Ideal Gas Thermodynamic Properties of Six Chloroethanes

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The thermodynamic properties: C_p°, S°, $H^\circ-H_0^\circ$, $-(G^\circ-H_0^\circ)/T$, ΔHf°, ΔGf°, and log K_f for chloroethane, 1,1-dichloroethane, 1,1,1-trichloroethane, 1,1,1,2-tetrachloroethane, pentachloroethane, and hexachloroethane in the ideal gaseous state in the temperature range from 0 to 1500 K and at 1 atm were evaluated by statistical thermodynamic methods based on a rigid-rotor harmonic-oscillator model. The internal rotation contributions to thermodynamic functions were calculated by using a partition function formed by summation of internal rotation energy levels. The internal rotation barrier heights (in kcal mol^{-1}) employed for generation of the energy levels for each of the above six chloroethanes are: 3.69, 3.54, 5.08, 10.38, 14.43, and 14.7, respectively. The calculated heat capacities and entropies are compared with available experimental data. The derived 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: Chloroethane with a symmetry top; ideal gas thermodynamic properties; internal rotation; internal rotation barrier heights; torsional fundamental.

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1. Introduction

The ideal gas thermodynamic properties: heat capacity (C_p°), entropy (S°), 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 ($\log K_f$) for six chloroethanes have been evaluated by the statistical thermodynamic method based on a rigid-rotor harmonic-oscillator model. These properties are tabulated at temperatures from 0 to 1500 K and at a pressure of one atmosphere. The procedures for selection, evaluation, and calculation of data are similar to those used in "Ideal Gas Thermodynamic Properties of Eight Chloro- and Fluoromethanes" by Rodgers, Chao, Wilhoit, and Zwolinski (1974). Units, symbols, fundamental constants, and auxiliary data which were described in that review also apply to the present work. The atomic masses are H = 1.008, C = 12.011, and Cl = 35.453.

Each of these six chloroethanes has hindered internal rotation about the C—C bond in the molecule, and at least one of the rotating groups is a symmetric top. The practicality of handling the internal rotation problem when one group is symmetric formed the basis of selection of this particular set of molecules. The internal rotation contributions to the thermodynamic properties for each compound were calculated by use of a partition function formed by summation of the internal rotation energy levels. These energy levels were obtained from an approximate solution of the Schroedinger equation using the adopted potential function $V = \frac{1}{2}V_3(1 - \cos 3\theta)$, where V_3 is the potential barrier height, and θ is the angle of internal rotation. A computer program, provided by J. Laane, Department of Chemistry, Texas A&M University (Lewis et al. 1972), was used to generate these energy levels. The input data required are the potential barrier height (V_3) and the internal rotational constant (F). The value of V_3 for each compound was evaluated from the adopted molecular structure and torsional frequency. The internal rotational constant F was derived from the reduced moment (I_r) using the relationship: $F = h/8\pi^2 cI_r$.

The calculated internal rotation energy levels up to about 15000 cm^{-1} were employed for evaluation of the internal rotation contributions to the thermodynamic properties for each compound, since the contributions from energy levels higher than 15000 cm^{-1} to these properties are insignificant even at the highest temperature, 1500 K, of the present tables. Since the maximum number of reliable energy levels which can be generated by Laane's computer program is about 150, and for 1,1,1,2-tetrachloroethane the highest energy level calculated by his computer program is 7000 cm^{-1}, the missing levels between the highest calculated energy level and the selected 15000 cm^{-1} limit were evaluated on the assumption of free internal rotation in this energy range. For example, 369 internal rotation energy levels were employed in calculations for the CH_2ClCCl_3 molecule of which 137 levels were obtained from the computer program, and the rest were derived from a free rotation model. For the last two compounds, $CHCl_2CCl_3$ and CCl_3CCl_3, because of their large reduced moments, the calculated highest energy levels by the computer program are still below their respective potential barrier heights. Thus, the free rotation model is no longer valid.

In order to resolve this problem, we used the semi-classical approximation of Pitzer and Gwinn (1942) for evaluation of the internal rotation contributions to thermodynamic properties for the last two chloroethanes. It is interesting to note that when we used this semi-classical approximation method to calculate the internal rotation contributions to thermodynamic properties for CH_2ClCCl_3, the results obtained are consistent with those derived by using internal rotation energy levels.

The basic molecular and thermochemical constants employed for calculation of the chemical thermodynamic properties for these six chloroethanes are summarized in table 7–1. The details of the selection and of the calculation procedures for each of the six chloroethanes are discussed in the following sections.

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 u$Å^2$
K	Equilibrium constant for a chemical reaction	
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

2. Chloroethane

The molecular and thermochemical properties of chloroethane (ethyl chloride) have been investigated by chemists for many years. The molecular structure of this compound was studied by electron diffraction by Bru (1933) and Beach and Stevenson (1939) and later by microwave spectroscopy by Wagner and Dailey (1954, 1955, 1957), Barchukov, Murina, and Prokhorov (1958), and Schwendeman and Jacobs (1962). The molecular structural parameters elucidated from four of these investigations are summarized in table 1–1.

Schwendeman and Jacobs examined the microwave spectra of $CH_3CH_2{}^{35}Cl$ and $CH_3CH_2{}^{37}Cl$ and derived the rotational constants (A, B, C) and the three principal moments of inertia (I_A, I_B, I_C) for each species. Combining their data with those reported previously for $CH_3CH_2{}^{35}Cl$, $CH_3CH_2{}^{37}Cl$, and $CH_2DCH_2{}^{35}Cl$, they obtained a complete set of structural parameters for chloroethane by means of the substitution method, as shown in table 1–1. Based on their reported values for I_A, I_B, and I_C for $CH_3CH_2{}^{35}Cl$ and $CH_3CH_2{}^{37}Cl$, the corresponding values for the chloroethane natural isotopic mixture are evaluated as: $I_A = 16.385$ u$Å^2$ (or 2.67985×10^{-39} g cm^2), $I_B = 92.5005$ u$Å^2$ (1.53600×10^{-38} g cm^2), and $I_C = 102.361$ u$Å^2$ (1.69974×10^{-38} g cm^2) by taking appropriately weighted averages of the values for the two isotopic species. The product of the principal moments of inertia ($I_aI_BI_C$) is obtained as 1.5281×10^5

TABLE 1–1. Structural data for chloroethane

Structural parameter[a]	Reference				
	Beach and Stevenson, 1939	Wagner and Dailey, 1957	Barchukov et al., 1958	Schwendeman and Jacobs, 1962	Selected
C–Cl	1.76±0.02	1.7785±0.0003	1.78	1.788±0.002	1.788
C–H(CH$_2$Cl)	(1.09)[b]	1.101±0.003	1.103	1.089±0.010	1.089
C–H(CH$_3$)	(1.09)	1.101±0.003	1.103	1.091±0.010	1.091
C–C	(1.54)	1.5495±0.0005	1.54	1.520±0.003	1.520
∠ CCCl	111.5±0.03	110.5±0.03	110.5	111.03±0.13	111.03
∠ HCH(CH$_2$Cl)	(109.5)	110.0±0.5	110.33	109.2±0.5	109.2
∠ HCC(CH$_2$Cl)	(109.5)		108.6	111.6±0.5	111.6
∠ HCH(CH$_3$)	(109.5)	110.0±0.5	109.47	108.5±0.5	108.5
∠ HCC(CH$_3$)	(109.5)				110.43[c]

[a] Bond distances, 10^{-8} cm; bond angle, degrees.
[b] Values in parentheses are estimated.
[c] Derived value.

u^{3}Å^6 (or 6.9966×10^{-115} g^3 cm^6). Adopting the selected structural parameters listed in table 1–1 and the usual atomic weights of natural isotope mixtures, the reduced moment of inertia (I_r) for internal rotation for chloroethane was derived to 2.779 uÅ^2 (or 4.615×10^{-40} g cm^2). The above values of $I_A I_B I_C$ and I_r were used in the calculation of the thermodynamic properties for chloroethane.

If the selected structural parameters given in table 1–1 are used to calculate the product of the three principal moments of inertia, the value $I_A I_B I_C = 1.5154 \times 10^5$ u^{3}Å^6 is obtained. Based on this $I_A I_B I_C$ value, the calculated entropies would be lower by a constant amount of $\frac{1}{2}R \ln (1.5281/1.5154) = 0.008$ cal K^{-1} mol^{-1}, and the values of Gibbs energy function $[-(G^\circ - H^\circ_0)/T]$ would be more positive by the same amount. The heat capacity and enthalpy values would not be changed.

TABLE 1–2. Vibrational assignments for chloroethane

Mode No.	Symmetry class	Reference
		Shimanouchi 1972
		Wavenumber in cm^{-1}
ν_1	a'	2967
ν_2	a'	2946
ν_3	a'	2881
ν_4	a'	1463
ν_5	a'	1448
ν_6	a'	1385
ν_7	a'	1289
ν_8	a'	1081
ν_9	a'	974
ν_{10}	a'	677
ν_{11}	a'	336
ν_{12}	a''	3014
ν_{13}	a''	2986
ν_{14}	a''	1448
ν_{15}	a''	1251
ν_{16}	a''	974
ν_{17}	a''	786
ν_{18}	a'' (torsion)	251

TABLE 1–3. Reported internal rotation barrier heights and torsional fundamentals of chloroethane

V_3, kcal mol^{-1}	ν_{18}, cm^{-1}	References
3.69	251	Shimanouchi, 1972
3.69	251	Durig et al., 1971
3.67	250.5	Fateley et al., 1970
	275	Strong et al., 1970
	251.5	Winther and Hummel, 1969
3.70	251	Allen et al., 1967
3.56	243	Shimanouchi, 1967
3.66		Möller et al., 1967
3.70	251.5	Fateley and Miller, 1963
3.69		Schwendeman and Jacobs, 1962
3.58	243	Fateley and Miller, 1961
3.56	242.5	Lide, 1959
2.9	220	Luft, 1955
3.0		Wagner and Dailey, 1954
2.7	215	Bernstein, 1949
4.7	280	Gordon and Giauque, 1948
2.7		Eucken and Franck, 1948
3.69	251	This work, 1972 (Selected)

Shimanouchi (1972) has critically reviewed the infrared and Raman data for chloroethane and assigned a complete set of vibrational fundamentals (see table 1–2) which values have been accepted for the computation of thermodynamic properties. Different vibrational fundamentals were assigned for chloroethane by Linnett (1940), Gordon and Giauque (1948), and Sheppard (1949).

Table 1–3 presents the torsional fundamentals and barrier heights for internal rotation for chloroethane reported in the literature. Since it is very likely that the molecular structures for CH$_3$CH$_2$Cl used by the various authors to derive the values of ν_{18} and V_3 listed in table 1–3 were not the same, only a limited comparison of these listed values can be made. A value of $V_3 = 1290.9$ cm^{-1} or 3.691 kcal mol^{-1} (corresponding to $\nu_{18} = 251$ cm^{-1}) was selected to generate 102 internal rotation energy levels for calculation.

By flame calorimetry, Fletcher and Pilcher (1971) measured the enthalpy of combustion of C_2H_5Cl (g) at 25 °C to be -337.73 ± 0.14 kcal mol^{-1}. Casey and Fordham (1951) determined the enthalpy of combustion of C_2H_5Cl (g) containing 90 percent by volume of H_2 (g) (to ensure adequate combustion without liberation of free Cl_2 (g)) to be -341 ± 2.5 kcal mol^{-1} at 293.15 K. The enthalpy change of reaction 1–1 was measured as -17.16 ± 0.06 kcal mol^{-1} at 521 K by Lacher et al. (1956).

$$C_2H_5Cl\,(g) + H_2\,(g) = C_2H_6\,(g) + HCl\,(g). \qquad (1\text{–}1)$$

The equilibrium constants of reaction 1–2 have been determined by Lane et al. (1953) in the temperature range 722–764 K, and by Howlett (1955), 448–528 K

$$C_2H_4\,(g) + HCl\,(g) = C_2H_5Cl\,(g). \qquad (1\text{–}2)$$

From their results, the respective enthalpy of formation, $\Delta Hf°(C_2H_5Cl$, g, 298.15), was evaluated. They are presented in table 1–4. The selected value for $\Delta Hf°(C_2H_5Cl$, g, 298.15) is -26.83 ± 0.18 kcal mol^{-1}. For the above calculations, the $\Delta Hf°$(g, 298.15) for C_2H_4 and C_2H_6 were obtained from APIRP 44 tables (Zwolinski et al., APIRP 44, 1972) and that for HCl was taken from TRCDP tables (Zwolinski et al., TRCDP, 1972).

Based on the adopted molecular and spectroscopic constants for C_2H_5Cl (g), the ideal gas thermodynamic functions, C_p°, $S°$, $-(G°-H_0^\circ)/T$, and $H°-H_0^\circ$, in the temperature range 100–1500 K were calculated by the statistical thermodynamic method using rigid-rotor and harmonic-oscillator approximations. From the selected $\Delta Hf°(C_2H_5Cl$, g, 298.15) and the enthalpy $(H°-H_0^\circ)$ and Gibbs energy function $[-(G°-H_0^\circ)/T]$ for C (graphite), H_2 (g), Cl (g) (see Rodgers et al., 1974), and C_2H_5Cl (g) (from table 1–5), the values of $\Delta Hf°$, $\Delta Gf°$, and log K_f in the same temperature range as the other thermodynamic functions were evaluated. The results are given in table 1–5.

TABLE 1–4. Enthalpy of formation data for chloroethane

$\Delta Hr°$ obs kcal mol^{-1}	Conditions	Method	$\Delta Hr°$ (298) kcal mol^{-1}	Reference	$\Delta Hf°$ (298) gas kcal mol^{-1}
-341 ± 2.5	293 K	combustion with H_2	-341 ± 2.5	Casey and Fordham, 1951	-23.5 ± 2.5
-18.4 ± 1.6	449 ~ 491 K	equilibrium	-18.1 ± 1.6	Lane et al., 1953	-27.7 ± 1.6
-17.43 ± 0.03	448 ~ 528 K	equilibrium	-17.16 ± 0.05	Howlett, 1955	-26.73 ± 0.05
-17.16 ± 0.06	521 K	hydrogenation	-16.56 ± 0.1	Lacher et al., 1956	-25.8 ± 0.1
-337.73 ± 0.14	298.15 K	flame calorimetry	-337.73 ± 0.14	Fletcher and Pilcher, 1971	-26.83 ± 0.18
				Selected value	-26.83 ± 0.18

TABLE 1–5. Ideal gas thermodynamic functions for chloroethane

Temp. 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	−26.418	−26.418	infinite
100.00	9.095	53.535	45.306	0.823	−24.792	−21.746	47.526
150.00	10.392	57.470	48.735	1.310	−25.258	−20.125	29.323
200.00	11.752	60.642	51.326	1.863	−25.778	−18.335	20.035
273.15	14.096	64.641	54.368	2.806	−26.570	−15.497	12.399
298.15	14.971	65.913	55.283	3.169	−26.830	−14.459	10.599
300.00	15.036	66.006	55.348	3.197	−26.849	−14.381	10.476
400.00	18.538	70.815	58.622	4.877	−27.814	−10.072	5.503
500.00	21.657	75.297	61.514	6.891	−28.611	−5.544	2.423
600.00	24.282	79.484	64.164	9.192	−29.249	−0.869	0.317
700.00	26.494	83.398	66.635	11.734	−29.749	3.905	−1.219
800.00	28.385	87.062	68.962	14.480	−30.129	8.739	−2.387
900.00	30.018	90.502	71.166	17.403	−30.403	13.616	−3.306

TABLE 1–5. Ideal gas thermodynamic functions for chloroethane—Continued

Temp. K	C°_p	S°	$-(G^\circ-H^\circ_0)/T$	$H^\circ-H^\circ_0$	ΔHf°	ΔGf°	log Kf
	cal K^{-1} mol^{-1}			kcal mol^{-1}			
1000.00	31.433	93.740	73.263	20.477	−30.581	18.527	−4.049
1100.00	32.662	96.795	75.265	23.683	−30.681	23.418	−4.653
1200.00	33.729	99.684	77.181	27.004	−30.723	28.358	−5.165
1300.00	34.658	102.421	79.018	30.424	−30.718	33.278	−5.595
1400.00	35.466	105.020	80.783	33.931	−30.674	38.220	−5.966
1500.00	36.171	107.491	82.482	37.514	−30.599	43.129	−6.284

TABLE 1–6. Comparison of calculated and experimental gas phase heat capacity and entropy data for chloroethane

Temp. K	C°_p cal K^{-1} mol^{-1}			S° cal K^{-1} mol^{-1}		
	obs	calc [a]	Ref	obs	calc [a]	Ref
200	11.82±0.1	11.75	Eucken and Franck, 1948			
280	14.02±0.1	14.33	Eucken and Franck, 1948			
285.37				65.31	65.27	Gordon and Giauque, 1948
313.15	15.7	15.50	Senftleben and Gladisch, 1949			
500				74.7±3	75.30	Lane et al., 1953
500				76.8±0.1	75.30	Howlett, 1955

[a] This work.

Comparison of calculated and experimental heat capacity and entropy data for C_2H_5Cl (g) is listed in table 1–6. Using thermal conductivity method, Eucken and Frank (1948) measured the vapor heat capacities of C_2H_5Cl at 200 and 280 K. Their results are in fair agreement with the present calculated values. The C°_p value reported by Senftleben and Gladisch (1949) is higher than the present value by 0.2 cal K^{-1} mol^{-1} at 313.15 K. Gordon and Giauque (1948) measured the low temperature heat capacities of crystal and liquid chloroethane in the temperature range 15 ~ 285.37 K. Based on S°_{15} (Debye extrapolation) = 0.50 cal K^{-1} mol^{-1}, ΔH°_m(134.80 K) = 1.064 kcal mol^{-1}, and ΔH°_v(285.37 K) = 5.892 kcal mol^{-1}, the third law entropy of C_2H_5Cl (g) was evaluated as 65.31 ± 0.1 cal K^{-1} mol^{-1}, which is in good agreement with the value 65.26 cal K^{-1} mol^{-1} obtained in this work. The two observed entropy values at 500 K were derived from the reported equilibrium data by the second law method. The calculated entropy is consistent with the average value of these two data points.

3. 1,1-Dichloroethane

The molecular structure of 1,1-dichloroethane has been studied by electron diffraction (Morino et al., 1949; Danford, 1954; Danford and Livingston, 1959) and microwave spectroscopy (Flygare, 1964). Their reported results are listed in table 2–1. Some structural parameters are still undetermined. The structure proposed by Flygare (1964) was adopted.

The infrared spectrum of 1,1-dichloroethane has been observed by Emschwiller and Lecomte (1937), Thompson and Torkington (1945, 1946), Daasch et al. (1954), and Durig et al. (1971). In addition, the Raman spectra of this compound were investigated by Pestemer (1930, 1931), Cleeton and Dufford (1931), Kohlrausch and Köppel (1934, 1935), and Bishui (1948).

Daasch et al. (1954) assigned 16 fundamental vibrational wavenumbers for CH_3CHCl_2 (g) and reported the two missing values for the complete vibrational assignment, $\nu_{12} = 2990$ cm^{-1} and $\nu_{18} = 239$ cm^{-1}, from the Raman spectrum of CH_3CHCl_2 (l). (See table 2–2 for

TABLE 2–1. Structural data for 1,1-dichloroethane

Structural parameter [a]	Reference				
	Morino et al., 1949	Danford, 1954	Danford and Livingston, 1959	Flygare, 1964	Selected
C—Cl	(1.77) [b]	1.795±0.02	1.795±0.02	1.766±0.01	1.766
C—H(CH_3)	(1.09)		(1.09)	(1.09)	1.09
C—H($CHCl_2$)	(1.09)		(1.09)	1.09	1.09
C—C	(1.54)	1.55±0.07	1.55±0.07	1.540±0.01	1.54
∠ClCC	112.5±2.0	110±4	110±4	111.0±0.5	111.0
∠HCC($CHCl_2$)	(109.5)		(109.47)	(111.29)	111.29
∠ClCCl	110±1	109.1±3.5	109.5±1.5	112.0±0.5	112.0
∠HCC(CH_3)	(109.5)		(109.47)	(108.73)	108.73
∠HCH(CH_3)				(110.2)	110.2

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

[b] Values in parentheses are estimated.

TABLE 2–2. Vibrational assignments for 1,1-dichloroethane

Mode No.	Symmetry Class	Reference		
		Daasch et al., 1954	Allen et al., 1967	Selected
		Wavenumber in cm^{-1}		
ν_1	a'	3012		3012
ν_2	a'	2941		2941
ν_3	a'	2873		2873
ν_4	a'	1445		1445
ν_5	a'	1383		1383
ν_6	a'	1282		1282
ν_7	a'	1094		1094
ν_8	a'	982		982
ν_9	a'	651		651
ν_{10}	a'	405	406	406
ν_{11}	a_1	277	275	275
ν_{12}	a''	2990		2990
ν_{13}	a''	1445		1445
ν_{14}	a''	1239		1239
ν_{15}	a''	1058		1058
ν_{16}	a''	705		705
ν_{17}	a''	317	318	318
ν_{18}	a'' (torsion)	239	222	231 [a]

[a] Based on Durig et al. (1971).

details.) Allen et al. (1967) have studied the far infrared and Raman spectra of CH_3CHCl_2 (l and g). They assigned three new wavenumbers, 275, 318, and 406 cm^{-1}, for CH_3CHCl_2 (g) and a torsional wavenumber, $\nu_{18}=222$ cm^{-1}, which was obtained from the Raman spectrum of liquid 1,1-dichloroethane. The torsional wavenumber, 239 cm^{-1}, reported by Daasch et al. (1954), was not observed by them. Durig et al. (1971) have investigated the infrared spectrum of CH_3CHCl_2 (g) in a 10-m variable-path-length cell. A weak band that appeared at 231 cm^{-1} in the spectrum was assigned as the methyl torsional mode. They also studied the infrared spectrum of CH_3CHCl_2 (c) from 140 to 400 cm^{-1} and observed the torsional mode at 232 cm^{-1}.

Based on a neutron inelastic scattering study, Brier et al. (1971) reported bands at 290 and ~ 230 cm^{-1}. The 290 cm^{-1} band is more intense, and they tentatively assigned it to the torsional mode for the gas as it was similar to the 298±10 cm^{-1} torsional band reported earlier by Brier (1970) for liquid 1,1-dichloroethane. Recently, Durig et al. (1972) recorded the infrared spectra of gaseous and solid CH_3CHCl_2 and CD_3CDCl_2. The corresponding Raman spectra of the gases and liquids have also been recorded and depolarization values have been measured. The internal torsional mode was observed at 196 cm^{-1} in the infrared spectrum of CD_3CDCl_2 (c). From the expected shift factor of 1.414 with deuteration, they estimated the torsional fundamental for CH_3CHCl_2 as 277 cm^{-1}. This assignment leaves unexplained the band at 232 cm^{-1} reported previously. According to Durig et al. (1972), the most reasonable explanation seems to be that it arose from an impurity in the sample used in the previous investigations.

Based on $\nu_{18}=231$ and 277 cm^{-1}, the corresponding internal rotation barrier heights were derived to be 3.54 and 4.89 kcal mol^{-1}, respectively. As the latter value seems unreasonably high, the torsional vibrational mode $\nu_{18}=231$ cm^{-1} (Durig et al., 1971) was selected. Other values of V_3 and ν_{18} that have been reported in

TABLE 2–3. Reported internal rotation barrier heights and torsional fundamentals 1,1-dichloroethane

V_3, kcal mol^{-1}	ν_{18}, cm^{-1}	References
4.89	277	Durig et al., 1972
3.50	231	Durig et al., 1971
3.50	232	Durig et al., 1971; for CH_3CHCl_2(c)
3.3	222	Allen et al., 1967
3.49±0.2 [a]		Wulff, 1963
3.55±0.45 [b]		Li and Pitzer, 1956
	240 [c]	Millikan; quoted by Li and Pitzer, 1956
2.95	215	Luft, 1955
3.75	239	Daasch et al., 1954
3.54	231	This work, 1972 (Selected)

[a] Calculated from thermal data on solid phase reported by Li and Pitzer (1956).

[b] Derived from the third law entropy at 298.15 K.

[c] Observed in an unpublished infrared spectrum of liquid 1,1-dichloroethane.

the literature for CH_3CHCl_2 (g) are listed in table 2–3. The other vibrational wavenumbers adopted for 1,1-dichloroethane (g) are listed in table 2–2.

Flygare (1964) calculated the three principal moments of inertia of the isotopic species $CH_3CH^{35,35}Cl_2$ and $CH_3CH^{35,37}Cl_2$ directly from the observed rotational constants A, B, and C. We assumed that the corresponding moments of inertia of the $CH_3CH^{37,37}Cl_2$ species could be estimated by addition of the differences in I_A, I_B, and I_C between $CH_3CH^{35,37}Cl_2$ and $CH_3CH^{35,35}Cl_2$ species to those for the $CH_3CH^{35,37}Cl_2$ species. From the reported three principal moments of inertia for $CH_3CH^{35,35}Cl_2$ and $CH_3CH^{35,37}Cl_2$ and those estimated values for $CH_3CH^{37,37}Cl_2$, the three principal moments of inertia of 1,1-dichloroethane natural isotopic mixture were evaluated to be: $I_A = 78.8154$ uÅ^2 (or 1.30875×10^{-38} g cm^2), $I_B = 159.239$ uÅ^2 (2.64421×10^{-38} g cm^2), and $I_C = 224.623$ uÅ^2 (3.72993×10^{-38} g cm^2). The product $I_A I_B I_C$ is 2.81913×10^6 u^{3}Å^6 (1.29078×10^{-113} g^3 cm^6), which was adopted for thermodynamic calculations in this study.

Based on the selected structural parameters for 1,1-dichloroethane given in table 2–1, the value of $I_A I_B I_C$ is obtained as 2.72546×10^6 u^{3}Å^6. By use of this $I_A I_B I_C$ value, each calculated entropy value would be 0.033 cal K^{-1} mol^{-1} lower than the previously calculated ones, and each calculated Gibbs energy function $[(G^\circ - H^\circ_0)/T]$ value would be more positive by the same amount. The values of heat capacities and enthalpies would not be changed.

The reduced moment of inertia (I_r) for internal rotation for 1,1-dichloroethane was evaluated as 3.158 uÅ^2 (or 5.243×10^{-40} g cm^2), based on the selected molecular structure as shown in table 2–1. From the torsional wavenumber, 231 cm^{-1}, and the above value of I_r, the internal rotation barrier, V_3, was derived as 3.545 kcal mol^{-1}, which is in excellent agreement with the value 3.550 ± 0.450 kcal mol^{-1} obtained by Li and Pitzer (1956) from the experimental third law entropy. By use of the method described in the introduction, 110 internal rotation energy levels below 16660 cm^{-1} were generated. These energy levels were employed for the computation of the internal rotation contributions to the thermodynamic properties.

Smith et al. (1953) determined the energy of combustion (ΔU_c) of CH_3CHCl_2 (l) by the "Quartz Wool" method. For the reaction 2–1, the value $\Delta U^\circ_c = 3005.9$ cal g^{-1} was reported

$$CH_3CHCl_2\ (l) + 2\tfrac{1}{2}O_2\ (g) = 2CO_2\ (g) + H_2O + 2HCl\ (600\ H_2O). \qquad (2\text{–}1)$$

This ΔU°_c value was recalculated as -3004.4 cal g^{-1} or -297.32 kcal mol^{-1} (see Rodgers et al., 1974, for details) which leads to $\Delta H^\circ_c = -297.61$ kcal mol^{-1} for CH_3CHCl_2 (l). From this data, one calculates $\Delta Hf^\circ(CH_3CHCl_2$, l, 298.15$) = -38.45$ kcal mol^{-1}, using auxiliary data for CO_2 (g), H_2O (l), and $HCl \cdot 600\ H_2O$ from Wagman et al. (1968). Li and Pitzer (1956) measured the enthalpy of vaporization for 1,1-dichloroethane by vaporizing through a suitable capillary tube into a bulb immersed in liquid nitrogen in order to maintain a constant pressure difference at constant flow rates. They obtained the enthalpy of vaporization at 293 K as 7409 ± 7 cal mol^{-1}. Using the Berthelot equation of state, critical constants and vapor pressure data from the TRCDP tables (Zwolinski et al., TRCDP, 1972) and $\Delta C_p = -12$ cal K^{-1} mol^{-1}, we calculated $\Delta H^\circ_v = 7.42$ kcal mol^{-1} at 293 K and 7.36 ± 0.10 kcal mol^{-1} at 298.15 K (see table 2–4). This leads to $\Delta Hf^\circ(CH_3CHCl_2$, g, 298$) = -31.09 \pm 0.2$ kcal mol^{-1}.

TABLE 2–4. Enthalpy of vaporization data for 1,1-dichloroethane

ΔH_v obs kcal mol^{-1}	Conditions	Methods	Reference	ΔH°_v (298) kcal mol^{-1}
7.409 ± 0.007	293 K	Calorimetric	Li and Pitzer, 1956	7.36 ± 0.01
7.401	293 K	Calculated from vapor pressure equation	Li and Pitzer, 1956	7.36
			Selected value:	7.36

Lacher et al. (1967) determined the enthalpy of reaction 2–2 at 250 °C and obtained $\Delta H^\circ_r(523\ K) = -34.65 \pm 0.12$ kcal mol^{-1}

$$CH_3CHCl_2\ (g) + 2H_2\ (g) = CH_3CH_3\ (g) + 2HCl\ (g). \qquad (2\text{–}2)$$

Adopting heat capacity data for H_2 (g) and HCl (g) from TRC Data Project Tables (Zwolinski et al., TRCDP, 1972) and for CH_3CH_3 (g) from APIRP 44 Tables (Zwolinski et al., APIRP 44, 1972), we calculated the enthalpy change of this reaction at 298.15 K as -33.30 kcal mol^{-1}. Based on $\Delta Hf^\circ(C_2H_6$, g, 298.15$) = -20.24$ (Zwolinski et al., APIRP 44, 1972) and ΔHf°(HCl, g, 298.15$) = -22.06$ kcal mol^{-1} (Zwolinski et al., TRCDP, 1972), we obtained $\Delta Hf^\circ(CH_3CHCl_2$, g, 298.15$) = -31.06 \pm 0.1$ kcal mol^{-1}, in excellent agreement with the above calorimetric value. The selected value is -31.1 ± 0.2 kcal mol^{-1}. These data are summarized in table 2–5.

TABLE 2–5. Enthalpy of formation data for 1,1-dichloroethane

$\Delta Hr°$ obs kcal mol^{-1}	Conditions	Method	$\Delta Hf°$ (l) kcal mol^{-1}	Reference	$\Delta Hf°$ (298) gas kcal mol^{-1}
−297.6	298 K	Combustion calorimetry	−38.45	Smith et al., 1953	−31.09
−34.65	523 K	Hydrogenation		Lacher et al., 1967	−31.06
				Selected value:	−31.1

Employing $\Delta Hf°(CH_3CHCl_2$, g, 298.15)=−31.1 kcal mol^{-1} from this work and enthalpy and Gibbs free energy function data for C (c), H_2 (g), and Cl_2 (g) from the TRC Data Project Tables, we derived the values of $\Delta Hf°$, $\Delta Gf°$, and $\log K_f$ for CH_3CHCl_2 (g) in the temperature range 100 to 1500 K. The results are presented in table 2–6.

TABLE 2–6. Ideal gas thermodynamic functions for 1,1-dichloroethane

Temp. 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	−31.168	−31.168	infinite
100.00	10.096	58.028	49.545	0.848	−29.442	−29.807	56.400
150.00	12.409	62.568	53.154	1.412	−29.865	−23.898	34.819
200.00	14.460	66.424	56.001	2.085	−30.293	−21.842	23.868
273.15	17.297	71.352	59.466	3.247	−30.905	−18.661	14.930
298.15	18.245	72.908	60.529	3.691	−31.100	−17.523	12.844
300.00	18.315	73.021	60.605	3.725	−31.114	−17.436	12.702
400.00	21.844	78.786	64.443	5.737	−31.814	−12.765	6.975
500.00	24.793	83.988	67.840	8.074	−32.366	−7.939	3.470
600.00	27.184	88.727	70.932	10.677	−32.786	−3.013	1.097
700.00	29.148	93.070	73.789	13.497	−33.096	1.978	−0.618
800.00	30.794	97.073	76.453	16.496	−33.313	7.004	−1.913
900.00	32.194	100.783	78.952	19.647	−33.447	12.053	−2.927
1000.00	33.395	104.24	81.310	22.928	−33.506	17.123	−3.742
1100.00	34.430	107.47	83.543	26.321	−33.505	22.160	−4.403
1200.00	35.324	110.51	85.665	29.809	−33.462	27.238	−4.961
1300.00	36.768	113.36	87.687	33.381	−33.383	32.290	−5.428
1400.00	36.768	116.06	89.618	37.025	−33.277	37.358	−5.832
1500.00	37.352	118.62	91.467	40.732	−33.148	42.391	−6.176

The low temperature heat capacities (14.17 to 294.26 K), melting point (176.18 K), and enthalpies of fusion (1881 cal mol^{-1}) and vaporization (7409 cal mol^{-1} at 293 K) have been determined by Li and Pitzer (1956). From these data, they calculated the entropy at 293 K as 72.58±0.15 cal K^{-1} mol^{-1}, which is in excellent agreement with the value 72.59 cal K^{-1} mol^{-1} obtained in this study. There are no vapor heat capacity measurements reported for CH_3CHCl_2 (g) in the literature for comparison.

4. 1,1,1-Trichloroethane

The 1,1,1-trichloroethane (CH_3CCl_3) molecule has two symmetric tops rotating around the C—C bond. The molecular structure of this molecule was determined by electron diffraction (Beach and Stevenson, 1939; Coutts and Livingston, 1953) and microwave spectroscopy (Ghosh et al., 1952; Holm et al., 1968). Holm et al. evaluated the complete set of molecular structural parameters for CH_3CCl_3 (g), and their values were adopted. The reported molecular parameters for CH_3CCl_3 by several investigators are listed in table 3–1. Based on the adopted molecular structure, the three principal moments of inertia were calculated as: $I_A=I_B=215.12$ uÅ^2 (or 3.5720×10^{-38} g cm^2) and $I_C=299.64$ uÅ^2 (or 4.9753×10^{-38} g cm^2). The values of $I_AI_BI_C$ and the reduced moment (I_r) were obtained as 1.3867×10^7 u^{3}Å^6 (or 6.3480×10^{-113} g^3 cm^6) and 3.196 uÅ^2 (or 5.306×10^{-40} g cm^2), respectively.

Pitzer and Hollenberg (1953) measured the infrared spectrum of this compound in the gaseous state in the range 130–430 cm^{-1}. They assigned 12 fundamental vibrations for three different classes of symmetry (see table 3–2 for numerical values) of which the torsional mode was assigned as 214 cm^{-1}. Since this torsional mode (ν_6) is inactive as a fundamental in either the

TABLE 3–1. Structural data for 1,1,1-trichloroethane

Structural parameter[a]	Reference				
	Black and Stevenson, 1939	Ghosh et al., 1952	Coutts and Livingston, 1953	Holm et al., 1968	Selected
C—Cl	1.76 ± 0.2	(1.767)	1.775 ± 0.02	1.7712 ± 0.0008	1.7712
C—H	(1.09)[b]	(1.09)	(1.09)	1.090 ± 0.002	1.090
C—C	(1.54)	1.55 ± 0.01	1.54 ± 0.04	1.541 ± 0.001	1.541
∠ClCC	109 ± 2	(109.47)	110.0 ± 1.5		109.52[c]
∠ClCCl	110 ± 2	(110.4)	109.0 ± 1.5	109.39 ± 0.25	109.39
∠HCC	(109.47)	(109.47)	(109.47)		108.52[c]
∠HCH		(109.5)	(109.5)	110.04 ± 0.25	110.04

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

[b] Value in parentheses are estimated.

[c] Derived value.

TABLE 3–2. Vibrational assignments for 1,1,1-trichloroethane

Mode no.	Symmetry class	Reference				
		El Sabban et al., 1951	Smith et al., 1952	Pitzer and Hollenberg, 1953	Evans and Bernstein, 1955	Selected
		Wavenumber in cm^{-1}				
ν_1	a_1	2954	2954	2954	2938	2954
ν_2	a_1	1381	1383	1383	1378	1383
ν_3	a_1	1012	1075	1075	1067	1075
ν_4	a_1	524	526	526	521	526
ν_5	a_1	343	344	344	343	344
ν_6	a_2 (torsion)	205±20[c]	213[c]	214[c]	....	278[b]
ν_7	e	3017	3017	3017	3005	3017
ν_8	e	1445	1427/1456[a]	1456	1444	1456
ν_9	e	1087	1089	1089	1081	1089
ν_{10}	e	720	725	725	712	725
ν_{11}	e	....	301	351	343	351
ν_{12}	e	....	241	239	239	239

[a] Split levels.

[b] Obtained from Durig et al. (1971), see text for details.

[c] Calculated value.

Raman or the infrared spectra, the value 214 cm^{-1} was derived from the combinations of this mode with the fundamentals of E symmetry. However, the combination bands 135, 154, and 172 cm^{-1} observed by Pitzer and Hollenberg (1953) were not found in the far infrared spectrum by Fateley and Miller (1963) and Durig et al. (1971): therefore, the value $\nu_6 = 214$ cm^{-1} was not accepted.

Durig et al. (1971) have investigated the far infrared and Raman spectra of solid CH_3CCl_3 and CD_3CCl_3, hoping to resolve the conflicting results obtained for the torsional fundamental and the barrier to internal rotation in 1,1,1-trichloroethane. From the spectra obtained, they found a relatively sharp band at 290 cm^{-1} in the infrared spectrum of CH_3CCl_3 (c) and the band shift to 206 cm^{-1} with deuteration. The shift factor of 1.41 is in excellent agreement with the theoretical value of 1.414 predicted by the Teller-Redlich product rule. By assuming that the shift for solidification is within the same range as that found for ethane, chloroethane, and dichloroethane, they assigned a torsional fundamental of 278 cm^{-1} for CH_3CCl_3 (g) which was adopted for the present calculations. The other fundamental vibrations have been adopted from those reported by Pitzer and Hollenberg (1953). The selected values, as well as some values reported by the previous investigators, are shown in table 3–2.

From $\nu_6 = 278$ cm^{-1} and $I_r = 3.196$ $uÅ^2$, the barrier height for internal rotation was calculated to be $V_3 = 5.08$ kcal mol^{-1}. This value is much higher than the values predicted from thermodynamic (Rubin et al., 1944) and microwave (Holm et al., 1968) studies. Table 3–3 presents a comparison of the various reported values for V_3 and ν_6 for CH_3CCl_3 (g). Nevertheless, the present V_3 value is consistent with those obtained by Rush (1967) and Stejskal et al. (1959). By use of the method described previously, 112 internal rotation levels up to 17300 cm^{-1} were generated.

The enthalpy of combustion (reaction 3–1) for 1,1,1-trichloroethane (l) at 298.15 K has been determined as

TABLE 3–3. Reported internal rotation barrier heights and torsional fundamentals of 1,1,1-trichloroethane

V_3, kcal mol^{-1}	ν_6, cm^{-1}	References
5.0	278	Durig et al., 1971
5.5 ^{a}	290	Durig et al., 1971
1.74±0.3		Holm et al., 1968
2.8	205	Allen et al., 1967
4.41		De Coen et al., 1967
5.8±0.45 ^{a,b}	300±12	Rush, 1967
3.73 ^{d}		Scott and Scheraga, 1965
5.7 ^{a,c}		Stejskal et al., 1959
3.0	214	Luft, 1955
2.97	214	Pitzer and Hollenberg, 1953
3.045	213	Smith et al., 1952
2.84	205±20	El Sabban et al., 1951
2.7±0.35	205	Rubin et al., 1944
5.08	278	This work, 1972 (Selected)

[a] For CH_3CCl_3 (c).

[b] Obtained in the neutron in elastic scattering investigation.

[c] Derived from the low-temperature solid phase nuclear magnetic resonance spin-lattice relaxation times.

[d] Theoretical calculation.

−266.70±0.15, −265.80±0.31, and −264.73±0.19 kcal mol^{-1} by Hu and Sinke (1969), Mansson et al. (1971), and Hu and Sinke (1971), respectively

$$CH_3CCl_3\ (l) + 2O_2\ (g) = 2CO_2\ (g) + 3HCl\ (600\ H_2O). \qquad (3\text{–}1)$$

Based on this reaction, the value of $\Delta Hf°(CH_3CCl_3$, l, 298.15) was calculated to be −40.87, −41.77, and −42.84 kcal mol^{-1}. According to Mansson et al. (1971), the value reported by Hu and Sinke (1969) was probably in error. The later value (Hu and Sinke, 1971) has not yet been published. Therefore, the $\Delta Hf°(CH_3CCl_3$, l, 298.15)=−41.77 kcal mol^{-1}, reported by Mansson et al., was adopted. The enthalpy of vaporization was measured calorimetrically as 7.754 (Hu and Sinke, 1971) and 7.761 kcal mol^{-1} (Mansson et al., 1971). An average value, $\Delta H_v^\circ(CH_3CCl_3$, l, 298.15)=7.76±0.02 kcal mol^{-1}, was adopted to derive the enthalpy of formation, $\Delta Hf°(CH_3CCl_3$, g, 298.15)=−34.01 kcal mol^{-1}. For evaluation of $\Delta Hf°(CH_3CCl_3$, l, 298.15), the auxiliary data for CO_2 (g) and $HCl \cdot 600\ H_2O$ were taken from Wagman et al. (1968).

The thermodynamic functions were calculated from the selected data in the rigid-rotor and harmonic-oscillator approximations. The results are presented in table 3–6.

Rubin et al. (1944) measured the low temperature heat capacities (12.29 to 299.59 K), the temperatures of transition (224.20 ± 0.03 K) and melting (240.2 ± 0.5 K), enthalpies of transition (1786±2 cal mol^{-1}), melting (450 ± 300 cal mol^{-1}, a rough value) and vaporization (7962 ± 12 cal mol^{-1} at 286.53 K) for CH_3CCl_3. Employing S_{15}=0.851 cal K^{-1} mol^{-1} (Debye extrapolation), they evaluated the entropy of the real gas at 286.53 K and 76.86 torr as 80.755±0.16, and the entropy for ideal gas at 286.53 K and 1 atm as 76.22±0.16 cal K^{-1} mol^{-1}. For corrections to the entropy of the ideal gas at 286.53 K and 1 atm, the following values were used: ΔS (gas imperfection)=0.002 and ΔS (correction to 1 atm)= −4.553 cal K^{-1} mol^{-1}. From the present statistical thermodynamical calculation, the value of $S^\circ_{286.53}$ is 75.62 cal K^{-1} mol^{-1}, which is lower than the third law entropy value by about 0.6 cal K^{-1} mol^{-1} at 286.53 K and 0.5 cal K^{-1} mol^{-1} at 298.15 K (see table 3–6). Because of the uncertainties involved in the measure-

TABLE 3–4. Enthalpy of vaporization data for 1,1,1-trichloroethane

ΔH_v obs kcal mol^{-1}	Conditions	Methods	Reference	ΔH_v° (298) kcal mol^{-1}
7.96±0.01	286.5 K and 76.86 torr	Giauque calorimeter	Rubin et al., 1944	7.81±0.05
7.76±0.02	298.15 K	Wadso calorimeter	Mansson et al., 1971	7.76±0.02
7.75	298.15 K	Calorimetric	Hu and Sinke, 1971	7.75
			Selected value:	7.76±0.02

TABLE 3–5. Enthalpy of formation data for 1,1,1-trichloroethane

$\Delta Hr°$ obs kcal mol^{-1}	Conditions	Method	$\Delta Hf°$ (298) liq. kcal mol^{-1}	Reference	$\Delta Hf°$ (298) gas kcal mol^{-1}
−266.70±0.15	liq., at 298.15 K	Combustion	−40.87	Hu and Sinke, 1969	−33.11±0.15
−265.80±0.31	liq., at 298.15 K	Combustion	−41.77	Mansson et al., 1971	−34.01±0.33
−264.73±0.19	liq., at 298.15 K	Combustion	−42.84	Hu and Sinke, 1971	−35.08±0.20
				Selected value:	−34.01±0.33

TABLE 3–6. Ideal gas thermodynamic functions for 1,1,1-trichloroethane

Temp. 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	−34.646	−34.646	infinite
100.00	11.251	58.665	49.905	0.876	−32.818	−28.208	61.649
150.00	14.792	63.917	53.719	1.530	−33.186	−25.822	37.622
200.00	17.651	68.579	56.862	2.343	−33.499	−23.316	25.479
273.15	21.044	74.600	60.824	3.763	−33.894	−19.532	15.627
298.15	22.071	76.488	62.059	4.302	−34.010	−18.207	13.346
300.00	22.145	76.624	62.149	4.343	−34.018	−18.107	13.191
400.00	25.717	83.504	66.647	6.743	−34.398	−12.740	6.961
500.00	28.517	89.556	70.636	9.460	−34.647	−7.298	3.190
600.00	30.682	94.955	74.247	12.425	−34.789	−1.813	0.660
700.00	32.381	99.818	77.559	15.581	−34.850	3.691	−1.152
800.00	33.747	104.234	80.621	18.890	−34.847	9.197	−2.512
900.00	34.871	108.275	83.473	22.322	−34.790	14.701	−3.570
1000.00	35.811	112.000	86.142	25.858	−34.682	20.205	−4.416
1100.00	36.606	115.451	88.651	29.480	−34.537	25.660	−5.098
1200.00	37.283	118.666	91.020	33.175	−34.369	31.144	−5.672
1300.00	37.864	121.674	93.264	36.933	−34.183	36.593	−6.152
1400.00	38.364	124.499	95.395	40.745	−33.983	42.049	−6.564
1500.00	38.797	127.161	97.425	44.604	−33.772	47.466	−6.916

ments by Rubin et al. (1944) on the melting point and the enthalpy of melting for CH_3CCl_3 (c), these discrepancies in entropies may not be real. In order to resolve this inconsistency, a redetermination of the third law entropy for CH_3CCl_3 (l) at 298.15 K by use of modern high precision low temperature calorimetry seems necessary.

TABLE 3–7. Comparison of calculated and experimental gas phase heat capacity and entropy data for 1,1,1-trichloroethane

Temp. K	S° cal K^{-1} mol^{-1}		
	obs	calc[a]	Ref
286.54	76.22±0.16	75.62	Rubin et al., 1944
298.15	76.97±0.16	76.49	Rubin et al., 1944

[a] This work.

5. 1,1,1,2-Tetrachloroethane

The molecular structure of 1,1,1,2-tetrachloroethane (CH_2ClCCl_3) has not been reported in the literature. The bond distances and angles used for calculations were estimated on an assumption that the structures of CH_2Cl and CCl_3 in the CH_2ClCCl_3 molecule are similar to those of the corresponding groups in CH_3CH_2Cl and CCl_3CCl_3. The C—C bond distance was estimated as the average of the C—C bond lengths in chloro- and hexachloroethanes. These estimated values are listed in table 4–1. Based on this molecular structure, the three principal moments of inertia were derived as: I_A = 266.12 uÅ^2 (or 4.4188×10^{-38} g cm^2), I_B=462.96 uÅ^2 (or 7.6871×10^{-38} g cm^2), and I_C=496.01 uÅ^2 (or 8.2359×10^{-38} g cm^2). The reduced moment for internal rotation (I_r) was calculated to be 40.28 uÅ^2 (6.688×10^{-39} g cm^2).

TABLE 4–1. Structural data for 1,1,1,2-tetrachloroethane

Structural parameters[a]	Reference
	Selected
C—Cl(CCl_3)	(1.77)[b]
C—Cl(CH_2Cl)	(1.79)
C—H(CH_2Cl)	(1.09)
C—C	(1.55)
∠ClCC(CCl_3)	(109.5)
∠ClCC(CH_2Cl)	(111.0)
∠ClCCl(CCl_3)	(109.4)
∠HCC	(111.6)
∠HCH	(109.2)

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

[b] Values in parentheses are estimated.

The infrared absorption spectrum of CH_2ClCCl_3 in the gaseous and liquid states has been observed by Bernstein (1950) and Nielsen, Liang, and Daasch (1953). Complete assignments of fundamental vibrational modes were made. Allen and Bernstein (1954) and Allen, Brier, and Lane (1967) studied the far infrared and Raman spectra of CH_2ClCCl_3 (l) and assigned vibrational fundamentals close to those reported by Nielsen, Liang, and Daasch (see table 4–2). The infrared spectrum of CH_2ClCCl_3 (l) has also been obtained by Silver and Wood (1963), Bolleter (1964), and Chanal et al. (1967). Plyler and Acquista (1956) reported three bands at 114, 122, and 157 cm^{-1} in the infrared spectrum of CH_2ClCCl_3 (g). The Raman spectrum of 1,1,1,2-tetrachloroethane in the liquid state has also been reported by Gerding and Haring (1955) and Barrett and Tobin (1966). The selected values of vibrational fundamentals are shown in table 4–2 in which several more recent assignments are summarized for comparison.

TABLE 4–2. Vibrational assignments for 1,1,1,2-tetrachloroethane

Mode No.	Symmetry Class	Reference					
		Bernstein 1950	Nielsen et al., 1953	Allen and Bernstein 1954	Silver and Wood, 1963	Allen et al. 1967	Selected
		Wavenumber in cm^{-1}					
ν_1	a'	2980	2959	2961			2960
ν_2	a'	1415	1283	1280			1283
ν_3	a'	1280	1206	1200			1206
ν_4	a'	960	1055	1055			1055
ν_5	a'	730	822	810			822
ν_6	a'	718	757	750			757
ν_7	a'	525	551	550			551
ν_8	a'	381	381	380	384	380	380
ν_9	a'	336	334	335	334	330	330
ν_{10}	a'	308	242	240	245	243	243
ν_{11}	a'	242	157	157	159	159	158
ν_{12}	a''	3000	3020	3000			3020
ν_{13}	a''	1205	1426	1415			1426
ν_{14}	a''	1060	958	958			958
ν_{15}	a''	818	731	730			730
ν_{16}	a''	750	308	305	312	307	307
ν_{17}	a''	157	242	240	267		267
ν_{18}	a'' (torsion)	188	116	117	123	118	116

Based on the adopted torsional fundamental, 116 cm^{-1}, and derived I_r, we calculated $V_3 = 10.38$ kcal mol^{-1}. Two values for $V_3(CH_2ClCCl_3, g)$ were reported, i.e., 10.0 kcal mol^{-1} by Allen, Brier, and Lane (1967) and 12.4 kcal mol^{-1} by Silver and Wood (1963). Allen, Brier, and Lane (1967) employed $\nu_{torsion} = 116$ cm^{-1} and F (rotational constant) $= 0.4293$ cm^{-1} to derive the V_3 value. Based on a slightly different molecular structure, the F value was calculated as 0.4185 cm^{-1} for the present work. Silver and Wood assigned the torsional frequency for CH_2CCCl_3 as 123 cm^{-1}; and based on an unreported molecular structure, they obtained a higher potential barrier. The above values of V_3 and $\nu_{torsion}$, together with other reported results in the literature, are summarized in table 4–3.

TABLE 4–3. Reported internal rotation barrier heights and torsional fundamentals of 1,1,1,2-tetrachloroethane

V_3, kcal mol^{-1}	ν_{18}, cm^{-1}	References
10.0	116	Allen, Brier and Lane, 1967
12.4	123	Silver and Wood, 1963
	114	Plyler and Acquista, 1956
6	70	Luft, 1955
	117	Allen and Bernstein, 1954
	116	Nielsen, Liang and Daasch, 1953
	118	Bernstein, 1950
10.38	116	This work, 1972 (Selected)

The internal rotation contributions to thermodynamic properties were computed using 369 internal rotation levels up to 14994 cm^{-1}. These levels were generated with $V_3 = 10.38$ kcal mol^{-1} and $I_r = 40.28$ uÅ^2. It is interesting to mention that the thermodynamic functions thus obtained are in excellent agreement with those calculated using $\nu_{18} = 116$ cm^{-1} by Pitzer's semi-classical approximation method (Pitzer and Gwinn, 1942). The following table shows the results obtained by use of these two different methods.

T K	Values calculated			
	Using energy levels		Using Pitzer's approximation	
	C_p°	S°	C_p°	S°
100	1.600	3.374	1.604	3.371
298.15	2.005	5.396	2.006	5.395
500	2.116	6.459	2.117	6.459
1000	2.348	8.010	2.338	8.007
1500	2.250	8.953	2.218	8.964

These results suggest the usefulness of Pitzer's semi-classical approximation method in cases when it is impractical to calculate the full set of internal rotation levels. Such situations arise, for example, in molecules like the pentachloro- and hexachloroethanes, which have high V_3 and I_r values.

The enthalpies of formation for CH_2ClCCl_3 in the liquid and gaseous states have not been measured. The value of $\Delta Hf^\circ(CH_2ClCCl_3$, g, 298.15) for the present work was estimated by a variable increment method. From ΔHf°(g, 298.15) $= -34.0$, -26.8, and

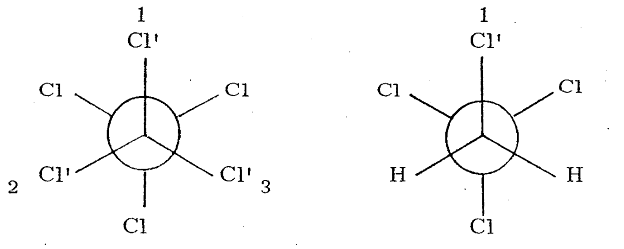
TABLE 4–4. Ideal gas thermodynamic functions for 1,1,1,2-tetrachloroethane

Temp. 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	−36.9	−36.9	infinite
100.00	13.49	64.70	54.83	0.987	−34.9	−29.8	65.1
150.00	17.06	70.87	59.17	1.754	−35.1	−27.2	39.7
200.00	19.95	76.19	62.78	2.682	−35.4	−24.5	26.8
273.15	23.51	82.94	67.30	4.275	−35.6	−20.5	16.4
298.15	24.59	85.05	68.70	4.876	−35.7	−19.2	14.0
300.00	24.67	85.20	68.80	4.922	−35.7	−19.1	13.9
400.00	28.36	92.83	73.88	7.582	−35.9	−13.5	7.4
500.00	31.16	99.48	78.35	10.56	−36.0	−7.9	3.4
600.00	33.28	105.4	82.37	13.79	−36.0	−2.2	0.8
700.00	34.93	110.6	86.03	17.20	−35.8	3.4	−1.1
800.00	36.24	115.4	89.41	20.77	−35.6	9.0	−2.4
900.00	37.30	119.7	92.54	24.44	−35.4	14.5	−3.5
1000.00	38.17	123.7	95.45	28.22	−35.2	20.1	−4.4
1100.00	38.88	127.3	98.19	32.07	−34.9	25.5	−5.1
1200.00	39.47	130.8	100.8	35.99	−34.6	31.0	−5.7
1300.00	39.96	133.9	103.2	39.96	−34.2	36.5	−6.1
1400.00	40.36	136.9	105.5	43.98	−33.9	41.9	−6.5
1500.00	40.69	139.7	107.7	48.03	−33.6	47.3	−6.9

−20.24 kcal mol^{-1} for CH_3CCl_3, CH_3CH_2Cl (this work), and C_2H_6 (API 44 tables), respectively, we calculated $\Delta Hf^\circ(CH_2ClCCl_3, g, 298.15) = -40.56$ kcal mol^{-1}, using the approximation that $\Delta Hf^\circ(CCl_3CH_2Cl) = \Delta Hf^\circ(CH_3CCl_3) + \Delta Hf^\circ(CH_3CH_2Cl) - \Delta Hf^\circ(C_2H_6)$. Then we refined the derived value by addition of a correction called the configuration energy (Benson et al., 1969), E_{conf}. The E_{conf} value for C_2Cl_6 was derived as

$$\Delta Hf^\circ(C_2Cl_6) - [2\,\Delta Hf^\circ(CH_3CCl_3) - \Delta Hf^\circ(C_2H_6)]$$
$$= -33.2 - (-68.0 + 20.24)$$
$$= 14.6 \text{ kcal mol}^{-1},$$

which involves three Cl—Cl—Cl configurational interactions (see figure 1). Since there are only 1/3 of such interactions in the CH_2ClCCl_3 molecule, the E_{conf} value for 1,1,1,2-tetrachloroethane was evaluated as $\frac{1}{3}(14.6) = 4.9$ kcal mol^{-1}. This leads to



Three Cl–Cl'–Cl interactions in C_2Cl_6 molecule

One Cl–Cl'–Cl interaction in CH_2ClCCl_3

FIGURE 1. The Cl–Cl–Cl configurational interactions in C_2Cl_6 and CH_2ClCCl_3 molecules.

$$\Delta Hf^\circ(CH_2ClCCl_3, g, 298.15) = -40.56 + 4.9$$
$$= -35.7 \pm 1.0 \text{ kcal mol}^{-1},$$

which was adopted.

By use of the above selected data, the thermodynamic functions for 1,1,1,2-tetrachloroethane (g) were evaluated. The results are presented in table 4–4. There are no third law entropies, vapor heat capacities, or equilibrium data available in the literature for checking the calculated values.

6. Pentachloroethane

The molecular structure of pentachloroethane ($CHCl_2CCl_3$) has not been reported in the literature. The molecular parameters used for calculation of the moments of inertia were estimated based on an assumption that the structural parameters for the CCl_3 and the $CHCl_2$ group in CCl_3CHCl_2 are similar to those of the corresponding groups in the C_2Cl_6 and CH_3CHCl_2 molecules. Employing the adopted structural parameters, as listed in table 5–1, the three principal moments of inertia were calculated to be:

$$I_A = 429.6 \text{ uÅ}^2 \text{ (or } 7.133 \times 10^{-38} \text{ g cm}^2),$$

$$I_B = 532.1 \text{ uÅ}^2 \text{ (or } 8.835 \times 10^{-38} \text{ g cm}^2),$$

and

$$I_C = 685.5 \text{ uÅ}^2 \text{ (or } 1.138 \times 10^{-37} \text{ g cm}^2).$$

The internal rotation reduced moment (I_r) was obtained as 105.1 uÅ^2 (or 1.745×10^{-38} g cm^2). Morino, Yamaguchi, and Mizushima (1944) studied the molecular structure of pentachloroethane by electron diffraction.

Allen, Brier, and Lane (1967) observed the infrared and Raman spectra of pentachloroethane in the liquid and gaseous states and assigned vibrational fundamentals. Vibrational assignments were also reported by Allen and Bernstein (1954), Neilsen, Liang, and Daasch (1953), and Blaine (1963). Their

TABLE 5–1. Structural data for pentachloroethane

Structural parameter [a]	Reference
	Selected
C—Cl(CCl$_3$)	(1.769) [b]
C—Cl(CHCl$_2$)	(1.766)
C—H	(1.09)
C—C	(1.564)
∠CCCl(CHCl$_2$)	(111.0)
∠ClCC(CCl$_3$)	(110.0)
∠HCC	(111.3)
∠ClCCl(CHCl$_2$)	(112.0)

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

[b] Values in parentheses are estimated.

results are summarized in table 5–2 in which the selected fundamentals for pentachloroethane (g) are also listed for comparison. The infrared spectrum of this compound has been observed by Chanal et al. (1967), Bolleter (1964), Plyler and Acquista (1956), Thompson and Torkington (1945), Vierling and Mecke (1936), Stair and Coblentz (1935), and Timm and Mecke (1935). Its Raman spectrum was investigated by Gerding and Haring (1955), Gerding and Rijnders (1946), Mizushima, Morino, Kawano, and Otai (1944), and Bonino and Brüll (1929).

Based on the adopted values for the torsional fundamental (ν_{18}) and I_r, we calculated the potential barrier height for internal rotation (V_3) as 14.43 kcal mol^{-1}. Table 5–3 summarizes the values of V_3 and I_r reported in the literature for pentachloroethane (g). The internal rotation contributions to thermodynamic functions were evaluated by use of the semi-classical approximation method suggested by Pitzer and Gwinn (1942).

The enthalpy of vaporization was calorimetrically determined by Eftring (1938), and his result was used by Kirkbride (1956) for calculation of $\Delta Hf°(C_2HCl_5$, g, 298.15). In the absence of better data, Eftring's value was adopted for calculation. The vapor pressures of pentachloroethane (l) have been determined by Nelson (1930, 298.3–435.4 K), Herz and Rathmann (1912, 342–431 K), and Staedel (1882, 411.2–449.3 K). We tried to use these data points for fitting to an Antoine equation and found that these three sets of vapor pressure measurements were not consistent. Using the derived Antoine constants, we calculated the enthalpy of vaporization at the boiling point (433.68 K) as 8.9 kcal mol^{-1}. Based on the vapor pressure data of Nelson, the value of $\Delta H_v^\circ(C_2HCl_5$, l, 433.5) was obtained as 9.04 kcal mol^{-1} and $\Delta H_v^\circ(C_2HCl_5$, l, 298.15)$=$11.6 kcal mol^{-1}. (See table 5–4). These calculated ΔH_v° values were not used.

Smith et al. (1953) determined the standard enthalpy change for the combustion reaction 5–1 as -204.89 kcal mol^{-1} at 298.15 (corrected value)

$$C_2HCl_5(l)+2H_2O(l)+O_2(g) \\ =2CO_2(g)+5HCl(600\ H_2O). \qquad (5\text{–}1)$$

Employing $\Delta Hf°(298.15)$ values for H_2O (l), CO_2(g), and HCl · 600H$_2$O (aq) from Wagman et al. (1968), we derived the value $\Delta Hf°(C_2HCl_5$, l, 298.15) $= -45.70 \pm 0.6$ kcal mol^{-1}. From this value and $\Delta H_v^\circ(C_2HCl_5$, l, 298.15) $=$ 10.9 kcal mol^{-1}, the $\Delta Hf°(C_2HCl_5$, g, 298.15) was evaluated to be -34.8 ± 1.0 kcal mol^{-1}. Since there was no other $\Delta Hf°$ value available for pentachloroethane (g), this value was adopted.

TABLE 5–2. Vibrational assignments for pentachloroethane

Mode No.	Symmetry class	Reference				
		Nielsen et al., 1953	Allen et al., 1954	Blaine, 1963	Allen et al., 1967	Selected
		Wavenumber in cm^{-1}				
ν_1	a'	2995	2985			2990
ν_2	a'	1252	1253			1253
ν_3	a'	1021	1022			1021
ν_4	a'	820	820			820
ν_5	a'	724	724			724
ν_6	a'	585	582			582
ν_7	a'	404	404		404	404
ν_8	a'	327	326		325	325
ν_9	a'	278	278		278	278
ν_{10}	a'	224	225		225	225
ν_{11}	a'	176	175	175.5	178	175
ν_{12}	a''	1210	1208			1209
ν_{13}	a''	835	836			835
ν_{14}	a''	771	770			771
ν_{15}	a'	327	326		325	325
ν_{16}	a''	238	238		238	238
ν_{17}	a''	166	165	164.5	165	165
ν_{18}	a'' (torsion)	85	82	85	85	85

Based on the above selected values, the thermodynamic properties for pentachloroethane in the ideal gaseous state in the temperature range 100 to 1500 K were calculated by use of rigid-rotor and harmonic-oscillator approximations. The results are presented in table 5–6. No experimental heat capacity and entropy data were available in the literature for comparisons of entropy values.

TABLE 5–3. Reported internal rotation barrier heights and torsional fundamentals of pentachloroethane

V_3, kcal mol^{-1}	ν_{18}, cm^{-1}	References
14.2	85	Allen, Brier, and Lane, 1967
	85±1.5	Blaine, 1963
9	65	Luft, 1955
	82	Allen and Bernstein, 1954
	85	Nielsen, Liang, and Daasch, 1953
14.43	85	This work, 1972 (Selected)

7. Hexachloroethane

The molecular structure of hexachloroethane (CCl_3CCl_3, g) has been determined by electron diffraction by many investigators (Morino and Kimura, 1947; Hassel and Viervoll, 1947; Morino and Iwasaki, 1949;

TABLE 5–4. Enthalpy of vaporization data for pentachloroethane

ΔH_v obs kcal mol^{-1}	Conditions	Methods	Reference	ΔH_v° (298) kcal mol^{-1}
10.9	293.15 K	calorimetric measurement	Kirkbride, 1956; this value was measured by E. Eftring, Dissertation, Lund, 1938	10.9±0.5
9.04	433.5 K, 1 atm	calculated from vapor pressure equation	Nelson, 1930	11.6
			Selected value:	10.9±0.5

TABLE 5–5. Enthalpy of formation data for pentachloroethane

ΔHr° obs kcal mol^{-1}	Conditions	Method	ΔHf° (298) kcal mol^{-1}	Reference	ΔHf° (298) gas kcal mol^{-1}
−204.9±0.6	292 K	combustion calorimetry	−45.70±0.6	Smith et al., 1953	−34.80±1.0
				Selected value:	−34.8±1.0

TABLE 5–6. Ideal gas thermodynamic functions for pentachloroethane

Temp. 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	−36.63	−36.63	infinite
100.00	15.564	67.556	56.809	1.075	−34.46	−28.66	62.63
150.00	19.877	74.727	61.618	1.966	−34.65	−25.71	37.46
200.00	23.189	80.916	65.687	3.046	−34.76	−22.71	24.82
273.15	27.085	88.744	70.840	4.890	−34.80	−18.30	14.64
298.15	28.219	91.165	72.444	5.582	−34.80	−16.79	12.31
300.00	28.299	91.340	72.560	5.634	−34.80	−16.68	12.15
400.00	31.957	100.013	78.369	8.658	−34.69	−10.64	5.82
500.00	34.523	107.436	83.458	11.989	−34.48	−4.66	2.04
600.00	36.345	113.901	88.005	15.537	−34.21	1.28	−0.47
700.00	37.686	119.609	92.120	19.242	−33.90	7.17	−2.24
800.00	38.709	124.711	95.881	23.064	−33.56	13.02	−3.56
900.00	39.516	129.319	99.344	26.977	−33.20	18.82	−4.57
1000.00	40.166	133.517	102.555	30.962	−32.82	24.59	−5.37
1100.00	40.697	137.371	105.547	35.006	−32.42	30.28	−6.02
1200.00	41.133	140.931	108.349	39.098	−32.02	35.98	−6.55
1300.00	41.493	144.238	110.984	43.230	−31.62	41.63	−7.00
1400.00	41.790	147.325	113.471	47.395	−31.27	47.27	−7.38
1500.00	42.035	150.216	115.825	51.587	−30.81	52.86	−7.70

TABLE 6–1. Structural data for hexachloroethane

Structural parameter[a]	Reference				
	Morino and Iwasaki, 1949	Swick et al., 1954	Morino and Hirota, 1958	Almenningen et al., 1964	Selected
C – Cl	1.77 ± 0.02	1.74 ± 0.01	1.775	1.769 ± 0.003	1.769
C – C	1.54 ± 0.07	1.57 ± 0.06	1.46	1.564 ± 0.014	1.564
∠ ClCC		109.7 ± 0.5	111.5	110.0 ± 0.5	110.0

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

Swick et al., 1954; Morino and Hirota, 1958; and Almenningen et al., 1964). The structural parameters reported by the more recent investigators are listed in table 6–1. Those given by Almenningen et al. were adopted for the present work.

Incomplete vibrational assignments were made for CCl_3CCl_3 (g) from Raman spectra by Hamilton and Cleveland (1944), Gerding and Haring (1946), and Mizushima et al. (1949). The infrared spectrum of hexachloroethane has been observed by Hirota (1958), Carney et al. (1961), Bolleter (1964), Watari and Aida (1967), and Chanal et al. (1967) from which vibrational fundamentals were derived and reported. Recently, Shimanouchi (1972) has critically reviewed the infrared and Raman spectral data and assigned 12 fundamentals for CCl_3CCl_3 (g). (See table 6–2 for numerical values.) His assigned values were adopted here, except the value of ν_4 (torsion) which was given at 61 cm^{-1}.

Using this value, $\nu_4 = 61$ cm^{-1}, we calculated the internal rotation potential barrier, $V_3 = 10.4$ kcal mol^{-1}, for the hexachloroethane molecule. This V_3 value seems low compared to our adopted $V_3 = 14.43$ kcal mol^{-1} for $CHCl_2CCl_3$ (g) which has only 5 Cl atoms in the molecule and might be expected to have a lower barrier than CCl_3CCl_3 (g). Allen et al. (1967) reported the torsional mode as 79 cm^{-1} and $V_3 = 17.5$ kcal mol^{-1} based on a private communication from Shimanouchi; however, in his recent work, Shimanouchi (1972) selected 61 cm^{-1} as ν_4 for CCl_3CCl_3 (g). Due to inconsistency, neither 61 nor 79 cm^{-1} was accepted.

Karle (1966) presented a method for determining the barrier height for hindered internal rotation from electron-diffraction data. His reported value of 14.7 kcal mol^{-1}, which was based on a structure consistent with our selected molecular structure, was adopted in this work. From $V_3 = 14.7$ kcal mol^{-1} and a reduced moment for internal rotation, $I_r = 146.95$ uÅ^2, the torsional fundamental (ν_4) was derived as 73 cm^{-1}. Because of the high barrier height and large reduced moment for internal rotation for CCl_3CCl_3 (g), the contributions to the thermodynamic functions have been calculated using the semi-classical approximation of Pitzer and Gwinn (1942). Other values of V_3 and ν_4 reported in the literature are summarized in table 6–3.

TABLE 6–2. Vibrational assignments for hexachloroethane

Mode No.	Symmetry class	Reference		
		Karle, 1966	Shimanouchi, 1972	Selected
		Wavenumber in cm^{-1}		
ν_1	a_{1g}		975	975
ν_2	a_{1g}		431	431
ν_3	a_{1g}		170	170
ν_4	a_{1u} (tor.)	73	61	73
ν_5	a_{2u}		675	675
ν_6	a_{2u}		372	372
ν_7	e_g		778	778
ν_8	e_g		271	271
ν_9	e_g		114	114
ν_{10}	e_u		859	859
ν_{11}	e_u		340	340
ν_{12}	e_u		223	223

TABLE 6–3. Reported internal rotation barrier heights and torsional fundamentals of hexachloroethane

V_3, kcal mol^{-1}	ν_4, cm^{-1}	Reference
10.4	61	Shimanouchi, 1972
17.5	79	Allen et al., 1967
14.7	73	Karle, 1966 [a]
11.0		Karle, 1966 [b]
12.8		Karle, 1966 [c]
10.8 ± 3.0		Morino and Hirota, 1958
12.0	65	Luft, 1955
⩾ 7 ± 1		Swick, Karle, and Karle, 1954
10–15		Morino and Iwasaki, 1949
12 ± 2	65	Mizushima et al., 1949
14.7	73	This work, 1972 (Selected)

[a] Calculation based on a molecular structure determined by Almenningen et al. (1964).

[b] Calculation based on a molecular structure determined by Morino and Hirota (1958).

[c] Calculation based on a molecular structure determined by Swick et al. (1954).

The vapor pressures of hexachloroethane (c, l) have been measured by Lee (1935, 335–512 K), Ivin and Dainton (1947, 286–447 K), and Nitta and Seki (1941, 290–343 K). The reported data points were fitted to the Antoine equation by the least squares techniques, and the enthalpies of sublimation, ΔH_s°(c), were evaluated from the derived Antoine constants at 298 K and 351 K for data of Nitta and Seki and of Lee, Ivin and Dainton, respectively. The values of ΔH_s°(351) were converted to 298.15 K employing C_p° (C_2Cl_6, g) from the present work, and C_p°(C_2Cl_6, c) and enthalpies of transition from

TABLE 6–4. Enthalpy of sublimation data for hexachloroethane

ΔHs obs kcal mol^{-1}	Conditions	Methods	Reference	$\Delta H_s°(298)$ kcal mol^{-1}
13.5±0.4	351 K	Antoine equation with $\Delta C_p^\circ = -23.2$ cal K^{-1} mol^{-1} at 351 K	Lee, 1935	17.3±0.4
13.3±0.4	351 K	Antoine equation with $\Delta C_p^\circ = -23.2$ cal K^{-1} mol^{-1} at 351 K	Ivin and Dainton, 1947	17.0±0.4
14.5±0.4	298 K	Antoine equation	Nitta and Seki, 1941	14.5±0.4
12.35±0.4	351 K	Antoine equation	Lee, 1935; Ivin and Dainton, 1947	16.1±0.4
16.1±0.9	298 K	From $\Delta Hf°$ of crystal and gas	Smith et al., 1953; Puyo et al., 1963	16.1±0.9
			Selected value	16.5±0.5

Seki and Momotani (1950). We have combined the vapor pressure data of Lee (1935) and Ivin and Dainton (1947) and fitted 39 data points to the Antoine equation. Based on the derived Antoine constants, we obtained ΔH_s° (298.15) = 16.1 kcal mol^{-1}.

Using the derived Antoine constants, we calculated the ΔC_p° for sublimation and found that the value of ΔC_p° was essentially zero, i.e., the obtained ΔC_p° value was much too positive. In order to improve the evaluation of ΔH_s°, we fixed $\Delta C_p^\circ(351)$, a temperature at the middle of the temperature range of the data points, at -23.2 cal K^{-1} mol^{-1}, which was an experimental value, and then refitted the vapor pressure data to the Antoine equation. This procedure yields $\Delta H_s^\circ(298.15) = 17.0$ to 17.3 kcal mol^{-1}. An average value of 16.5 ± 0.5 kcal mol^{-1} was adopted. The results are summarized in table 6–4.

By the quartz wool method, Smith et al. (1953) measured the enthalpy of combustion of hexachloroethane (c) as -172.36 kcal mol^{-1} at 292 K. Employing auxiliary data from Wagman et al. (1968), $\Delta Hf°$ (C_2Cl_6, C, 298.15) = -49.74 was calculated. Kirkbride (1956) determined for reaction 6–1, $\Delta Hr°(298.15\text{ K}) = -32 \pm 2$ kcal mol^{-1} and the enthalpy of solution of C_2Cl_6 (c) in C_2Cl_4 (l) as 4.7 kcal mol^{-1}

$$C_2Cl_4(l) + Cl_2(g) = C_2Cl_6\ (sol). \qquad (6\text{–}1)$$

Therefore, taking $\Delta Hf°(C_2Cl_4, l, 298.15) = -12.5$ kcal mol^{-1} (Wagman et al., 1968), we calculated $\Delta Hf°(C_2Cl_6, c, 298.15) = -49.5$ kcal mol^{-1}. Incorporating the above two $\Delta Hf°(C_2Cl_6, c, 298.15)$ values with the selected enthalpy of sublimation (table 6–4), we obtained $\Delta Hf°$ (C_2Cl_6, g, 298.15) = -33.2 and -33.0 kcal mol^{-1}, respectively.

Puyo et al. (1963) determined the equilibrium constant $K_p = 0.8$ atm at 776 K for reaction 6–2, which yields $\Delta Gr°$ (776 K) = 0.344 kcal mol^{-1}.

$$C_2Cl_6(g) = C_2Cl_4(g) + Cl_2(g) \qquad (6\text{–}2)$$

From $\Delta Gr°$(776 K) and $\Delta Sr°(776\text{ K}) = 37.13$ cal K^{-1} mol^{-1} ($S°$ for C_2Cl_4 taken from JANAF tables; $S°$ for C_2Cl_6 from the present work; and $S°$ for Cl_2 from TRC Data Project tables), we evaluated $\Delta Hr°(776\text{ K}) = 29.16$ kcal mol^{-1} and $\Delta Hr°(298.15\text{ K}) = 30.69$ kcal mol^{-1}. Adopting $\Delta Hf°(C_2Cl_4, g, 298.15) = -2.9$ kcal mol^{-1} (Wagman et al., 1968) and $\Delta Hr°(298.15\text{ K}) = 30.7$ kcal

TABLE 6–5. Enthalpy of formation data for hexachloroethane

$\Delta Hr°$ kcal mol^{-1}	Conditions	Method	$\Delta Hr°$ (298) kcal mol^{-1}	Reference	$\Delta Hf°$ (298) gas kcal mol^{-1}
−172.36±0.5	292 K, crystal	Combustion, Quartz Wool method	−49.7±0.5	Smith et al., 1953	−33.2±0.7
−37±2	298 K, 1 atm, C_2Cl_4 soln.	$C_2Cl_4(l) \pm Cl_2(g) \rightarrow C_2Cl_6(c)$	−49.5±2	Kirkbride, 1956	−33.0±2
29.16±0.3	776 K, gas phase	$C_2Cl_6 \rightleftharpoons C_2Cl_4 + Cl_2$	30.7±0.3	Puyo et al., 1963	−33.6±0.8
				Selected value	−33.2±1

TABLE 6–6. Ideal gas thermodynamic functions for hexachloroethane

Temp. 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	−35.92	−35.92	infinite
100.00	18.448	67.476	55.285	1.219	−33.53	−26.69	58.33
150.00	23.571	75.982	60.804	2.277	−33.60	−23.25	33.87
200.00	27.362	83.305	65.535	3.554	−33.53	−19.80	21.64
273.15	31.535	92.485	71.558	5.716	−33.30	−14.81	11.85
298.15	32.680	95.297	73.432	6.519	−33.20	−13.13	9.62
300.00	32.760	95.500	73.567	6.580	−33.19	−13.00	9.47
400.00	36.206	105.434	80.331	10.041	−32.71	−6.34	3.46
500.00	38.395	113.766	86.208	13.779	−32.17	0.19	−0.08
600.00	39.823	120.901	91.410	17.695	−31.62	6.61	−2.18
700.00	40.795	127.118	96.076	21.729	−31.06	12.94	−4.04
800.00	41.484	132.613	100.307	25.845	−30.52	19.19	−5.24
900.00	41.993	137.529	104.174	30.020	−29.99	25.37	−6.16
1000.00	42.378	141.975	107.736	34.239	−29.46	31.51	−6.89
1100.00	42.676	146.028	111.035	38.492	−28.94	37.55	−7.46
1200.00	42.909	149.752	114.109	42.772	−28.44	43.59	−7.94
1300.00	43.091	153.194	116.984	47.073	−27.94	49.57	−8.33
1400.00	43.232	156.393	119.686	51.389	−27.46	55.53	−8.67
1500.00	43.341	159.379	122.234	55.718	−26.99	61.44	−8.95

mol^{-1}, we calculated $\Delta Hf^\circ(C_2Cl_6$, g, 298.15$)=-33.6$ ± 0.8 kcal mol^{-1}. The adopted value for $\Delta Hf^\circ(C_2Cl_6$, g, 298.15) is -33.2 ± 1 kcal mol^{-1} as shown in table 6–5.

The ideal gas thermodynamic functions were calculated using these selected data and the rigid-rotor harmonic-oscillator approximation. They are presented in table 6–6. No experimental vapor heat capacity or third law entropies were available from the literature for comparisons with the calculated values.

8. Comparison

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 in tables 7–2 and 7–3. The minor differences are probably due to the use of different molecular, spectroscopic, and thermochemical data for evaluation of these properties.

TABLE 7–1. Molecular and thermochemical constants for the six chloroethanes

	CH_3CH_2Cl	CH_3CHCl_2	CH_3CCl_3	CH_2ClCCl_3	$CHCl_2CCl_3$	CCl_3CCl_3
Mole weight	64.515	98.960	133.405	167.850	202.295	236.740
Point group	C_s	C_s	C_{3v}	C_s	C_s	D_{3d}
Symmetry number, total*	3	3	9	3	3	18
Ground state configuration	${}^1A'$	${}^1A'$	${}^1A'$	${}^1A'$	${}^1A'$	${}^1A_{1g}$
Product of three principal moments of inertia, g^3 cm^6	6.9966×10^{-115}	1.2908×10^{-113}	6.3480×10^{-113}	2.7975×10^{-112}	7.1727×10^{-112}	1.3865×10^{-111}
Reduced moment of internal rotation, g cm^2	4.615×10^{-40}	5.243×10^{-40}	5.306×10^{-40}	6.688×10^{-39}	1.745×10^{-38}	2.440×10^{-38}
Torsional fundamental, cm^{-1}	251	231	278	116	85	73
Potential barrier height for internal rotation, kcal mol^{-1}	3.69	3.54	5.08	10.38	14.43	14.7
Vibrational fundamentals, cm^{-1}	see table 1–2	see table 2–2	see table 3–2	see table 4–2	see table 5–2	see table 6–2
Enthalpy of formation at 298.15 K, kcal mol^{-1}	−26.83	−31.10	−34.01	−35.7	−34.80	−33.20

*Total symmetry number = external symmetry number × internal symmetry number (symmetry number of the rotating top).

TABLE 7–2. Comparison of the ideal gas thermodynamic data at 1 atm and 298.15 K for the six chloroethanes

	CH_3CH_2Cl			CH_3CHCl_2			CH_3CCl_3			CH_2ClCCl_3			$CHCl_2CCl_3$			CCl_3CCl_3		
	C_p°	S°	$-\Delta Hf^\circ$	C_p°	S°	$-\Delta Hf^\circ$	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}	cal K^{-1} mol^{-1}		kcal mol^{-1}	cal K^{-1} mol^{-1}		kcal mol^{-1}
Landolt-Bornstein, 1961	14.90	65.67	25.09	18.22	72.82		22.37	77.03		24.57	85.11		28.18	90.94		32.65	94.77	
Wagman et al., 1968 (NBS TN–270–3)	15.01	65.94	26.81	18.22	72.90	30.93	22.3	77.2		24.55	85.07		28.14	90.95		32.7	95.3	33.9
Stull, Westrum, and Sinke, 1969	14.99	65.93	26.70	18.22	72.39	31.05							28.14	90.95	34.00	32.59	94.77	33.80
JANAF, 1969																33.21	95.07	32.08
Glushko et al., 1970 (USSR)	15.01	65.99	25.7	18.2	72.3	30.6	22.2	77.1		24.6	85.1		28.2	90.9		32.6	94.8	34.0
This Work, 1972	14.97	65.91	26.83	18.24	72.38	31.10	22.07	76.49	34.01	24.59	85.05	35.7	28.22	91.16	34.80	32.68	95.30	33.20

TABLE 7–3. Comparison of the ideal gas thermodynamic data at 1 atm and 700 K for the six chloroethanes

	CH_3CH_2Cl			CH_3CHCl_2			CH_3CCl_3			CH_2ClCCl_3			$CHCl_2CCl_3$			CCl_3CCl_3		
	C_p°	S°	$-\Delta Hf^\circ$	C_p°	S°	$-\Delta Hf^\circ$	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}	cal K^{-1} mol^{-1}		kcal mol^{-1}	cal K^{-1} mol^{-1}		kcal mol^{-1}
Landolt-Bornstein, 1961	26.72	83.24	27.99	29.18			31.95	100.3		34.68			37.52			40.65		
Stull, Westrum, and Sinke, 1969	26.53	83.44	29.61	29.21	93.07	33.04							37.53	119.27	33.15	40.63	126.49	31.72
JANAF, 1969																41.06	127.24	29.79
This Work, 1972	26.49	83.40	29.75	29.15	93.07	33.10	32.38	99.82	34.85	34.93	110.61	35.81	37.69	119.61	33.90	40.80	127.12	31.06

FIGURE 1. The Cl—Cl—Cl configurational interactions in C_2Cl_6 and CH_2ClCCl_3 molecules

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