalpy of reaction for reaction (5).

$$CH_3Br\,(l)+\frac{1}{2}\,H_2\,(g)=CH_4\,(g)+\frac{1}{2}\,Br_2\,(l) \qquad (5)$$

They obtained ΔH_r° (5, 298) $=-3.30\pm0.30$ kcal mol^{-1}. From this value, ΔHf° (CH_3Br, l, 298) $=-14.58$ kcal mol^{-1} is obtained using auxiliary data given in table 2. Egan and Kemp [34] measured the enthalpy of vaporization $\Delta H_v=5.715$ kcal mol^{-1} calorimetrically at 276.66 K. Their reference temperature was 273.10 K. Hence 276.66 K corresponds to 276.71 K with 273.15 K as the reference temperature. The correction to the ideal gas was made using the Berthelot equation of state (6) and relevant critical data [33] to give ΔH_v° (276.71) $=5.76$ kcal mol^{-1}.

$$v_g=RT/P+(9/128)(RT_c/P_c)(1-6T_c^2/T^2) \qquad (6)$$

The liquid phase heat capacity data of Egan and Kemp combined with the gas phase heat capacity (this work) yields $\Delta H_v^\circ(298)=5.56\pm0.05$ kcal mol^{-1}. This value combined with ΔHf°(CH_3Br, l, 298) $=-14.58$ kcal mol^{-1} gives ΔHf°(CH_3Br, g, 298) $=-9.02\pm0.35$ kcal mol^{-1}. This value is in excellent agreement with that of Fowell et al. The available ΔHf° (CH_3Br, g, 298) values are summarized in table 5. ΔHf° (CH_3Br, g, 298) $=-9.02\pm0.36$ kcal mol^{-1} is adopted in this work. This is in good agreement with Cox and Pilcher's recommendation of -9.1 ± 0.3 kcal mol^{-1} [6].

TABLE 5. Enthalpy of formation data for bromomethane (CH_3Br)

Author(s)	ΔHf°(g, 298) kcal mol^{-1}
Bak (1948)	-8.64 ± 0.14
NBS Circular 500 (1952)	-8.5
Carson et al. (1952)	-8.6
Fowell et al. (1965)	-9.01 ± 0.36
Adams et al. (1966)	-9.02 ± 0.35
Wagman et al. (1968)	-8.4
Cox and Pilcher (1970)	$-9.1\ \pm0.3$
Selected (1973)	-9.02 ± 0.36

The ideal gas thermal functions were calculated using the data given in tables 3 and 4 and are presented in table 6.

Egan and Kemp [34] have reported experimental entropy of the real gas at its boiling point: S^r(CH_3Br, g, 276.71) $=57.74\pm0.1$ cal $K^{-1}\,\text{mol}^{-1}$. The correction for the ideal gas from the Berthelot equation using more recent critical constants [35] is 0.16. This gives S°(CH_3Br, g, 276.71) $=57.90\pm0.15$ cal K^{-1} mol^{-1} as compared to our calculated value of 58.02 ± 0.06 cal K^{-1} mol^{-1}.

3. Dibromomethane (Methylene Bromide)

Microwave studies were made for the first time by Krishnaji et al. [36] on two symmetric isotopic species $CH_2^{79}Br_2$ and $CH_2^{81}Br_2$. Chadwick and Millen [37] studied the microwave spectra of $CH_2^{79}Br_2$, $CH_2^{81}Br_2$, $CD_2^{79}Br_2$ and $CD_2^{81}Br_2$ species and recommended the structural parameters for CH_2Br_2 which are adopted in this work. These are given in table 3. Earlier studies have been summarized in ref. [15].

Shimanouchi [2] has critically reviewed the infrared and Raman spectral data for CH_2Br_2 and selected the

TABLE 6. Ideal gas thermodynamic properties of bromomethane (CH_3Br)

Temp.	C_p°	S°	$-(G^\circ-H_0^\circ)/T$	$H^\circ-H_0^\circ$	ΔHf°	ΔGf°	log Kf
K	cal deg^{-1} mol^{-1}			kcal mol^{-1}			
0	0.0000	0.0000	0.0000	0.0000	−5.340	−5.340	Infinite
100.00	7.973	49.367	41.415	0.795	−6.032	−6.644	14.52124
150.00	8.181	52.630	44.644	1.198	−6.367	−6.881	10.02627
200.00	8.658	55.043	46.954	1.618	−6.777	−6.992	7.64024
273.15	9.723	57.890	49.514	2.288	−8.736	−6.935	5.54893
298.15	10.147	58.760	50.253	2.536	−9.020	−6.750	4.94798
300.00	10.179	58.823	50.305	2.555	−9.041	−6.735	4.90640
400.00	11.938	61.992	52.839	3.661	−13.343	−5.113	2.79374
500.00	13.566	64.835	54.959	4.938	−13.875	−2.944	1.30887
600.00	14.978	67.436	56.824	6.367	−14.317	−0.775	0.28240
700.00	16.196	69.839	58.514	7.927	−14.680	1.512	−0.47219
800.00	17.259	72.072	60.071	9.601	−14.973	3.847	−1.05097
900.00	18.191	74.160	61.522	11.375	−15.202	6.213	−1.50860
1000.00	19.010	76.120	62.885	13.236	−15.373	8.606	−1.88090
1100.00	19.728	77.966	64.173	15.173	−15.497	10.998	−2.18512
1200.00	20.357	79.710	65.395	17.178	−15.583	13.421	−2.44437
1300.00	20.909	81.362	66.561	19.242	−15.641	15.839	−2.66271
1400.00	21.391	82.930	67.674	21.358	−15.672	18.275	−2.85279
1500.00	21.815	84.420	68.741	23.518	−15.684	20.694	−3.01509
Maximum uncertainty	±0.03	±0.06	±0.04	±0.03	±0.03	±0.05	±0.010

assignments for the liquid state. Recently Dennen et al. [38] have reported infrared measurements in the gaseous state and their assignments are in good agreement with those of Plyler et al. [39]. Brown et al. [40] studied the infrared and Raman spectra for various states for crystal structure determination. Their values in gaseous state compare very well with those of Dennen et al. We have therefore adopted Dennen et al.'s values in this work which are reported in table 4. Other references for infrared and Raman work are refs. [19] and [41] to [47].

The enthalpy of formation of CH_2Br_2 has not yet been measured. It has been shown by Bernstein [48] and Rodgers [49] that fairly accurate estimates can be made by applying the bond additivity scheme corrected for near neighbor bond interactions taken two at a time [50] or two and three at a time [51]. With Allen's scheme [51], the enthalpy of formation of CH_2Br_2 is related to the enthalpies of formation of CH_4, CH_3Br, $CHBr_3$ and CBr_4 by equation (7).

$$1.5\Delta Hf^\circ(CH_2Br_2, g, 298) = -0.25[\Delta Hf^\circ(CH_4, g, 298) + \Delta Hf^\circ(CBr_4, g, 298)] + \Delta Hf^\circ(CH_3Br, g, 298) + \Delta Hf^\circ(CHBr_3, g, 298) \tag{7}$$

Using ΔHf° (CH_4) (table 1) and values adopted in this work for other compounds, ΔHf° (CH_2Br_2, g, 298)$=-3.53\pm0.8$ kcal mol^{-1} is obtained which is adopted.

The ideal gas thermal functions are calculated using the data given in tables 3 and 4 and are presented in table 7. No experimental gaseous heat capacity or entropy are available for comparison of the calculated values.

4. Tribromomethane (Bromoform)

Williams et al. [52] made microwave measurement on four isotopic species $CH^{79}Br_3$, $CH^{81}Br_3$, $CD^{79}Br_3$ and $CD^{81}Br_3$ from which they calculated the structural parameters. These are consistent with the earlier work summarized in ref. [15]. The values of Williams et al. are adopted in this work and are given in table 3.

Shimanouchi [3] has critically reviewed the infrared and Raman spectral data. He has selected assignments for the gaseous state except for two which are not observed in the gaseous state and hence were selected from Raman data on the liquid state. Recently Berger and Cichon [53] have reported more accurate vibrational frequencies for this molecule from their infrared measurements for gaseous state. Only ν_6 was recorded for liquid state. They compare very well with Shimanouchi's values. Their assignments are adopted in this work and are presented in table 4. Other references on infrared and Raman work are refs. [19] and [54] to [58].

The enthalpy of formation of $CHBr_3$ reported in NBS Circular 500 [25] is 6.0 kcal mol^{-1} at 298 K. More recent NBS compilation [4] recommends ΔHf°($CHBr_3$, g, 298)$=4.0$ kcal mol^{-1}. The other value available in the literature is 19.0 kcal mol^{-1} from Bernstein [48] which is calculated from the bond dissociation data. Furuyama et al. [59] recommend Bernstein's value on the basis that the second difference in the enthalpy of formation (ΔHf°) for the series $CH_4 \rightarrow CBr_4$ is consistent with Bernstein's values and not with Wagman's [4] values.

TABLE 7. Ideal gas thermodynamic properties of dibromomethane (CH_2Br_2)

Temp	C_p°	S°	$-(G^\circ-H_0^\circ)/T$	$H^\circ-H_0^\circ$	ΔHf°	ΔGf°	log Kf
K	cal deg^{-1} mol^{-1}			kcal mol^{-1}			
0	0.0000	0.0000	0.0000	0.0000	1.589	1.589	Infinite
100.00	9.204	58.479	50.082	0.840	0.987	−1.112	2.43074
150.00	9.967	62.351	53.561	1.318	0.594	−2.079	3.02964
200.00	10.917	65.344	56.145	1.840	0.136	−2.902	3.17088
273.15	12.497	68.978	59.110	2.696	−3.174	−3.828	3.06294
298.15	13.038	70.096	59.984	3.015	−3.530	−3.868	2.83533
300.00	13.077	70.177	60.047	3.039	−3.555	−3.869	2.81882
400.00	15.049	74.217	63.097	4.448	−11.328	−2.397	1.30955
500.00	16.632	77.753	65.682	6.036	−11.641	−0.128	0.05605
600.00	17.879	80.900	67.961	7.764	−11.878	2.198	−0.80053
700.00	18.884	83.734	70.015	9.603	−12.057	4.559	−1.42348
800.00	19.718	86.312	71.893	11.535	−12.187	6.943	−1.89682
900.00	20.425	88.676	73.628	13.543	−12.275	9.340	−2.26794
1000.00	21.030	90.860	75.244	15.616	−12.325	11.749	−2.56781
1100.00	21.553	92.890	76.757	17.746	−12.344	14.145	−2.81030
1200.00	22.006	94.785	78.181	19.925	−12.341	16.564	−3.01669
1300.00	22.399	96.562	79.527	22.145	−12.321	18.968	−3.18887
1400.00	22.742	98.235	80.804	24.403	−12.286	21.387	−3.33870
1500.00	23.040	99.814	82.020	26.692	−12.240	23.785	−3.46550
Maximum uncertainty	±0.04	±0.12	±0.10	±0.04	±0.03	±0.16	±0.025

We find that for the other series $CH_4 \rightarrow CCl_4$, not the second difference but the third difference in the enthalpy of formation is almost constant (±1 kcal mol^{-1}) as shown below [60].

ΔHf°(298) [27]

CH_4	−17.88			
		+1.71		
CH_3Cl	−19.59		−1.50	
		+3.21		−2.91
CH_2Cl_2	−22.80		+1.41	
		+1.80		−2.09
$CHCl_3$	−24.60		+3.50	
		−1.70		
CCl_4	−22.90			

For the CH_4 CI_4 series, the third difference cannot be obtained as the experimental value for CI_4 is not available. As seen below the second difference is not constant.

ΔHf°(298) [This work]

CH_4	−17.88		
		−21.17	
CH_3I	+ 3.29		+3.94
		−25.11	
CH_2I_2	+28.4		−3.11
		−22.0	
CHI_3	+50.4		

This means that the trigonal interactions are significant and should not be neglected. The $CH_4 \rightarrow CF_4$ series cannot be checked for the "differences" due to nonavailability of experimental data for CH_3F.

The values reported by Wagman et al. for $CHBr_3$ and CBr_4 satisfy the above finding very well. Hence we have adopted ΔHf°($CHBr_3$, g, 298) = 4.0±0.8 kcal mol^{-1}.

The ideal gas thermodynamic functions have been calculated using the data given in tables 3 and 4, and are presented in table 8. There are no experimental data on gaseous heat capacity and entropy available for comparison.

5. Tetrabromomethane

The electron diffraction studies of tetrabromomethane by Lister and Sutton [61] and Finbak et al. [62] are in excellent agreement. The selected values based upon these authors' studies are given in table 3. Other work on structural parameters is summarized in ref. [15].

Shimanouchi [1] has critically reviewed the infrared and Raman spectral data. His assignments are adopted in this work and are presented in table 4. Other references on infrared and Raman work are refs. [19, 39, 57 and 63].

The enthalpy of formation of CBr_4 reported by NBS Circular 500 [5] is 12.0 kcal mol^{-1}. More recent NBS compilation recommends ΔHf°(CBr_4, g, 298) = 19.0 kcal mol^{-1}. Bernstein [48] reports it to be 38. kcal mol^{-1} based on the calculations from dissociation energy data. For the same reason given for $CHBr_3$ we have adopted ΔHf°(CBr_4, g, 298) = 19.0±1.0 kcal mol^{-1}.

The ideal gas thermal functions calculated using the data given in tables 3 and 4 are presented in table 9. No experimental data on gaseous heat capacity and entropy are available for comparison.

TABLE 8. Ideal gas thermodynamic properties of tribromomethane ($CHBr_3$)

Temp.	C_p°	S°	$-(G^\circ-H_0^\circ)/T$	$H^\circ-H_0^\circ$	ΔHf°	ΔGf°	Log Kf
K	cal deg^{-1} mol^{-1}			kcal mol^{-1}			
0	0.0000	0.0000	0.0000	0.0000	10.250	10.250	Infinite
100.00	11.588	63.706	54.412	0.929	9.783	6.585	−14.39200
150.00	13.215	68.727	58.385	1.551	9.399	5.068	−7.38468
200.00	14.612	72.723	61.485	2.247	8.966	3.690	−4.03242
273.15	16.419	77.552	65.162	3.384	4.400	1.978	−1.58288
298.15	16.964	79.014	66.263	3.802	4.000	1.775	−1.30123
300.00	17.003	79.119	66.342	3.833	3.972	1.762	−1.28343
400.00	18.800	84.270	70.200	5.628	−7.188	3.313	−1.81007
500.00	20.090	88.612	73.460	7.576	−7.232	5.942	−2.59729
600.00	21.027	92.362	76.305	9.634	−7.233	8.578	−3.12441
700.00	21.734	95.658	78.839	11.774	−7.208	11.212	−3.50041
800.00	22.290	98.598	81.128	13.976	−7.163	13.841	−3.78116
900.00	22.741	101.251	83.219	16.228	−7.100	16.463	−3.99764
1000.00	23.115	103.666	85.145	18.522	−7.020	19.082	−4.17038
1100.00	23.430	105.885	86.931	20.849	−6.930	21.674	−4.30625
1200.00	23.697	107.935	88.597	23.206	−6.832	24.282	−4.42230
1300.00	23.926	109.841	90.159	25.588	−6.731	26.866	−4.51654
1400.00	24.123	111.622	91.629	27.990	−6.626	29.460	−4.59885
1500.00	24.293	113.292	93.018	30.411	−6.518	32.028	−4.66645
Maximum uncertainty	±0.10	±0.24	±0.21	±0.05	±0.04	±0.33	±0.055

TABLE 9. Ideal gas thermodynamic properties of tetrabromomethane (CBr_4)

Temp	C_p°	S°	$-(G^\circ-H_0^\circ)/T$	$H^\circ-H_0^\circ$	ΔHf°	ΔGf°	log Kf
K	cal deg^{-1} mol^{-1}			kcal mol^{-1}			
0	0.0000	0.0000	0.0000	0.0000	26.100	26.100	Infinite
100.00	15.170	65.268	54.488	1.078	25.827	21.897	−47.85640
150.00	17.709	71.944	59.241	1.905	25.514	20.001	−29.14083
200.00	19.444	77.287	63.106	2.836	25.166	18.215	−19.90465
273.15	21.296	83.640	67.786	4.331	19.422	15.911	−12.73039
298.15	21.782	85.526	69.195	4.869	19.000	15.606	−11.43912
300.00	21.815	85.661	69.296	4.909	18.971	15.584	−11.35324
400.00	23.195	92.144	74.228	7.166	4.500	17.442	−9.52984
500.00	24.005	97.414	78.355	9.530	4.779	20.643	−9.02308
600.00	24.505	101.838	81.910	11.957	5.053	23.790	−8.66549
700.00	24.829	105.642	85.035	14.425	5.311	26.892	−8.39617
800.00	25.050	108.973	87.823	16.920	5.554	29.960	−8.18460
900.00	25.206	111.933	90.341	19.433	5.784	32.997	−8.01272
1000.00	25.321	114.595	92.635	21.959	6.005	36.015	−7.87098
1100.00	25.407	117.012	94.743	24.496	6.217	38.991	−7.74671
1200.00	25.473	119.226	96.693	27.040	6.418	41.973	−7.64431
1300.00	25.525	121.267	98.505	29.590	6.608	44.922	−7.55209
1400.00	25.567	123.160	100.200	32.145	6.791	47.876	−7.47378
1500.00	25.600	124.925	101.790	34.703	6.965	50.799	−7.40143
Maximum uncertainty	±0.19	±0.42	±0.37	±0.06	±0.03	±0.60	±0.100

6. Iodomethane (Methyl Iodide)

Miller et al. [13] have made microwave measurements on four isotopic species $^{12}CH_3\,^{127}I$, $^{13}CH_3\,^{127}I$, $^{12}CD_3\,^{127}I$, and $^{12}CHD_2\,^{127}I$ from which the structural parameters were calculated. Costain [14] recalculated the structural parameters using the data of Miller et al., taking into account the changes in the average bond distances with isotopic substitution. Recently Duncan [64], and Matsuura and Overend [65] have reported the equilibrium structure of CH_3I and their values are in good agreement with each other. As Matsuura and Overend have used observed values of rotational constant (A_0) and rotation-vibration interaction constants in determining the equilibrium structure, we have adopted their values in this work and are listed in table 3. Earlier studies have been summarized in ref. [15].

Shimanouchi [2] has critically reviewed the infrared and Raman spectral data and selected the assignments for the gaseous state. These assignments are adopted in this work and listed in table 4. The other references for infrared and Raman work are refs. [19, 21, and 66 to 73].

The enthalpy of formation at 298 K of CH_3I (g) reported in NBS Circular 500 [25] is 4.9 kcal mol^{-1} obtained from the measurement of heat of combustion data of Thomsen [26]. The more recent NBS compilation [4] recommends $\Delta Hf^\circ(CH_3I, g, 298) = 3.1$ kcal mol^{-1}.

Carson et al. [74] obtained $\Delta Hf^\circ(CH_3I, g, 298) = 3.1 \pm 1.3$ kcal mol^{-1}. Their value depends on a complex thermochemical cycle involving both the heat of combustion of mercury dimethyl and its reaction with alcoholic solution of iodine.

Carson et al. [75] made a careful study of the enthalpy of reaction (8):

$$CH_3I(l) + \tfrac{1}{2}H_2(g) = CH_4(g) + \tfrac{1}{2}I_2(C) \qquad (8)$$

They obtained $\Delta H_r(8, CH_3I, 1, 298) = -15.0 \pm 0.3$ kcal mol^{-1} and $\Delta Hf^\circ(CH_3I, 1, 298) = -2.9$ kcal mol^{-1}.

$\Delta H^\circ_v(298) = 6.7 \pm 0.3$ of CH_3I was calculated from equation (1) using the literature vapor pressure data [76]. This combined with ΔHf° in liquid state of Carson et al. gives $\Delta Hf^\circ(CH_3I, g, 298) = +3.8 \pm 0.5$ kcal mol^{-1}.

Golden et al. [77] and Goy and Pritchard [78] have independently made the study of chemical equilibrium of reaction (9). Golden et al. reported ΔGf° values at 605.6 K, 630.4 K, and 666.9 K.

$$CH_3I(g) + HI(g) \rightleftharpoons CH_4(g) + I_2(g) \qquad (9)$$

From the experimental ΔGf° values, the enthalpies of reaction ΔH°_{rT} were obtained and converted to $\Delta H^\circ_r(9, 298)$ using equation (4). S° and C°_p needed for the calculation were taken from JANAF [10] for HI and I_2, from API [32] for CH_4 and from this work for CH_3I. The average $\Delta H^\circ_r(CH_3I, g, 298) = 12.56 \pm 0.26$ kcal mol^{-1}. This value combined with enthalpies of formation of CH_4, HI, and I_2 (table 1) gives $\Delta Hf^\circ(CH_3I, g, 298) = 3.27 \pm 0.28$ kcal mol^{-1}.

Goy and Pritchard [78] carried out the equilibrium measurements at nine temperatures between 585 K and 748 K. From their data we recalculated the average $\Delta H^\circ_r(CH_3I, g, 298) = 12.60 \pm 0.10$ and $\Delta Hf^\circ(CH_3I, g, 298. = 3.31 \pm 0.12$ kcal mol^{-1} following the same procedure given above. This value is in excellent agreement with that of Golden et al. We have adopted $\Delta Hf^\circ(CH_3I, g, 298) = 3.29 \pm 0.28$ kcal mol^{-1}, an average of Golden et al. and of Goy and Pritchard. The available $\Delta Hf^\circ(g, 298)$ are summarized in table 10. Our selection is corroborated by Cox and Pilcher's [6] recommendation of 3.4 ± 0.3 for $\Delta Hf^\circ(g, 298)$.

The ideal gas thermal functions have been calculated using the data given in tables 3 and 4, and are presented in table 11. No experimental gaseous heat capacity and entropy data are available for comparison.

7. Diiodomethane (Methylene Iodide)

The electron diffraction studies made by Hugill [79] and Bastiansen [80] are in excellent agreement. They have reported only the bond length C—I and bond angle ICI. Bond length C—H and bond angle HCH were estimated in this work by averaging the values of these parameters in other halomethanes. The values adopted here are given in table 3.

TABLE 10. Enthalpy of formation data for iodomethane (CH_3I)

Author(s)	ΔHf°(g, 298) kcal mol^{-1}
NBS Circular 500 (1952)	4.9
Carson et al. (1949)	3.1 ± 1.3
Carson et al. (1961)	3.8 ± 0.5
Golden et al. (1965)	3.27 ± 0.28
Goy and Pritchard (1965)	3.31 ± 0.12
Wagman et al. (1968) (NBS Compilation)	3.1
Cox and Pilcher (1970)	3.4 ± 0.3
Selected (1973)	3.29 ± 0.28

Plyler and Benedict [81], Voelz et al. [82] and Marzocchi et al. [83] have made infrared measurements in the liquid state. Their assignments are in very good agreement. In this work we have adopted the assignments of Marzocchi et al. being most recent and reliable and they are listed in table 4.

Berthelot's measurements of heat of combustion [27] yield $\Delta Hf^\circ(CH_2I_2, 1, 298) = 16.0$ kcal mol^{-1}. Wagman et al. [4] have also recommended this liquid value for $\Delta Hf^\circ(CH_2I_2, 1, 298)$ and $\Delta Hf^\circ(CH_2I_2, g, 298) = 27.0$ kcal mol^{-1}.

The available vapor pressure data were used by TRC [4, 84] and fitted to the Antoine equation (10):

$$\log P(\mathrm{mm}) = A - B/(C + t(^\circ C)) \qquad (10)$$

Their constants $A = 6.961$, $B = 1575.0$, $C = 204.0$ were used in equation (1) to yield $\Delta H^\circ_v(298) = 12.2 \pm 0.5$ kcal mol^{-1}. Dreisbach [85] also reported the same value for ΔH°_v. His source appears to be the same as TRC. This $\Delta H^\circ_v(298)$ value combined with $\Delta Hf^\circ(1, 298) = 16.0$ kcal mol^{-1}, yields $\Delta Hf^\circ(CH_2I_2, g, 298) = 28.2$ kcal mol^{-1}. Stull et al. [5] recommend the same value.

Recently Furuyama et al. [86] have carried out the measurements on the chemical equilibrium of the reaction (11)

$$2CH_3I(g) \rightleftharpoons CH_2I_2(g) + CH_4(g), \qquad (11)$$

at two temperatures 332 °C and 278 °C.

They reported $\Delta Hf^\circ(CH_2I_2, g, 298) = 29.2 \pm 1$ kcal mol^{-1}. However, $\Delta H_r(298)$ obtained from the experimental data at 332 °C and 278 °C differ considerably. As reported by them, the reaction is very slow below 300 °C. Hence in our calculations we have considered the data at 332 °C only. Neglecting one outlying value at 331.7 °C, $K_{av} = 1.25 \times 10^{-2}$. This value (using equation (4)) yields $\Delta H^\circ_r(CH_2I_2, 298) = 3.64 \pm 1$ kcal mol^{-1}. The S° and C°_p needed in the calculation were taken from API [5] for CH_4 and from this work for CH_3I and CH_2I_2. This value combined with ΔHf° of CH_4 (table 1)

TABLE 11. Ideal gas thermodynamic properties of iodomethane (CH_3I)

Temp	C_p°	S°	$-(G^\circ-H_0^\circ)/T$	$H^\circ-H_0^\circ$	ΔHf°	ΔGf°	log Kf
K	cal deg^{-1} mol^{-1}			kcal mol^{-1}			
0	0.0000	0.0000	0.0000	0.0000	5.569	5.569	Infinite
100.00	8.005	51.016	43.060	0.796	4.847	4.155	−9.08098
150.00	8.328	54.312	46.295	1.203	4.508	3.880	−5.65271
200.00	8.924	56.784	48.619	1.633	4.113	3.730	−4.07568
273.15	10.095	59.732	51.213	2.327	3.498	3.682	−2.94571
298.15	10.536	60.635	51.965	2.585	3.290	3.715	−2.72290
300.00	10.569	60.701	52.019	2.604	3.275	3.719	−2.70895
400.00	12.331	63.985	54.609	3.750	0.546	4.059	−2.21751
500.00	13.916	66.911	56.782	5.065	−5.268	5.500	−2.40402
600.00	15.276	69.571	58.695	6.526	−5.682	7.694	−2.80255
700.00	16.449	72.016	60.426	8.113	−6.022	9.952	−3.10718
800.00	17.473	74.281	62.018	9.811	−6.293	12.254	−3.34769
900.00	18.375	76.392	63.499	11.604	−6.505	14.585	−3.54162
1000.00	19.168	78.370	64.888	13.482	−6.662	16.942	−3.70257
1100.00	19.867	80.231	66.199	15.435	−6.773	19.295	−3.83364
1200.00	20.479	81.986	67.442	17.452	−6.850	21.679	−3.94827
1300.00	21.017	83.647	68.626	19.528	−6.898	24.057	−4.04439
1400.00	21.487	85.222	69.755	21.654	−6.922	26.452	−4.12926
1500.00	21.901	86.719	70.837	23.823	−6.928	28.830	−4.20048
Maximum uncertainty	±0.02	±0.06	±0.04	±0.04	±0.03	±0.06	±0.009

and CH_3I (this work) gives $\Delta Hf^\circ(CH_2I_2, g, 298)=28.37$ kcal mol^{-1}. $\Delta Hf^\circ(CH_2I_2, g, 298.15)=28.37\pm1.0$ kcal mol^{-1} is adopted in this work. This is in excellent agreement with the one mentioned earlier. Various values of $\Delta Hf^\circ(298)$ are tabulated in table 12.

Ideal gas thermal functions calculated using the data given in tables 3 and 4 are presented in table 13. No experimental gaseous heat capacity and entropy data are availabe for comparison.

8. Triiodomethane (Iodoform)

The electron diffraction studies made by Hugil [79] and Bastiansen [80] are in excellent agreement. They reported only bond length C—I, and bond angle ICI. As mentioned in section 7, the C—H value which is used is obtained by averaging the values of this parameter in other halomethanes. These parameters are listed in table 3.

Infrared and Raman measurements have been made in solid state for CHI_3 [87, 88, 89]. The assignments reported by various authors are in good agreement. We have adopted the assignments from infrared measurement except ν_3 which is the Raman value and they are listed in table 4.

TABLE 12. Enthalpy of formation data for diiodomethane (CH_2I_2)

Author(s)	ΔHf°(g, 298) kcal mol^{-1}
Berthelot (1901)	28.2
Wagman (1968)	27.0
Furuyama et al. (1968)	29.2±1.0
Stull (1969)	28.2
Selected value (1973)	28.37±1.0

Wagman et al. [4] have reported $\Delta Hf^\circ(CHI_3, S, 298)=33.7$ kcal mol^{-1} which was presumably obtained from the enthalpy of combustion measured by Berthelot [23]. The enthalpy of sublimation, $\Delta H_s^\circ(298)=16.7$ kcal mol^{-1}, is listed by Jones [90] and is based on the vapor pressure measurements by Nitta and Seki [91]. Combining the two, one obtains $\Delta Hf^\circ(CHI_3, g, 298)=50.4\pm1$ kcal mol^{-1} which is adopted in this work. The same value is reported by Stull et al. [5].

Ideal gas thermodynamic functions are calculated using the data from tables 3 and 4 and are presented in table 14. No experimental gaseous heat capacity and entropy data are available for comparison.

9. Tetraiodomethane

The electron diffraction studies made by Finbak and Hassel [92] and Lister and Sutton [93] are in good agreement. The average of these two investigations is adopted in this work which is presented in table 3.

Shimanouchi [1] has critically evaluated the assignments for CI_4 based upon the infrared and Raman measurements of Stammreich et al. [94] in solid state. These assignments are adopted in this work and are given in table 4.

The enthalpy of formation of CI_4 has not yet been measured. As in the case of CH_2Br_2 (section 3), enthalpy of formation is calculated using equation (12).

$$\begin{aligned}\Delta Hf^\circ(CI_4, g, 298)=&-\Delta Hf^\circ(CH_4, g, 298)\\&-6\Delta Hf^\circ(CH_2I_2, g, 298)+4\Delta Hf^\circ(CH_3I, g, 298)\\&+4\Delta Hf^\circ(CHI_3, g, 298)\qquad(12)\end{aligned}$$

Using $\Delta Hf^\circ(CH_4, g, 298)=-17.88$ kcal mol^{-1} and the

TABLE 13. Ideal gas thermodynamic properties of diiodomethane (CH_2I_2)

Temp	C_p°	S°	$-(G^\circ-H_0^\circ)/T$	$H^\circ-H_0^\circ$	ΔHf°	ΔGf°	log Kf
K	cal deg^{-1} mol^{-1}			kcal mol^{-1}			
0	0.0000	0.0000	0.0000	0.0000	30.562	30.562	Infinite
100.00	9.600	61.682	53.019	0.866	29.926	27.677	−60.48812
150.00	10.495	65.734	56.617	1.368	29.538	26.635	−38.80690
200.00	11.594	68.901	59.305	1.919	29.120	25.731	−28.11716
273.15	13.257	72.762	62.407	2.829	28.504	24.588	−19.67329
298.15	13.798	73.947	63.325	3.167	28.300	24.242	−17.76969
300.00	13.838	74.032	63.391	3.192	28.285	24.218	−17.64252
400.00	15.739	78.284	66.597	4.675	23.654	23.118	−12.63092
500.00	17.217	81.962	69.310	6.326	12.765	24.024	−10.50106
600.00	18.367	85.207	71.695	8.107	12.572	26.296	−9.57819
700.00	19.293	88.110	73.836	9.992	12.431	28.595	−8.92778
800.00	20.064	90.738	75.787	11.961	12.334	30.912	−8.44487
900.00	20.721	93.140	77.584	14.001	12.272	33.238	−8.07130
1000.00	21.288	95.353	79.251	16.102	12.245	35.575	−7.77483
1100.00	21.779	97.406	80.810	18.256	12.245	37.895	−7.52905
1200.00	22.205	99.320	82.273	20.456	12.263	40.236	−7.32799
1300.00	22.576	101.112	83.654	22.695	12.298	42.565	−7.15576
1400.00	22.900	102.797	84.962	24.969	12.344	44.902	−7.00955
1500.00	23.182	104.387	86.204	27.274	12.400	47.220	−6.87998
Maximum uncertainty	±0.04	±0.15	±0.13	±0.05	±0.03	±0.21	±0.125

TABLE 14. Ideal gas thermodynamic properties of triiodomethane (CHI_3)

Temp	C_p°	S°	$-(G^\circ-H_0^\circ)/T$	$H^\circ-H_0^\circ$	ΔHf°	ΔGf°	log Kf
K	cal deg^{-1} mol^{-1}			kcal mol^{-1}			
0	0.0000	0.0000	0.0000	0.0000	52.294	52.294	infinite
100.00	12.756	68.468	58.328	1.014	51.820	48.402	−105.78297
150.00	14.319	73.943	62.665	1.692	51.466	46.770	−68.14320
200.00	15.713	78.257	66.041	2.443	51.103	45.260	−49.45757
273.15	17.438	83.420	70.028	3.658	50.577	43.209	−34.57213
298.15	17.942	84.969	71.216	4.100	50.400	42.542	−31.18376
300.00	17.978	85.080	71.301	4.134	50.387	42.494	−30.95652
400.00	19.596	90.487	75.444	6.017	43.918	40.171	−21.94851
500.00	20.729	94.989	78.916	8.037	27.985	40.749	−17.81125
600.00	21.542	98.844	81.924	10.152	28.028	43.298	−15.77129
700.00	22.157	102.213	84.586	12.339	28.091	45.838	−14.31133
800.00	22.644	105.205	86.980	14.579	28.168	48.370	−13.21401
900.00	23.042	107.895	89.157	16.864	28.254	50.890	−12.35775
1000.00	23.375	110.341	91.155	19.186	28.354	53.406	−11.67176
1100.00	23.656	112.582	93.003	21.538	28.461	55.892	−11.10475
1200.00	23.897	114.651	94.721	23.916	28.571	58.391	−10.63441
1300.00	24.103	116.572	96.329	26.316	28.685	60.870	−10.23316
1400.00	24.281	118.365	97.840	28.735	28.798	63.352	−9.88961
1500.00	24.435	120.046	99.265	31.171	28.913	65.810	−9.58853
Maximum uncertainty	±0.10	±0.32	±0.30	±0.05	±0.03	±0.46	±0.066

ΔHf° values adopted in this work for other compounds, we obtained $\Delta Hf^\circ(CI_4, g, 298) = 62.24$ kcal mol^{-1}.

Furuyama et al. [86] estimated $\Delta Hf^\circ(CI_4, g, 298.15) = 95.1$ kcal mol^{-1} assuming second difference in ΔHf° values of the series $CH_4 \rightarrow CI_4$ to be constant. However, in the present study, the trigonal interactions are assumed important in these molecules and hence $\Delta Hf^\circ(CI_4, g, 298) = 62.24 \pm 1$ kcal mol^{-1} is adopted.

The ideal gas thermal functions calculated using the data from tables 3 and 4 are presented in table 15. No experimental gaseous heat capacity and entropy data are available for comparison.

10. Comparison

The thermodynamic functions, C_p°, S°, and ΔHf° computed in this work are compared with the available important compilations [4, 5, 95, 96, 97] at 298 and 700 K in tables 16 to 19. In general the agreement of these values with each other is quite satisfactory except for the enthalpy of formation reported by Gurvich et al. [97] at 700 K. It is clear that they have made some error in their calculations.

TABLE 15. Ideal gas thermodynamic properties of tetraiodomethane (CI_4)

Temp	C_p°	S°	$-(G^\circ-H_0^\circ)/T$	$H^\circ-H_0^\circ$	ΔHf°	ΔGf°	Log Kf
K	cal deg^{-1} mol^{-1}			kcal mol^{-1}			
0	0.0000	0.0000	0.0000	0.0000	64.056	64.056	infinite
100.00	17.345	71.587	59.088	1.250	63.833	59.614	−130.28508
150.00	19.400	79.035	64.556	2.172	63.580	57.559	−83.86296
200.00	20.931	84.835	68.926	3.182	63.332	55.590	−60.74596
273.15	22.513	91.612	74.130	4.775	62.968	52.822	−42.26354
298.15	22.906	93.601	75.681	5.343	62.840	51.894	−38.03922
300.00	22.933	93.743	75.791	5.385	62.831	51.827	−37.75558
400.00	23.996	100.501	81.158	7.737	54.591	48.509	−26.50424
500.00	24.586	105.925	85.587	10.169	33.658	48.971	−21.40525
600.00	24.938	110.441	89.364	12.647	33.965	52.005	−18.94271
700.00	25.162	114.303	92.657	15.152	34.249	54.988	−17.16807
600.00	25.312	117.674	95.578	17.676	34.511	57.935	−15.82694
900.00	25.418	120.662	98.202	20.213	34.753	60.848	−14.77596
1000.00	25.494	123.344	100.585	22.759	34.983	63.742	−13.93068
1100.00	25.552	125.776	102.766	25.311	35.201	66.593	−13.23075
1200.00	25.596	128.002	104.778	27.869	35.403	69.447	−12.64803
1300.00	25.630	130.052	106.644	30.430	35.597	72.275	−12.15050
1400.00	25.658	131.952	108.385	32.995	35.777	75.099	−11.72339
1500.00	25.680	133.723	110.015	35.562	35.950	77.896	−11.34942
Maximum uncertainty	±0.19	±0.59	±0.54	±0.06	±0.02	±0.086	±0.125

TABLE 16. Comparison of the ideal gas thermodynamic properties at 1 atm and 298 K for bromomethanes

	CH_3Br			CH_2Br_2			$CHBr_3$			CBr_4		
	C_p°	S°	$-\Delta Hf^\circ$	C_p°	S°	$-\Delta Hf^\circ$	C_p°	S°	$-\Delta Hf^\circ$	C_p°	S°	$-\Delta Hf^\circ$
	cal K^{-1} mol^{-1}		kcal mol^{-1}	cal K^{-1} mol^{-1}		kcal mol^{-1}	cal K^{-1} mol^{-1}		kcal mol^{-1}	cal K^{-1} mol^{-1}		kcal mol^{-1}
Gelles and Pitzer (1953) [95]	10.14	58.82		13.09	70.02		16.99	79.03		21.80	85.53	
Landolt-Bornstein (1961) [96]	10.11	58.75	8.51	13.09	70.08	1.00	16.99	79.03	−4.49	21.80	85.54	−12.00
Gurvich et al., (1962) (USSR) [97]		58.77	8.49		70.12	1.13		79.08	−10.16		85.58	−20.19
Wagman et al., (1968) (NBS TN–270–3) [4]	10.14	58.86	8.40	13.07	70.06		17.02	79.07	−4.0	21.79	85.55	−19.00
Stull, Westrum, and Sinke (1969) [5]	10.14	58.75	9.00		70.08	1.0		79.03	−6.0		85.53	−12.00
This work (1973)	10.15	58.76	9.02	13.04	70.10	3.50	16.96	79.01	−4.0	21.78	85.53	−19.00

TABLE 17. Comparison of the ideal gas thermodynamic properties at 1 atm. and 298 K for iodomethanes

	CH_3I			CH_2I_2			CHI_3			CI_4		
	C_p°	S°	$-\Delta Hf^\circ$	C_p°	S°	$-\Delta Hf^\circ$	C_p°	S°	$-\Delta Hf^\circ$	C_p°	S°	$-\Delta Hf^\circ$
	cal K^{-1} mol^{-1}		kcal mol^{-1}	cal K^{-1} mol^{-1}		kcal mol^{-1}	cal K^{-1} mol^{-1}		kcal mol^{-1}	cal K^{-1} mol^{-1}		kcal mol^{-1}
Gelles and Pitzer (1953) [95]	10.55	60.47		13.83	73.88							
Landolt-Bornstein, (1961) [96]	10.40	60.46	−4.90	13.83	76.84							
Gurvich, et al. (1962) (USSR) [97]		60.63	−4.10		74.12	−27.11		85.10	−51.13			
Wagman et al., (1968) (NBS TN-270-3) [4]	10.54	60.71	−3.1	13.79	74.00	−27.00	17.92	85.1		22.91	93.65	
Stull, Westrum, and Sinke (1969) [5]	10.55	60.71	−3.34	13.83	73.88	−28.2	17.91	85.00	−50.40		93.61	
This work, (1973)	10.54	60.64	−3.29	13.80	73.95	−28.4	17.94	84.97	−50.40	22.91	93.60	−62.42

TABLE 18. Comparison of the ideal gas thermodynamic properties at 1 atm. and 700 K for bromomethanes

	CH_3Br			CH_2Br_2			$CHBr_3$			CBr_4		
	C_p°	S°	$-\Delta Hf^\circ$	C_p°	S°	$-\Delta Hf^\circ$	C_p°	S°	$-\Delta Hf^\circ$	C_p°	S°	$-\Delta Hf^\circ$
	cal K^{-1} mol^{-1}		kcal mol^{-1}	cal K^{-1} mol^{-1}		kcal mol^{-1}	cal K^{-1} mol^{-1}		kcal mol^{-1}	cal K^{-1} mol^{-1}		kcal mol^{-1}
Gelles and Pitzer (1953) [95]	16.19	69.88		18.91	83.69		21.76	95.69		24.84	105.65	
Landolt-Bornstein, (1961) [96]	16.19	69.83	17.85	18.92	83.77	9.46	21.76	95.70	5.11	24.83		
Gurvich et al. (1962) (USSR) [97]		69.85	31.03		83.76	−7.72		95.77	18.153		105.70	−29.75
Stull, Westrum, and Sinke, (1969) [5]	16.19	69.83	14.66									
This work (1973)	16.20	69.84	14.68	18.88	83.73	12.06	21.73	95.66	7.21	24.83	105.64	−5.31

TABLE 19. Comparison of the ideal gas thermodynamic properties at 1 atm and 700 K for iodomethanes

	CH_3I			CH_2I_2			CHI_3			CI_4		
	C_p°	S°	$-\Delta Hf^\circ$	C_p°	S°	$-\Delta Hf^\circ$	C_p°	S°	$-\Delta Hf^\circ$	C_p°	S°	$-\Delta Hf^\circ$
	cal K^{-1} mol^{-1}		kcal mol^{-1}	cal K^{-1} mol^{-1}		kcal mol^{-1}	cal K^{-1} mol^{-1}		kcal mol^{-1}	cal K^{-1} mol^{-1}		kcal mol^{-1}
Gelles and Pitzer (1953) [95]	16.48	71.88		19.30	88.05							
Landolt-Bornstein (1961) [96]	16.43	72.04	4.37	19.30								
Gurvich et al. (1962) [97]		72.06	−9.72		88.23	33.93		102.32	−59.35			
Stull, Westrum, and Sinke, (1969) [5]	16.48	72.12	5.96	19.30	88.06	−12.34	22.13	102.22	−28.08			
This work (1973)	16.45	72.02	6.02	19.29	88.11	−12.51	22.16	102.21	−28.09	25.16	114.30	−33.83

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