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Cite as: Journal of Physical and Chemical Reference Data **5**, 571 (1976); <https://doi.org/10.1063/1.555539>  
Published Online: 15 October 2009

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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 chloro- and fluoro-substituted methanes and ethanes [1-3]<sup>1</sup>, 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  $\text{CHClF}_2$  and  $b_2$  band in  $\text{CCl}_2\text{F}_2$ , 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  $\text{C} = 12.011$ ,  $\text{H} = 1.0079$ ,  $\text{F} = 18.99840$ , and  $\text{Cl} = 35.453$  were used. Throughout this paper,  $1\text{\AA} = 10^{-8}\text{ cm} = 10^{-10}\text{ m}$ ,  $1\text{ kcal} = 1000\text{ cal} = 4184\text{ J}$ , and  $1\text{ cm}^{-1}$  is equivalent to  $11.96267\text{ J}\cdot\text{mol}^{-1}$ . The conversion factor  $505379\text{ MHz}\cdot\text{amu}\cdot\text{\AA}^2$  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  $\Delta H_f^\circ$  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  $\Delta H_f^\circ$  values for  $\text{CH}_2\text{ClF}$

and  $\text{CHCl}_2\text{F}$ . 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  $\Delta H_f^\circ$ ,  $\Delta G_f^\circ$ , and  $\log K_f$  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)<sup>2</sup>

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  $\text{CH}_2\text{Cl}^{35}\text{F}$  and  $\text{CH}_2\text{Cl}^{37}\text{F}$  and derived structural parameters on the basis of an assumed  $\text{H}-\text{C}-\text{H}$  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  $\text{CH}_2\text{ClF}$  belongs to the point group  $\text{C}_s$  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  $\text{CH}_2\text{ClF}$  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  $\text{CH}_2\text{ClF}$ .

<sup>1</sup>Figures in brackets indicate the literature references.

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<sup>2</sup>A 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 Hudlický, M., *Organic Fluorine Chemistry*, Plenum Press, New York-London (1971), p. 19.

A simple correlation scheme [16] led to  $\Delta H_f^\circ(\text{CH}_2\text{ClF}) = -62.7 \text{ kcal}\cdot\text{mol}^{-1}$  when the selected values of  $\Delta H_f^\circ$  for  $\text{CF}_4$  and  $\text{CCl}_4$  [1] and for  $\text{CH}_4$  [17] were used. To the contrary, a more recent bond energy-group contribution scheme [18] gave  $-64.0 \text{ kcal}\cdot\text{mol}^{-1}$ . The triatomic additivity method of Somayajulu and Zwolinski [7] has been very satisfactorily applied to a large number of substituted alkanes. This method yields a value for  $\Delta H_f^\circ(\text{CH}_2\text{ClF}) = -63.2 \text{ kcal}\cdot\text{mol}^{-1}$  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  $\text{CHClF}_2$  was investigated by both electron diffraction [8] and microwave [19, 20] techniques. The rotational constants for the isotopic species,  $\text{CHCl}^{35}\text{F}_2$  and  $\text{CHCl}^{37}\text{F}_2$ , 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  $\text{CHClF}_2$  molecule has the same point group and symmetry species of vibrational modes as for  $\text{CH}_2\text{ClF}$ . The Raman spectrum for the liquid  $\text{CHClF}_2$  was repeatedly recorded [12, 21, 22]. The vibrational fundamentals were revised due to the possible existence of  $\text{CHF}_3$  [21] and  $\text{CCl}_2\text{F}_2$  [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  $365 \text{ cm}^{-1}$  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  $400 \text{ cm}^{-1}$  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  $1116 \text{ cm}^{-1}$  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  $\text{CHClF}_2$  in the endothermic reaction  $2\text{CHClF}_2 \rightleftharpoons \text{C}_2\text{F}_4 + 2\text{HCl}$  in a spherical bomb. To eliminate the effects of possible side reactions, they extrapolated the values of the equilibrium constant  $K_p$  and obtained  $K_p = 0.087 \text{ atm}$  at  $873.15 \text{ K}$ . They then derived  $\Delta H_f^\circ(\text{CHF}_2\text{Cl}) = -112.3 \text{ kcal}\cdot\text{mol}^{-1}$  from this  $K_p$  value with the aid of tabulated thermodynamic functions. When the JANAF [28] thermodynamic values were used,  $\Delta H_f^\circ(\text{CHClF}_2) = -115.1 \text{ kcal}\cdot\text{mol}^{-1}$  was obtained. However, Cox and Pilcher [29] recommended  $-115.6 \text{ kcal}\cdot\text{mol}^{-1}$  which is exactly the same as the value predicted by Somayajulu

TABLE 1. The selected molecular and chemical constants of the six chlorofluoromethanes<sup>a</sup>

Compound	$\text{CH}_2\text{ClF}$	$\text{CHClF}_2$	$\text{CHCl}_2\text{F}$	$\text{CClF}_3$	$\text{CCl}_2\text{F}_2$	$\text{CCl}_3\text{F}$
Molecular weight	68.4782	86.4687	102.9233	104.4592	120.9138	137.3684
Symmetry number	1	1	1	3	2	3
Principal moments of inertia <sup>b</sup>						
$I_a, 10^{-40} \text{ g}\cdot\text{cm}^2$	20.080	82.004	120.267	146.52 <sup>c</sup>	203.29 <sup>d</sup>	344.698
$I_b, 10^{-40} \text{ g}\cdot\text{cm}^2$	147.644	173.858	255.350	253.99 <sup>c</sup>	324.64 <sup>d</sup>	344.698
$I_c, 10^{-40} \text{ g}\cdot\text{cm}^2$	162.382	240.489	358.880	253.99 <sup>c</sup>	373.85 <sup>d</sup>	496.68 <sup>e</sup>
Vibrational fundamentals, $\text{cm}^{-1}$	2993 ( <i>a'</i> ) 1468 ( <i>a'</i> ) 1351 ( <i>a'</i> ) 1236 ( <i>a'</i> ) 760 ( <i>a'</i> ) 385 ( <i>a'</i> ) 3048 ( <i>a''</i> ) 1068 ( <i>a''</i> ) 1001 ( <i>a''</i> )	3026 ( <i>a'</i> ) 1312 ( <i>a'</i> ) 1178 ( <i>a'</i> ) 806 ( <i>a'</i> ) 598 ( <i>a'</i> ) 419 ( <i>a'</i> ) 1343 ( <i>a''</i> ) 1115 ( <i>a''</i> ) 369 ( <i>a''</i> )	3026 ( <i>a'</i> ) 1316 ( <i>a'</i> ) 1083 ( <i>a'</i> ) 742 ( <i>a'</i> ) 456 ( <i>a'</i> ) 274 ( <i>a'</i> ) 1240 ( <i>a''</i> ) 802 ( <i>a''</i> ) 365 ( <i>a''</i> )	1212 ( <i>e</i> ) 563 ( <i>e</i> ) 350 ( <i>e</i> ) 1105 ( <i>a</i> <sub>1</sub> ) 782 ( <i>a</i> <sub>1</sub> ) 476 ( <i>a</i> <sub>1</sub> )	1101 ( <i>a</i> <sub>1</sub> ) 667 ( <i>a</i> <sub>1</sub> ) 458 ( <i>a</i> <sub>1</sub> ) 261 ( <i>a</i> <sub>1</sub> ) 322 ( <i>a</i> <sub>2</sub> ) 922 ( <i>b</i> <sub>1</sub> ) 433 ( <i>b</i> <sub>1</sub> ) 1159 ( <i>b</i> <sub>2</sub> ) 446 ( <i>b</i> <sub>2</sub> )	847 ( <i>e</i> ) 394 ( <i>e</i> ) 241 ( <i>e</i> ) 1085 ( <i>a</i> <sub>1</sub> ) 535 ( <i>a</i> <sub>1</sub> ) 350 ( <i>a</i> <sub>1</sub> )
Standard enthalpy of formation $\Delta H_f^\circ$ (g, 298.15), $\text{kcal}\cdot\text{mol}^{-1}$	$-63.2 \pm 2.0^f$	$-115.6 \pm 1.4$	$-68.1 \pm 2.1^f$	$-169.2 \pm 0.9$	$-117.9 \pm 0.6$	$-68.1 \pm 0.4$

<sup>a</sup>Symbols in parentheses after wavenumbers denote the vibrational symmetry species.

<sup>b</sup>Obtained from rotational constants unless otherwise indicated.

<sup>c</sup>Calculated from  $r(\text{C}-\text{F}) = 1.328 \text{ \AA}$ ,  $r(\text{C}-\text{Cl}) = 1.751 \text{ \AA}$ ,  $r(\text{F}\cdots\text{F}) = 2.158 \text{ \AA}$ , and  $r(\text{F}\cdots\text{Cl}) = 2.539 \text{ \AA}$  [38].

<sup>d</sup>Calculated from  $r(\text{C}-\text{F}) = 1.35 \text{ \AA}$ ,  $r(\text{C}-\text{Cl}) = 1.74 \text{ \AA}$ ,  $r(\text{F}\cdots\text{F}) = 2.21 \text{ \AA}$ ,  $r(\text{F}\cdots\text{Cl}) = 2.52 \text{ \AA}$ , and  $r(\text{Cl}\cdots\text{Cl}) = 2.90 \text{ \AA}$  [8].

<sup>e</sup>Calculated from  $r(\text{C}-\text{F}) = 1.40 \text{ \AA}$ ,  $r(\text{C}-\text{Cl}) = 1.76 \text{ \AA}$ ,  $r(\text{F}\cdots\text{Cl}) = 2.56 \text{ \AA}$ , and  $r(\text{Cl}\cdots\text{Cl}) = 2.91 \text{ \AA}$  [8].

<sup>f</sup>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  $\Delta H_f^\circ(\text{CHClF}_2) = -115.6$  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.

#### 4. Dichlorofluoromethane (F 21)

The structural parameters of the gaseous  $\text{CHCl}_2\text{F}$  were first determined by the electron diffraction method [8]. McLay [32] measured the frequencies for the low rotational transitions in the microwave spectra of  $\text{C}^{12}\text{HCl}_2^{35}\text{F}$  and  $\text{C}^{12}\text{HCl}_2^{35}\text{Cl}^{37}\text{F}$  and obtained the rotational constants. The allowance for the isotopic effect was made and the principal moments of inertia

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

$T$	$C_p^\circ$	$S^\circ$	$-(G^\circ - H_0^\circ)/T$	$H^\circ - H_0^\circ$	$\Delta H_f^\circ$	$\Delta G_f^\circ$	$\log K_f$
K	$\text{cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$			$\text{kcal} \cdot \text{mol}^{-1}$			
0	0	0	0	0	-61.46	-61.46	$\infty$
50	7.95	47.48	39.53	0.398	-61.92	-61.34	268.12
100	8.20	53.04	45.05	0.799	-62.13	-60.68	132.62
150	8.75	56.47	48.32	1.222	-62.38	-59.91	87.28
200	9.46	59.08	50.69	1.677	-62.65	-59.04	64.52
273.15	10.75	62.21	53.37	2.415	-63.06	-57.65	46.13
298.15	11.25	63.17	54.15	2.689	-63.20	-57.11	41.87
300	11.28	63.24	54.21	2.710	-63.21	-57.12	41.61
400	13.29	66.76	56.92	3.939	-63.72	-55.01	30.05
500	15.08	69.93	59.21	5.360	-64.15	-52.78	23.07
600	16.57	72.81	61.24	6.945	-64.49	-50.47	18.38
700	17.79	75.46	63.08	8.665	-64.76	-48.11	15.02
800	18.81	77.91	64.79	10.496	-64.97	-45.71	12.49
900	19.66	80.17	66.37	12.421	-65.13	-43.30	10.51
1000	20.39	82.28	67.86	14.424	-65.24	-40.86	8.93
1100	21.01	84.25	69.26	16.495	-65.31	-38.43	7.64
1200	21.54	86.11	70.59	18.623	-65.36	-35.98	6.55
1300	22.00	87.85	71.85	20.800	-65.38	-33.53	5.64
1400	22.39	89.49	73.05	23.020	-65.39	-31.06	4.85
1500	22.73	91.05	74.20	25.276	-65.38	-28.62	4.17

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

$T$	$C_p^\circ$	$S^\circ$	$-(G^\circ - H_0^\circ)/T$	$H^\circ - H_0^\circ$	$\Delta H_f^\circ$	$\Delta G_f^\circ$	$\log K_f$
K	$\text{cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$			$\text{kcal} \cdot \text{mol}^{-1}$			
0	0	0	0	0	-114.09	-114.09	$\infty$
50	7.96	50.13	42.18	0.398	-114.46	-113.64	496.72
100	8.43	55.74	47.70	0.803	-114.72	-112.72	246.35
150	9.59	59.36	51.01	1.253	-114.97	-111.67	162.70
200	10.88	62.30	53.48	1.764	-115.20	-110.54	120.79
273.15	12.74	65.97	56.34	2.629	-115.51	-108.78	87.03
298.15	13.35	67.11	57.20	2.955	-115.60	-108.08	79.22
300	13.39	67.19	57.26	2.979	-115.61	-108.11	78.76
400	15.63	71.36	60.28	4.434	-115.93	-105.56	57.68
500	17.45	75.05	62.87	6.092	-116.17	-102.94	45.00
600	18.87	78.37	65.18	7.911	-116.35	-100.28	36.53
700	19.97	81.36	67.28	9.856	-116.47	-97.59	30.47
800	20.84	84.09	69.21	11.898	-116.55	-94.89	25.92
900	21.54	86.58	71.01	14.018	-116.59	-92.17	22.38
1000	22.10	88.88	72.68	16.201	-116.61	-89.46	19.55
1100	22.57	91.01	74.25	18.436	-116.60	-86.75	17.24
1200	22.96	92.99	75.73	20.713	-116.58	-84.03	15.30
1300	23.29	94.84	77.13	23.026	-116.55	-81.32	13.67
1400	23.57	96.58	78.46	25.369	-116.51	-78.60	12.27
1500	23.80	98.22	79.72	27.738	-116.46	-75.90	11.06

we obtained for the naturally abundant  $\text{CHCl}_2\text{F}$  are given in table 1.

The molecule of  $\text{CHCl}_2\text{F}$  belongs to the same point group as do  $\text{CH}_2\text{ClF}$  and  $\text{CHClF}_2$ . The vibrational spectra of  $\text{CHCl}_2\text{F}$  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  $1240\text{ cm}^{-1}$  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  $\text{CHCl}_2\text{F}$  at 298.15 K has not been experimentally determined. It was calculated either as  $-71.7\text{ kcal}\cdot\text{mol}^{-1}$  from the simple correlation [16] or as  $-66.7\text{ kcal}\cdot\text{mol}^{-1}$  from the bond energy-group contribution scheme [18]. The value of  $-67.7\text{ kcal}\cdot\text{mol}^{-1}$  derived [28] from the change in heat of atomization by successive replacement of F by Cl in the  $\text{CHF}_3$  to  $\text{CHCl}_3$  series is, of course, a rough approximation. In view of the general validity of the triatomic additivity method of Somayajulu and Zwolinski [7], we calculated  $\Delta H_f^\circ(\text{CHCl}_2\text{F}) = -68.1\text{ kcal}\cdot\text{mol}^{-1}$ . This has been adopted and is given in table 1.

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

## 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  $\text{CClF}_3$ . 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.

The molecule of  $\text{CClF}_3$  belongs to the point group  $\text{C}_{3v}$ . Three of its six vibrational modes are of symmetry species  $e$  while the remaining are of symmetry species  $a_1$ . 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.

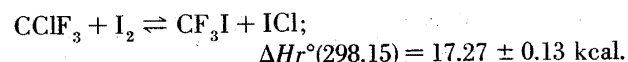
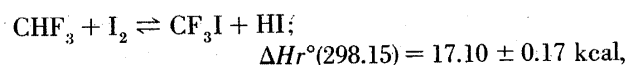
Two independent measurements [42, 43] of the enthalpy for the reaction  $\text{CClF}_3(\text{g}) + 4\text{K}(\text{s}) \rightleftharpoons \text{KCl}(\text{s}) + 3\text{KF}(\text{s}) + \text{C}(\text{s})$  respectively led to  $\Delta H_f^\circ(\text{CClF}_3)$  equal to  $-162 \pm 3$  and  $-171 \pm 1\text{ kcal}\cdot\text{mol}^{-1}$ , using  $\Delta H_f^\circ(\text{KF}, \text{s}) = -134.5\text{ kcal}\cdot\text{mol}^{-1}$  and  $\Delta H_f^\circ(\text{KCl}, \text{s}) = -104.2\text{ kcal}\cdot\text{mol}^{-1}$  [44]. The carbon produced in the reaction was found by x-ray diffraction to be in amorphous form and an assumed enthalpy decrease of  $2.5\text{ kcal}\cdot\text{mol}^{-1}$  for the transition to graphite was made [43]. The value

TABLE 4. Ideal gas thermodynamic functions of dichlorofluoromethane (F 21)

$T$	$C_p^\circ$	$S^\circ$	$-(G^\circ - H_0^\circ)/T$	$H^\circ - H_0^\circ$	$\Delta H_f^\circ$	$\Delta G_f^\circ$	$\log K_f$
K	$\text{cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$			$\text{kcal}\cdot\text{mol}^{-1}$			
0	0	0	0	0	-66.76	-66.76	$\infty$
50	8.00	51.82	43.86	0.398	-67.14	-66.29	289.76
100	8.99	57.60	49.42	0.818	-67.38	-65.35	142.82
150	10.52	61.53	52.83	1.305	-67.60	-64.29	93.67
200	11.99	64.76	55.42	1.868	-67.79	-63.15	69.01
273.15	13.96	68.79	58.48	2.819	-68.03	-61.42	49.14
298.15	14.58	70.04	59.39	3.175	-68.10	-60.77	44.55
300	14.62	70.13	59.46	3.202	-68.11	-60.77	44.27
400	16.78	74.65	62.71	4.777	-68.34	-58.28	31.84
500	18.44	78.58	65.50	6.542	-68.50	-55.75	24.37
600	19.70	82.06	67.97	8.452	-68.60	-53.19	19.37
700	20.66	85.17	70.21	10.472	-68.66	-50.61	15.80
800	21.41	87.98	72.26	12.577	-68.69	-48.03	13.12
900	22.01	90.54	74.15	14.749	-68.68	-45.45	11.04
1000	22.51	92.88	75.91	16.976	-68.66	-42.86	9.37
1100	22.92	95.05	77.55	19.248	-68.61	-40.30	8.01
1200	23.26	97.06	79.09	21.557	-68.56	-37.72	6.87
1300	23.55	98.93	80.55	23.897	-68.50	-35.15	5.91
1400	23.79	100.69	81.92	26.265	-68.43	-32.58	5.09
1500	24.00	102.33	83.23	28.655	-68.36	-30.02	4.38

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

From the equilibrium constant measurements for the following two reactions

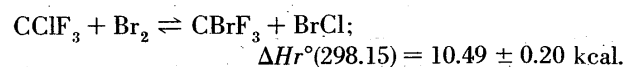
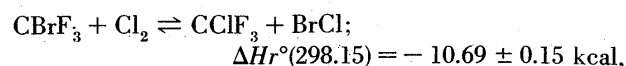
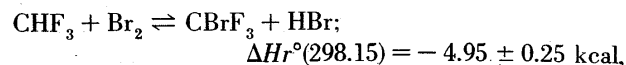


Lord, Goy, and Pritchard [49] derived  $\Delta H_r^\circ$  by the third-law method and obtained

$$\Delta H_f^\circ(\text{CClF}_3) = \Delta H_f^\circ(\text{CHF}_3) - 2.37 \pm 0.30 \text{ kcal} \cdot \text{mol}^{-1}. \quad (1)$$

They then derived  $\Delta H_f^\circ(\text{CClF}_3) = -167.5$  kcal  $\cdot$  mol $^{-1}$  by use of  $\Delta H_f^\circ(\text{CHF}_3) = -165.1$  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  $\Delta H_r^\circ$  by the third-law method.



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

$$\Delta H_f^\circ(\text{CClF}_3) = \Delta H_f^\circ(\text{CHF}_3) - 2.8 \pm 0.3 \text{ kcal} \cdot \text{mol}^{-1}. \quad (2)$$

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  $\Delta H_f^\circ(\text{CHF}_3) = -166.6 \pm 0.8$  kcal  $\cdot$  mol $^{-1}$  [28] we finally obtained  $\Delta H_f^\circ(\text{CClF}_3) = -169.2$  kcal  $\cdot$  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.

TABLE 5. Ideal gas thermodynamic functions of chlorotrifluoromethane ( $F_{13}$ )

$T$	$C_p^\circ$	$S^\circ$	$-(G^\circ - H_0^\circ)/T$	$H^\circ - H_0^\circ$	$\Delta H_f^\circ$	$\Delta G_f^\circ$	$\log K_f$
K	$\text{cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$			$\text{kcal} \cdot \text{mol}^{-1}$			
0	0	0	0	0	-167.98	-167.98	$\infty$
50	7.97	49.52	41.57	0.398	-168.28	-167.05	730.17
100	8.79	55.21	47.11	0.810	-168.57	-165.71	362.15
150	10.66	59.11	50.48	1.295	-168.82	-164.22	239.27
200	12.66	62.46	53.06	1.879	-169.00	-162.66	177.75
273.15	15.22	66.79	56.17	2.901	-169.16	-160.31	128.27
298.15	15.98	68.16	57.12	3.291	-169.20	-159.38	116.83
300	16.03	68.26	57.19	3.321	-169.20	-159.44	116.15
400	18.53	73.23	60.59	5.055	-169.29	-156.17	85.33
500	20.32	77.57	63.56	7.003	-169.29	-152.90	66.83
600	21.60	81.40	66.22	9.103	-169.25	-149.62	54.50
700	22.50	84.80	68.64	11.310	-169.18	-146.35	45.69
800	23.17	87.85	70.85	13.595	-169.10	-143.09	39.09
900	23.66	90.60	72.90	15.937	-169.01	-139.85	33.96
1000	24.03	93.12	74.80	18.322	-168.90	-136.61	29.86
1100	24.31	95.42	76.57	20.740	-168.80	-133.40	26.50
1200	24.54	97.55	78.23	23.183	-168.69	-130.18	23.71
1300	24.72	99.52	79.79	25.646	-168.59	-126.97	21.35
1400	24.86	101.36	81.27	28.125	-168.50	-123.76	19.32
1500	24.98	103.07	82.66	30.617	-168.40	-120.58	17.57

### 6. Dichlorodifluoromethane (F 12)

The discrepancies in some of the structural parameters of the  $\text{CCl}_2\text{F}_2$  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  $\text{CCl}_2\text{F}_2$  have been adopted to calculate the principal moments of inertia. The values are given in table 1.

The  $\text{CCl}_2\text{F}_2$  molecule belongs to the point group  $C_{2v}$  and has nine vibrational modes, i.e.,  $4a_1$ ,  $a_2$ ,  $2b_1$ , and  $2b_2$ . Among the Raman [25, 33, 40] and infrared [23, 34] spectra, the vibrational fundamentals were nearly consistently assigned except for one fundamental representing the  $\text{CF}_2$  rocking mode. A band was observed at  $877\text{ cm}^{-1}$  in the liquid-phase Raman [33] and at  $885\text{ cm}^{-1}$  in the infrared [34]. However, no band in the vicinity of these two wavenumbers appeared in the gas-phase Raman [25, 40] and infrared [23] spectra. The very weak band at  $640\text{ cm}^{-1}$  was observed only in the Raman work [25]. Plyler and Benedict [23] observed the slight minima at 446 and  $473\text{ cm}^{-1}$  in their infrared absorption curves. The absence of a band at around  $473\text{ cm}^{-1}$  in the Raman data seemed to favor the choice of  $446\text{ cm}^{-1}$  which would likely be overshadowed by the intense neighboring bands at 433 and  $458\text{ cm}^{-1}$ . This choice, which was also preferred by a normal coordinate analysis [54], was found to be reasonable when referred to the Shimanouchi's selected values [55] for the  $\text{CF}_2$  rocking mode in other molecules. Therefore, we have selected  $446\text{ cm}^{-1}$  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  $\text{CCl}_2\text{F}_2 + 4\text{K} \rightleftharpoons 2\text{KF} + 2\text{KCl} + \text{C}$ ,  $\Delta H_f^\circ(\text{CCl}_2\text{F}_2)$  was determined to be  $-111 \pm 2\text{ kcal} \cdot \text{mol}^{-1}$  [42] or  $-112 \pm 2\text{ kcal} \cdot \text{mol}^{-1}$  [43]. When potassium in the reaction was replaced by sodium,  $\Delta H_r^\circ(298.15) = -354.1 \pm 1.3\text{ kcal}$  led to [45]  $\Delta H_f^\circ(\text{CCl}_2\text{F}_2) = -112.1 \pm 1.2\text{ kcal} \cdot \text{mol}^{-1}$ . The auxiliary data used therein are those indicated previously for  $\text{CClF}_3$ . A least squares fit to several heats of reaction with JANAF auxiliary values [28, 56] gave  $\Delta H_f^\circ(\text{CCl}_2\text{F}_2) = -117.5 \pm 2\text{ kcal} \cdot \text{mol}^{-1}$  which is larger than the Cox and Pilcher [29] selected value  $-114.8\text{ kcal} \cdot \text{mol}^{-1}$ . Petersen and Pitzer [57] obtained  $\log K = -3.0$  for the gas-phase reaction  $2\text{CClF}_3 + \text{CCl}_4 \rightleftharpoons 3\text{CCl}_2\text{F}_2$  at 400 K. We derived  $\Delta H_r^\circ(298.15) = 7.59\text{ kcal}$  from the third-law calculations. With the selected values  $\Delta H_f^\circ(\text{CClF}_3) = -169.2\text{ kcal} \cdot \text{mol}^{-1}$  of this work and  $\Delta H_f^\circ(\text{CCl}_4) = -22.90\text{ kcal} \cdot \text{mol}^{-1}$  [1],  $\Delta H_f^\circ(\text{CCl}_2\text{F}_2) = -117.9\text{ kcal} \cdot \text{mol}^{-1}$  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  $\pm 0.6\text{ kcal} \cdot \text{mol}^{-1}$  for the derived  $\Delta H_f^\circ(\text{CCl}_2\text{F}_2)$ . The values of  $\Delta H_f^\circ(\text{CCl}_2\text{F}_2)$  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  $-115.9\text{ kcal} \cdot \text{mol}^{-1}$ .

Table 6 shows the calculated thermodynamic properties. Comparisons with the measured heat capacities [58-60] will be given in section 8.

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

$T$	$C_p^\circ$	$S^\circ$	$-(G^\circ - H_0^\circ)/T$	$H^\circ - H_0^\circ$	$\Delta H_f^\circ$	$\Delta G_f^\circ$	$\log K$
K	$\text{cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$			$\text{kcal} \cdot \text{mol}^{-1}$			
0	0	0	0	0	-116.90	-116.90	$\infty$
50	8.03	51.72	43.76	0.398	-117.20	-115.97	506.91
100	9.48	57.63	49.35	0.828	-117.48	-114.63	250.53
150	11.83	61.92	52.84	1.361	-117.68	-113.16	164.88
200	14.01	65.63	55.59	2.008	-117.80	-111.64	121.99
273.15	16.58	70.39	58.93	3.131	-117.89	-109.37	87.50
298.15	17.31	71.87	59.95	3.555	-117.90	-108.51	79.54
300	17.36	71.98	60.03	3.587	-117.90	-108.53	79.06
400	19.69	77.32	63.70	5.447	-117.89	-105.41	57.59
500	21.28	81.89	66.89	7.500	-117.81	-102.29	44.71
600	22.37	85.87	69.73	9.686	-117.70	-99.20	36.13
700	23.14	89.38	72.29	11.964	-117.58	-96.12	30.01
800	23.69	92.51	74.63	14.307	-117.45	-93.07	25.42
900	24.09	95.33	76.77	16.696	-117.31	-90.03	21.86
1000	24.39	97.88	78.76	19.121	-117.17	-87.00	19.01
1100	24.62	100.22	80.60	21.572	-117.03	-84.00	16.69
1200	24.80	102.37	82.33	24.044	-116.90	-80.99	14.75
1300	24.95	104.36	83.95	26.532	-116.77	-78.01	13.11
1400	25.06	106.21	85.47	29.032	-116.65	-75.02	11.71
1500	25.16	107.94	86.91	31.544	-116.53	-72.06	10.50

## 7. Trichlorofluoromethane (F 11)

The agreement in the structural parameters of  $\text{CCl}_3\text{F}$  between the two electron diffraction investigations [8, 61] is within estimated uncertainties. From the most intense lines of the transitions  $J=1 \rightarrow 2$  in hyperfine microwave spectra, Long, Williams, and Weatherly [62] derived the rotational constants,  $A=B=2465.39$  MHz for  $\text{CCl}_3^{35}\text{F}$  and  $A=2463.22$  MHz and  $B=2398.50$  MHz for  $\text{CCl}_3^{35}\text{Cl}^{37}\text{F}$ . These result in the principal moments of inertia,  $I_a=I_b=340.398 \times 10^{-40}$  g·cm<sup>2</sup> for  $\text{CCl}_3^{35}\text{F}$  and  $I_a=340.698 \times 10^{-40}$  and  $I_b=349.892 \times 10^{-40}$  g·cm<sup>2</sup> for  $\text{CCl}_3^{35}\text{Cl}^{37}\text{F}$ . We have calculated  $I_a=I_b=344.698 \times 10^{-40}$  g·cm<sup>2</sup> for the naturally abundant species  $\text{CCl}_3\text{F}$  with  $\text{Cl}=35.453$ . The largest principal moment with respect to the C—F axis,  $I_c=496.68 \times 10^{-40}$  g·cm<sup>2</sup>, was calculated from the structural parameters of Brockway [8].

The molecule of  $\text{CCl}_3\text{F}$  has the point group  $\text{C}_{3v}$  with three singlet  $a_1$  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 Raman of Hozer and Moser [25] have been selected together with a missing  $a_1$  mode which appeared very intensely at 1085 cm<sup>-1</sup> in the gas-phase infrared spectra [23, 63].

From the heats of reaction  $\text{CCl}_3\text{F}(\text{g}) + 4\text{K}(\text{s}) \rightleftharpoons \text{KF}(\text{s}) + 3\text{KCl}(\text{s}) + \text{C}(\text{amor.})$ ,  $\Delta H_f^\circ(\text{CCl}_3\text{F})$  was determined to be either  $-70 \pm 4$  kcal·mol<sup>-1</sup> [43] or  $-62 \pm 1$  kcal·mol<sup>-1</sup> [42]. By exploding a mixture of  $\text{H}_2$ ,  $\text{O}_2$ , and  $\text{CO}$  with  $\text{CCl}_3\text{F}$ ,  $\Delta H_f^\circ(\text{CCl}_3\text{F}) = -66.4 \pm 2.1$  kcal·mol<sup>-1</sup> was found [47]. The compiled value of  $-64.0$  kcal·mol<sup>-1</sup> [29] is too small when compared with  $-69.0 \pm 1.5$  kcal·mol<sup>-1</sup> derived [28, 56] from a least squares fit to several heats of reaction. The value  $\log K = -4.5$  of Petersen and Pitzer [57] for the gas-phase reaction  $\text{CClF}_3 + 2\text{CCl}_4 \rightleftharpoons 3\text{CCl}_3\text{F}$  at 400 K led to  $\Delta H_f^\circ(298.15) = 10.59$  kcal by the third-law calculations. With the selected values  $\Delta H_f^\circ(\text{CClF}_3) = -169.2$  kcal·mol<sup>-1</sup> of this work and  $\Delta H_f^\circ(\text{CCl}_4) = -22.90$  kcal·mol<sup>-1</sup> [1], we have obtained  $\Delta H_f^\circ(\text{CCl}_3\text{F}) = -68.1$  kcal·mol<sup>-1</sup>. The auxiliary data,  $\Delta H_f^\circ$  for  $\text{CClF}_3$  and  $\text{CCl}_4$ , were determined fairly accurately by direct experimental measurements. As for  $\text{CCl}_2\text{F}_2$ , the possible error in  $\log K$  is less than one unit [57] and consequently introduces an uncertainty of  $\pm 0.6$  kcal·mol<sup>-1</sup> in  $\Delta H_f^\circ(\text{CCl}_3\text{F})$ . For comparison,  $\Delta H_f^\circ(\text{CCl}_3\text{F})$  was calculated to be  $-68.8$ ,  $-72.9$ , and  $-69.0$  kcal·mol<sup>-1</sup> respectively 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)

$T$	$C_p$	$S^\circ$	$-(G^\circ - H_0^\circ)/T$	$H^\circ - H_0^\circ$	$\Delta H_f^\circ$	$\Delta G_f^\circ$	$\log K_f$
K	cal·K <sup>-1</sup> ·mol <sup>-1</sup>			kcal·mol <sup>-1</sup>			
0	0	0	0	0	-67.35	-67.35	$\infty$
50	8.15	52.18	44.21	0.399	-67.64	-66.33	289.92
100	10.37	58.41	49.87	0.854	-67.90	-64.91	141.81
150	13.13	63.15	53.53	1.443	-68.05	-63.38	92.34
200	15.42	67.25	56.46	2.159	-68.11	-61.81	67.54
273.15	17.96	72.46	60.06	3.385	-68.11	-59.50	47.61
298.15	18.66	74.06	61.17	3.843	-68.10	-58.68	43.01
300	18.71	74.17	61.25	3.878	-68.10	-58.66	42.73
400	20.84	79.87	65.21	5.863	-67.99	-55.53	30.34
500	22.22	84.68	68.64	8.021	-67.83	-52.43	22.92
600	23.13	88.82	71.67	10.291	-67.66	-49.36	17.98
700	23.75	92.43	74.38	12.637	-67.48	-46.33	14.46
800	24.19	95.63	76.84	15.035	-67.30	-43.32	11.83
900	24.50	98.50	79.09	17.470	-67.13	-40.33	9.79
1000	24.74	101.10	81.16	19.933	-66.95	-37.35	8.16
1100	24.92	103.46	83.08	22.416	-66.78	-34.41	6.84
1200	25.05	105.64	84.87	24.914	-66.62	-31.47	5.73
1300	25.17	107.65	86.55	27.426	-66.47	-28.55	4.80
1400	25.25	109.51	88.12	29.947	-66.32	-25.63	4.00
1500	25.33	111.26	89.61	32.476	-66.18	-22.73	3.31



### 8. Comparisons

Benning, McHarness, Markwood, and Smith [30] employed a non-adiabatic calorimeter to measure the vapor heat capacities of  $\text{CHClF}_2$ ,  $\text{CHCl}_2\text{F}$ , and  $\text{CCl}_3\text{F}$  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  $C_p^\circ$  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  $S=63.781 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  for  $\text{CHClF}_2$  vapor at 232.50 K and 1 atm from heat capacity data. This was converted into  $S^\circ=63.93 \pm 0.28 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  which is in agreement with our calculated value  $64.00 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  within experimental uncertainty.

Vanderkooi and de Vries [52] utilized the wire-ribbon method in calorimetry to obtain  $C_p=14.10 \pm 0.38 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  for gaseous  $\text{CClF}_3$  at 300 K and in the micron of mercury pressure range. We can safely assume that  $C_p^\circ=C_p+R=16.09 \pm 0.38 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  which is in good agreement with our calculated value,  $16.03 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ .

For  $\text{CCl}_3\text{F}$  gas, Osborne, Garner, Doescher, and Yost [66] obtained from adiabatic calorimetric measurements the third-law entropy,  $S=73.907 \pm 0.1 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  at 290.40 K and 602.5 mm Hg that eventually resulted in  $S^\circ=73.58 \pm 0.1 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  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,  $S^\circ$  was found to be  $73.55 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ . Our calculated value of  $73.57 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  is in excellent agreement.

By use of a flow calorimeter Buffington and Gilkey [58] measured the real gas  $C_p$  for  $\text{CCl}_2\text{F}_2$  at 1 atm and in the temperature range of 273.15 ~ 323.05 K. These  $C_p$  values were converted into the ideal gas  $C_p^\circ$ . Eucken and Bertram [59] obtained  $C_p^\circ(\text{g})$  in the same temperature range. Here, again,  $C_p^\circ=C_p+R$ , and as shown in table 8, our calculated  $C_p^\circ$  favor Buffington and Gilkey values at high temperature and Eucken and Bertram at low temperature. The discrepancies, however, are within the experimental uncertainty of  $\pm 0.2 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ . Mashi [60] measured  $C_p$  of a 99.8 mol percent sample with a flow calorimeter and obtained  $C_p^\circ$  by extrapolation to zero pressure. Table 8 illustrates a satisfactory agreement in comparisons with our calculated  $C_p^\circ$ .

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

$\text{CHClF}_2$			$\text{CHCl}_2\text{F}$			$\text{CCl}_3\text{F}$			$\text{CCl}_2\text{F}_2$			
T/K	$C_p^\circ/\text{cal K}^{-1} \text{mol}^{-1}$		T/K	$C_p^\circ/\text{cal K}^{-1} \text{mol}^{-1}$		T/K	$C_p^\circ/\text{cal K}^{-1} \text{mol}^{-1}$		T/K	$C_p^\circ/\text{cal K}^{-1} \text{mol}^{-1}$		
	[30] <sup>a</sup>	calcd.		[30] <sup>a</sup>	calcd.		[30] <sup>a</sup>	calcd.		[58] <sup>b</sup>	[59] <sup>b</sup>	calcd.
322.95	13.52	13.94	310.75	14.37	14.88	310.95	18.57	18.99	273.15	16.92	16.71	16.58
364.55	14.35	14.88	358.75	15.65	15.96	314.55	18.70	19.08	298.15	17.60	17.49	17.33
407.75	15.59	15.79	407.45	16.94	16.92	358.85	19.94	20.08	323.05	18.09	18.28	17.98
						407.35	21.00	20.96				
$\text{CHClF}_2$			$\text{CClF}_3$			$\text{CCl}_3\text{F}$			$\text{CCl}_2\text{F}_2$			
T/K	$S^\circ/\text{cal K}^{-1} \text{mol}^{-1}$		T/K	$C_p^\circ/\text{cal K}^{-1} \text{mol}^{-1}$		T/K	$S^\circ/\text{cal K}^{-1} \text{mol}^{-1}$		T/K	$C_p^\circ/\text{cal K}^{-1} \text{mol}^{-1}$		
	[31] <sup>c</sup>	calcd.		[52] <sup>d</sup>	calcd.		[66] <sup>e</sup>	calcd.		[60] <sup>f</sup>		calcd.
232.50	63.94	64.00	300.00	16.09	16.03	290.40	73.58	73.57	243.15		15.67	15.61
									273.15		16.65	16.58
									318.15		17.95	17.85
									363.15		19.05	18.93

<sup>a</sup> 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.

<sup>b</sup> Estimated uncertainty  $\pm 0.2 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  may be subject to larger error.

<sup>c</sup> Uncertainty  $\pm 0.28 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ .

<sup>d</sup> Uncertainty  $\pm 0.38 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ .

<sup>e</sup> Uncertainty  $\pm 0.1 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ .

<sup>f</sup> Uncertainty  $\pm 0.02 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  excluding errors due to extrapolation to zero pressure.

The recommended values of  $C_p^\circ$ ,  $S^\circ$ , 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  $C_p^\circ$  and  $S^\circ$  are in excellent agreement among the various sources, except for  $S^\circ$  of  $\text{CClF}_3$  by Landolt-Bornstein [68] and  $C_p^\circ$  and  $S^\circ$  of  $\text{CHClF}_2$  by JANAF [28].

## 9. Acknowledgments

This study was supported by the NBS Office of Standard Reference Data under the contract number 2-35730. The cost for computer utilization was partially financed by the Texas Engineering Experiment Station. We are grateful to Dr. A. S. Rodgers for literature help and to the reviewers and the editor of this Journal

TABLE 9-1. Comparison of the ideal gas thermodynamic data at 1 atm and 298.15 K for the six chlorofluoromethanes

	$\text{CH}_2\text{ClF}$			$\text{CHClF}_2$			$\text{CHCl}_2\text{F}$		
	$C_p^\circ$	$S^\circ$	$-\Delta H_f^\circ$	$C_p^\circ$	$S^\circ$	$-\Delta H_f^\circ$	$C_p^\circ$	$S^\circ$	$-\Delta H_f^\circ$
	cal K <sup>-1</sup> mol <sup>-1</sup>		kcal mol <sup>-1</sup>	cal K <sup>-1</sup> mol <sup>-1</sup>		kcal mol <sup>-1</sup>	cal K <sup>-1</sup> mol <sup>-1</sup>		kcal mol <sup>-1</sup>
Landolt-Bornstein, 1961.....	11.26	63.17	68.1	13.36	67.14	117.1	14.58	70.00	70.0
Wagman, et al., 1968.....	11.24	63.17		13.35	67.11		14.56	70.02	
JANAF, 1970.....	11.24	63.17	62.6	13.65	67.13	115.1	14.58	70.07	67.7
Glushko, et al., 1970.....	11.24	63.17	61.5	13.35	67.12	110.0	14.57	70.06	64.0
This work, 1975.....	11.25	63.17	63.2	13.35	67.11	115.6	14.58	70.04	68.1
	$\text{CClF}_3$			$\text{CCl}_2\text{F}_2$			$\text{CCl}_3\text{F}$		
	$C_p^\circ$	$S^\circ$	$-\Delta H_f^\circ$	$C_p^\circ$	$S^\circ$	$-\Delta H_f^\circ$	$C_p^\circ$	$S^\circ$	$-\Delta H_f^\circ$
	cal K <sup>-1</sup> mol <sup>-1</sup>		kcal mol <sup>-1</sup>	cal K <sup>-1</sup> mol <sup>-1</sup>		kcal mol <sup>-1</sup>	cal K <sup>-1</sup> mol <sup>-1</sup>		kcal mol <sup>-1</sup>
Landolt-Bornstein, 1961.....	15.97	68.24	170.9	17.28	71.85	112.1	18.62	73.92	70.0
Wagman, et al., 1968.....	15.98	68.16	166.0	17.27	71.86	114.0	18.66	74.05	66.0
JANAF, 1970.....	15.99	68.17	169.2	17.31	71.91	117.5	18.65	74.00	69.0
Glushko, et al., 1970.....	15.99	68.17	169.7	17.31	71.92	113.3	18.65	74.02	66.5
This work, 1975.....	15.98	68.16	169.2	17.31	71.87	117.9	18.66	74.06	68.1

TABLE 9-2. Comparison of the ideal gas thermodynamic data at 1 atm and 700 K for the six chlorofluoromethanes

	$\text{CH}_2\text{ClF}$			$\text{CHClF}_2$			$\text{CHCl}_2\text{F}$		
	$C_p^\circ$	$S^\circ$	$-\Delta H_f^\circ$	$C_p^\circ$	$S^\circ$	$-\Delta H_f^\circ$	$C_p^\circ$	$S^\circ$	$-\Delta H_f^\circ$
	cal K <sup>-1</sup> mol <sup>-1</sup>		kcal mol <sup>-1</sup>	cal K <sup>-1</sup> mol <sup>-1</sup>		kcal mol <sup>-1</sup>	cal K <sup>-1</sup> mol <sup>-1</sup>		kcal mol <sup>-1</sup>
Landolt-Bornstein, 1961.....	17.79			19.97			20.67		
JANAF, 1970.....	17.79	75.46	64.2	20.27	81.69	115.8	20.66	85.20	68.3
This work, 1975.....	17.79	75.46	64.8	19.97	81.36	116.5	20.66	85.17	68.7
	$\text{CClF}_3$			$\text{CCl}_2\text{F}_2$			$\text{CCl}_3\text{F}$		
	$C_p^\circ$	$S^\circ$	$-\Delta H_f^\circ$	$C_p^\circ$	$S^\circ$	$-\Delta H_f^\circ$	$C_p^\circ$	$S^\circ$	$-\Delta H_f^\circ$
	cal K <sup>-1</sup> mol <sup>-1</sup>		kcal mol <sup>-1</sup>	cal K <sup>-1</sup> mol <sup>-1</sup>		kcal mol <sup>-1</sup>	cal K <sup>-1</sup> mol <sup>-1</sup>		kcal mol <sup>-1</sup>
Landolt-Bornstein, 1961.....	22.49	84.68	170.9				23.72	92.28	69.5
JANAF, 1970.....	22.50	84.81	169.2	23.14	89.42	117.2	23.75	92.37	68.4
This work, 1975.....	22.50	84.80	169.2	23.14	89.38	117.6	23.75	92.43	67.5

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.

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