Ideal gas thermodynamic properties of six chlorofluoromethanes

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Ideal Gas Thermodynamic Properties of Six Chlorofluoromethanes

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Spectroscopic and thermal data were reviewed. The selected values for the principal moments of inertia, the vibrational fundamentals, and the standard enthalpy of formation at 298.15 K for each of the six chlorofluoromethanes were used to derive the chemical thermodynamic properties of molecules from 0 to 1500 K, based on the rigid-rotor harmonic-oscillator approximation. The calculated values are in accord with experimental heat capacities and entropies.

Key words: Chlorofluoromethanes; ideal gas thermodynamic functions; principal moments of inertia; standard enthalpy of formation; vibrational fundamentals.

1. Introduction

As a continuing part in a series of studies on chloroand fluoro-substituted methanes and ethanes [1-3], the six mixed chlorofluoromethanes were investigated. These compounds are frequently used as coolants and propellants. In recent months, some concern has been expressed that chlorofluoromethanes may accumulate in the air to an extent sufficient to deplete the ozone in the upper atmosphere [4]. This work provides reference data on the thermodynamic properties which should be useful in investigations of the thermal stability and kinetics of reaction of these compounds in the stratosphere.

For each of the chlorofluoromethanes concerned, molecular structure and the vibrational fundamentals are generally well determined, except for the assignments of the lowest a' band in CHClF and b1 band in CCl3F, which were found to be less certain. Whenever observed rotational constants were not available, the principal moments of inertia were calculated from the selected structural parameters. The most recent fundamental 1973 physical constants [5] and the recommended masses [6] with C = 12.011, H = 1.0079, F = 18.99840, and Cl = 35.453 were used. Throughout this paper, 1 Å = 10^-10 cm = 10^-10 m, 1 kcal = 1000 cal = 4184 J, and 1 cm^-1 is equivalent to 11.96267 J·mol^-1. The conversion factor 505379 MHz·amu·Å^2 has been used to calculate principal moments of inertia from rotational constants reported in the literature.

Chemical thermodynamic properties were calculated for the harmonic-oscillator rigid-rotor model. Comparisons were made with available experimental data. Unless otherwise mentioned, the symbol ΔH^° stands for the standard enthalpy of formation in the ideal gaseous state at 298.15 K. No experimental work was carried out to determine the ΔH^° values for CH₂ClF and CHClF. The values were estimated by means of the general triatomic additivity (GTA) method [7], in which the contributing terms were determined by correlation of selected experimental data on key halogenated alkanes. The basic thermodynamic data for the four chemical elements as given in reference [1] were used to generate the values of ΔH^°, ΔG^°, and log Kf for the six chlorofluoromethanes at various temperatures. The six chlorofluoromethanes are discussed below in the standard order of arrangement of the elements.

2. Chlorofluoromethane (F 31)^2

The molecular structure of chlorofluoromethane in the gaseous phase was first studied by the electron diffraction method [8]. Muller [9] measured the microwave spectra for the isotopic species CH₃Cl²F and CH₃Cl²F² and derived structural parameters on the basis of an assumed H-C-H angle [10, 11]. The principal moments of inertia reported in table 1 are derived from the rotational constants of Muller [9] and correspond to the atomic mass of 35.453 for chlorine. These were used to calculate the rotational contributions to the thermodynamic properties for naturally occurring mixtures of isotopes.

The molecule of CH₂ClF belongs to the point group C₂ and has nine vibrational modes. Of these, six modes belong to the a' species while the remainder belong to the a'' species. A Raman spectrum of a liquid sample was recorded [12] and only seven fundamentals were assigned [13]. Most of the assignments were confirmed by Plyler and Lamb [14] in an infrared spectrum for the gaseous phase. Another infrared study of the gaseous CH₂ClF was reported [15], but no vibrational assignments were given. Consequently, the complete assignment of Plyler and Lamb [14] is adopted and tabulated in table 1.

No experimental measurements have ever been made for the standard enthalpy of formation for CH₂ClF.

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1Figures in brackets indicate the literature references.

2A system of nomenclature consisting of the letter F (for fluorocarbon) and a number has grown up for convenience in referring to the chlorofluorinated hydrocarbons and will be used here. For a description of the system see Hudlicky, M., Organic Fluorine Chemistry, Plenum Press, New York-London (1971), p. 19.
A simple correlation scheme [16] led to $\Delta H^\alpha(\text{CH}_2\text{CIF}) = -62.7$ kcal mol$^{-1}$ when the selected values of $\Delta H^\alpha$ for CF$_4$ and CCl$_4$ [1] and for CH$_4$ [17] were used. To the contrary, a more recent bond energy-group contribution scheme [18] gave $-64.0$ kcal mol$^{-1}$. The triatomic additivity method of Somayajulu and Zwoinski [7] has been very satisfactorily applied to a large number of substituted alkanes. This method yields a value for $\Delta H^\alpha(\text{CH}_2\text{CIF}) = -63.2$ kcal mol$^{-1}$ which is adopted and listed in table 1.

The selected values in table 1 were used for the calculations of chemical thermodynamic properties. The results are given in table 2. No experimental thermal data are available for comparison.

3. Chlorodifluoromethane (F 22)

The molecular structure of the gaseous CHCIF$_2$ was investigated by both electron diffraction [8] and microwave [19, 20] techniques. The rotational constants for the isotopic species, CHCl$^{18}$F$_2$ and CHCl$^{17}$F$_2$, determined by Beeson et al. [19] and by McLay and Mann [20] are in excellent agreement. The principal moments listed in table 1 are derived from the observed rotational constants with an adjustment for the natural isotopic abundance of C and Cl.

The CHCIF$_2$ molecule has the same point group and symmetry species of vibrational modes as for CH$_2$CIF. The Raman spectrum for the liquid CHCIF$_2$ was repeatedly recorded [12, 21, 22]. The vibrational fundamentals were revised due to the possible existence of CHF$_3$ [21] and CCl$_2$F$_2$ [22] as impurities in the sample.

The gaseous phase was also investigated by means of infrared [23, 24] and Raman [25, 26] spectra. The observed fundamentals are generally in good agreement, except for three modes. The lowest band at about 365 cm$^{-1}$ was found in the infrared with weak intensity for the gas [23] and with medium intensity for the liquid [22], whereas a weak band at 400 cm$^{-1}$ was recorded in the Raman for the gas [25, 26]. This weak band was also observed in the infrared spectrum of the gas [24]. The two bands at 1178 and 1116 cm$^{-1}$ were observed only in the gas-phase infrared [23, 24]. These two bands with medium and strong intensities, for a sample of greater than 99 mole percent purity, cannot be overlooked. While the vibrational fundamentals assigned in the Raman work [25, 26] are apparently somewhat ambiguous, the agreement between the two infrared studies [23, 24] is quite good. We have elected to select the recent values of Weissman, Meister, and Cleveland [24]. The adopted vibrational fundamentals are given in table 1.

Edwards and Small [27] studied the pyrolysis of CHClF$_3$ in the endothermic reaction 2CHClF$_3$ $\rightarrow$ C$_2$F$_4$ + 2HCl in a spherical bomb. To eliminate the effects of possible side reactions, they extrapolated the values of the equilibrium constant $K_p$ and obtained $K_p = 0.087$ atm at 873.15 K. They then derived $\Delta H^\alpha(\text{CHClF}_3) = -112.3$ kcal mol$^{-1}$ from this $K_p$ value with the aid of tabulated thermodynamic functions. When the JANAF [28] thermodynamic values were used, $\Delta H^\alpha(\text{CHClF}_3) = -115.1$ kcal mol$^{-1}$ was obtained. However, Cox and Pilcher [29] recommended $-115.6$ kcal mol$^{-1}$ which is exactly the same as the value predicted by Somayajulu.

### Table 1. The selected molecular and chemical constants of the six chlorofluoromethanes

<table>
<thead>
<tr>
<th>Compound</th>
<th>CHClF</th>
<th>CHCIF$_2$</th>
<th>CHClF</th>
<th>CCIF$_3$</th>
<th>CCl$_2$F$_2$</th>
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<td>1</td>
<td>1</td>
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<td>2</td>
<td>3</td>
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<td>3026 (a')</td>
<td>3026 (a')</td>
<td>1212 (e)</td>
<td>1101 (a)</td>
<td>847 (e)</td>
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<td>1312 (a')</td>
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<td>667 (a)</td>
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<td>$\nu_{5}$</td>
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<td>446 (b)</td>
<td>446 (b)</td>
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$^a$Symbols in parentheses after wavenumbers denote the vibrational symmetry species.

$^b$Obtained from rotational constants unless otherwise indicated.

$^c$Calculated from $r(C-C) = 3.132$ Å, $r(C-CI) = 1.751$ Å, $r(F-CI) = 2.158$ Å, and $r(F-CI) = 2.539$ Å [38].

$^d$Calculated from $r(C-F) = 1.35$ Å, $r(C-CI) = 1.74$ Å, $r(F-CF) = 2.21$ Å, $r(F-CI) = 2.52$ Å, and $r(F-CI) = 2.90$ Å [39].

$^e$Calculated from $r(C-F) = 1.40$ Å, $r(C-CI) = 1.76$ Å, $r(F-CF) = 2.56$ Å, and $r(C-CI) = 2.91$ Å [8].

$^f$Calculated from the correlation method [7].
and Zwolinski [7]. The simple scheme [16] and the bond energy-group contribution scheme [18] give −118.7 and −113.9 kcal·mol⁻¹, respectively. We have therefore selected ΔH_f°(CHClF_2) = −115.6 kcal·mol⁻¹ as is given in table 1.

The calculated thermodynamic properties were tabulated in table 3. Comparisons with the experimental heat capacities [30] and the third-law entropy [31] will be discussed in section 8.

### Table 2. Ideal gas thermodynamic functions of chlorofluoromethane (F 31)

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### Table 3. Ideal gas thermodynamic functions of chlorodifluoromethane (F 22)

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The structural parameters of the gaseous CHClF were first determined by the electron diffraction method [8]. McLay [32] measured the frequencies for the low rotational transitions in the microwave spectra of C¹HClF²F and C¹HClF²Cl³F and obtained the rotational constants. The allowance for the isotopic effect was made and the principal moments of inertia

we obtained for the naturally abundant CHClF are given in table 1.

The molecule of CHClF belongs to the same point group as do CH₂ClF and CHClF₂. The vibrational spectra of CHClF were observed in the Raman [21, 22, 26, 33] and infrared [23, 24, 34]. Taking the phase shift into consideration, the vibrational assignments from the Raman of liquid [21, 22, 33] are generally in accord with those from the infrared of gas [23, 24]. The strong band at 1240 cm⁻¹ which was observed elsewhere [21–24, 33, 34], however, was not assigned in the gas-phase Raman work [26]. The nine vibrational fundamentals assigned by Weissman, Meister, and Cleveland [24] from their infrared absorption spectrum of gas have been selected and are given in table 1.

The standard enthalpy of formation for the gaseous CHClF at 298.15 K has not been experimentally determined. It was calculated either as −71.7 kcal·mol⁻¹ from the simple correlation [16] or as −66.7 kcal·mol⁻¹ from the bond energy-group contribution scheme [18]. The value of −67.7 kcal·mol⁻¹ derived [28] from the vibrational fundamentals. The values are listed in table 1.

The molecule of CCIF₃ belongs to the same point group C₃v as the remaining are of symmetry species a₁. The vibrational fundamentals observed in the Raman [25, 39–41] and infrared [23, 34] are generally in good agreement. Based on the gas-phase infrared spectrum of Plyler and Benedict [23] and Raman spectra of Claassen [40], Taylor [41], and Holzer and Moser [25], we have selected the sharp and intense bands as the vibrational fundamentals. The values are listed in table 1.

Two independent measurements [42, 43] of the enthalpy for the reaction CCIF₃ (g) + 4K (s) ⇌ KCl (s) + 3KF (s) + C (s) respectively led to ΔH°(CCIF₃) equal to −162 ± 3 and −171 ± 1 kcal·mol⁻¹, using ΔH°(KF, s) = −134.5 kcal·mol⁻¹ and ΔH°(KCl, s) = −104.2 kcal·mol⁻¹ [44]. The carbon produced in the reaction was found by x-ray diffraction to be in amorphous form and an assumed enthalpy decrease of 2.5 kcal·mol⁻¹ for the transition to graphite was made [43]. The value

5. Chlorotrifluoromethane (F 13)

The infrared [34], microwave [35], and electron diffraction [36–38] techniques have been applied to the investigation of the molecular structure of CCIF₃. The discrepancies among the electron diffraction measurements are within the experimental uncertainties. Since all the rotational constants have not been determined experimentally, the most reliable structural parameters, obtained by Bartell and Brockway [38], were used to calculate the principal moments of inertia that are given in table 1.

Table 4 summarizes the calculated thermodynamic properties. The observed heat capacities [30] will be compared in section 8.

Table 4. Ideal gas thermodynamic functions of dichlorotrifluoromethane (F 21)

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of $-331 \pm 1$ kcal for the heat of reaction was obtained [45] when potassium was replaced by sodium. This value led to $\Delta H^\circ (\text{CCIF}_3) = -171.8 \pm 0.9$ kcal $\cdot$ mol$^{-1}$, using $\Delta H^\circ (\text{C}, \text{amorphous}) = 3.95$ kcal $\cdot$ mol$^{-1}$ and $\Delta H^\circ (\text{NaCl}, \text{s}) = -98.48$ kcal $\cdot$ mol$^{-1}$ [45], and $\Delta H^\circ (\text{NaF}, \text{s}) = -136.17 \pm 0.3$ kcal $\cdot$ mol$^{-1}$ [46]. Side reactions were noticed in all cases, although the effect on $\Delta H^\circ$ was claimed to be small. By measuring the enthalpy change in the explosion of $\text{CCIF}_3$ with a $\text{CO} + \text{O}_2 + \text{H}_2$ mixture, $\Delta H^\circ (\text{CCIF}_3) = -166.2 \pm 2.2$ kcal $\cdot$ mol$^{-1}$ was obtained [47]. All the aforementioned studies utilized the old value of $\Delta H^\circ (\text{HF}, \text{aq})$ [44] which was later found [48] to be in error.

From the equilibrium constant measurements for the following two reactions

$$\text{CHF}_3 + \text{I}_2 \rightleftharpoons \text{CF}_3\text{I} + \text{HI};$$
$$\Delta H^\circ (298.15) = 17.10 \pm 0.17 \text{ kcal},$$
$$\text{CCIF}_3 + \text{I}_2 \rightleftharpoons \text{CF}_3\text{I} + \text{ICl};$$
$$\Delta H^\circ (298.15) = 17.27 \pm 0.13 \text{ kcal.}$$

Lord, Goy, and Pritchard [49] derived $\Delta H^\circ$ by the third-law method and obtained

$$\Delta H^\circ (\text{CCIF}_3) = \Delta H^\circ (\text{CF}_3\text{I}) - 2.37 \pm 0.30 \text{ kcal} \cdot \text{mol}^{-1}.$$  \hfill (1)

They then derived $\Delta H^\circ (\text{CCIF}_3) = -167.5$ kcal $\cdot$ mol$^{-1}$ by use of $\Delta H^\circ (\text{CF}_3\text{I}) = -165.1$ kcal $\cdot$ mol$^{-1}$ which was considered to be slightly too small and was later revised [28, 48]. Coomber and Whittle [50] also measured the equilibrium constants for the forward and reverse reactions in the gaseous phase and obtained the mean values of $\Delta H^\circ$ by the third-law method.

$$\text{CHF}_3 + \text{Br}_2 \rightleftharpoons \text{CBF}_3 + \text{HBr};$$
$$\Delta H^\circ (298.15) = -4.95 \pm 0.25 \text{ kcal},$$
$$\text{CBrF}_3 + \text{Cl}_2 \rightleftharpoons \text{CCIF}_3 + \text{BrCl};$$
$$\Delta H^\circ (298.15) = -10.69 \pm 0.15 \text{ kcal},$$
$$\text{CCIF}_3 + \text{Br}_2 \rightleftharpoons \text{CBrF}_3 + \text{BrCl};$$
$$\Delta H^\circ (298.15) = 10.49 \pm 0.20 \text{ kcal}.$$

Adopting $\Delta H^\circ (\text{Br}_2) = 7.39$ kcal $\cdot$ mol$^{-1}$, $\Delta H^\circ (\text{BrCl}) = 3.48$ kcal $\cdot$ mol$^{-1}$ and $\Delta H^\circ (\text{HBr}) = -8.70$ kcal $\cdot$ mol$^{-1}$ [51], Coomber and Whittle found

$$\Delta H^\circ (\text{CCIF}_3) = \Delta H^\circ (\text{CHF}_3) - 2.8 \pm 0.3 \text{ kcal} \cdot \text{mol}^{-1}.$$  \hfill (2)

This is in good agreement with eq (1) and the average value of $-2.6 \pm 0.3$ kcal $\cdot$ mol$^{-1}$ has been chosen in this work. By use of $\Delta H^\circ (\text{CHF}_3) = -166.6 \pm 0.8$ kcal $\cdot$ mol$^{-1}$ [28] we finally obtained $\Delta H^\circ (\text{CCIF}_3) = -169.2 \text{ kcal} \cdot \text{mol}^{-1}$ which was adopted. For comparison, values of $-173.0, -169.8$, and $-169.3$ kcal $\cdot$ mol$^{-1}$ were calculated respectively from the simple correlation [16], the triatomic additivity method [7], and the bond energy-group contribution scheme [18].

In table 5, the calculated thermodynamic properties are given. The comparison with the single datum of heat capacity [52] will be illustrated in section 8.

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6. Dichlorodifluoromethane (F 12)

The discrepancies in some of the structural parameters of the CCl₂F₂ molecule between the two electron diffraction studies [8, 53] exceed experimental uncertainties. In view of the internal consistency among the structural parameters of a series of mixed fluorochloromethanes observed by Brockway [8], his values for CCl₂F₂ have been adopted to calculate the principal moments of inertia. The values are given in table 1.

The CCl₂F₂ molecule belongs to the point group C₂ᵥ and has nine vibrational modes, i.e., 4a₁, a₂, 2b₁, and 2b₂. Among the Raman [25, 33, 40] and infrared [23, 34] spectra, the vibrational fundamentals were nearly consistently assigned except for one fundamental representing the CF₂ rocking mode. A band was observed at 877 cm⁻¹ in the liquid-phase Raman [33] and at 885 cm⁻¹ in the infrared [34]. However, no band in the vicinity of these two wavenumbers appeared in the infrared absorption curves. The absence of a band at 446 cm⁻¹ in the Raman work [25]. Plyler and Benedict [23] observed the slight minima at 446 and 473 cm⁻¹ in their infrared absorption curves. This choice, which was also preferred by Petersen and Pitzer [57], was found to be reasonable when referred to the Shimanouchi's selected values [55] for the CF₂ rocking mode in other molecules. Therefore, we have selected 446 cm⁻¹ and the other eight fundamentals from the sharp and intense bands in the infrared of Plyler and Benedict [23] and in the Raman of Claassen [40] and of Holzer and Moser [25]. The selected values are tabulated in table 1.

From the heat of reaction for CCl₂F₂ + 4K = 2KF + 2KCl + C, ΔHf°(CCl₂F₂) was determined to be -111±2 kcal mol⁻¹ [42] or -112±2 kcal mol⁻¹ [43]. When potassium in the reaction was replaced by sodium, ΔHf°(298.15) = -354.1±1.3 kcal led to [45] ΔHf°(CCl₂F₂) = -112.1±2 kcal mol⁻¹. The auxiliary data used therein are those indicated previously for CClF₂. A least squares fit to several heats of reaction with JANAF auxiliary values [28, 56] gave ΔHf°(CCl₂F₂) = -117.5±2 kcal mol⁻¹ which is larger than the Cox and Pilcher [29] selected value -114.8 kcal mol⁻¹. Petersen and Pitzer [57] obtained log K = -3.0 for the gas-phase reaction 2CCIF₂ + CCl₂ = 3CCl₂F₂ at 400 K. We derived ΔHf°(298.15) = 7.59 kcal from the third-law calculations. With the selected values ΔHf°(CCl₂F₂) = -169.2 kcal mol⁻¹ of this work and ΔHf°(CCl₂) = -22.90 kcal mol⁻¹ [1], ΔHf°(CCl₂F₂) = -117.9 kcal mol⁻¹ was obtained and adopted as given in table 1. Petersen and Pitzer [57] indicated that it is unlikely that log K is in error by more than one unit which is equivalent to ±0.6 kcal mol⁻¹ for the derived ΔHf°(CCl₂F₂). The values of ΔHf°(CCl₂F₂) calculated respectively from the triatomic additivity method [7], the simple correlation [16], and the bond energy-group contribution scheme [18] are -118.0, -123.0, and -115.9 kcal mol⁻¹.

Table 6 shows the calculated thermodynamic properties. Comparisons with the measured heat capacities [38–60] will be given in section 8.

### Table 6. Ideal gas thermodynamic functions of dichlorodifluoromethane (F 12)

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7. Trichlorofluoromethane (F 11)

The agreement in the structural parameters of CCl₃F between the two electron diffraction investigations [8, 61] is within estimated uncertainties. From the most intense lines of the transitions J=1→2 in hyperfine microwave spectra, Long, Williams, and Weatherly [62] derived the rotational constants, A=B=2465.39 MHz for CCl₂FP and A=2463.22 MHz and B=2398.50 MHz for CCl₂CPF. These result in the principal moments of inertia, Iₓ=340.398×10⁻⁴⁰ g·cm² for CCl₂FP and Iₓ=340.698×10⁻⁴⁰ and Iₓ=349.892×10⁻⁴⁰ g·cm² for CCl₂CPF. We have calculated Iₓ=Iₓ=344.698×10⁻⁴⁰ g·cm² for the naturally abundant species CCl₃F with Cl=35.453. The largest principal moment with respect to the C—F axis, Iₓ=496.68×10⁻⁴⁰ g·cm², was calculated from the structural parameters of Brockway [8].

The molecule of CCl₃F has the point group C₃v, with three singlet a₁ and three doublet e symmetry species. Infrared [23, 34, 63, 64] and Raman [25, 65] techniques have been employed to investigate its vibrational modes. The vibrational degeneracies given in the infrared work [34] appeared to be in error. As given in table 1, the five directly observed bands in the gas-phase infrared spectra very intensely at 1085 cm⁻¹ in the gas-phase infrared spectra [23, 63].

From the heats of reaction CCl₃F (g)+4K (s)⇌KF (s)+3KCl (s)+C (amor.), ΔH_f°C(ClClF) was determined to be either −70±4 kcal·mol⁻¹ [43] or −62±1 kcal·mol⁻¹ [42]. By exploding a mixture of H₂, O₂, and CO with CCl₃F, ΔH_f°C(ClClF)=-66±2.1 kcal·mol⁻¹ was found [47]. The compiled value of −64.0 kcal·mol⁻¹ [29] is too small when compared with −69.0±1.5 kcal·mol⁻¹ derived [28, 56] from a least squares fit to several heats of reaction. The value log K=−4.5 of Petersen and Fitzer [57] for the gas-phase reaction CClFₓ+(2CClₓ⇌3CClF at 400 K led to ΔH_r°(298.15)=10.59 kcal by the third-law calculations. With the selected values ΔH_f°(CClFₓ)=−169.2 kcal·mol⁻¹ of this work and ΔH_f°(CClₓ)=−22.90 kcal·mol⁻¹ [1], we have obtained ΔH_f°(CClₓ)=−68.1 kcal·mol⁻¹. The auxiliary data, ΔH_f° for CClₓ, were determined fairly accurately by direct experimental measurements. As for CClₓFₓ, the possible error in log K is less than one unit [57] and consequently introduces an uncertainty of ±0.6 kcal·mol⁻¹ in ΔH_f°(CClₓ). For comparison, ΔH_f°(CClₓ) was calculated to be −68.8, −72.9, and −69.0 kcal·mol⁻¹ repectively from the triatomic additivity method [7], the simple correlation [16], and the bond energy-group contribution scheme [18].

The calculated thermodynamic properties are given in table 7. Comparisons with the observed heat capacities [30] and the third-law entropy [66] will be made in section 8.

Table 7. Ideal gas thermodynamic functions of trichlorofluoromethane (F 11)

<table>
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<tr>
<th>T</th>
<th>G</th>
<th>S</th>
<th>(G°−H°)/T</th>
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8. Comparisons

Benning, McHarness, Markwood, and Smith [30] employed a non-adiabatic calorimeter to measure the vapor heat capacities of CHClF₂, CHCl₂F, and CCl₄F at 1 atm (where 1 atm = 760 mm Hg = 101325 Pa). They pointed out that the measured heat capacities are quite good at the high temperature end, but are too low by as much as 4 to 8 percent in the low temperature range, due probably to heat losses. Table 8 shows that our calculated $C_p$ values are in good agreement at high temperature and are about 3 percent higher as compared with those of Benning et al.

Nielsen and White [31] derived $S$ = 63.781 cal·K⁻¹·mol⁻¹ for CHClF₂ vapor at 232.50 K and 1 atm from heat capacity data. This was converted into $S$ = 63.93 ± 0.28 cal·K⁻¹·mol⁻¹ which is in agreement with our calculated value 64.00 cal·K⁻¹·mol⁻¹ within experimental uncertainty.

Vanderkooi and de Vries [52] utilized the wire-ribbon method in calorimetry to obtain $C_p$ = 14.10 ± 0.38 cal·K⁻¹·mol⁻¹ for gaseous CHClF₂ at 300 K and in the micron of mercury pressure range. We can safely assume that $C_p$ = $C_e$ + $R$ = 16.09 ± 0.38 cal·K⁻¹·mol⁻¹ which is in good agreement with our calculated value, 16.03 cal·K⁻¹·mol⁻¹.

For CCl₄F gas, Osborne, Garner, Doescher, and Yost [66] obtained from adiabatic calorimetric measurements the third-law entropy, $S$ = 73.907 ± 0.1 cal·K⁻¹·mol⁻¹ at 290.40 K and 602.5 mm Hg that eventually resulted in $S$ = 73.58 ± 0.1 cal·K⁻¹·mol⁻¹ at 290.40 K and 1 atm with the aid of the Berthelot equation. When the TRC h-table [67] of the second virial coefficient was used for gas imperfection correction, $S$ was found to be 73.55 cal·K⁻¹·mol⁻¹. Our calculated value of 73.57 cal·K⁻¹·mol⁻¹ is in excellent agreement.

By use of a flow calorimeter Buffington and Gilkey [58] measured the real gas $C_p$ for CCl₄F₂ at 1 atm and in the temperature range of 273.15–323.05 K. These $C_p$ values were converted into the ideal gas $C_p$ (g) in the same temperature range. Here, again, $C_p$ = $C_p$ (g) + $R$, and as shown in table 8, our calculated $C_p$ favor Buffington and Gilkey values at high temperature and Eucken and Bertram at low temperature. The discrepancies, however, are within the experimental uncertainty of ±0.2 cal·K⁻¹·mol⁻¹. Mashi [60] measured $C_p$ of a 99.8 mol percent sample with a flow calorimeter and obtained $C_p$ by extrapolation to zero pressure. Table 8 illustrates a satisfactory agreement in comparisons with our calculated $C_p$.

### Table 8. Comparisons of calculated values of $C_p$ and $S^\circ$ with experimental data

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<th>T/K</th>
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*a The authors indicated that the measured heat capacities are probably reliable at high temperature but are too low due to heat losses by as much as 4 to 8 percent at low temperature.

*Estimated uncertainty ±0.2 cal·K⁻¹·mol⁻¹ may be subject to larger error.

*Uncertainty ±0.28 cal·K⁻¹·mol⁻¹.

*Uncertainty ±0.38 cal·K⁻¹·mol⁻¹.

*Uncertainty ±0.1 cal·K⁻¹·mol⁻¹.

*Uncertainty ±0.02 cal·K⁻¹·mol⁻¹ excluding errors due to extrapolation to zero pressure.
The recommended values of $C_p$, $S^0$, and $\Delta H_f^\circ$ of this work are compared with those of other major compilations [17, 28, 68, 69] at 298.15 K and 700 K in tables 9–1 and 9–2, respectively. Apparently, the values of $\Delta H_f^\circ$ are scattered. However, the values of $C_p$ and $S^0$ are in excellent agreement among the various sources, except for $S^0$ of CClF$_3$ by Landolt-Bornstein [68] and $C_p$ and $S^0$ of CHClF by JANAF [28].

9. Acknowledgments

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for their valuable suggestions. The preparation of the manuscript by the Editorial Office of the Thermodynamics Research Center at the Texas A&M University is acknowledged.

10. References