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A. S. Rodgers, J. Chao, R. C. Wilhoit, and B. J. Zwolinski

Ideal Gas Thermodynamic Properties of Eight Chloro- and Fluoromethanes

A. S. Rodgers, J. Chao, R. C. Wilhoit, and B. J. Zwolinski

Thermodynamics Research Center, Department of Chemistry, Texas A&M University, College Station, Texas 77843

The structural data, vibrational assignments, enthalpies of vaporization and formation for chloromethane, dichloromethane, trichloromethane, tetrachloromethane, fluoromethane, difluoromethane, trifluoromethane, and tetrafluoromethane were critically reviewed. Based on the selected best values, the thermodynamic properties for each of these eight chloro- and fluoromethanes were calculated by statistical thermodynamic methods using the rigid-rotor harmonic-oscillator approximations. The derived entropies and heat capacities are compared with the available third law entropies and vapor heat capacities. The calculated values of C_p°, S°, and ΔHf° at 298.15 and 700 K are compared with those reported in the other major compilations.

Key words: Chloromethane; fluoromethane; ideal gas thermodynamic properties; critical evaluation of thermodynamic properties.

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1. Introduction

1.1. Scope and Objectives

This report is the first in a series on the critical review, evaluation, and calculation of the ideal gas thermodynamic properties of the fluorine and chlorine derivatives of methane and ethane. The properties tabulated are: heat capacity, C_p°; entropy, S°; relative enthalpy, $H^\circ - H_0^\circ$; the Gibbs energy function, $(G^\circ - H_0^\circ)/T$; enthalpy of formation, ΔHf°; Gibbs energy of formation, ΔGf°; and logarithm of the equilibrium constant of formation, log K_f. Values are given at temperatures from 0 to 1500 K. The first four properties have been calculated from the partition functions based on the usual rigid-rotor harmonic-oscillator approximations. Enthalpies of formation have been derived from selected experimental data such as enthalpies of combustion and enthalpies of halogenation of an ethene, where available, or from correlation methods where there are no experimental data. Enthalpies of formation at various temperatures, as well as Gibbs energies of formation and log K_f, are calculated from the related data by the usual thermodynamic formulae. Properties of the elements used in these calculations are listed in section 1.6. In addition, certain other experimental data, such as vapor pressure, enthalpy of vaporization, and third law entropy, have been selected and listed as auxiliary information.

Except for hexachloroethane, the fluoro-, chloro-, and fluorochloro-substituted methanes and ethanes are either gases at room temperature and one atmosphere or low boiling liquids. Most of these compounds are thermally stable and many are used extensively in industry as solvents, refrigerants, and heat transfer fluids. The ideal gas properties are useful approximations to the real gas properties and serve as convenient starting points for the tabulation of properties of the real gases and the condensed states.

Each compound is discussed in a separate section which includes identification of sources of data and their references, selections of the "best" values, comparisons of observed and recommended values, estimates of uncertainties, and tables of the selected values of the molecular parameters and of the thermodynamic properties at selected temperatures. All selected values except the enthalpy of formation of fluoromethane are derived from experimental measurements reported in the literature.

1.2. Definitions of Properties and Symbols

The symbols recommended in "Manual of Symbols and Terminology for Physicochemical Quantities and Units," McGlashan, International Union of Pure and Applied Chemistry, Butterworths, London, 1970, are used throughout. Symbols used in this report, which include some additional specifications, are listed below.

Symbol	Description	Units
C_p	Heat capacity at constant pressure	cal K^{-1}mol^{-1}
H	Enthalpy ($H = U + PV$)	cal mol^{-1}
ΔHf	Enthalpy of formation of a compound from its elements	kcal mol^{-1}
ΔH_c	Enthalpy of combustion of a compound with oxygen to yield CO_2(g), H_2O(l) and other products as specified	kcal mol^{-1}
ΔH_v	Enthalpy of vaporization of a liquid to a gas at equilibrium vapor pressure	kcal mol^{-1}
ΔH_s	Enthalpy of sublimation of a solid to a gas at equilibrium vapor pressure	kcal mol^{-1}
I	Moment of inertia of a molecule	g cm^2 or uÅ^2
K	Equilibrium constant for a chemical reaction	

Symbol	Description	Units
K_f	Equilibrium constant of formation of a compound from its elements	
$H-H_0$	Enthalpy at given temperature minus the enthalpy at zero K	cal mol^{-1}
G	Gibbs energy ($G=H-TS$)	cal mol^{-1}
ΔGf	Gibbs energy of formation of a compound from its elements	kcal mol^{-1}
$G-H_0$	Gibbs energy at given temperature minus the enthalpy at zero K	cal mol^{-1}
ΔHr	Enthalpy change for a chemical reaction	kcal mol^{-1}
P	Pressure	atm
S	Entropy	cal $K^{-1}mol^{-1}$
T	Temperature, Kelvin scale	K
U	Internal energy	cal mol^{-1}
ΔUc	Change in internal energy for combustion of a compound in oxygen	kcal mol^{-1}
M	Molecular weight	
V	Volume	cm^3 mol^{-1}
ν	Vibrational frequency (expressed in wavenumber equivalent)	cm^{-1}

Physical states are indicated by the following abbreviations

g	gas
l	liquid
c	crystal
aq	aqueous solution

The superscript, °, written after any symbol indicates a property of the substance in its standard state. The standard state of liquids and crystals is the thermodynamically stable state at one atmosphere and at the temperature specified. The standard state of a gas is the hypothetical ideal gas at one atmosphere and at the temperature specified. When needed, additional descriptive information such as the formula of the compound, the state, the moles of water per mole of solute for an aqueous solution, and the temperature are placed in parentheses following the symbol of a property. The number "298" when written within parentheses represents the temperature 298.15 K, or 25°C. Other temperatures are written completely with the appropriate unit symbol, K, or °C, included.

1.3. Units and Physical Constants

This review employs SI units (Page and Vigoureaux, 1970), except for the specification of energy in calories (1 cal = 4.184 J, exactly). The currently accepted atomic weights (The Commission of Atomic Weights, 1970): carbon, 12.011; hydrogen, 1.008; chlorine, 35.453; and fluorine, 18.9984, were used in the calculations. The fundamental physical constants used in the calculations were adopted from Taylor, Parker, and Langenberg (1969). These values have been provisionally recommended by the National Bureau of Standards.

1.4. Uncertainties

The uncertainties associated with the various selected values in this report reflect the judgment of the authors about the accuracy of these values. Wherever possible, they include the effect of both systematic and random errors. When an observed property value is taken from a single source, only the uncertainty estimate of the original author is generally used. When a value is selected from among more than one source, the extent of agreement among the different sources is considered in assigning an uncertainty. Uncertainties in the calculated ideal gas thermodynamic properties are obtained by observing the effects of changing the molecular parametric data by amounts corresponding to their estimated uncertainties.

1.5. Calculation of Ideal Gas Thermodynamic Properties

The ideal gas values of C_p°, S°, $H^\circ-H_0^\circ$, $(H^\circ-H_0^\circ)/T$, and $(G^\circ-H_0^\circ)/T$ have been calculated from the molecular partition functions for the rigid-rotor harmonic-oscillator model as described by Mayer and Mayer (1940) and other textbooks on statistical thermodynamics. In this approximation, the partition function for the molecule is assumed to be a product of terms for translational, rotational, vibrational, and electronic degrees of freedom. Wherever possible, the calculated values of entropy and heat capacity are compared with experimental third law entropy and heat capacity for the gas phase. Vibrational frequencies selected by Shimanouchi (1972) were adopted for all the chloro- and fluoromethanes except difluoromethane.

The selected molecular and thermochemical constants which were used for calculation of the ideal gas thermodynamic properties for the eight chloro- and fluoromethanes are summarized in table 1–1.

1.6. Auxiliary Data

The following enthalpies of formation, as reported in National Bureau of Standards Technical Note 270–3 (Wagman et al., 1968), were used in converting

TABLE 1-1. Molecular and thermochemical constants for the eight chloro- and fluoromethanes

	CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4	CH_3F	CH_2F_2	CHF_3	CF_4
Molecular weight	50.488	84.933	119.378	153.823	34.0334	52.0238	70.0142	88.0046
Point group	C_{3v}	C_{2v}	C_{3v}	T_d	C_{3v}	C_{2v}	C_{3v}	T_d
Symmetry number	3	2	3	12	3	2	3	12
Ground state configuration	$^1A_1$	$^1A_1$	$^1A_1$	$^1A_1$	$^1A_1$	$^1A_1$	$^1A_1$	$^1A_1$
Product of the three principal moments of inertia, $g^3\ cm^6 \times 10^{114}$	0.0211546	1.9306	32.8237	118.973	0.0059373	0.122690	0.968210	3.15975
Vibrational frequencies, cm^{-1}	see Table 2-1	see Table 3-1	see Table 4-2	see Table 5-2	see Table 6-1	see Table 7-1	see Table 8-2	see Table 9-2
Enthalpy of formation at 298.15 K, kcal mol^{-1}	-19.59 ± 0.16	-22.8 ± 0.2	-24.6 ± 0.2	-22.90 ± 0.14	-56.8 ± 2	-108.2 ± 0.2	-165.7 ± 1	-223.02 ± 0.2

experimental data to standard thermodynamic properties:

$$\Delta Hf^\circ(H_2O, l, 298) = -68.315 \text{ kcal mol}^{-1},$$

$$\Delta Hf^\circ(CO_2, g, 298) = -94.051 \text{ kcal mol}^{-1},$$

$$\Delta Hf^\circ(HCl, aq, 298) = -39.952 \text{ kcal mol}^{-1}.$$

The enthalpy of formation of liquid and aqueous hydrogen fluoride is still unsettled at this time. Based on the available current information and on personal communications with Ward Hubbard and his coworkers of the Argonne National Laboratory, we have adopted the values,

$$\Delta Hf^\circ(HF, l, 298) = -72.55 \text{ kcal mol}^{-1}, \text{ and}$$

$$\Delta Hf^\circ(HF, aq, 25\ H_2O, 298) = -77.011 \text{ kcal mol}^{-1},$$

TABLE 1-2. Thermodynamic properties of elements

	Carbon, graphite, C		Hydrogen, gas, H_2^*		Chlorine, gas, Cl_2		Fluorine, gas, F_2	
T, K	$H^\circ - H^\circ_0$ cal mol^{-1}	$(G^\circ - H^\circ_0)/T$ cal K^{-1} mol^{-1}	$H^\circ - H^\circ_0$ cal mol^{-1}	$(G^\circ - H^\circ_0)/T$ cal K^{-1} mol^{-1}	$H^\circ - H^\circ_0$ cal mol^{-1}	$(G^\circ - H^\circ_0)/T$ cal K^{-1} mol^{-1}	$H^\circ - H^\circ_0$ cal mol^{-1}	$(G^\circ - H^\circ_0)/T$ cal K^{-1} mol^{-1}
100	14.7	−0.081	758.9	−16.798	696.0	−38.189	694.7	−33.746
150	43.5	−0.166	1046.0	−19.733	1051.4	−41.019	1043.2	−36.564
200	92.5	−0.276	1361.6	−21.712	1422.0	−43.048	1394.9	−38.567
273.15	202.8	−0.469	1853.3	−23.801	1992.7	−45.292	1923.8	−40.750
298.15	251.2	−0.530	2023.7	−24.418	2194.3	−45.933	2109.6	−41.638
300	255.0	−0.536	2036.4	−24.462	2209.3	−45.978	2123.5	−41.412
400	502.0	−0.837	2730.9	−26.422	3038.8	−48.130	2893.7	−43.469
500	821.0	−1.157	3429.4	−27.948	3892.5	−49.846	3699.4	−45.101
600	1198.0	−1.488	4129.4	−29.201	4761.0	−51.279	4531.5	−46.464
700	1622.0	−1.821	4831.5	−30.264	5638.8	−52.512	5382.9	−47.639
800	2082.0	−2.150	5537.1	−31.187	6523.5	−53.594	6248.7	−48.674
900	2569.0	−2.472	6248.1	−32.002	7413.2	−54.559	7125.9	−49.600
1000	3074.0	−2.790	6966.2	−32.734	8306.9	−55.431	8012.3	−50.439
1100	3595.0	−3.080	7692.5	−33.400	9203.9	−56.226	8906.6	−51.207
1200	4232.0	−3.380	8428.0	−34.010	10104.	−56.956	9808.0	−51.915
1300	4682.0	−3.660	9173.7	−34.574	11007.	−57.632	10716.	−52.572
1400	5242.0	−3.940	9929.9	−35.099	11912.	−58.261	11630.	−53.185
1500	5810.0	−4.200	10696.9	−35.589	12819.	−58.849	12549.	−53.760

*Normal.

The data for graphite were taken from National Bureau of Standards Report 6928, Table B-39, by William Evans, 1960, for the range 0 to 1200 K, and from West and Ishihara, "Advances in Thermophysical Properties at Extreme Temperatures and Pressures", American Society for Testing and Materials, Philadelphia, Pa., 1965. Data for hydrogen, chlorine, and fluorine were obtained from tables 2-s, 2-u, 9-2-s, 9-2-u, 10-2-s, and 10-2-u of the Thermodynamics Research Center Data Project, Texas A&M University (Zwolinski et al., TRCDP, 1972). The listed values of $H^\circ - H^\circ_0$ at 298.15 K for C (c), H_2 (g), and Cl_2 (g) are consistent with those reported and recommended by the CODATA Task Group as the final set of key values for thermodynamics — Part I (International Council of Scientific Unions, 1971).

for this report. The selected enthalpies of formation for CH_2F_2 and CHF_3 are dependent on the value of ΔHf for aqueous HF. A change in this value by an amount Δx will result in a corresponding change of $2\Delta x$ for the ΔHf of the CH_2F_2 and $3\Delta x$ for CHF_3. The selected enthalpy of formation for CF_4 is not affected by the enthalpy of formation of HF.

The thermodynamic properties of the elements used in the calculation of ΔHf°, ΔGf°, and log K_f for the various compounds are listed in table 1–2.

2. Chloromethane

The values of rotational constants, A_e and B_e, for chloromethane (methyl chloride), $CH_3{}^{35}Cl$, were calculated by Duncan (1970) from the best estimates of values of A_0, the microwave values of B_0, and the interaction terms, α_r^A and α_r^B. The corresponding moments of inertia for isotope $CH_3{}^{35}Cl$ were derived as $I_A = 5.3576 \times 10^{-40}$ g cm^2 (3.2264 uÅ^2) and $I_B = I_C = 62.5967 \times 10^{-40}$ g cm^2 (37.6968 uÅ^2). The moments of inertia for isotope $CH_3{}^{37}Cl$ were obtained as: $I_A = 5.3576 \times 10^{-40}$ g cm^2 (3.2264 uÅ^2) and $I_B = I_C = 63.5796 \times 10^{-40}$ g cm^2 (38.2887 uÅ^2), where the value of I_A is the same as that for $CH_3{}^{35}Cl$, since the atomic mass of ^{35}Cl and ^{37}Cl is not involved. The value of I_B for $CH_3{}^{37}Cl$ was estimated by addition to the value of I_B ($CH_3{}^{35}Cl$) the difference in moments of inertia (I_B) between $CH_3{}^{37}Cl$ and $CH_3{}^{35}Cl$, which were derived based on the molecular parameters obtained by Duncan (1970).

Based on the values of I_A, I_B, and I_C for $CH_3{}^{35}Cl$ and $CH_3{}^{37}Cl$, the corresponding values for CH_3Cl isotopic mixture were calculated to be: $I_A = 5.3576 \times 10^{-40}$ g cm^2 and $I_B = I_C = 62.8372 \times 10^{-40}$ g cm^2. The moment of inertia for the isotopic mixture was evaluated as $I = W_{35}I_{35} + W_{37}I_{37}$, where W_{35}, W_{37} and I_{35}, I_{37} are the percent natural abundance and moment of inertia for $CH_3{}^{35}Cl$ and $CH_3{}^{37}Cl$, respectively. The product of the three principal moments of inertia for CH_3Cl was obtained as 2.1155×10^{-116} g^3 cm^6 (4620.2 u^{3}Å^6), which was adopted.

TABLE 2–1. Vibrational assignments for chloromethane

Mode No.	Symmetry class	Reference
		Shimanouchi 1972
		Wavenumber in cm^{-1}
ν_1	a_1	2937
ν_2	a_1	1355
ν_3	a_1	732
ν_4	e	3039
ν_5	e	1452
ν_6	e	1017

Shimanouchi (1972) has critically reviewed the infrared and Raman data for CH_3Cl, and his assignments, given in table 2–1, are selected.

The enthalpy of formation of CH_3Cl was listed in NBS Circular 500 (Rossini et al., 1952) as: $\Delta Hf^\circ(CH_3Cl$, g, 298) = −19.6 kcal mol^{-1} and was based upon the very early results of Thomsen (1908). The more recent NBS compilation (Wagman et al., 1968) gives: $\Delta Hf^\circ(CH_3Cl$, g, 298) = −19.32 kcal mol^{-1}.

The enthalpy of hydrogenation of CH_3Cl (reaction 2–1) has been measured at 521 K in a flow calorimeter by Lacher and coworkers (1956a, b). They obtained for reaction 2–1: $\Delta Hr^\circ(521\text{ K}) = -19.67 \pm 0.5$ kcal mol^{-1}

$$CH_3Cl(g) + H_2(g) \rightarrow CH_4(g) + HCl(g). \qquad (2\text{–}1)$$

The enthalpy change for this reaction has been corrected to 298.15 K using heat capacity data for $CH_4(g)$ $H_2(g)$ (Zwolinski et al., API44, 1972), HCl(g) (JANAF, 1971), and $CH_3Cl(g)$ (this work) to yield:

$$\Delta Hr^\circ(298\text{ K}) = -19.28 \pm 0.05 \text{ kcal mol}^{-1}.$$

This data, combined with $\Delta Hf^\circ(CH_4$, g, 298) = −19.88 and ΔHf°(HCl, g, 298) = −22.20 kcal mol^{-1} (Wagman et al., 1968), yield:

$$\Delta Hf^\circ(CH_3Cl, g, 298) = -20.67 \pm 0.05 \text{ kcal mol}^{-1}.$$

Lacher and coworkers (1956a, b) noted difficulty in obtaining complete reaction with CH_3Cl and, using infrared analysis, estimated that hydrogenation was 99.5 percent complete.

Fletcher and Pilcher (1971) have measured the enthalpy of combustion of $CH_3Cl(g)$ in a flame calorimeter using aqueous arsenious oxide to insure complete conversion of Cl_2 to HCl. They obtained

$$\Delta Hr^\circ(298\text{ K}) = -182.6 \pm 0.12 \text{ kcal mol}^{-1}$$

for reaction (2–2),

$$CH_3Cl(g) + \tfrac{3}{2}O_2(g) \rightarrow CO_2(g) + H_2O(l) + HCl \cdot 600\,H_2O. \qquad (2\text{–}2)$$

From this,

$$\Delta Hf^\circ(CH_3Cl, g, 298) = -19.59 \pm 0.16 \text{ kcal mol}^{-1}$$

may be obtained by using auxiliary data of Wagman et al. (1968). This differs significantly from the result of Lacher et al. (1956a, b) and suggests that the extent of hydrogenation of CH_3Cl may have been overestimated by these researchers.

Fletcher and Pilcher (1971) have also studied the combustion of ethyl and isopropyl chlorides in the same

TABLE 2–2. Enthalpy of formation data for chloromethane

ΔHr° (obs) kcal mol^{-1}	Conditions	Method	ΔHr° (298) kcal mol^{-1}	Reference	ΔHf°(g, 298) kcal mol^{-1}
−19.67 ± 0.05	Gas phase, 521 K	Hydrogenation	−19.28 ± 0.05	Lacher et al., 1956 (a, b)	−20.67 ± 0.05
				Wagman et al., 1968	−19.32
−182.6 ± 0.12	Gas phase, 298 K	Flame calorimeter	−182.6 ± 0.12	Fletcher and Pilcher, 1971	−19.59 ± 0.16
				Selected	−19.59 ± 0.16

TABLE 2–3. Ideal gas thermodynamic properties for chloromethane

T, K	C_p°	S°	$-(C^\circ-H_0^\circ)/T$	$H^\circ-H_0^\circ$	ΔHf°	ΔGf°	Log *Kf*
	cal K^{-1} mol^{-1}			kcal mol^{-1}			
0	0.0	0.0	0.0	0.0	−17.695	−17.696	infinite
100.00	7.955	46.795	38.846	0.795	−18.402	−17.143	37.465
150.00	8.060	50.034	42.070	1.195	−18.639	−16.465	23.989
200.00	8.401	52.393	44.368	1.605	−18.936	−15.696	17.151
273.15	9.335	55.138	46.898	2.251	−19.424	−14.440	11.554
298.15	9.737	55.973	47.624	2.489	−19.590	−13.969	10.239
300.00	9.767	56.033	47.675	2.507	−19.602	−13.933	10.150
400.00	11.514	59.080	50.154	3.571	−20.242	−11.943	6.525
500.00	13.188	61.833	52.218	4.807	−20.799	− 9.804	4.285
600.00	14.661	64.371	54.035	6.202	−21.267	− 7.560	2.754
700.00	15.937	66.729	55.682	7.733	−21.651	− 5.242	1.637
800.00	17.050	68.931	57.202	9.384	−21.961	− 2.876	0.786
900.00	18.022	70.997	58.621	11.138	−22.205	− 0.475	0.115
1000.00	18.873	72.941	59.957	12.984	−22.388	1.955	−0.427
1100.00	19.617	74.775	61.221	14.909	−22.522	4.383	−0.871
1200.00	20.266	76.510	62.424	16.904	−22.617	6.844	−1.246
1300.00	20.833	78.156	63.571	18.960	−22.681	9.300	−1.563
1400.00	21.329	79.718	64.669	21.068	−22.720	11.771	−1.838
1500.00	21.762	81.205	65.722	23.223	−22.737	14.231	−2.074

calorimeter and have obtained good agreement with ΔHf° obtained from equilibrium data on these compounds. For these reasons,

$$\Delta Hf^\circ(\mathrm{CH_3Cl, g, 298}) = -19.59 \pm 0.16\ \mathrm{kcal\,mol^{-1}}$$

has been adopted. These experimental results are summarized in table 2–2.

The rigid-rotor harmonic-oscillator approximation (Mayer and Mayer, 1940) has been used with the above selected data (see table 1–1) to calculate the ideal gas thermodynamic properties for CH_3Cl, as shown in table 2–3.

Messerly and Aston (1940) have measured the entropy of the real gas at its boiling point:

$$S^r(\mathrm{CH_3Cl, g, 248.96\ K}) = 54.15 \pm 0.15\ \mathrm{cal\,K^{-1}\,mol^{-1}}.$$

The correction to the ideal gas state which they obtained at this temperature from the Berthelot equation of state was: $S^\circ - S^r = 0.12$ *cal* K^{-1} mol^{-1}. Thus, the entropy of the ideal gas was:

$$S^\circ(\mathrm{CH_3Cl, g, 248.96\ K}) = 54.27 \pm 0.15\ \mathrm{cal\,K^{-1}\,mol^{-1}}.$$

The value calculated in this work is:

$$S^\circ(\mathrm{CH_3Cl, g, 248.96\ K}) = 54.290\ \mathrm{cal\ K{-}1\ mol^{-1}},$$

well within the experimental error. However, the entropy at this low temperature is not a sensitive test of the calculated functions as a 5 percent increase in the fundamental frequencies gave only a 0.1 percent decrease (0.05 cal K^{-1} mol^{-1}) in the calculated entropy.

3. Dichloromethane

From microwave study, Myers and Gwinn (1952) obtained the rotational constants, A_0, B_0, and C_0, for dichloromethane (methylene chloride) isotopes, $CH_2{}^{35,35}Cl_2$, $CH_2{}^{35,37}Cl_2$ and $CH_2{}^{37,37}Cl_2$. Based on their reported rotational constants, we calculated the three principal moments of inertia for CH_2Cl_2 as :

$$I_A = 2.6274 \times 10^{-39}\ \mathrm{g\ cm^2}\ (15.826\ \mathrm{u\AA^2}),$$

$$I_B = 2.6509 \times 10^{-38}\ \mathrm{g\ cm^2}\ (159.642\ \mathrm{u\AA^2}),$$

and

$$I_C = 2.7719 \times 10^{-38}\ \mathrm{g\ cm^2}\ (166.927\ \mathrm{u\AA^2}).$$

TABLE 3–1. Vibrational assignments for dichloromethane

Mode No.	Symmetry class	Reference
		Shimanouchi, 1972
		Wavenumber in cm^{-1}
v_1	a_1	2999
v_2	a_1	1467
v_3	a_1	717
v_4	a_1	282
v_5	a_2	1153
v_6	b_1	3040
v_7	b_2	898
v_8	b_2	1268
v_9	b_2	758

The product $I_A I_B I_C$ was derived to be 1.9306×10^{-114} g^3 cm^6 (421650 u^{3}Å^6) and was adopted for calculation.

Shimanouchi (1972) has critically reviewed the infrared and Raman data on CH_2Cl_2, and his assignments, given in table 3–1, were selected.

The enthalpy of vaporization of CH_2Cl_2 is needed to determine the enthalpy of formation in the gas phase. Mathews (1926) measured ΔH_v calorimetrically at 313.65 K and obtained: $\Delta H_v(313.65\ \mathrm{K}) = 6.68 \pm 0.02$ kcal mol^{-1}. The correction to the ideal gas was made using Berthelot's equation of state and relevant critical data (Zwolinski et al., TRCDP, 1972) which gave:

$$\Delta H_v^\circ(313.65\ \mathrm{K}) = 6.74 \pm 0.03\ \mathrm{kcal\ mol^{-1}}.$$

The liquid phase heat capacity data have been reviewed (Stull, Westrum, and Sinke, 1969) and below 320 K, $C_p(CH_2Cl_2, l) = 17.06 + 0.023\ T(\mathrm{K})$. The data, combined with the gas phase heat capacity calculated in this work, yield:

$$\Delta H_v^\circ(298\ \mathrm{K}) = 6.93 \pm 0.03\ \mathrm{kcal\ mol^{-1}}.$$

The equilibrium vapor pressure data have been critically evaluated by the TRC Data Project (Zwolinski et al., TRCDP, 1972) and correlated to the Antoine equation for vapor pressure (P^e). The enthalpy of vaporization may be calculated from the Antoine constants (B, C) using the Clapeyron equation:

$$\Delta H_v = T\Delta V \frac{dP^e}{dT} = T\Delta V \frac{2.3026\,BP^e}{(t+C)^2}, \qquad (3\text{–}1)$$

where $\Delta V = V(\mathrm{g}) - V(\mathrm{l})$; T and t are temperatures in K and °C, respectively.

The change in volume on vaporization was calculated using the Berthelot equation of state with

$$P_c = 60.0\ \mathrm{atm\ and}\ T_c = 510\ \mathrm{K}$$

for the gas and $d_l^{25} = 1.316$ g cm^{-3} (Zwolinski et al., TRCDP, 1972) for the liquid. After correcting to the ideal gas, reaction 3–1 gave:

$$\Delta H_v^\circ(CH_2Cl_2, 298) = 6.94\ \mathrm{kcal\ mol^{-1}}.$$

These values are in excellent agreement and yield the selected value:

$$\Delta H_v^\circ(CH_2Cl_2, 298) = 6.94 \pm 0.02\ \mathrm{kcal\ mol^{-1}}.$$

A summary of these data is given in table 3–2.

Eftring (1938) has measured the enthalpy of combustion of dichloromethane, and his data have been corrected by Smith et al. (1953). One of the corrections made by Smith (1953) was for the oxidation reaction of arsenious oxide to arsenic oxide (3–2).

$$As_2O_3(aq) + O_2(g) \rightarrow As_2O_5(aq). \qquad (3\text{–}2)$$

The value used by Eftring was 19.6 cal/milliequivalent Cl_2 ($\Delta Hr^\circ(298\ \mathrm{K}) = 78.4$ kcal mol^{-1}), and Smith et al. corrected this to 18.6 cal/milliequivalent Cl_2. Wagman et al. (1968) gave $\Delta Hr^\circ(298\ \mathrm{K}) = -76.6$ kcal mol^{-1}, corresponding to 19.15 cal/milliequivalent Cl_2 for undissociated arsenic acid.

Thus to make the enthalpy of combustion given by Smith et al. compatible with the newest $\Delta Hr^\circ(298\ \mathrm{K})$ for reaction 3–1, one must add 65 percent of the As_2O_3 correction to the "corrected" enthalpy of combustion. Thus for CH_2Cl_2, Smith et al. (1953) gave

$$\Delta U_c/M = -1701.4\ \mathrm{cal\ g^{-1}}$$

and

$$\Delta U/M(As_2O_3) = 3.2\ \mathrm{cal\ g^{-1}}.$$

TABLE 3–2. Enthalpy of vaporization data for dichloromethane

ΔHv (obs) kcal mol^{-1}	Conditions	Methods	Reference	ΔHv° (298) kcal mol^{-1}
6.69	1 atm, 313.5 K	Calorimetric	Mathews, 1926	6.93
6.90	435.6 torr, 298.15 K	Vapor pressure, Antoine equation.	Zwolinski et al., TRCDP, 1972.	6.94
			Selected	6.94

Therefore, the best value is

$$\Delta U_c/M = -1701.4 + (0.65)(3.2) = -1699.3 \text{ cal g}^{-1}$$

$$CH_2Cl_2(l) + O_2(g) \rightarrow CO_2(g) + 2HCl \cdot 600\ H_2O. \quad (3\text{–}3)$$

Consequently, $\Delta Hr°(298\text{ K}) = -144.3$ kcal mol^{-1} for reaction 3–3, $\Delta Hf°(CH_2Cl_2$, l, 298) = −29.40, and $\Delta Hf°(CH_2Cl_2$, g, 298) = −22.5 ± 0.2 kcal mol^{-1}, using auxiliary data from Wagman et al. (1968) and $\Delta H_v°(298\text{ K})$ adopted here.

Hu and Sinke (1969) have measured the energy of combustion of liquid CH_2Cl_2 in a rotating bomb calorimeter with aqueous arsenious oxide. Their data, reduced in an analogous manner to that above, gave: $\Delta Hf°(CH_2Cl_2$, l, 298) = −29.7 ± 0.2 kcal mol^{-1}. Lacher, Amador, and Park (1967) have measured the enthalpy change of reaction 3–4 at 523 K and have obtained: $\Delta Hr°(523\text{ K}) = -40.05 \pm 0.15$ kcal mol^{-1}

$$CH_2Cl_2(g) + 2H_2(g) \rightarrow CH_4(g) + 2HCl(g). \quad (3\text{–}4)$$

This result is corrected to 298 K using the heat capacity data for $CH_4(g)$ and $H_2(g)$ from the API44 Tables (Zwolinski et al., API44, 1972), for HCl(g) from JANAF (1971), and for $CH_2Cl_2(g)$ from this work. This correction yields: $\Delta Hr°(298\text{ K}) = -39.1 \pm 0.2$ kcal mol^{-1}, for reaction 3–4. When this result is combined with $\Delta Hf°(CH_4$, g, 298) = −17.88 and $\Delta Hf°$(HCl, g, 298) = −22.020 kcal mol^{-1} (Wagman et al., 1968), one obtains $\Delta Hf°(CH_2Cl_2$, g, 298) = −22.8 ± 0.2 kcal mol^{-1}. These experimental results and the selected value, $\Delta Hf°$ (CH_2Cl_2, g, 298) = −22.8 ± 0.2 kcal mol^{-1}, are summarized in table 3–3.

The rigid-rotor harmonic-oscillator approximation (Mayer and Mayer, 1940) has been used with the above selected data to calculate the ideal gas thermodynamic functions for CH_2Cl_2. These calculations are presented in table 3–4. There are no experimental data for entropy or gas phase heat capacity with which these functions may be compared.

4. Trichloromethane

The structural parameters for trichloromethane (chloroform) deduced from microwave studies are sum-

TABLE 3–3. Enthalpy of formation data for dichloromethane

$\Delta Hr°$ (obs) kcal mol^{-1}	Conditions	Method	$\Delta Hr°$ (298) kcal mol^{-1}	Reference	$\Delta Hf°$(g, 298) kcal mol^{-1}
−40.07 ± 0.14	1 atm, 523 K, gas phase.	Hydrogenation	−39.09	Lacher et al., 1967	−22.8 ± 0.2
−144.38	liq at 298 K	Combustion	−144.38	Smith et al., 1953	−22.5 ± 0.2
−144.00 ± 0.2	liq at 298 K	Combustion	−144.00 ± 0.2	Hu and Sinke, 1969	−22.8 ± 0.2
				Selected	−22.8 ± 0.2

TABLE 3–4. Ideal gas thermodynamic properties for dichloromethane

T, K	$C_p°$	$S°$	$-(G°-H_0°)/T$	$H°-H_0°$	$\Delta Hf°$	$\Delta Gf°$	log Kf
	cal K^{-1} mol^{-1}			kcal mol^{-1}			
0	0.0	0.0	0.0	0.0	−21.16	−21.16	infinite
100.00	8.547	53.813	45.721	0.809	−21.82	−20.23	44.204
150.00	9.268	57.412	49.051	1.254	−22.05	−19.38	28.238
200.00	10.126	60.192	51.500	1.738	−22.30	−18.45	20.165
273.15	11.627	63.565	54.292	2.533	−22.68	−16.99	13.594
298.15	12.164	64.606	55.114	2.830	−22.80	−16.46	12.066
300.00	12.204	64.682	55.172	2.853	−22.81	−16.42	11.962
400.00	14.237	68.477	58.035	4.177	−23.26	−14.22	7.769
500.00	15.934	71.843	60.466	5.689	−23.62	−11.92	5.210
600.00	17.296	74.873	62.619	7.353	−23.90	−9.55	3.479
700.00	18.403	77.625	64.569	9.139	24.11	7.14	2.230
800.00	19.321	80.144	66.361	11.027	−24.28	−4.71	1.286
900.00	20.095	82.466	68.023	12.999	−24.39	−2.25	0.547
1000.00	20.755	84.618	69.576	15.042	−24.47	0.22	−0.048
1100.00	21.322	86.624	71.036	17.147	−24.51	2.68	−0.532
1200.00	21.809	88.500	72.414	19.304	−24.52	5.16	−0.939
1300.00	22.231	90.263	73.920	21.506	−24.52	7.63	−1.283
1400.00	22.596	91.924	74.961	23.748	−24.50	10.11	−1.578
1500.00	22.913	93.494	76.145	26.024	−24.46	12.58	−1.833

TABLE 4-1. Structural data for trichloromethane

Structural parameter[a]	Reference			
	Ghosh, Trambarulo, and Gordy, 1952	Wolfe 1956	Jen and Lide 1962	Selected
C−H	1.073 ± 0.02	1.073[b]	1.100 ± 0.004	1.100 ± 0.004
C−Cl	1.767	1.762	1.758 ± 0.001	1.758 ± 0.001
∠ ClCCl	110.40	110.92	111.3 ± 0.2	111.3 ± 0.2

[a] Bond distances, 10^{-8} cm; bond angle, degrees.

[b] Assumed value.

TABLE 4-2. Vibrational assignments for trichloromethane

Mode No.	Symmetry class	Reference
		Shimanouchi 1972
		Wavenumber in cm^{-1}
ν_1	a_1	3034
ν_2	a_1	680
ν_3	a_1	363
ν_4	e	1220
ν_5	e	774
ν_6	e	261

marized in table 4−1. The more recent results of Jen and Lide (1962) are adopted, as their analysis included not only the data of Ghosh, Trambarulo, and Gordy (1952), but new results on $^{13}CH^{35}Cl_3$ also. The adopted parameters are consistent with earlier electron diffraction studies which are summarized in "Interatomic Distances" (1958).

Shimanouchi (1972) has critically reviewed the infrared and Raman data for trichloromethane, and his assignments, given in table 4−2, were selected.

Mathews (1926) has measured the enthalpy of vaporization calorimetrically at 333.3 K and has obtained

$$\Delta H_v(333.3\ \text{K}) = 7.02\ \text{kcal mol}^{-1}.$$

The correction to ideal gas is made using the Berthelot equation of state and $P_c = 54$ atm, $T_c = 536.5$ K (Zwolinski et al., TRCDP, 1972) to yield

$$\Delta H_v^\circ(333.3\ \text{K}) = 7.08\ \text{kcal mol}^{-1}.$$

Stull, Westrum, and Sinke (1969) reviewed the C_p° data for the liquid and so

$$C_p^\circ(\text{CHCl}_3, \text{l}, T) = 21.86 + 0.018T \qquad (240 \leqslant T \leqslant 330\ \text{K}),$$

thus

$$\Delta H_v^\circ(298\ \text{K}) = 7.49\ \text{kcal mol}^{-1}.$$

Patton (1952) has measured ΔH_v calorimetrically at 298 K and has obtained

$$\Delta H_v(\text{CHCl}_3, 298) = 7.44\ \text{kcal mol}^{-1},$$

and $P_{eq} = 199.1$ torr, so that ΔH_v° ($CHCl_3$, 298) = 7.46 kcal mol^{-1}, which is in good agreement with Mathews (1926). A mean of these data, summarized in table 4−3, is adopted. The data of Kolossowsky and Alimov (1934) appear too high.

Smith et al. (1953) have corrected the measurements of Eftring (1938) for the enthalpy change of reaction 4−1.

$$\text{CHCl}_3(\text{l}) + \text{H}_2\text{O}(\text{l}) + \tfrac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 3\text{HCl}\cdot 600\,\text{H}_2\text{O}. \qquad (4\text{−}1)$$

The measurements were made using quartz wool moistened with aqueous arsenious oxide to insure complete conversion of Cl_2 to HCl. When these data are corrected as explained in part 3, then for reaction 4−1

$$\Delta Hr^\circ(298\ \text{K}) = -112.6\ \text{kcal mol}^{-1},$$

and $\Delta Hf^\circ(\text{CHCl}_3, \text{l}, 298) = -32.61$, using auxiliary data

TABLE 4-3. Enthalpy of formation data for trichloromethane

ΔHv (obs) kcal mol^{-1}	Conditions	Methods	Reference	ΔHv° (298) kcal mol^{-1}
7.02	1 atm, 333.3 K	Calorimetric	Mathews, 1926	7.49
7.44	199.1 torr, 298 K	Calorimetric	Patton, 1952	7.46
7.69	295 K	Calorimetric	Kolosovskii and Alimov, 1934	7.67
			Selected	7.48

TABLE 4–4. Enthalpy of formation data for trichloromethane

$\Delta Hr°$ (obs) kcal mol^{-1}	Conditions	Method	$\Delta Hr°$ (298) kcal mol^{-1}	Reference	$\Delta Hf°$ (g, 298) kcal mol^{-1}
−112.6	liq, 293 K	Combustion	−112.6	Smith et al., 1953	−25.12
−113.1±0.2	liq, 298 K	Combustion	−113.1±0.2	Hu and Sinke, 1969	−24.62±0.2
				Selected	−24.6±0.2

TABLE 4–5. Ideal gas thermodynamic properties for trichloromethane

T, K	C_p°	S°	$-(G^\circ-H_0^\circ)/T$	$H^\circ-H_0^\circ$	ΔHf°	ΔGf°	Log Kf
	cal K^{-1} mol^{-1}			kcal mol^{-1}			
0	0.0	0.0	0.0	0.0	−23.43	−23.43	infinite
100.00	9.637	57.180	48.816	0.836	−24.03	−21.73	47.498
150.00	11.414	61.432	52.340	1.364	−24.21	−20.54	29.934
200.00	12.978	64.934	55.062	1.974	−24.36	−19.30	21.090
273.15	15.007	69.287	58.305	3.000	−24.55	−17.42	13.936
298.15	15.627	70.628	59.282	3.383	−24.60	−16.76	12.288
300.00	15.671	70.725	59.353	3.412	−24.60	−16.71	12.176
400.00	17.747	75.532	62.813	5.088	−24.77	−14.96	7.680
500.00	19.266	79.664	65.780	6.942	−24.86	−11.37	4.969
600.00	20.378	83.280	68.401	8.927	−24.90	− 8.66	3.156
700.00	21.217	86.487	70.760	11.009	−24.92	− 5.96	1.859
800.00	21.872	89.365	72.909	13.165	−24.90	− 3.25	0.887
900.00	22.398	91.973	74.885	15.379	−24.86	− 0.54	0.132
1000.00	22.831	94.356	76.714	17.641	−24.80	2.16	−0.473
1100.00	23.191	96.549	78.419	19.943	−24.73	4.84	−0.962
1200.00	23.494	98.580	80.016	22.277	−24.65	7.54	−1.372
1300.00	23.751	100.471	81.517	24.640	−24.57	10.21	−1.717
1400.00	23.971	102.239	82.935	27.026	−24.48	12.89	−2.013
1500.00	24.160	103.900	84.278	29.433	−24.38	15.56	−2.267

from Wagman et al. (1968). Therefore, $\Delta Hf^\circ(\mathrm{CHCl_3}, \mathrm{g}, 298) = -25.12$ kcal mol^{-1}.

Hu and Sinke (1969) have measured the enthalpy of reaction 4–1 in a rotating bomb calorimeter, using aqueous arsenious oxide to assure complete conversion of $\mathrm{Cl_2}$ to HCl. They obtained $\Delta Hr^\circ(298\ \mathrm{K}) = -113.1 \pm 0.2$ kcal mol^{-1} and, therefore,

$$\Delta Hf^\circ(\mathrm{CHCl_3}, \mathrm{g}, 298) = -24.62 \pm 0.2\ \mathrm{kcal\ mol^{-1}}.$$

These two values are consistent with one another and are summarized in table 4–4. The more recent work of Hu and Sinke (1969) in a rotating bomb calorimeter has been adopted.

These selected data have been used to calculate the ideal gas thermodynamic properties in the rigid-rotor harmonic-oscillator approximation. The results are presented in table 4–5. There are no experimental heat capacity or entropy measurements with which to compare these calculations.

5. Tetrachloromethane

Electron diffraction studies of tetrachloromethane (carbon tetrachloride) made by Karle and Karle (1949) and by Bartell, Brockway, and Schwendeman (1955) are in excellent agreement. The selected parameters and data are summarized in table 5–1.

Shimanouchi (1972) has critically reviewed the infrared and Raman data for tetrachloromethane, and his assignments, given in table 5–2, were selected.

Mathews (1926) measured the enthalpy of vaporization of tetrachloromethane calorimetrically at 348.6 K and obtained $\Delta H_v(348.6\ \mathrm{K}) = 7.16$ kcal mol^{-1}. This value is corrected to the ideal gas state using the Berthelot equation of state and $P_c = 44.97$, $T_c = 556.3$, and $P_{\mathrm{eq}} = 1$ atm (nominal) (Zwolinski et al., TRCDP, 1972); thus, $\Delta H_v^\circ(348.6\ \mathrm{K}) = 7.24$ kcal mol^{-1}. Stull, Westrum, and Sinke (1969) have summarized the experimental data on liquid heat capacities and have found:

$$C_p^\circ(\mathrm{CCl_4}, \mathrm{l}, T) = 27.65 + 0.013\,T \qquad (250 < T < 340\ \mathrm{K}).$$

These data are combined with $C_p^\circ(\mathrm{CCl_4}, \mathrm{g}, T)$ of this work to obtain $\Delta H_v^\circ(298) = 7.82$ kcal mol^{-1}.

Kolossowsky and Alimov (1934) measured the enthalpy of vaporization at 295 and 295.5 K. Their data were corrected in a similar fashion ($P_{\mathrm{eq}} = 0.13$ atm (Hildebrand and McDonald, 1959)) to that of Mathews

TABLE 5–1. Stuctural data for tetrachloromethane

Structural Parameter[a]	Reference		
	Karle and Karle 1949	Bartell, Brockway, and Schwendeman, 1955	Selected
C—Cl	1.77 ± 0.01	1.769 ± 0.005	1.769 ± 0.005
∠ClCCl	109.47	109.47	109.47

[a]Bond distances, 10^{-8} cm; bond angle, degrees.

TABLE 5–2. Vibrational assignments for tetrachloromethane

Mode No.	Symmetry class	Reference
		Shimanouchi, 1972
		Wavenumber in cm^{-1}
ν_1	a_1	458
ν_2	e	217
ν_3	f_2	776
ν_4	f_2	314

(1926) to yield $\Delta H_v^\circ(295\ K) = 7.84$ and $\Delta H_v^\circ(295.5\ K) = 7.87$ kcal mol^{-1}.

Pitzer (1941) measured the enthalpy of vaporization in a flow calorimeter at 349.8 K and obtained $\Delta H_v(349.8\ K) = 7.17 \pm 0.02$ kcal mol^{-1}. This yields $\Delta H_v^\circ(298) = 7.83 \pm 0.03$ kcal mol^{-1}.

Hildebrand and McDonald (1959) measured the enthalpy of vaporization calorimetrically at 298 K and obtained $\Delta H_v(298) = 7.746 \pm 0.005$ kcal mol^{-1}, which yields $\Delta H_v^\circ(298) = 7.762 \pm 0.01$ kcal mol^{-1} ($P_{eq} = 0.15$ atm). An error of ±0.03 kcal mol^{-1} was estimated for the data of Mathews (1926), and an average taken of this value, Pitzer's (1941), and Hildebrand and McDonald's (1959) weighted inversely to their errors. These data and the selected value are summarized in table 5–3.

Bodenstein, Gunter, and Hoffmeister (1926) measured the enthalpy change of reaction 5–1,

$$CCl_4(g) + 2H_2(g) \rightarrow C(s) + 4HCl(g) \qquad (5\text{–}1)$$

and obtained $\Delta Hr^\circ(293\ K) = -62.6 \pm 0.4$ kcal mol^{-1}. Their calorimeter was calibrated with the formation reaction for HCl(g). A value of $\Delta Hf^\circ(HCl, g, 298) = -22.0$ kcal mol^{-1} was used and is consistent with accepted values today (Wagman et al., 1968). Thus,

$$\Delta Hf^\circ(CCl_4, g, 298) - \Delta Hf^\circ(C, s, 298) = -25.6 \pm 0.4 \text{ kcal mol}^{-1}.$$

Domalski and Armstrong (1967) summarized the available data on the observed enthalpy of formation of solid carbon (soot) and concluded that ΔHf° (C, s, 298) = 3 ± 1 kcal mol^{-1} was reasonable in the absence of other data. This leads to $\Delta Hf^\circ(CCl_4, g, 298) = -22.6 \pm 1$ kcal mol^{-1}.

Smith et al. (1953) have measured the enthalpy of combustion of CCl_4 (reaction 5–2) using a static calorimeter and quartz wool moistened with aqueous arsenious oxide to assure complete conversion of Cl_2 to HCl

$$CCl_4(l) + 2H_2O(l) \rightarrow CO_2(g) + 4HCl \cdot 600H_2O. \qquad (5\text{–}2)$$

When their data were corrected as indicated in section 3 and combined with the necessary ΔHf° (Wagman et al., 1968), one obtains: $\Delta Hf^\circ(CCl_4, l, 298) = -30.4 \pm 0.5$ kcal mol^{-1}.

TABLE 5–3. Enthalpy of vaporization data for tetrachloromethane

ΔHv (obs) kcal mol^{-1}	Conditions	Methods	Reference	ΔHv° (298) kcal mol^{-1}
7.16	1 atm, 348.6 K	Calorimetric	Mathews, 1926	7.82
7.86	295 K	Calorimetric	Kolosovskii and Alimov, 1934	7.84
7.89	295.5 K	Calorimetric	Kolosovskii and Alimov, 1934	7.87
7.746±0.005	0.15 atm, 298 K	Calorimetric	Hildebrand and McDonald, 1959	7.762±0.01
7.170±0.02	1 atm, 349.8 K	Calorimetric	Pitzer, 1941	7.83 ±0.03
			Selected	7.79 ±0.03

TABLE 5–4. Enthalpy of formation data for tetrachloromethane

ΔHr° (obs) kcal mol^{-1}	Conditions	Method	ΔHr° (298) kcal mol^{-1}	Reference	ΔHf° (g, 298) kcal mol^{-1}
-62.57 ± 0.35	gas, 293.2 K	Hydrogenation	-62.57	Bodenstein, Gunter and Hoffmeister, 1926	$-22.6\ \pm1$
-86.35 ± 0.5	liquid, 295 K	Combustion	-86.35	Smith et al., 1953	$-22.6\ \pm0.5$
$-22.3\ \pm2$	solution, 298 K	Chlorination, $CHCl_3$	-22.3	Kirkbride, 1956	$-24.3\ \pm2$
	gas, 298 K	Explosion in H_2+O_2		Baibuz, 1961	$-24.6\ \pm2$
-86.02 ± 0.14	liquid, 298 K	Combustion	-86.02	Hu and Sinke, 1969	-22.90 ± 0.14
	gas, 630–720 K	Equilibrium with $COCl_2$	$-16.8\ \pm0.3$	Lord and Pritchard, 1969	-27.35 ± 0.3
				Selected	-22.90 ± 0.14

Kirkbride (1956) measured the enthalpy change for reaction 5–3 and obtained $\Delta Hr^\circ(298)=-22.3\pm2$ kcal mol^{-1}

$$CHCl_3(l)+Cl_2(g)\rightarrow CCl_4(soln)+HCl(g). \quad (5\text{–}3)$$

Wagman et al. (1968) gave the enthalpy of solution of tetrachloromethane in trichloromethane. It is small compared to the experimental error and can be neglected, so that $\Delta Hf^\circ(CCl_4, l, 298)=-32.1\pm2$ kcal mol^{-1}, using $\Delta Hf^\circ(CHCl_3, l, 298)$ from this work and ΔHf°(HCl, g, 298) from Wagman et al. (1968).

Baibuz (1961) has determined the enthalpy of formation of tetrachloromethane from its effect on explosions of $H_2(g)$ and $O_2(g)$. They deduced: $\Delta Hf^\circ(CCl_4, g, 298)=-24.6\pm2$ kcal mol^{-1}.

Hu and Sinke (1969) have measured the enthalpy change of reaction 5–2 in a rotating bomb calorimeter using aqueous arsenious oxide to assure complete comversion of Cl_2 to HCl. They obtained for reaction 5–2

$$\Delta Hr^\circ(298)=-86.02\pm0.14 \text{ kcal mol}^{-1},$$

from which one can obtain $\Delta Hf^\circ(CCl_4, l, 298)=-30.69\pm0.14$ kcal mol^{-1}. These data are summarized in table 5–4 from which it is seen that the above values are all consistent, within their experimental error, with the very careful study of Hu and Sinke (1969). Consequently, we have adopted $\Delta Hf^\circ(CCl_4, g, 298)=-22.90\pm0.14$ kcal mol^{-1}.

Lord and Pritchard (1969) have measured the equilibrium constant for reaction (5–4) over the range 630–720 K

$$CCl_4(g)+CO_2(g)\rightleftarrows 2COCl_2(g). \quad (5\text{–}4)$$

Their data were reduced using free energy functions (JANAF, 1971) in excellent agreement with those calculated here. They obtained: $\Delta Hr^\circ(298)=16.8\pm0.3$ kcal mol^{-1} for reaction 5–4 which when combined with ΔHf° data from Wagman et al. (1968) yields $\Delta Hf^\circ(CCl_4, g, 298)=-27.4\pm0.3$ kcal mol^{-1}. This result is totally out of line with the other data summarized in table 5–4 and indicates that either Lord and Pritchard had not reached equilibrium in their system, which seems unlikely, or that $\Delta Hf^\circ(COCl_2, g, 298)$ ought to be -50.1 ± 0.4 kcal mol^{-1} rather than -52.3 kcal mol^{-1} (Wagman et al., 1968).

The rigid-rotor harmonic-oscillator approximation (Mayer and Mayer, 1940) has been used with the above selected data to calculate the ideal gas thermodynamic properties for CCl_4. These are presented in table 5–5.

Pitzer (1941) has measured the heat capacity of CCl_4 in a flow calorimeter at 1 atm and has obtained: $C_p(CCl_4, g, 380\ K)=22.05\pm0.1$ and $C_p(CCl_4, g, 426\ K)=22.42\pm0.1$ cal K^{-1} mol^{-1}. These data are corrected to the ideal gas state by means of the Berthelot equation of state and yield: $C_p^\circ(CCl_4, g, 380\ K)=21.70\pm0.1$ and $C_p^\circ(CCl_4, g, 426\ K)=22.12\pm0.1$ cal K^{-1} mol^{-1}. Montgomery and DeVries (1942) similarly measured the heat capacity of CCl_4 and obtained $C_p(CCl_4, g, 380\ K)=21.81\pm0.06$ cal K^{-1} mol^{-1} which yields $C_p^\circ(CCl_4, g, 380\ K)=21.47\pm0.08$ cal K^{-1} mol^{-1}. Our calculated values are 21.61 and 22.28 cal K^{-1} mol^{-1} at 380 and 426 K, respectively. This is only in fair agreement with the work of Pitzer (1941) and at odds with that of Montgomery and DeVries (1942). *A uniform variation in the* assigned fundamentals of 1 percent results in a variation of ±0.06 cal K^{-1} mol^{-1} in C_p° at 380 and 426 K. Since this is a reasonable upper limit to the error in the fundamental assignment, one must conclude that there is an

TABLE 5–5. Ideal gas thermodynamic properties for tetrachloromethane

T, K	C_p°	S°	$-(G^\circ-H_0^\circ)/T$	$H^\circ-H_0^\circ$	ΔHf°	ΔGf°	Log Kf
	cal K^{-1} mol^{-1}			kcal mol^{-1}			
0	0.0	0.0	0.0	0.0	−22.383	−22.383	infinite
100.00	11.303	57.075	48.238	0.884	−22.905	−19.559	42.747
150.00	14.375	62.264	52.072	1.529	−22.999	−17.862	26.025
200.00	16.735	66.738	55.192	2.309	−23.009	−16.146	17.643
273.15	19.266	72.352	59.057	3.632	−22.939	−13.642	10.915
298.15	19.936	74.069	60.245	4.122	−22.900[a]	−12.796	9.380
300.00	19.982	74.192	60.330	4.159	−22.896	−12.733	9.276
400.00	21.920	80.230	64.575	6.262	−22.699	− 9.373	5.121
500.00	23.089	85.258	68.223	8.517	−22.470	− 6.069	2.653
600.00	23.824	89.537	71.428	10.866	−22.236	− 2.810	1.023
700.00	24.307	93.248	74.286	13.274	−22.008	0.410	−0.128
800.00	24.638	96.517	76.865	15.722	−21.789	3.597	−0.983
900.00	24.874	99.433	79.213	18.198	−21.579	6.759	−1.641
1000.00	25.048	102.064	81.369	20.695	−21.375	9.904	−2.164
1100.00	25.179	104.457	83.361	23.206	−21.178	13.007	−2.584
1200.00	25.280	106.653	85.211	25.729	−20.992	16.115	−2.935
1300.00	25.359	108.679	86.940	28.262	−20.815	19.198	−3.227
1400.00	25.423	110.561	88.560	30.801	−20.647	22.278	−3.478
1500.00	25.475	112.317	90.086	33.346	−20.484	25.339	−3.692

[a] While this paper was in proof, Mendenhall, Golden, and Benson reported a value of −22.4 ± 0.4 kcal mol^{-1} for ΔHf° (CCl_4, g, 298). J. Phys. Chem. **77**, 2707 (1973).

TABLE 5–6. Comparison of calculated and experimental gas phase heat capacity and entropy data for tetrachloromethane

T, K	C_p°, cal K^{-1} mol^{-1}			S°, cal K^{-1} mol^{-1}		
	obs	calc	Ref	obs	calc	Ref
380	21.47 ± 0.06	21.61	Montgomery and DeVries, 1942			
380	21.70 ± 0.1	21.61	Pitzer, 1941			
426	22.16 ± 0.1	22.28	Pitzer, 1941			
298.15				74.59	74.07	Lord and Blanchard, 1936
298.15				74.75	74.07	Stull, 1937
298.15				73.61 ± 0.15	74.07	Hicks, Hooley, and Stephenson, 1944[a]
298.15				77.03 ± 0.15	74.07	Hildebrand and McDonald, 1959[a]

[a] Recalculated.

error in the work of Montgomery and DeVries, though its source is not at all clear.

The entropy of CCl_4 has been measured by Lord and Blanchard (1936), Stull (1937), Hicks, Hooley, and Stephenson (1944), and by Hildebrand and McDonald (1959). These latter two authors were in agreement with regard to the thermal data, but Hildebrand and McDonald (1959) preferred an extrapolation from 18 K to 0 K using three Debye functions with $\theta = 70$ K and four Einstein functions with $\theta = 98$ K. This procedure fits the C_p data from 18 to 32 K while that of Hicks, Hooley, and Stephenson (1949) did not. The results were: $S^\circ(CCl_4$, l, 298$) = 51.67 \pm 0.15$ (Hildebrand and McDonald, 1959) and 51.25 ± 0.05 cal K^{-1} mol^{-1} (Hicks, Hooley, and Stephenson, 1949). Using the value for $\Delta H_v^\circ(298)$ adopted here and $P_{eq} = 0.15$ atm (Hildebrand and McDonald, 1959), one obtains $S^\circ(CCl_4$, g, 298$) = 74.03 \pm 0.15$ cal K^{-1} mol^{-1}. This is in excellent agreement with our calculated value of 74.07 cal K^{-1} mol^{-1}. Again, if the fundamental assignment is estimated to be accurate to 1 percent, then an error of ±0.10 cal K^{-1} mol^{-1} is obtained for the calculated entropy. The entropy and heat capacity data are summarized in table 5–6.

6. Fluoromethane

The infrared absorption spectrum of CH_3F was studied by Andersen et al. (1956). Their analysis of the fine structure gave reliable rotational constants. Their evaluated value of $I_A = 5.492 \times 10^{-40}$ g cm^2 (3.3074 uÅ^2) for CH_3F was adopted. Based on the microwave investigation by Gilliam et al. (1949), they reported the moment of intertia I_B for $^{12}CH_3F$ and $^{13}CH_3F$ as 19.79488 and 20.33113 uÅ^2, respectively. From these I_B values, we evaluated the other two principal moments of inertia for CH_3F as $I_B = I_C = 3.2880 \times 10^{-39}$ g cm^2 (19.8008 uÅ^2). The product $I_A I_B I_C$ was calculated to be 5.9373 × 10^{-117} g^3 cm^6 (1296.7 u^{3}Å^6), which was used in this study.

The infrared and Raman spectral data have been critically evaluated by Shimanouchi (1972) and his assignments, given in table 6–1, were adopted.

The enthalpy of formation of CH_3F has not been measured. Simple estimates of enthalpies of formation for fluorohydrocarbons based upon bond additives are notoriously bad (Rodgers, 1967); however, corrections for near neighbor bond interactions taken two at a time (Zahn, 1934) or two and three at a time (Allen, 1959) lead to significantly better results (Bernstein, 1965; Rodgers, 1967). The enthalpy of formation of CH_3F, based on the treatment of Allen (1959), may be related to the enthalpies of formation of CH_4, CH_2F_2, CHF_3, and CF_4 by reaction 6–1

TABLE 6–1. Vibrational assignments for fluoromethane

Mode No.	Symmetry class	Reference
		Shimanouchi 1972
		Wavenumber in cm^{-1}
ν_1	a_1	2930
ν_2	a_1	1464
ν_3	a_1	1049
ν_4	e	3006
ν_5	e	1467
ν_6	e	1182

$$\Delta Hf^\circ(CH_3F, g, 298) = 0.25[\Delta Hf^\circ(CF_4, g, 298) + \Delta Hf^\circ(CH_4, g, 298)] + 1.5[\Delta Hf^\circ(CH_2F_2, g, 298)] - \Delta Hf^\circ(CHF_3, g, 298). \tag{6–1}$$

Thus using $\Delta Hf^\circ(CH_4, g, 298) = -17.88$ (Wagman et al., 1968) and the values adopted in this work for the other compounds, one obtains $\Delta Hf^\circ(CH_3F, g, 298) = -56.8$ kcal mol^{-1}. We estimate the error at ±2 kcal mol^{-1}. (Using this formula to "estimate" $\Delta Hf^\circ(CH_3Cl, g, 298)$ using our selected data yields −19.8 kcal mol^{-1}.)

The ideal gas thermodynamic properties have been calculated using these selected data and the rigid-rotor harmonic-oscillator approximation (Mayer and Mayer, 1940). These calculations are presented in table 6–2. There are no experimental data with which to compare these calculations.

TABLE 6–2. Ideal gas thermodynamic properties for fluoromethane

T, K	C_p°	S°	$-(G^\circ - H_0^\circ)/T$	$H^\circ - H_0^\circ$	ΔHf°	ΔGf°	LogKf
	cal K^{-1} mol^{-1}			kcal mol^{-1}			
0	0.0	0.0	0.0	0.0	−54.88	−54.88	infinite
100.00	7.949	44.356	36.407	0.795	−55.59	−54.31	118.69
150.00	7.964	47.581	39.630	1.193	−55.82	−53.62	78.122
200.00	8.084	49.884	41.919	1.593	−56.12	−52.84	57.740
273.15	8.656	52.475	44.413	2.202	−56.62	−51.57	41.259
298.15	8.963	53.246	45.122	2.422	−56.80	−51.09	37.449
300.00	8.987	53.302	45.172	2.439	−56.81	−51.05	37.191
400.00	10.556	56.093	47.561	3.413	−57.51	−49.02	26.785
500.00	12.258	58.632	49.524	4.554	−58.14	−46.83	20.468
600.00	13.836	61.009	51.242	5.860	−58.68	−44.51	16.214
700.00	15.234	63.250	52.799	7.315	−59.13	−42.12	13.149
800.00	16.457	65.366	54.239	8.901	−59.49	−39.66	10.834
900.00	17.525	67.367	55.587	10.602	−59.78	−37.16	9.024
1000.00	18.454	69.263	56.861	12.402	−60.01	−34.63	7.569
1100.00	19.261	71.060	58.071	14.288	−60.18	−32.10	6.377
1200.00	19.963	72.767	59.225	16.250	−60.31	−29.53	5.378
1300.00	20.572	74.389	60.330	18.278	−60.40	−26.96	4.532
1400.00	21.102	75.934	61.390	20.362	−60.47	−24.38	3.805
1500.00	21.564	77.406	62.409	22.496	−60.52	−21.80	3.176

7. Difluoromethane

Lide (1952) recorded and analyzed the K-band microwave spectrum of the slightly asymmetric rotor CH_2F_2. From the three lines of lowest J values, the rotational constants for difluoromethane (methylene fluoride) were determined. Based on his reported values of A_0, B_0, and C_0 for $^{12}CH_2F_2$ and $^{13}CH_2F_2$, we derived the three principal moments of inertia for CH_2F_2 as $I_A = 1.7084 \times 10^{-39}$ g cm^2, $I_B = 7.9144 \times 10^{-39}$ g cm^2, and $I_C = 9.0740 \times 10^{-39}$ g cm^2 and the product $I_A I_B I_C =$ 1.22690×10^{-115} g^3 cm^6 (26796 u^{3}Å^6), which was adopted in this work.

The infrared and Raman spectra of CH_2F_2 have been investigated by Stewart and Nielsen (1949), Rank, Shull, and Pace (1950), and by Plyler and Benedict (1951). These data are summarized in table 7–1. Aside from an inverted assignment of ν_2 and ν_5 by Stewart and Nielsen (1949), the data are in excellent accord except for a minor discrepancy at ν_3. Plyler and Benedict (1951) measured the spectra of 18 halogenated methanes, studied over the range 2 – 38μm using a grating spectrometer. Purity of all samples was checked carefully, and assignments were determined by Raman polarization data and were checked with correlation diagrams. For these reasons, their assignments have been adopted.

Neugebauer and Margrave (1958) measured the enthalpy change of reaction 7–1

$$CH_2F_2(g) + O_2(g) \rightarrow CO_2(g) + 2HF \cdot 25\,H_2O(aq), \qquad (7\text{–}1)$$

in a rotating bomb calorimeter. They made six determinations with apparently random errors to obtain $\Delta Hr°(298) = -139.83 \pm 0.2$ kcal mol^{-1}. They also ob-

TABLE 7–1. Vibrational assignments for difluoromethane

Mode No.	Symmetry class	Reference			
		Stewart and Nielsen, 1949	Rank, Shull and Pace, 1950	Plyler and Benedict, 1951	Selected
		Wavenumber in cm^{-1}			
ν_1	1_1	2949	2963	2949	2949
ν_2		1262	1508	1508	1508
ν_3		1116	1078	1116	1116
ν_4		528.6	532	529	529
ν_5	a_2	1510.6	1262	1262	1262
ν_6	b_1	3015.2	3030	3012	3012
ν_7		1176.1	1170	1176	1176
ν_8	b_2	1435.4	1435	1435	1435
ν_9		1089.7	1089	1090	1090

TABLE 7–2. Ideal gas thermodynamic properties for difluoromethane

T, K	$C_p°$	$S°$	$-(G°-H_0°)/T$	$H°-H_0°$	$\Delta Hf°$	$\Delta Gf°$	logKf
	cal K^{-1} mol^{-1}			kcal mol^{-1}			
0	0.0	0.0	0.0	0.0	−106.37	−106.37	infinite
100.00	8.006	49.444	41.488	0.796	−107.04	−105.46	230.476
150.00	8.290	52.736	44.723	1.202	−107.30	−104.61	152.416
200.00	8.768	55.182	47.044	1.628	−107.59	−103.67	113.283
273.15	9.808	58.059	49.621	2.305	−108.05	−102.16	81.743
298.15	10.245	58.936	50.366	2.555	−108.20	−101.62	74.486
300.00	10.279	59.000	50.419	2.574	−108.21	−101.57	73.996
400.00	12.218	62.219	52.974	3.698	−108.80	−99.27	54.238
500.00	14.096	65.151	55.120	5.015	−109.30	−96.83	42.323
600.00	15.719	67.869	57.021	6.508	−109.72	−94.29	34.346
700.00	17.079	70.397	58.754	8.150	−110.06	−91.69	28.628
800.00	18.216	72.754	60.358	9.917	−110.32	−89.05	24.327
900.00	19.170	74.956	61.859	11.787	−110.53	−86.38	20.975
1000.00	19.976	77.019	63.273	13.746	−110.68	−83.68	18.288
1100.00	20.659	78.956	64.612	15.779	−110.79	−80.99	16.091
1200.00	21.242	80.779	65.884	17.874	−110.86	−78.27	14.254
1300.00	21.741	82.499	67.096	20.024	−110.92	−75.55	12.701
1400.00	22.169	84.127	68.255	22.220	−110.95	−72.82	11.367
1500.00	22.539	85.669	69.365	24.456	−110.97	−70.10	10.213

tained good agreement between the moles of $CO_2(g)$ and 0.5 times the moles of $HF \cdot 25\ H_2O(aq)$. Settle, Greenberg, and Hubbard (1971) have recently determined ΔHf°(HF, l, 298) $= -72.55 \pm 0.06$ kcal mol^{-1}, and Johnson, Smith, and Hubbard (1971) have determined the enthalpy of solution of HF(l), so that ΔHf° ($HF \cdot 25\ H_2O$, aq, 298) $= -77.011$ kcal mol^{-1}. (Compare to ΔHf° ($HF \cdot 25\ H_2O$, aq, 298) $= -76.292$ kcal mol^{-1} (Wagman et al., 1968)). This, combined with ΔHf° (CO_2, g, 298) (Wagman et al., 1968), leads to ΔHf° (CH_2F_2, g, 298) $= -108.2 \pm 0.2$ kcal mol^{-1} which was adopted.

The ideal gas thermodynamic properties have been calculated using the selected data given here and the rigid-rotor harmonic-oscillator approximation (Mayer and Mayer, 1940). These calculations are summarized in table 7–2. There are no experimental data on S° or C_p° of CH_2F_2 with which these calculations may be compared.

8. Trifluoromethane

Bernstein and Herzberg (1948) analyzed the high resolution infrared spectrum of trifluoromethane (fluoroform) in the 1 to 2.5 μm region and obtained 48.8440 uÅ^2 for the moment of inertia perpendicular to the symmetry axis. They then assumed tetrahedral angles and a C—H distance of 1.09 Å to calculate the C—F distance given in table 8–1. Gilliam, Edwards, and Gordy (1949) measured the microwave spectrum of $^{12}CHF_3$ and deduced 48.8388 ± 0.0002 uÅ^2 for the perpendicular moment of inertia, in excellent agreement with Bernstein and Herzberg (1948). Later, Ghosh, Trambarulo, and Gordy (1952) measured the microwave spectra of $^{13}CHF_3$ and $^{12}CDF_3$ and were thus able to uniquely define all three structural parameters. These are the parameters adopted in this work, and, as can be seen in table 8–1, they are in excellent agreement with the electron diffraction work of Thornton (1954) and also consistent with earlier studies ("Interatomic Distances," 1958).

The infrared and Raman spectral data for CHF_3 have been critically evaluated by Shimanouchi (1972), and his assignments, summarized in table 8–2, were adopted.

Neugebauer and Margrave (1958) determined the enthalpy change of reaction 8–1

$$CHF_3(g) + \tfrac{1}{2}O_2(g) + H_2O(l) \rightarrow CO_2(g) + 3HF \cdot 25H_2O, \qquad (8\text{–}1)$$

in a rotating bomb calorimeter. They made five determinations and noted that for each run the quantity, $y =$ moles $CO_2 - \frac{1}{3}$ moles HF, was positive to varying degrees and that traces of $CF_4(g)$ were observed in the products roughly proportional to y. This led them to suggest the occurrence of the following side reaction, 8–2

$$CHF_3(g) + \tfrac{1}{2}O_2(g) \rightarrow \tfrac{1}{4}CO_2(g) + \tfrac{3}{4}CF_4(g) + \tfrac{1}{2}H_2O(l). \qquad (8\text{–}2)$$

If one assumes that the entire discrepancy, y, can be attributed to reaction 8–2, then ΔHf°(CHF_3, g, 298) may be calculated using ΔHf°(CF_4, g, 298) $= -223.02$ kcal mol^{-1} (this work) and other auxiliary data in section 1.6. The average of the value so obtained is ΔHf°(CHF_3, g, 298) $= -166.1 \pm 1.3$ kcal mol^{-1}. However, there is a marked trend in the calculated values to be more negative with increasing values of "y" suggesting that this procedure overcorrects for the side reaction. It is also possible to ignore the presence of side reactions and calculate ΔHf°(CHF_3, g, 298) based on the $CO_2(g)$ analyses. When this is done, no significant trend is observed, and ΔHf°(CHF_3, g, 298) $= -165.14 \pm 0.5$ kcal mol^{-1} is obtained.

TABLE 8–2. Vibrational assignments for trifluoromethane

Mode no.	Symmetry class	Reference
		Shimanouchi, 1972
		Wavenumber in cm^{-1}
ν_1	a_1	3036
ν_2	a_1	1117
ν_3	a_1	700
ν_4	e	1372
ν_5	e	1152
ν_6	e	507

TABLE 8–1. Structural data for trifluoromethane

Structural parameter[a]	Reference				
	Bernstein and Herzberg, 1948	Gilliam, Edwards, and Gordy, 1949	Thornton 1954	Ghosh, Trambarulo, and Gordy, 1952	Selected
C—H	1.09[b]	1.111[b]		1.098 ± 0.02	1.098
C—F	1.329	1.326 ± 0.013	1.334 ± 0.005	1.332	1.332
∠ FCF	109.47[b]	110 ± 3[b]	108.47	108.80	108.80
∠ HCF					110.13

[a] Bond distances, 10^{-8} cm; bond angle, degrees.

[b] Assumed.

TABLE 8–3. Enthalpy of formation data for trifluoromethane

$\Delta Hr°$ (obs) kcal mol^{-1}	Conditions	Method	$\Delta Hr°$ (298) kcal mol^{-1}	Reference	$\Delta Hf°$ (g, 298) kcal mol^{-1}
-90.1 ± 1.3	298 K, 30 atm	Rotating bomb combustion with correction for CF_4		Neugebauer and Margrave, 1958	-166.4 ± 1.3
-91.33 ± 0.5	298 K, 30 atm	Rotating bomb combustion without correction for CF_4		Neugebauer and Margrave, 1958	-165.1 ± 0.5
				Selected	-165.7 ± 1

TABLE 8–4. Ideal gas thermodynamic properties for trifluoromethane

T, K	C_p°	$S°$	$-(G°-H_0^\circ)/T$	$H°-H_0^\circ$	$\Delta Hf°$	$\Delta Gf°$	log Kf
	cal K^{-1} mol^{-1}			kcal mol^{-1}			
0	0.0	0.0	0.0	0.0	−164.04	−164.04	infinite
100.00	8.101	51.591	43.622	0.797	−164.68	−162.49	355.122
150.00	8.809	54.992	46.875	1.217	−164.95	−161.34	235.069
200.00	9.863	57.666	49.248	1.683	−165.22	−160.09	174.939
273.15	11.609	60.995	51.959	2.468	−165.59	−158.16	126.542
298.15	12.222	62.038	52.761	2.766	−165.70	−157.47	115.429
300.00	12.267	62.114	52.819	2.789	−165.71	−157.42	114.679
400.00	14.611	65.970	55.633	4.135	−166.11	−154.59	84.464
500.00	16.591	69.451	58.054	5.698	−166.42	−151.67	66.296
600.00	18.159	72.620	60.222	7.439	−166.66	−148.70	54.164
700.00	19.386	75.516	62.203	9.319	−166.83	−145.69	45.488
800.00	20.354	78.170	64.035	11.308	−166.96	−142.66	38.974
900.00	21.129	80.614	65.744	13.383	−167.04	−139.62	33.905
1000.00	21.759	82.874	67.345	15.529	−167.09	−136.57	29.847
1100.00	22.277	84.973	68.853	17.731	−167.11	−133.53	26.530
1200.00	22.707	86.930	70.279	19.981	−167.12	−130.47	23.761
1300.00	23.068	88.762	71.631	22.270	−167.11	−127.41	21.420
1400.00	23.373	90.483	72.917	24.593	−167.10	−124.35	19.412
1500.00	23.632	92.105	74.142	26.943	−167.08	−121.30	17.674

Since the presence of CF_4(g) clearly indicates some side reaction is taking place, but it appears "y" is not a quantitative measure of its extent, we shall adopt an unweighted average of these two calculations, namely, $\Delta Hf°(CHF_3$, g, 298$) = -165.7 \pm 1$ kcal mol^{-1}. These results are summarized in table 8–3.

The ideal gas thermodynamic properties have been calculated using the data selected here and the rigid-rotor harmonic-oscillator approximation (Mayer and Mayer, 1940). These calculations are summarized in table 8–4.

Vanderkooi and DeVries (1956) used the wire ribbon method to determine the heat capacity (constant volume) of CHF_3 at 298 K as a function of pressure ($<$ 0.005 torr) and extrapolated their data to obtain $C_v^\circ(CHF_3$, g, 298$) = 10.23 \pm 0.13$ cal K^{-1} mol^{-1}. This leads to $C_p^\circ(CHF_3$, g, 298$) = 12.22 \pm 0.13$ cal K^{-1} mol^{-1}, in excellent agreement with our calculated value, 12.27 cal K^{-1} mol^{-1}.

Valentine, Brodale, and Giauque (1962) have obtained low temperature thermochemical data on CHF_3 solid and liquid from 15 K to its boiling point at 190.97 K, including $\Delta H_v(CHF_3$, 190.97 K$) = 3.994 \pm 0.004$ kcal mol^{-1}, to obtain $S^r(CHF_3$, g, 1 atm, 190.97 K$) = 57.01$. The Berthelot equation of state and $T_c = 298.89$ K and $P_c = 47.73$ atm (Zwolinski et al., TRCDP, 1972) are used to obtain $S° - S^r = 0.13$ cal K^{-1} mol^{-1}, so that $S°(CHF_3$, g, 190.97 K$) = 57.14$ cal K^{-1} mol^{-1}, in excellent agreement with the calculated value, 57.22 cal K^{-1} mol^{-1}. These data are summarized in table 8–5.

TABLE 8–5. Comparison of calculated and experimental gas phase heat capacity and entropy data for trifluoromethane

T, K	$C°$, cal K^{-1} mol^{-1}			$S°$, cal K^{-1} mol^{-1}		
	obs	calc	Ref	obs	calc	Ref
300	12.22±0.13	12.27	Vanderkooi and DeVries, 1956			
190.97				57.14	57.22	Valentine, Brodale and Giauque, 1962

TABLE 9–1. Structural data for tetrafluoromethane

Structural parameter [a]	Reference					
	Alcock and Hurst, 1951	Bowen, 1954	Thornton, 1954	Hoffman and Livingston, 1953	Brockway, 1954	Selected
C–F	1.33±0.02	1.337±0.022	1.322±0.005	1.317±0.005	1.323±0.005	1.321±0.003

[a] Bond distances, 10^{-8} cm; bond angle, degrees.

9. Tetrafluoromethane

The structure of tetrafluoromethane (carbon tetrafluoride) has been studied by Alcock and Hurst (1951), using neutron diffraction; and by Bowen (1954), Thornton (1954), Hoffman and Livingston (1953), and Brockway (1954), using the electron diffraction technique. The last three authors have estimated errors of ±0.005 Å, so that the selected value was obtained as an unweighted average of these yielding: C—F = 1.321 ± 0.003 Å. References to earlier and less accurate work may be found in "Interatomic Distances" (1958). The structural data are summarized in table 9–1.

Shimanouchi (1972) has critically reviewed the infrared and Raman spectral data on CF_4 and his fundamental assignments, given in table 9–2, have been adopted.

Early calorimetric data on CF_4 was frequently obtained from reactions leading to poorly characterized products; as a result, values for $\Delta Hf°$ (CF_4, g, 298) differing by 20 to 30 kcal mol^{-1} were reported. Patrick (1961) has summarized this earlier work, and it shall not be dealt with in this report.

Scott, Good, and Waddington (1955) and Good, Scott, and Waddington (1956) used a rotating bomb calorimeter to determine $\Delta Hr°(298) = -160.3 \pm 0.9$ kcal mol^{-1} for reaction 9–1,

$$C_2F_4(\text{poly}) + O_2(g) + 2H_2O(l) \rightarrow 2CO_2(g) + 4HF \cdot 10H_2O, \qquad (9\text{–}1)$$

and $\Delta Hr°(298) = -118.8 \pm 0.5$ kcal mol^{-1} for reaction 9–2,

$$C_2F_4(\text{poly}) + O_2(g) \rightarrow CF_4(g) + CO_2(g). \qquad (9\text{–}2)$$

TABLE 9–2. Vibrational assignments for tetrafluoromethane

Mode no.	Symmetry class	Reference Shimanouchi, 1972 Wavenumber in cm^{-1}
ν_1	a_1	908
ν_2	e	435
ν_3	f_2	1283
ν_4	f_2	632

By combining these data with the appropriate auxiliary data from section 1.6 and $\Delta Hf°(HF \cdot 10H_2O, aq, 298) = -76.968$ kcal mol^{-1} (Settle, Greenberg, and Hubbard, 1971; Johnson, Smith, and Hubbard, 1971), one calculates $\Delta Hf°(CF_4, g, 298) = -223.7 \pm 1$ kcal mol^{-1}.

Neugebauer and Margrave (1956) have studied the enthalpy changes of the gas phase explosions of C_2F_4 pure and mixed with hydrogen (reactions 9–3 and 9–4,

$$C_2F_4(g) \rightarrow C\,(\text{amp}) + CF_4(g) \qquad (9\text{–}3)$$

$$C_2F_4(g) + 2H_2(g) \rightarrow 2C\,(\text{amp}) + 4HF \cdot 15H_2O \qquad (9\text{–}4)$$

They obtained $\Delta Hr°(298) = -63.57 \pm 0.4$ for reaction 9–3 and $\Delta Hr°(298) = -147.8 \pm 1$ kcal mol^{-1} for reaction 9–4.

In addition, they determined from combustion studies of the "soot" produced in their reactions that $\Delta Hf°$(C, amp, 298) = 1.7 ± 0.2 kcal mol^{-1}. These data, combined with $\Delta Hf°(\text{HF} \cdot 15\text{H}_2\text{O}, \text{aq}, 298) = -76.991$ kcal mol^{-1} (Settle, Greenberg, and Hubbard, 1971; Johnson, Smith, and Hubbard, 1971), yield $\Delta Hf°(\text{CF}_4, \text{g}, 298) = -222.0 \pm 1$ kcal mol^{-1}.

Cox, Gundry, and Head (1965) studied the enthalpy of combustion of $\text{C}_{12}\text{F}_{22}$ in a rotating bomb calorimeter with and without hydrogen-containing material added. From this, they deduced the enthalpy change of reaction 9–5, $\Delta Hr°(298) = -41.38 \pm 0.3$ kcal mol^{-1}

$$\text{CF}_4(\text{g}) + 2\text{H}_2\text{O(l)} \rightarrow \text{CO}_2(\text{g}) + 4\text{HF} \cdot 20\text{H}_2\text{O}. \qquad (9\text{–}5)$$

Using the auxiliary data from Wagman et al. (1968) and $\Delta Hf°(\text{HF} \cdot 20\text{H}_2\text{O}, \text{aq}, 298) = -77.004$ kcal mol^{-1} (Settle, Greenberg, and Hubbard, 1971; Johnson, Smith, and Hubbard, 1971), one calculates $\Delta Hf°(\text{CF}_4, \text{g}, 298) = -224.1 \pm 0.3$ kcal mol^{-1}.

Wood, Lagow, and Margrave (1967) obtained a sample of C_2F_4 polymer from Scott, Good, and Waddington (1955) and reacted it with 4 atm of fluorine in a nickel-lined calorimeter. Their data give for reaction 9–6, $\Delta Hr°(298) = -246.84 \pm 0.07$ kcal mol^{-1}

$$\text{C}_2\text{F}_4(\text{poly}) + 2\text{F}_2(\text{g}) \rightarrow 2\text{CF}_4(\text{g}). \qquad (9\text{–}6)$$

From the enthalpy change for reaction 9–1 determined by Scott, Good, and Waddington (1955), one can calculate $\Delta Hf°(\text{C}_2\text{F}_4, \text{poly}, 298) = -199.0 \pm 0.9$ kcal mol^{-1}. Incorporating this value with $\Delta Hr°(298)$ for reaction 9–6 yields $\Delta Hf°(\text{CF}_4, \text{g}, 298) = -222.9 \pm 0.9$ kcal mol^{-1}.

Domalski and Armstrong (1967) studied the same reaction (9–6) but with 15 atm fluorine which, they report, surpressed the formation of higher perfluoroalkanes. They obtained $\Delta Hr°(298) = -247.92 \pm 0.07$ kcal mol^{-1} [compare to $\Delta Hr°(298) = -246.84$ kcal mol^{-1} of Wood, Lagow, and Margrave (1967)]. As above, this yields $\Delta Hf°(\text{CF}_4, \text{g}, 298) = -223.5 \pm 0.9$ kcal mol^{-1}. These workers have also studied the enthalpy of formation of CF_4 (reaction 9–7) with 15–20 atm fluorine.

$$\text{C(graphite)} + 2\text{F}_2(\text{g}) \rightarrow \text{CF}_4(\text{g}) \qquad (9\text{–}7)$$

They obtained $\Delta Hf°(\text{CF}_4, \text{g}, 298) = -222.87 \pm 0.4$ kcal mol^{-1}.

Greenberg and Hubbard (1968) also determined the enthalpy of formation of CF_4 (reaction 9–7) in a bomb calorimeter using 25 atm of fluorine. They obtained $\Delta Hf°(\text{CF}_4, \text{g}, 298) = -223.05 \pm 0.18$ kcal mol^{-1} which is in excellent agreement with that reported by Domalski and Armstrong (1967). If one combines the enthalpy change of reaction 9–6 obtained by Domalski and Armstrong (1967) (the high fluorine pressure makes this the preferred datum) with that of reaction 9–2 measured by Scott, Good, and Waddington (1956), one has $\Delta Hr°(298) = -129.1 + 0.5$ kcal mol^{-1} for reaction 9–8.

$$\text{CO}_2(\text{g}) + 2\text{F}_2 \rightarrow \text{CF}_4(\text{g}) + \text{O}_2(\text{g}), \qquad (9\text{–}8)$$

from which one may calculate $\Delta Hf°(\text{CF}_4, \text{g}, 298) = -223.17 \pm 0.5$ kcal mol^{-1}.

These last three determinations of $\Delta Hf°(\text{CF}_4, \text{g}, 298)$ have all been independent of $\Delta Hf°(\text{HF} \cdot n\text{H}_2\text{O}, \text{aq}, 298)$. The selected value has been obtained as an average of these three determinations weighted inversely to their experimental errors; thus $\Delta Hf°(\text{CF}_4, \text{g}, 298) = -223.02 \pm 0.2$ kcal mol^{-1}. These data and our selected value are summarized in table 9–3.

It is interesting to note that the average of all the data of table 9–3, again weighted inversely to their errors, is $\Delta Hf°(\text{CF}_4, \text{g}, 298) = -223.22$ kcal mol^{-1}. The work of Cox, Gundry, and Head (1965) deviates from this average by 0.9 kcal mol^{-1}, essentially three times the experimental deviation. If we eliminate this value, the average then becomes $\Delta Hf°(\text{CF}_4, \text{g}, 298) = -223.03$ kcal mol^{-1}, indicating that the data for $\Delta Hf°(\text{CF}_4, \text{g}, 298)$ are in excellent agreement with the new determinations of $\Delta Hf°(\text{HF}, \text{l}, 298)$ and $\Delta Hf°(\text{HF} \cdot n\text{H}_2\text{O}, \text{aq}, 298)$ of Settle, Greenberg, and Hubbard (1971) and Johnson, Smith, and Hubbard (1971). They have been adopted for use in this report.

The rigid-rotor harmonic-oscillator approximation (Mayer and Mayer, 1940) has been used with these selected data to calculate the ideal gas thermodynamic functions for CF_4. These calculations are summarized in table 9–4.

The entropy of CF_4 has been determined from low temperature thermal studies by Eucken and Schroder (1938) at 122 K and by Smith and Pace (1969) at 145.12 K (normal boiling point). Their data were corrected to the ideal gas state using the Berthelot equation of state and $P_c = 36.9$ atm and $T_c = 227.5$ K (Zwolinski et al., TRCDP, 1972). As can be seen in table 9–5, the agreement between the experimental data and our calculations is excellent. However, the vibrational contribution to the entropy at these temperatures is only of the order of 2 percent, so that this is not a sensitive test of the fundamental assignment or of the validity of the rigid-rotor harmonic-oscillator approximation.

Hwang and Martin (1964) have measured the constant volume heat capacity at 10 to 16 atm and from 300 to 470 K. The correction $C_v^\circ - C_v^r$ was determined from the Berthelot equation of state which gives:

$$C_v^\circ - C_v^r = -\frac{108\,RT_c^3P}{128\,T^3P_c} + \frac{1}{R}\left[\frac{108\,RT_c^3P}{128\,T^3P_c}\right]^2. \qquad (9\text{–}9)$$

The authors' lowest pressure data were reduced to C_v° values using eq 9–9. The uncertainty in this correction is estimated at ±0.1 cal K^{-1} mol^{-1}. The data, summarized in table 9–5, are in excellent accord with the calculated C_p° indicating no significant correction for anharmonicity is needed up to temperatures of 500 K for CF_4.

Table 9–3. Enthalpy of formation data for tetrafluoromethane

$\Delta Hr°$ (obs) kcal mol^{-1}	Conditions	Method	$\Delta Hr°$(298) kcal mol^{-1}	Reference	$\Delta Hf°$ (g, 298) kcal mol^{-1}
−118.8±0.5	298 K and 30 atm O_2	Rotating bomb calorimeter		Scott, Good and Waddington, 1955; Good, Scott and Waddington, 1956	−223.7±1.
−84.23±1.0	298 K and 30 atm H_2	Bomb calorimeter		Neugebauer and Margrave, 1956	−222.0±1.
−41.38±0.3	298 K and 30 atm O_2	Rotating bomb calorimeter		Cox, Gundry and Head, 1965	−224.1±0.3
−246.84±0.07	298 K and 4 atm F_2	Bomb calorimeter		Wood, Lagow and Margrave, 1967	−222.9±0.9
−247.92±0.07	298 K and 15 atm F_2	Bomb calorimeter		Domalski and Armstrong, 1967	−223.5±0.9
−222.87±0.4	298 K and 15 atm F_2	Bomb calorimeter		Domalski and Armstrong, 1967	−222.87±0.4
−223.09±0.18	298 K and 15 atm F_2	Bomb calorimeter		Greenberg and Hubbard, 1968	−223.04±0.18
−129.1±0.5	298 K and 15 atm F_2	Combination of data		Scott, Good and Waddington, 1955; Good, Scott and Waddington, 1956; Domalski and Armstrong, 1967	−223.17±0.5
				Selected	−223.02±0.2

Table 9–4. Ideal gas thermodynamic properties for tetrafluoromethane

T, K	C_p°	S°	$-(G^\circ-H_0^\circ)/T$	$H^\circ-H_0^\circ$	ΔHf°	ΔGf°	$\log Kf$
	cal K^{-1} mol^{-1}			kcal mol^{-1}			
0	0.0	0.0	0.0	0.00	−221.591	−221.591	infinite
100.00	8.304	50.733	42.731	0.800	−222.196	−219.108	478.858
150.00	9.590	54.317	46.021	1.244	−222.477	−217.501	316.898
200.00	11.319	57.309	48.477	1.766	−222.708	−215.805	235.820
273.15	13.811	61.212	51.375	2.687	−222.955	−213.235	170.611
298.15	14.589	62.456	52.252	3.042	−223.020	−212.345	155.653
300.00	14.645	62.546	52.315	3.069	−223.025	−212.278	154.644
400.00	17.302	67.140	55.459	4.673	−223.209	−208.665	114.009
500.00	19.289	71.226	58.211	6.507	−223.304	−205.017	89.613
600.00	20.740	74.878	60.690	8.512	−223.341	−201.356	73.344
700.00	21.798	78.159	62.955	10.642	−223.338	−197.693	61.722
800.00	22.579	81.123	65.044	12.863	−223.308	−194.029	53.006
900.00	23.165	83.818	66.983	15.152	−223.261	−190.372	46.228
1000.00	23.612	86.283	68.791	17.491	−223.199	−186.713	40.806
1100.00	23.959	88.550	70.486	19.871	−223.129	−183.085	36.376
1200.00	24.233	90.647	72.080	22.281	−223.059	−179.438	32.680
1300.00	24.453	92.596	73.584	24.716	−222.990	−175.806	29.556
1400.00	24.631	94.415	75.007	27.170	−222.923	−172.171	26.877
1500.00	24.777	96.119	76.359	29.641	−222.860	−168.550	24.558

TABLE 9–5. Comparison of calculated and experimental gas phase heat capacity and entropy data for tetrafluoromethane

T, K	C_p°, cal K^{-1} mol^{-1}			S°, cal K^{-1} mol^{-1}		
	obs	calc	Ref	obs	calc	Ref
122				52.49 ± 0.3	52.43	Eucken and Schroder, 1938
145.12				54.04 ± 0.13	54.00	Smith and Pace, 1969
303	14.74 ± 0.15	14.74	Hwang and Martin, 1964			
323	15.31 ± 0.15	15.32	Hwang and Martin, 1964			
373	16.63 ± 0.15	16.65	Hwang and Martin, 1964			
423	17.85 ± 0.15	17.81	Hwang and Martin, 1964			
473	18.91 ± 0.15	18.81	Hwang and Martin, 1964			

10. Comparison

The thermodynamic functions, C_p°, S°, and ΔHf°, recommended in this report are compared with those in several other major compilations at 298.15 and 700 K in tables 10–1 through 10–4. In general, the agreement is quite good at 298.15 K but scatter appreciably at 700 K. This undoubtedly reflects the fact that choices in molecular parameters are more critical for the calculated functions at higher temperatures. Furthermore, it seems clear that some error was made in calculating the enthalpy of formation of the chloromethanes reported by Gurvich et al. (1962) at 700 K.

TABLE 10–1. Comparison of the ideal gas thermodynamic data at 1 atm and 298.15 K for chloromethanes

	CH_3Cl			CH_2Cl_2			$CHCl_3$			CCl_4		
	C_p°	S°	$-\Delta Hf^\circ$	C_p°	S°	$-\Delta Hf^\circ$	C_p°	S°	$-\Delta Hf^\circ$	C_p°	S°	ΔHf°
	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}
Landolt-Bornstein, 1961	9.73	55.81	19.6	12.21	64.58		15.70	70.65	24.0	19.93	74.02	25.5
Gurvich et al., 1962 (USSR)		55.86	20.6		64.60	22.4		70.72	24.9		74.11	24.6
Wagman et al., 1968 (NBS TN–270–3)	9.74	56.04	19.3	12.18	64.56	22.1	15.70	70.65	24.7	19.91	74.03	24.6
Stull, Westrum and Sinke, 1969	9.74	56.04	20.6	12.22	64.59	22.8	15.71	70.66	24.2	20.02	74.12	24.0
JANAF, 1969	9.73	55.99	20.7	12.16	64.57	22.8	15.63	70.63	24.7	19.93	74.02	22.9
This work, 1972	9.74	55.97	19.6	12.16	64.61	22.8	15.63	70.63	24.6	19.94	74.07	22.9

TABLE 10–2. Comparison of the ideal gas thermodynamic data at 1 atm and 298.15 K for fluoromethanes

	CH_3F			CH_2F_2			CHF_3			CF_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}
Landolt-Bornstein, 1961	8.94	53.25	59.0	10.27	58.80	105.5	21.21	62.02	162.6	14.63	62.62	217.0
Gurvich et al., 1962 (USSR)		53.24	67.9		58.94	117.9		62.04	169.9		62.47	219.9
Wagman et al., 1968 (NBS TN–270–3)	8.96	53.25		10.25	58.94	106.8	12.20	62.04	164.5	14.60	62.50	221.0
Stull, Westrum and Sinke, 1969	8.96	53.25	55.9	10.25	58.94	108.2	12.20	62.04	166.7	14.68	62.50	223.0
JANAF, 1969	8.96	53.25	56.0	10.24	58.94	107.7	12.20	62.03	166.6	14.59	62.45	223.0
This Work, 1972	8.96	53.25	56.8	10.25	58.94	108.2	12.22	62.04	165.7	14.59	62.46	223.0

TABLE 10–3. Comparison of the ideal gas thermodynamic data at 1 atm and 700 K for chloromethanes

	CH_3Cl			CH_2Cl_2			$CHCl_3$			CCl_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}
Landolt-Bornstein, 1961	15.92	66.54	21.68	18.47	77.65		21.22	86.50	24.3	24.31	93.19	24.6
Gurvich et al., 1962 (USSR)		66.78	15.3		77.67	16.1		86.62	17.2		93.30	15.5
Stull, Westrum, and Sinke, 1969	15.93	66.81	22.7	18.47	77.75	24.1	21.27	86.58	24.5	24.61	93.44	23.0
JANAF, 1969	15.92	66.73	22.7	18.40	77.59	24.2	21.22	86.49	25.0	24.31	93.20	22.1
This Work, 1972	15.94	66.73	21.7	18.40	77.63	24.1	21.22	86.49	24.9	24.31	93.25	22.0

TABLE 10–4. Comparison of the ideal gas thermodynamic data at 1 atm and 700 K for fluoromethanes

	CH_3F			CH_2F_2			CHF_3			CF_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}
Landolt-Bornstein, 1961	15.20	63.22	61.42	17.11	70.29	107.4	19.36	75.48	163.7	21.85	78.67	217.4
Gurvich et al, 1962 (USSR)		63.22	63.04		70.40	112.3		75.50	163.4		78.20	212.3
Stull, Westrum and Sinke, 1969	15.23	63.27	58.22	17.08	70.41	110.1	19.36	75.58	167.8	21.99	78.32	223.3
JANAF, 1969	15.23	63.25	58.33	17.08	70.39	109.6	19.36	75.48	167.8	21.80	78.16	223.4
This Work, 1972	15.23	63.25	59.1	17.08	70.40	110.1	19.38	75.52	166.8	21.80	78.16	223.3

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