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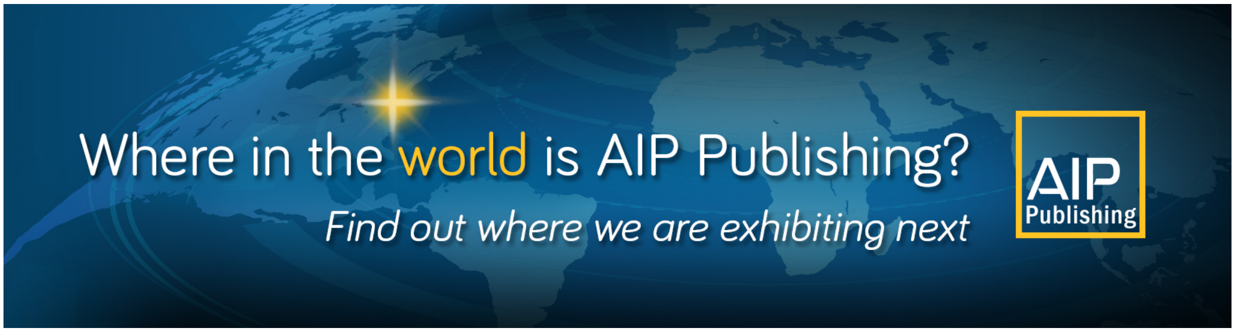

Ideal Gas Thermodynamic Properties of Six Fluoroethanes

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The molecular structural parameters, the vibrational fundamentals, the potential barrier height to internal rotation, and the standard enthalpy of formation for each of the six fluoroethanes in which at least one of the internally rotating groups is a symmetric top have been extensively studied and recommended values selected. Chemical thermodynamic properties of molecules in the ideal gas state at temperatures from 0 to 1500 K have been calculated with the rigid-rotor harmonic-oscillator approximation. The calculated values are in a very good agreement with the existing third-law entropies.

Key words: Barrier height to internal rotation; fluoroethanes with a symmetric top; ideal gas thermodynamic functions; reduced and principal moments of inertia; standard heat of formation; structural parameters; torsional mode; vibrational fundamentals.

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1. Introduction

This is the third part in a series of studies on halogenated alkanes with one and two carbon atoms [1,2][1] to provide a useful reference source of standard data on the ideal gas thermodynamic properties derived from available information on spectroscopic and calorimetric measurements. The most recent fundamental physical constants [3] together with the recommended mass units, C = 12.011, H = 1.008, and F = 18.9984, have been used.

The structural parameters and the vibrational fundamentals of C_2H_5F, CH_3CHF_2, CH_3CF_3, CH_2FCF_3, C_2HF_5, and C_2F_6 have been selected from experimental data. The parameters of 1,1,1,2-tetrafluoroethane were estimated by correlating properties of other fluoro- and chloromethanes and ethanes. The principal moments, if spectroscopically unavailable, and also the reduced moment for each molecule have been calculated with the Kilpatrick-Pitzer procedure [4,5]. A three-fold symmetric potential function for internal rotation about the C—C bond has been assumed for all the molecules except fluoroethane for which an additional six-fold term, V_6, was required to fit the observed torsional transitions [6]. The potential barrier height can be evaluated from the Mathieu equation [7], using the corresponding torsional fundamental and the reduced moment of the rotor in question. The ratio V_6/V_3 can also be estimated if higher torsional transitions have been observed. Energy levels of internal rotation, at least up to 15000 cm^{-1}, have been derived from the diagonalization of the Hamiltonian matrix [8][2]. Based on the selected values of principal moments of inertia, vibrational fundamentals and energy levels of internal rotation, the ideal gas thermodynamic properties, namely C_p°, S°, $H^\circ - H_0^\circ$ and $-(G^\circ - H_0^\circ)/T$ have been calculated in the rigid-rotor harmonic-oscillator approximation. Comparisons of calculated and observed values have been made whenever experimental data were available.

The standard enthalpies of formation in the ideal gaseous state ΔHf° (g, 298.15) for four fluoroethanes have been obtained from enthalpies of reaction or enthalpies of combustion, after making corrections to impose consistency with recent experimental data. Since calorimetric data are not available for C_2H_5F and CH_2FCF_3, the values of ΔHf° (g, 298.15) have been derived from correlative procedures. Based on the selected values of ΔHf° (g, 298.15) for the substance from this study and necessary input data on the elements, viz., $H^\circ - H_0^\circ$ and $-(G^\circ - H_0^\circ)/T$ for C (graphite), H_2 (g) and F_2 (g) from a previous study [1], the chemical thermodynamic property values of ΔHf°, ΔGf° and log Kf in the temperature range 0 to 1500 K and at 1 atm have been evaluated.

2. Fluoroethane (Ethyl Fluoride)

The structural parameters for fluoroethane were incompletely derived from an analysis of the observed rotational transitions in the microwave spectrum [9]. The molecule was considered to be a slightly asymmetric prolate rotor and stable in its staggered configuration. This conclusion was later confirmed, and the molecular structure was determined as completely as was feasible at that time from the microwave spectra of eleven isotopic derivatives of ethyl fluoride containing ^{13}C and deuterium [10]. Because of uncertainties in the structure derived from microwave spectra, Nygaard [11] reexamined all the previously reported absorption frequencies and employed a least squares method to obtain the principal moments of inertia and, consequently, the complete set of structural parameters taking into account vibration-rotation effects and bond shortening correction on isotopic substitution. Because of her systematic treatment of all available information, Nygaard's values for the principal moments and structural parameters along with the calculated reduced moment of inertia were selected and listed in table 1–1.

The fluoroethane molecule belongs to the C_s point group. A Raman spectrum for the liquid phase and infrared spectra for the liquid and vapor phases are available [12]. The low-frequency torsional bands were observed in an infrared [13] and a far-infrared [6] spectrum of the gas phase. Shimanouchi [14] critically reviewed the reported spectral data and selected the vibrational fundamentals listed in table 1–1 which were adopted for the calculation of thermodynamic properties.

The torsional fundamental for fluoroethane was determined from a very weak Raman line [12], microwave relative intensities [9], and torsional bands in infrared [13] and far-infrared [6] regions. The various values of the potential barrier to internal rotation were derived from the corresponding values of the torsional fundamental and reduced moment of inertia, as shown in table 2–1. The potential barrier obtained from splittings of torsional satellites in a microwave spectrum [16] was also listed. The reported values of $V_3 = 3306$ cal mol^{-1} and $V_6 = -15$ cal mol^{-1} were obtained from a fit of the four torsional transitions (0–1, 1–2, 2–3 and 3–4) at 242.7, 225.5, 208.4, and 117 cm^{-1} [6]. However, we have found that the use of the same V_3 and $V_6 = -7$ cal mol^{-1} gave a slightly better over-all fit to all the observed torsional transitions [6, 15], as shown in table 1–3, and that the torsional fundamental was calculated to be 243 cm^{-1}, which was the same as that selected by Shimanouchi [14]. Therefore, $V_3 = 3306$ cal mol^{-1} and $V_6 = -7$ cal mol^{-1} have been used in this work for the calculation of energy levels of hindered internal rotation. The barrier heights [17, 18] estimated from semi-empirical procedures have also been given in a footnote to table 1–2 for comparison.

Since no experimentally measured enthalpy of formation of ethyl fluoride has been found, it was estimated

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[1] Figures in brackets indicate the literature references.

[2] In keeping with the commonly accepted convention in this field, vibrational energies are expressed in their wavenumber (cm^{-1}) equivalents.

TABLE 1-1. The selected molecular and chemical constants[a] of fluoroethane

Property	Quantity	Property	Quantity
Molecular weight	48.060	Principal moments of inertia	
Symmetry number	3	I_A, g cm^2	23.2589×10^{-40}
Structural parameters[b]		I_B, g cm^2	89.5538×10^{-40}
C—F	1.398	I_C, g cm^2	102.125×10^{-40}
C—H(CFH_2)	1.095	Reduced moment of inertia, g cm^2	4.333×10^{-40}
C—H(*gauche*, CH_3)	1.090	Vibration fundamentals, cm^{-1}	
C—H(*trans*, CH_3)	1.091	Symmetry species a'	3003, 2941, 2915, 1479,
C—C	1.505		1449, 1395, 1365, 1108,
∠FCH	106.1		1048, 880, 415
∠FCC	109.7	Symmetry species a''	3003, 3003, 1449, 1277,
∠HCH(CFH_2)	108.8		1048, 810, 243[c]
∠HCH(*gauche, gauche*, CH_3)	108.9	Potential barrier parameters	
∠HCH(*gauche, trans*, CH_3)	108.7	V_3, cal mol^{-1}	3306
∠HCC(CFH_2)	112.9	V_6, cal mol^{-1}	−7
∠HCC(*gauche, gauche*, CH_3)	109.7	Enthalpy of formation	
∠HCC(*gauche, trans*, CH_3)	110.4[d]	$\Delta Hf°$(g, 298.15), kcal mol^{-1}	−62.9

[a] Throughout this paper 1 cal = 4.184 J.

[b] Bond distances in 10^{-8} cm and bond angles in degrees.

[c] Torsional mode.

[d] Calculated value.

TABLE 1-2. Reduced moment of inertia, torsional fundamental and barrier height[a] of fluoroethane

I_r, g cm$^2\times10^{40}$	Reference	ν_{18}, cm^{-1}	V_3, cal mol^{-1}	V_6, cal mol^{-1}	Reference
4.23	[12]	278	(3959)		[12]
4.359	[9]	300±40	(4260±150)[b]		[9]
?[c]			3306±31		[16]
4.415	[15][d]		3310±210		[15]
4.359	[9]	243.5			[13]
4.415	[10]	242.7	(3306)	(−15)	[6]
		243			[14]
4.333	This work	243	(3306)	(−7)	This work

[a] Values in parentheses were derived from the corresponding reduced moments and torsional fundamentals. In addition, 3150 cal mol^{-1} (corresponding to $\nu_{18}=250$ cm^{-1}) [17] and 3310 cal mol^{-1} (corresponding to $\nu_{18}=241$ cm^{-1}) [18] were estimated from semi-empirical procedures.

[b] Assumed $\nu_{18}=278$ cm^{-1}.

[c] Presumed $I_r=4.415\times10^{-40}$ g cm^2. See the next footnote.

[d] Through personal communication with the author of ref. [16].

indirectly as follows. The enthalpy of reaction (1–1) at 521.15 K, $\Delta Hr° = -22.88\pm0.37$ kcal, was measured [19] in a flow calorimeter using a palladium-on-carbon catalyst.

$$CFH_2CH_2CH_3\,(g) + H_2\,(g) \rightarrow CH_3CH_2CH_3\,(g) + HF\,(g) \qquad (1\text{–}1)$$

The correction for $\Delta Hr°$ from 521.15 K to 298.15 K was assumed to be the same as that of the similar reaction (1–2).

$$CFH_2CH_3\,(g) + H_2\,(g) \rightarrow CH_3CH_3\,(g) + HF\,(g) \qquad (1\text{–}2)$$

The correction of $\Delta Hr°$ from 521.15 K to 298.15 K was calculated to be 0.45 kcal, by using the enthalpy of CFH_2CH_3 (g) from this study, that of CH_3CH_3 (g) from reference [20], and for HF (g) and H_2 (g) from reference [21]. Thus $\Delta Hr° = -22.43\pm0.37$ kcal for reaction (1–1) at 298.15 K. The values, $\Delta Hf°$(HF, g, 298.15) = −65.34 kcal mol^{-1} [20] and $\Delta Hf°$ ($CH_3CH_2CH_3$, g, 298.15) = 25.02 ± 0.12 kcal mol^{-1} [22] led to $\Delta Hf°$ ($CFH_2CH_2CH_3$, g, 298.15) = −67.93 ± 0.39 kcal mol^{-1}. By use of the incremental contribution 4.98 ± 0.1 kcal mol^{-1} for —CH_2— at 298.15, the recommended value of $\Delta Hf°$ (CFH_2CH_3, g, 298.15) is − 62.9 ± 0.4 kcal mol^{-1}. The value of − 63.1 kcal mol^{-1} predicted by the method of triatomic additivity [23] is in a good agreement within the experimental uncertainty.

The ideal gas thermodynamic properties in table 1–4 are based on the selected values in table 1–1. There are no experimental values of C_p° and $S°$ available for comparisons.

TABLE 1-3. Calculated and observed values for torisional transitions and their splittings for fluoroethane

Transition	Wavenumber of torsional transition in cm^{-1}				Splitting of transitions in cm^{-1}	
	$-V_6$ cal mol^{-1}	Calculated[a] with $V_3=3306$ cal mol^{-1} & V_6	Observed[b]		Calculated with $V_3=3306$ cal mol^{-1} & V_6	Reference [6]
			Reference [12]	Reference [6]		
0-1	0	243.8 (243.8)	243.5			
	7	243.0 (243.0)				
	15	242.2 (242.2)		242.7 ± 0.5		
1-2	0	226.7 (226.8)	227			
	7	226.3 (226.3)				
	15	225.8 (225.8)		225.4 ± 0.4		
2 3	0	207.7 (206.5)	206		1.2[c]	
	7	207.6 (206.4)			1.2[c]	
	15	207.4 (206.3)		208.4 ± 0.4	1.1[c]	1.1[c,e]
3-4	0	174.9 (185.3)			10.4[d]	
	7	175.1 (185.5)			10.4[d]	
	15	175.4 (185.7)		177.0 ± 1.0 (187)	10.3[d]	9.5[d,e] (10.0)[d,f]

[a] Values without parentheses represent the transitions between A levels such as 0A–1A, 1A–2A, 2A–3A and 3A–4A. Similarly, values in parentheses represent the transitions between E levels such as 0E–1E, 1E–2E, 2E–3E and 3E–4E.

[b] Observed values are indistinguishable for A to A and E to E transitions, except 117 cm^{-1} for 3A,E–4A and 187 cm^{-1} for 3E–4E.

[c] The splitting between the transitions 2A–3A and 2E–3*E*.

[d] The splitting between the transitions 3E–4E and 3A–4A.

[e] Ref. [6].

[f] The difference between 187 cm^{-1} for 3E–4E and 177 cm^{-1} for 3A–4A.

TABLE 1-4. Ideal gas thermodynamic functions for fluoroethane

T	C_p°	S°	$-(G^\circ - H_0^\circ)/T$	$H^\circ - H_0^\circ$	ΔHf°	ΔGf°	log Kf
K	cal K^{-1} mol^{-1}			kcal mol^{-1}			
0	0	0	0	0	−59.35	−59.35	∞
100.00	8.94	51.44	43.24	0.820	−60.81	−57.77	126.26
150.00	10.04	55.27	46.65	1.295	−61.28	−56.16	81.82
200.00	11.23	58.32	49.19	1.826	−61.81	−54.37	59.41
273.15	13.38	62.13	52.16	2.723	−62.63	−51.51	41.21
298.15	14.21	63.34	53.05	3.068	−62.90	−50.44	36.98
300.00	14.28	63.42	53.11	3.094	−62.92	−50.40	36.72
400.00	17.71	68.00	56.27	4.694	−63.94	−46.07	25.17
500.00	20.86	72.30	59.05	6.626	−64.79	−41.51	18.14
600.00	23.56	76.35	61.60	8.850	−65.49	−36.79	13.40
700.00	25.85	80.16	63.98	11.324	−66.04	−31.95	9.98
800.00	27.82	83.74	66.23	14.010	−66.47	−27.05	7.39
900.00	29.52	87.12	68.36	16.879	−66.79	−22.10	5.37
1000.00	31.00	90.31	70.40	19.907	−67.01	−17.12	3.74
1100.00	32.3	93.3	72.3	23.07	−67.2	−12.1	2.41
1200.00	33.4	96.2	74.2	26.36	−67.2	−7.1	1.30
1300.00	34.4	98.9	76.0	29.75	−67.3	−2.1	0.36
1400.00	35.2	101.5	77.7	33.22	−67.3	2.9	−0.46
1500.00	35.9	103.9	79.4	36.78	−67.2	7.9	−1.15

3. 1,1-Difluoroethane

Solimene and Dailey [24] determined the principal moments of inertia of CF_2HCH_3 from an analysis of the microwave spectrum. They then calculated the values of the four structural parameters listed in table 2-1. The C−H distances and HCH angle identified by a superscript, [b], were transferred from various methyl halides [25]. Since this is the only source of structural information, it was used in our calculations.

TABLE 2–1. The selected molecular and chemical constants of 1,1-difluoroethane

Property	Quantity	Property	Quantity
Molecular weight	66.051	Principal moments of inertia	
Symmetry number	3	I_A, g cm^2	88.4133×10^{-40}
Structural parameters [a]		I_B, g cm^2	93.6347×10^{-40}
C—F	1.345	I_C, g cm^2	162.310×10^{-40}
C—H(CF_2H)	1.100 [b]	Vibrational fundamentals, cm^{-1}	
C—H(CH_3)	1.100 [b]	Symmetry species a'	3018, 2978, 2960, 1460, 1414, 1372, 1143, 1129, 868, 571, 470
C—C	1.540 [b]		
∠FCF	109.13		
∠HCH	110.22 [b]	Symmetry species a''	3001, 1460, 1360, 1171, 930, 383, 222 [c]
∠FCC	109.43		
∠HCC(CF_2H)	109.82	Barrier height V_3, cal mol^{-1}	3215
∠HCC(CH_3)	108.71 [d]	Enthalpy of formation	
Reduced moment of inertia, g cm^2	5.129×10^{-40}	$\Delta Hf°$(g, 298.15), kcal mol^{-1}	−119.7

[a] Bond distances in 10^{-8} cm and bond angles in degrees.

[b] Assumed value, see ref. [25].

[c] Torsional mode.

[d] Calculated value.

The 1,1-difluoroethane molecule has C_s symmetry. The infrared and Raman spectra of its vapor and liquid were observed by Smith, Saunders, Nielsen, and Ferguson [12] who found no evidence for the low torsional mode from their analysis. The selection of the vibrational assignments is based on their intensities. Both ν_3 and ν_4 show strong absorption in both infrared and Raman spectra. Therefore, the average values were selected for these two frequencies. Recommended values of fundamentals are also included in table 2–1.

TABLE 2–2. Reduced moment of inertia, torsional fundamental and barrier height [a] of 1,1-difluoroethane

I_r, g cm$^2 \times 10^{40}$	Reference	ν_{18}, cm^{-1}	V_3, cal mol^{-1}	Reference
5.01	[12]	250	(3947)	[12]
5.122	[24]	235 ± 47	(3570 ± 580)	[24]
?			3180 ± 17	[16]
? [b]		222 ± 2	(3210)	[26]
5.129	This work	222	(3215)	This work

[a] Values in parentheses were derived from the corresponding reduced moments and torsional fundamentals. In addition, $V_3 = 3330$ cal mol^{-1} was obtained from semi-empirical procedures [27].

[b] The authors of ref. [26] did not indicate the value of I_r. Presumably, 5.122×10^{-40} g cm^2 was used.

The reported values of the torsional mode, the barrier height V_3 and the reduced moment of inertia have been summarized in table 2–2. From a systematic comparison of the vibrational fundamentals for ethane, fluoroethane, 1,1-difluoroethane, and 1,1,1-trifluoroethane, the torsional fundamental was deduced [12]. It was also determined from the relative intensities of microwave spectral lines [24]. The barrier height V_3 was obtained from the average of the results derived from splittings of eight torsional satellites in a microwave spectrum [16]. Later, Fateley and Miller [26] observed the absorption band at 222 ± 2 cm^{-1} for the transition 0–1 between the torsional A levels and the first overtone at 430 cm^{-1} in the far-infrared spectrum of the gas. The intensities were sufficient for unambiguous identification. Both values are consistent with a barrier of 3215 cal mol^{-1} for internal rotation, in combination with our calculated reduced moment. Fateley and Miller reported a slightly different value of 3210 cal mol^{-1}. A value of V_3 from semi-empirical estimation [27] is also shown in a footnote to table 2–2.

Kolesov, Shtekher, Martynov, and Skuratov [28] measured the enthalpy of combustion (2–1) at 298.15 K.

$$CF_2HCH_3\,(g) + 2\tfrac{1}{2}\,O_2\,(g) + 39\,H_2O\,(\ell) \rightarrow 2\,CO_2\,(g) + 2\,HF \cdot 20\,H_2O\,(\ell) \qquad (2\text{–}1)$$

From chromatographic and mass spectrometric analyses the purity of CF_2HCH_3 sample was estimated to be greater than 99.5 mol percent. However, 0.4 wt. percent of CO_2 was detected when the sample passed through a system of absorption tubes. The sample was prepurified with Ascarite and then burned in a bomb calorimeter lined with platinum. The combustion products were determined quantitatively by analyses for CO_2 by weight and aqueous HF by titration. Less than 1 percent of unreacted CF_2HCH_3 was found in a mass spectrometric analysis, however, unburned CF_2HCH_3 could not affect the calculation of the heat of combustion. For the reaction (2–1) $\Delta Hr°$ (g, 298.15) was determined to be −289.7 ± 0.4 kcal based on CO_2 analysis and − 293.3 ± 1.1 kcal based on aqueous HF analysis. Kolesov et al. reported an unweighted average; $\Delta Hr°$ (g, 298.15) = − 291.5 ± 2 kcal. However, it appears to be better to adopt the average value of the two (CO_2 and HF) results weighted inversely to their experimental errors. This gives $\Delta Hr°$ (g, 298.15) = − 290.7 ± 1.5 kcal. Based on $\Delta Hf°$ ($HF \cdot 2H_2O$, ℓ, 298.15) = − 77.004 kcal mol^{-1} [29], we have obtained $\Delta Hf°$ (CF_2HCH_3, g, 298.15) = − 119.7 ± 1.5 kcal mol^{-1}

Ideal gas thermodynamic functions for CF_2HCH_3 have been calculated with the same procedures as that

TABLE 2–3. Ideal gas thermodynamic functions for 1,1-difluoroethane

T	$C_p°$	$S°$	$-(G°-H_0°)/T$	$H°-H_0°$	$\Delta Hf°$	$\Delta Gf°$	log Kf
K	cal K^{-1} mol^{-1}			kcal mol^{-1}			
0	0	0	0	0	−116.38	−116.38	∞
100.00	9.27	54.34	46.05	0.829	−117.79	−114.23	249.66
150.00	10.92	58.40	49.52	1.333	−118.27	−112.35	163.70
200.00	12.66	61.78	52.17	1.922	−118.76	−110.31	120.54
273.15	15.31	66.12	55.34	2.945	−119.47	−107.09	85.69
298.15	16.24	67.50	56.30	3.339	−119.70	−105.87	77.61
300.00	16.31	67.60	56.37	3.369	−119.72	−105.87	77.12
400.00	19.93	72.79	59.84	5.184	−120.56	−101.12	55.25
500.00	23.08	77.59	62.91	7.339	−121.24	−96.18	42.04
600.00	25.70	82.04	65.73	9.782	−121.78	−91.12	33.19
700.00	27.87	86.17	68.36	12.464	−122.21	−85.97	26.84
800.00	29.70	90.01	70.83	15.345	−122.52	−80.77	22.06
900.00	31.25	93.60	73.16	18.394	−122.75	−75.53	18.34
1000.00	32.57	96.96	75.38	21.587	−122.89	−70.27	15.36
1100.00	33.7	100.1	77.5	24.90	−123.0	−65.03	12.29
1200.00	34.7	103.1	79.5	28.32	−123.0	−59.7	10.88
1300.00	35.5	105.9	81.4	31.84	−123.0	−54.5	9.16
1400.00	36.3	108.6	83.3	35.43	−122.9	−49.2	7.68
1500.00	36.9	111.1	85.0	39.09	−122.9	−43.9	6.40

for CFH_2CH_3 and tabulated in table 2–3. There are no experimental thermodynamic data for comparisons.

4. 1,1,1-Trifluoroethane (Methyl Fluoroform)

1,1,1-Trifluorethane is also called Freon "F-143." The molecular structure was investigated by electron diffraction measurements [30–33] and by microwave techniques [34–36]. Structural data were also reported in references [37, 38]. By considering the completeness of the structural parameters and their experimental uncertainties, we have selected the values of Edgell, Miller and Amy [36] and calculated the principal moment I_C and the reduced moment I_r. The principal moments, I_A and I_B, were obtained from the rotational constants [36]. Table 3–1 summarizes the selected values.

The CF_3CH_3 molecule has C_{3v} symmetry. The vibrational modes of species a_1 and e are active both in the infrared and Raman, whereas the torsional oscillation of species a_2 is inactive in both cases. A liquid Raman spectrum was observed [39] and vibrational assignments were made [40]. Drastically conflicting assignments for some vibrational modes based on infrared spectra have been published [41–43]. Later, a complete assignment of vibrational fundamentals based on Raman and infrared spectra [37, 44] in gaseous phase was made that appears consistent and reliable. The mean value of the doubly degenerate mode ν_{12} derived from five binary combination bands [43] is 365 cm^{-1}; however 368 cm^{-1} was chosen [43] to agree with the earlier assignment from a liquid Raman spectrum [40]. A weak and diffuse Raman band at 365 cm^{-1} [37] and a strong infrared band with Q branch at 367 cm^{-1} [44] were observed later. More recently, a single strong band at 365 cm^{-1} in an infrared spectrum of purified CF_3CH_3 was found [45]. We have selected the vibra-

TABLE 3–1. The selected molecular and chemical constants of 1,1,1-trifluoroethane

Property	Quantity	Property	Quantity
Molecular weight	84.041	Principal moments of inertia	
Symmetry number	9	$I_A = I_B$, g cm^2	161.84
Structural parameters [a]		I_C, g cm^2	152.28
C—F	1.335	Vibrational fundamentals, cm^{-1}	
C—H	1.085	Symmetry species a_1	2975, 1408, 1280, 830, 602
C—C	1.530	Symmetry species a_2	220 [c]
∠FCF	107.87 [b]	Symmetry species e	3035, 1443, 1233, 970, 541
∠HCH	110.60 [b]		365
∠FCC	111.03	Barrier height V_3, cal mol^{-1}	3167
∠HCC	108.32	Enthalpy of formation	
Reduced moment of inertia, g cm^2	5.141×10^{-40}	$\Delta Hf°$(g, 298.15), kcal mol^{-1}	−178.2

[a] Bond distances in 10^{-8} cm and bond angles in degrees.

[b] Calculated value.

[c] Torsional mode.

tional fundamentals, as shown in table 3–1, of Smith, Brown, Nielsen, Smith, and Liang [44], except for $\nu_{12}=365$ cm^{-1} of Catalano and Pitzer [45] and for the torsional mode described below.

Various values for the barrier height to internal rotation have been estimated from fitting a third-law entropy [40, 41], from a heat capacity at constant volume [46] and also from low temperature heat capacity data [47]. These values cannot be reliable in view of the controversial vibrational assignments employed in the calculations. The values of the torsional mode obtained from microwave relative intensity measurements [48, 49] and infrared combination bands of CF_3CH_3 gas [37, 38, 42, 45] scatter widely. Recently, Brier and Higgins [50] estimated the torsional fundamental $\nu_6=220\pm15$ cm^{-1} corresponding to $V_3=3170\pm250$ cal mol^{-1} from neutron inelastic scattering measurements. A torsional band that is active only in the solid phase was observed at 220 cm^{-1} in a far-infrared spectrum by Durig, Craven, Lau, and Bragin [51]. They then estimated 3100 cal mol^{-1} for the barrier in gas phase. We have thus selected 220 cm^{-1} as the torsional fundamental and have obtained $V_3=3167$ cal mol^{-1} based on the reduced moment of this work. The reported values of the torsional mode, the barrier height and the corresponding reduced moment, when available, have been listed in table 3–2.

TABLE 3–2. Reduced moment of inertia, torsional fundamental and barrier height [a] of 1,1,1-trifluoroethane

I_r, g cm^2 × 10^{40}	Reference	ν_6, cm^{-1}	V_3, cal mol^{-1}	Reference
5.125	[31]		3540 ± 400 [b]	[40]
[c]			3250 [b]	[41]
[d]		165 ± 25	(1470 ± 470)	[48]
[d]		218	(3000 ± 200) [e]	[42]
[f]		238	(3290)	[37]
[d]		234 ± 40	(3480)	[49]
5.11	[30]	238	(3660)	[44]
[f]			(3370 ± 200)	[46]
5.11	[30]	216	(3040)	[45]
5.125	[31]		(3250 ± 200)	[47]
5.122	?	220 ± 15	(3170 ± 250)	[50]
?		220	(3100)	[51]
5.141	This work	220	(3167)	This work

[a] Values in parentheses were derived from the corresponding reduced moments and torsional fundamentals. In addition, 3350 cal mol^{-1} was estimated from semi-empirical procedures [27].

[b] Derived from calorimetric and spectral data.

[c] The value was not indicated, but presumably was derived from the structural parameters [31].

[d] The value was not indicated, but presumably was derived from the structural parameters [34].

[e] Indirectly inferred from infrared combination bands, 172 cm^{-1} and 218 cm^{-1} proposed as likely for the torsional mode. The latter assignment was considered more likely with a barrier height of 3210 cal mol^{-1}, however, 3000 ± 200 cal mol^{-1} was preferred.

[f] The value was not indicated, but presumably was derived from the structural parameters [30].

Kolesov, Martynov, and Skuratov [52] measured the enthalpy of combustion of CF_3CH_3 gas in a bomb calorimeter lined with platinum. The fractionally distilled CF_3CH_3 sample was checked by mass spectrometry and was free from fluorine-containing impurities. An optimal gas mixture of 2 atm of CF_3CH_3 and 6 atm of oxygen was ignited by electric current. The combustion products of the reaction (3–1) at 298.15 K were determined from analyses of CO_2 by weight and aqueous HF by

$$CF_3CH_3(g)+2\ O_2(g)+135\ H_2O\ (\ell)\rightarrow 2\ CO_2(g)+3\ HF\cdot 45\ H_2O\ (\ell) \qquad (3\text{–}1)$$

titration. The results were in excellent agreement and the average value ΔU_c (g, 298.15) = −240.4 kcal was obtained. While about 2 percent of CF_3CH_3 gas did not react, no evidence of intermediate combustion products was found. The enthalpy of the reaction (3–1) was then taken as ΔHr° (g, 298.15) = −241.0±0.4 kcal. By use of the standard value ΔHf° (CO_2, g, 298.15) = −94.051 kcal mol^{-1} [53] and ΔHf° ($HF\cdot 45\ H_2O$, ℓ, 298.15) = −77.028 kcal mol^{-1} [29], we obtained ΔHf° (CF_3CH_3) = −178.2±0.4 kcal mol^{-1}. In a kinetic study, Ferguson and Whittle [54] determined ΔHr° (g, 298.15) = 106.7±0.5 kcal for reaction (3–2).

$$CF_3H\ (g)\rightarrow CF_3\cdot(g)+H\cdot(g) \qquad (3\text{–}2)$$

By adopting ΔHf° (CF_3H, g, 298.15) = −165.7±1 kcal mol^{-1} [1] and ΔHf° (H·, g, 298.15) = 52.095 kcal mol^{-1} [20] we obtained ΔHf° (CF_3, g, 298.15) = −111.1±1 kcal mol^{-1}. In an analysis of kinetic data from six different laboratories, Rodgers and Ford [55] derived ΔHr° (g, 298.15) = 101.2±1.1 kcal for reaction (3–3).

$$CF_3CH_3(g)\rightarrow CF_3\cdot(g)+CH_3\cdot(g) \qquad (3\text{–}3)$$

This led to ΔHf° (CF_3CH_3, g, 298.15) = −178.2±1.6 kcal mol^{-1} by using ΔHf° ($CH_3\cdot$, g, 298.15) = 34.1±0.5 kcal mol^{-1} [56]. This is in excellent agreement with the calorimetric value. The method of triatomic additivity [23] predicted ΔHf° (CF_3CH_3, g, 298.15) = −177.8 kcal mol^{-1} within the uncertainty of both experimental determinations. Table 3–3 summarizes experimental data for the enthalpy of formation of CF_3CH_3 gas. We have selected ΔHf° (CF_3CH_3, g, 298.15) = −178.2± 0.4 kcal mol^{-1}.

Ideal gas thermodynamic functions have been calculated and are listed in table 3–4. When the third-law entropy 63.95±0.10 cal K^{-1} mol^{-1} [40] for the ideal gas of CF_3CH_3 at 224.40 K and 0.9330 atmosphere is converted to one atmosphere, it is 63.89±0.1 cal K^{-1} mol^{-1}. This is in good agreement with our calculated value of 63.82 cal K^{-1} mol^{-1}.

5. 1,1,1,2-Tetrafluoroethane

The CFH_2CF_3 molecule has two very close principal moments of inertia and can therefore be regarded as an

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

Primary data		Auxiliary data		ΔHf° (g, 298.15) in kcal mol^{-1}
ΔHr° in kcal for reaction	Reference	ΔHf° (298.15) in kcal mol^{-1}	Reference	
ΔHr° (g, 298.15) $= -241.0 \pm 0.4$ for $CF_3CH_3 + 2O_2 + 135H_2O(\ell) \rightarrow 2CO_2 + 3HF \cdot 45H_2O(\ell)$	[52]	$\Delta Hf^\circ(CO_2, g) = -94.051$ $\Delta Hf^\circ(HF \cdot 45H_2O, \ell) = -77.028$	[53] [29]	$\Delta Hf^\circ(CF_3CH_3) = -178.2 \pm 0.4$
ΔHr° (g, 298.15) $= 106.7 \pm 0.5$ for $CF_3H \rightarrow CF_3\cdot + H\cdot$	[54]	$\Delta Hf^\circ(CF_3H, g) = -165.7 \pm 1$ $\Delta Hf^\circ(H\cdot, g) = 52.059$	[1] [20]	$\Delta Hf^\circ(CF_3\cdot) = -111.1 \pm 1$
ΔHr° (g, 298.15) $= 101.2 \pm 1.1$ for $CF_3CH_3 \rightarrow CF_3\cdot + CH_3\cdot$	[55]	$\Delta Hf^\circ(CH_3\cdot, g) = 34.1 \pm 0.5$ $\Delta Hf^\circ(CF_3\cdot, g) = -111.1 \pm 1$	[56] This work	$\Delta Hf^\circ(CF_3CH_3) = -178.2 \pm 1.6$

Selected value: $\Delta Hf^\circ(CF_3CF_3) = -178.2 \pm 0.4$

TABLE 3–4. Ideal gas thermodynamic functions for 1,1,1-trifluoroethane

T	Cp°	S°	$-(G^\circ - H^\circ_0)/T$	$H^\circ - H^\circ_0$	ΔHf°	ΔGf°	log Kf
K	cal K^{-1} mol^{-1}			kcal mol^{-1}			
0	0	0	0	0	−175.15	−175.15	∞
100.00	9.60	54.04	45.68	0.836	−176.53	−172.12	376.17
150.00	11.90	58.35	49.21	1.372	−177.00	−169.82	247.42
200.00	14.30	62.11	51.97	2.027	−177.44	−167.35	182.87
273.15	17.67	67.07	55.36	3.198	−178.02	−163.56	130.86
298.15	18.76	68.67	56.41	3.654	−178.20	−162.11	118.83
300.00	18.84	68.78	56.49	3.688	−178.21	−162.13	118.11
400.00	22.75	74.76	60.32	5.774	−178.82	−156.68	85.60
500.00	25.90	80.18	63.76	8.213	−179.27	−151.09	66.04
600.00	28.38	85.13	66.91	10.932	−179.61	−145.42	52.97
700.00	30.36	89.66	69.85	13.872	−179.84	−139.70	43.61
800.00	31.98	93.83	72.59	16.992	−180.00	−133.95	36.59
900.00	33.32	97.67	75.16	20.259	−180.09	−128.19	31.13
1000.00	34.44	101.24	77.59	23.648	−180.12	−122.41	26.75
1100.00	35.4	104.6	79.9	27.14	−180.10	−116.66	23.18
1200.00	36.2	107.7	82.1	30.72	−180.0	−110.9	20.19
1300.00	36.9	110.6	84.2	34.38	−180.0	−105.1	17.67
1400.00	37.5	113.4	86.2	38.10	−179.9	−99.3	15.51
1500.00	38.0	116.0	88.1	41.88	−179.8	−93.6	13.64

accidentally symmetric top. Structural parameters were assumed [57], since there are no direct experimental data. The structural parameters of CFH_2CF_3 were obtained by correlation of trends in observed properties of other fluoro- and chloromethanes and ethanes, and are listed in table 4–1. The calculated principal and reduced moments of inertia are also tabulated.

The molecule of CFH_2CF_3 belongs to the C_s point group. In a far-infrared spectrum of the gas, Danti and Wood [57] observed four low-frequency bands. Edgell, Riethof, and Ward [58] observed both the infrared spectrum of the gas and the Raman spectrum of the liquid and then made a complete assignment of the vibrational fundamentals. Nielsen and Halley [59], who seemed unaware of the work by Edgell et al., also observed an infrared spectrum of the gas and Raman spectra of the gas and the liquid. However, only two strong sharp bands were found in the Raman spectrum of gas. The conflicting assignments [58, 59], as shown in table 4–2, led us to make an extensive analysis of vibrational modes for halogenated methanes and ethanes. It is possible that the band at 1431 cm^{-1} in the gas infrared may shift to 1459 cm^{-1} in the liquid Raman spectrum [58], but it seems more appropriate to consider them as two different fundamentals corresponding to 1427 cm^{-1} and 1461 cm^{-1} [59]. The very weak band at 1067 cm^{-1} [58] may be due to an impurity. The assignment of the two bands at 972.4 cm^{-1} and 908 cm^{-1} [58] should be exchanged so that they are the CC stretching mode of a' symmetry and the CH_2 rocking mode of a'' symmetry. Similarly the assignment of the 407 cm^{-1} and 358 cm^{-1} bands should be exchanged so that they are the CCF deformation of a' and the CF_3 rocking of a'' symmetry, respectively. It is not known why the infrared peak at 1375 cm^{-1}, which is in excellent agreement with 1374 cm^{-1} [58], was not chosen [59]. This band may either represent the CF_3 stretching of a'' or the CH_2 twisting of a'', though the wavenumber

TABLE 4.1. The selected molecular and chemical constants of 1,1,1,2-tetrafluoroethane

Property	Quantity	Property	Quantity
Molecular weight	102.032	Principal moments of inertia	
Symmetry number	3	I_A, g cm^2	155.1×10^{-40}
Structural parameters [a]		I_b, g cm^2	306.9×10^{-40}
C—F (CF_3)	1.335	I_C, g cm^2	304.3×10^{-40}
C—F (CFH_2)	1.39	Vibration fundamentals, cm^{-1}	
C—H	1.09	Symmetry species a'	2984, 1464, 1427, 1298,
C—C	1.525		1103, 973, 842, 665, 549,
∠FCF	108.0[b]		408, 225
∠FCC (CF_3)	110.9	Symmetry species a''	3013, 1374, 1182, 885, 539,
∠FCC (CFH_2)	109.7		352, 120[c]
∠HCH	108.8	Barrier height V_3, cal mol^{-1}	4428
∠HCC	109.8	Enthalpy of formation	
Reduced moment of inertia, g cm^2	26.06×10^{-40}	ΔHf° (g, 298.15), kcal mol^{-1}	−216.1

[a] Bond distances in 10^{-8} cm and bond angles in degrees.

[b] Calculated value.

[c] Torsional mode.

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

Mode no.	Symmetry class	Reference					Selected[a]
		[57]	[58]		[59]		
		Infrared (g)	Infrared (g)	Raman (ℓ)	Infrared (g)	Raman (ℓ)	
		Wavenumber in cm^{-1}					
ν_1	a'		2984	2989	2984	2990[b]	2984
ν_2	a'		1431	1459	1464	1461	1464
ν_3	a'		1296	1284	1427	1428	1427
ν_4	a'		1096	1084	1298	1290	1298
ν_5	a'		1067	1061	1103	1081	1103
ν_6	a'		908		972	968	972
ν_7	a'		843.5	837	843	839[c]	842
ν_8	a'		666.2	660	665	663	665
ν_9	a'		550.2	548	549	548	549
ν_{10}	a'	409		358	408	410	408
ν_{11}	a'	225	201				225
ν_{12}	a''		3015	3030	3013	2990	3013
ν_{13}	a''		1374	1389	1182	1178	1374
ν_{14}	a''		1189	1173	665	663	1182
ν_{15}	a''		972.4	968	539	534	885
ν_{16}	a''		541.4		352	358	539
ν_{17}	a''	350		407			352
ν_{18}[d]	a''	120 ± 2		124			120

[a] The assignments [58, 59] are so inconsistent that the selection of vibrational fundamentals is explained in the text.

[b] A strong sharp band at 2984 cm^{-1} was observed in the Raman spectrum of gas.

[c] A strong sharp band at 841 cm^{-1} was observed in the Raman spectrum of gas.

[d] Torsional mode.

seems slightly, but not unreasonably, high. As was indicated [59], 665 cm^{-1} was assumed to be a superimposition of a' and a'' and so was 225 cm^{-1}. However, it was also indicated [59] that one of the three weak bands near 1065, 885, and 770 cm^{-1} should replace the a'' fundamental at 665 cm^{-1}. The CH_2 rocking mode of a'' is most likely at 885 cm^{-1} which may be equivalent to 908 cm^{-1} [58]. The superimposed a'' band at 225 cm^{-1} should be dropped since the bands at 539 and 352 cm^{-1} represent the CF_3 deformation and the CF_3 rocking, respectively. The final selected vibrational fundamentals are shown in table 4–2.

In a far-infrared spectrum Danti and Wood [57] first observed the torsional mode for the 0–1 transition at 120±2 cm^{-1} which has been selected and leads to a barrier height of 4428 cal mol^{-1} with our value for the reduced moment. The torsional fundamental has also been estimated from a liquid Raman [58] and a gas infrared [60, 61] spectrum. Table 4–3 summarizes the reported values of the observed torsional fundamental, the derived barrier height and the corresponding reduced moment.

TABLE 4–3. Reduced moment of inertia, torsional fundamental and barrier height [a] of 1,1,1,2-tetrafluoroethane

I_r, g cm^2 × 10^{40}	Reference	ν_{18}, cm^{-1}	V_3, cal mol^{-1}	Reference
25.24 [b]	[57]	120±2	(4200±150)	[57]
		124		[58]
26.22 [c]		124 [d]	(4577)	[e]
24.77 [f]		111	(3650±100)	[60, 61]
26.06	This work	120	(4428)	This work

[a] Values in parentheses were derived from the corresponding reduced moments and torsional fundamentals. In addition, 3620 cal mol^{-1} was estimated [18] from semi-empirical procedures [27].

[b] Calculated from an assumed structure.

[c] Calculated from the similar structural parameters [57].

[d] Adopted from ref. [58].

[e] Ward, C. R., and Ward, C. H., J. Mol. Spectrosc. **12**, 289 (1964).

[f] Calculated from F = 1.13 cm^{-1}.

No experimental measurements of the enthalpy of formation for CFH_2CF_3 have been found. It has been shown experimentally [55] that ΔHr° [(4–1), 298.15] = −15.3±1.6 kcal rather than a value of 0.0±1.0 kcal, which would be expected from Benson's group additivity [62].

$$CH_3CH_3\,(g) + CF_3CF_3\,(g) \rightarrow CF_3CH_3\,(g) + CF_3CH_3\,(g) \qquad (4\text{–}1)$$

$$CFH_2CH_3\,(g) + CF_3CF_3\,(g) \rightarrow CFH_2CF_3\,(g) + CF_3CH_3\,(g) \qquad (4\text{–}2)$$

$$CF_2HCH_3\,(g) + CF_3CF_3\,(g) \rightarrow CF_2HCF_3\,(g) + CF_3CH_3\,(g) \qquad (4\text{–}3)$$

This breakdown of additivity could be due to nonadditive dipole-dipole interactions between the very polar CF_3 and the CH_3 moieties. Indeed, the enthalpy of reaction (4–1) has been qualitatively accounted for [55] on this basis. Similarly ΔHr° [(4–3), 298.15] = 1.6±1.7 kcal may be derived using selected data from this work. It is readily seen that such dipole-dipole interactions become less important in the reaction series (4–1) to (4–3) in good accord with these data. Thus, we have estimated ΔHr° [(4–2), 298.15] = 0.5 {ΔHr° [(4–1), 298.15] + ΔHr° [(4–3), 298.15]} = −8.5 kcal. This leads to ΔHf° (CFH_2CF_3, g, 298.15) = −214.1±2 kcal mol^{-1} which has been adopted in this work. This interpolation procedure was also tested on the selected values for the enthalpy of formation for the analogous chloroethanes [2] and good agreement was obtained between the estimated and selected values of ΔHf° ($CClH_2CCl_3$, g, 298.15).

Ideal gas thermodynamic functions for CFH_2CF_3 have been calculated and are given in table 4–4. There are no experimental values of C_p° and S° available to make comparisons.

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

T	C_p°	S°	$-(G^\circ-H_0^\circ)/T$	$H^\circ-H_0^\circ$	ΔHf°	ΔGf°	log Kf
K	cal K^{-1} mol^{-1}			kcal mol^{-1}			
0	0	0	0	0	−211.41	−211.41	∞
100.00	11.07	59.18	50.11	0.908	−212.68	−207.97	454.52
150.00	13.47	64.12	53.98	1.521	−213.11	−205.53	299.45
200.00	15.93	68.33	57.05	2.255	−213.49	−202.94	221.76
273.15	19.46	73.82	60.82	3.550	−213.96	−198.99	159.22
298.15	20.62	75.58	61.99	4.051	−214.10	−197.46	144.74
300.00	20.70	75.70	62.07	4.090	−214.11	−197.52	143.89
400.00	24.90	82.25	66.31	6.376	−214.55	−191.92	104.86
500.00	28.23	88.18	70.10	9.040	−214.84	−186.23	81.40
600.00	30.76	93.56	73.57	11.995	−215.00	−180.49	65.74
700.00	32.70	98.46	76.78	15.172	−215.08	−174.72	54.55
800.00	34.20	102.92	79.77	18.520	−215.09	−168.96	45.16
900.00	35.40	107.02	82.58	22.002	−215.04	−163.19	39.63
1000.00	36.36	110.81	85.21	25.591	−214.95	−157.43	34.41
1100.00	37.2	114.3	87.7	29.27	−214.8	−151.7	30.14
1200.00	37.8	117.6	90.1	33.02	−214.7	−146.0	26.58
1300.00	38.4	120.6	92.3	36.83	−214.5	−140.2	23.58
1400.00	38.9	123.5	94.4	40.69	−214.4	−134.5	21.00
1500.00	39.3	126.2	96.4	44.60	−214.2	−128.8	18.77

TABLE 5–1. The selected molecular and chemical constants of pentafluoroethane

Property	Quantity	Property	Quantity
Molecular weight	120.022	Principal moments of inertia	
Symmetry number	3	I_A, g cm^2	227.367×10^{-40}
Structural parameters [a]		I_B, g cm^2	346.826×10^{-40}
C—F (CF_3)	1.335	I_C, g cm^2	418.355×10^{-40}
C—F (CF_2)	1.345	Reduced moment of inertia, g cm^2	55.278×10^{-40}
C—H	1.100 [b]	Vibrational fundamentals, cm^{-1}	
C—C	1.520	Symmetry species a'	3008, 1393, 1309, 1218,
∠FCF (CF_3)	108.14		1111, 867, 725, 577, 523,
∠FCF (CF_2H)	109.06		361, 246
∠FCH	109.30 [c]	Symmetry species a''	1359, 1198, 1145, 508,
∠FCC (CF_3)	110.77 [c]		413, 216, 82 [d]
∠FCC (CF_2H)	109.58	Barrier height V_3, cal mol^{-1}	4338
∠HCC	110.00 [b]	Enthalpy of formation	
		$\Delta Hf°$ (g, 298.15), kcal mol^{-1}	−264.0

[a] Bond distances in 10^{-8} cm and bond angles in degrees.
[b] Assumed value [63].
[c] Calculated value.
[d] Torsional mode.

6. Pentafluoroethane

Tipton, Britt, and Boggs [63] determined the molecular structure of CF_2HCF_3 by fitting the observed rotational constants obtained from the microwave spectrum. By use of the most recent fundamental physical constants [3], the principal moments and the reduced moment of inertia have been derived, respectively, from the rotational constants and the structural parameters [63]. The recommended values are given in table 5–1.

The molecule CF_2HCF_3 has C_s symmetry. Gas-phase infrared and Raman spectra and a liquid-phase infrared spectrum were observed by Nielsen, Claassen, and Moran [64]. A study in the far-infrared region for the gaseous compound was reported by Brown, Claque, Heitkamp, Koster, and Danti [65]. An infrared spectrum of the gas and Raman and infrared spectra of the liquid were examined by Kinumaki and Kozuka [18]. The selected values for the vibrational fundamentals are listed in table 5–1. Nielsen's [64] values have been selected for the ten higher fundamentals. Brown's et al. [65] values have been selected for the lower fundamentals except for the CF_2 rocking (ν_{17}) and torsion (ν_{18}) fundamentals for which Kinumaki and Kozuka's values [18] have been selected.

The torsional fundamental was determined from the intensity ratio of the ground-state and excited-state transitions in a microwave spectrum [63]. The determination of this mode from an infrared spectrum of the gas [60] was also reported [61]. Taking into consideration the overlap of higher transitions (1 2, 2 3, . . .), the 0 1 torsional transition was assigned at 74.2 cm^{-1} which is higher by 0.8 cm^{-1} than the actually measured absorption maximum (73.4 cm^{-1}) in the far-infrared spectrum [65]. However, Kinumaki and Kozuka [18] observed the torsional band with its center at 82 cm^{-1} and the absorption maximum of the lower wing at 74 cm^{-1} in an infrared spectrum of the gas. We have thus selected 82 cm^{-1} as the torsional fundamental and derived $V_3=4338$ cal mol^{-1} with the use of the reduced moment of this work. The values of the torsional fundamental and the reduced moment together with the derived barrier height are given in table 5–2.

TABLE 5–2. Reduced moment of inertia, torsional fundamental and barrier height [a] of pentafluoroethane

I_r, g cm$^2\times10^{40}$	Reference	ν_{18}, cm^{-1}	V_3, cal mol^{-1}	Reference
55.445	[63]	73.4 ± 0.2 [b]	(3510 ± 100)	[63]
?		74.2	(3350)	[65]
c		82	(4400)	[18]
55.54 [d]		75.5	(3700 ± 100)	[60, 61]
55.278	This work	82	(4338)	This work

[a] Values in parentheses were derived from the corresponding reduced moments and torsional fundamentals. In addition, 4020 cal mol^{-1} was estimated [18] from semi-empirical procedures [27].
[b] Adopted from Clague, A. D. H., and Danti, A., Proc. Int. Symp. Mol. Struct. Spectros., Columbus, Ohio, 1965. The actual band at 74 ± 10 cm^{-1} was observed.
[c] Presumably the structural parameters of ref. [63] were used.
[d] Calculated from F = 0.504 cm^{-1}.

Ferguson and Whittle [54] measured equilibrium constants for reaction (5–1) and derived a second-law enthalpy of reaction $\Delta Hr°=5.8\pm0.2$ kcal at 746.15 K from their data and that of an earlier work [66].

$$CF_3CF_2Br\ (g)+HBr\ (g)\rightarrow CF_3CF_2H\ (g)+Br_2\ (g) \qquad (5\text{–}1)$$

The integration of $\Delta C_p°$ converts $\Delta Hr°$ (746.15) to $\Delta Hr°$ (298.15) $=6.4\pm0.2$ kcal. Values of $C_p°$ for CF_3CF_2H from this work and for Br_2 and HBr from [67] were used while the heat capacity of CF_3CF_2Br was estimated by Benson's group additivity procedure [62, 68]. On the other hand, Lacher, Casali, and Park [69] measured $\Delta Hr^\circ = -38.35 \pm 0.65$ kcal for the gas-phase reaction (5–2) at 376.15 K.

$$CF_2CF_2\,(g) + Br_2\,(g) \rightarrow CF_2BrCF_2Br\,(g) \qquad (5\text{–}2)$$

Values of C_p° for CF_2CF_2 are available [67]. In the same way, we have calculated ΔHr° (298.15) $= -38.26 \pm 0.65$ kcal for the reaction (5–2). Accepting ΔHf° (CF_2CF_2, g, 298.15) $= -157.4 \pm 0.7$ kcal mol^{-1} [67] and ΔHf° (Br_2, g, 298.15) $= 7.39$ kcal mol^{-1} [53], ΔHf° (CF_2BrCF_2Br, g, 298.15) $= -188.3 \pm 1$ kcal mol^{-1} was obtained. One can estimate ΔHf° (CF_3CF_2Br, g, 298.15) $= \frac{1}{2}[\Delta Hf^\circ$ (CF_3CF_3, g, 298.15) $+ \Delta Hf^\circ$ (CF_2BrCF_2Br, g, 298.15)$] = -254.6 \pm 0.9$ kcal mol^{-1}. This leads to ΔHf° (CF_3CF_2H, g, 298.15) $= -264.3 \pm 0.9$ kcal mol^{-1} using ΔHf° (HBr, g, 298.15$= -8.7$ kcal mol^{-1} and ΔHr° (298.15) for the reaction (5–1). Recently, $\Delta Hr^\circ = 16.18 \pm 0.78$ kcal was measured [70] for the reaction (5–3) at 518.15 K.

$$CF_3CF_2I\,(g) + I\cdot(g) \rightarrow CF_3CF_2\cdot(g) + I_2\,(g) \qquad (5\text{–}3)$$

The value of ΔHr° (518.15) was corrected to ΔHr° (298.15) $= 16.44 \pm 0.78$ kcal and from ΔHf° (CF_3CF_2I, g, 298.15) $= -239.7 \pm 1.0$ kcal mol^{-1} [70] one obtained ΔHf° ($CF_3CF_2\cdot$, g, 298.15) $= -212.66 \pm 1.3$ kcal mol^{-1}. Taking ΔHf° (H$\cdot$, g, 298.15) $= 52.095$ kcal mol^{-1} [20] and the bond-dissociation energy $D(CF_3CF_2\text{—}H) = 103.0 \pm 1$ kcal mol^{-1} [71], one can calculate ΔHf° (CF_3CF_2H, g, 298.15) $= -263.6 \pm 1.6$ kcal mol^{-1}. This value is in good agreement with -264.3 ± 0.9 kcal mol^{-1}. Therefore the weighted average of the two results, ΔHf° (CF_3CF_2H, g, 298.15) $= -264.0 \pm 1.1$ kcal mol^{-1} was selected. The value -266.5 kcal mol^{-1} predicted from the triatomic additivity procedure [23] seems slightly too high. These enthalpy data are summarized in table 5–3.

The calculated ideal gas thermodynamic functions are given in table 5–4. No experimental values of C_p° and S° are available for comparisons.

TABLE 5–3. Enthalpy of formation data for pentafluoroethane

Primary data		Auxiliary data		ΔHf°(g, 298.15) kcal mol^{-1}
ΔHr° in kcal for reaction	Reference	ΔHf°(g, 298.15) in kcal mol^{-1}	Reference	
ΔHr° (g, 376.15)[a] $= -38.35 \pm 0.65$ for	[69]	ΔHf° (CF_2CF_2) $= -157.4 \pm 0.7$	[67]	
$CF_2CF_2 + Br_2 \rightarrow CF_2BrCF_2Br$		ΔHf° (Br_2) $= 7.39$	[53]	
ΔHr° (g, 746.15)[b] $= 5.8 \pm 0.2$ for	[54]	ΔHf° (HBr) $= -8.7$	[53]	
$CF_3CF_2Br + HBr \rightarrow CF_3CF_2H + Br_2$				-264.3 ± 0.9
ΔHr° (g, 518.15)[c] $= 16.18 \pm 0.78$ for	[70]	ΔHf° (H$\cdot$) $= 52.095$	[20]	
$CF_3CF_2I + I\cdot \rightarrow CF_3CF_2\cdot + I_2$		$D(CF_3CF_2\text{—}H) = 103 \pm 1$	[71]	-263.6 ± 1.6

[a] Corrected to ΔHr° (g, 298.15) $= -38.26 \pm 0.65$ kcal.
[b] Corrected to ΔHr° (g, 298.15) $= 6.4 \pm 0.2$ kcal.
[c] Corrected to ΔHr° (g, 298.15) $= 16.44 \pm 0.78$ kcal.

Selected value: -264.0 ± 1.1

TABLE 5–4. Ideal gas thermodynamic functions for pentafluoroethane

T	C_p°	S°	$-(G^\circ - H_0^\circ)/T$	$H^\circ - H_0^\circ$	ΔHf°	ΔGf°	log Kf
K	cal K^{-1} mol^{-1}			kcal mol^{-1}			
0	0	0	0	0	−261.69	−261.69	∞
100.00	12.14	61.44	51.82	0.962	−262.87	−257.58	562.94
150.00	15.10	66.92	55.97	1.643	−263.27	−254.84	371.31
200.00	17.93	71.66	59.31	2.469	−263.57	−251.99	275.36
273.15	21.69	77.81	63.46	3.921	−263.91	−247.69	198.18
298.15	22.88	79.76	64.74	4.478	−264.00	−246.00	180.32
300.00	22.97	79.90	64.84	4.520	−264.01	−246.09	179.28
400.00	27.20	87.11	69.52	7.036	−264.26	−240.08	131.17
500.00	30.50	93.55	73.69	9.929	−264.37	−234.02	102.29
600.00	32.94	99.34	77.49	13.107	−264.37	−227.94	83.03
700.00	34.76	104.56	80.99	16.496	−264.31	−221.88	69.27
800.00	36.12	109.30	84.24	20.043	−264.20	−215.82	58.96
900.00	37.17	113.61	87.27	23.710	−264.06	−209.78	50.94
1000.00	37.98	117.57	90.10	27.469	−263.88	−203.75	44.53
1100.00	38.6	121.2	92.8	31.30	−263.7	−197.8	39.29
1200.00	39.2	124.6	95.3	35.19	−263.5	−191.8	34.93
1300.00	39.6	127.8	97.7	39.13	−263.3	−185.8	31.24
1400.00	40.0	130.7	99.9	43.11	−263.1	−179.8	28.07
1500.00	40.3	133.5	102.1	47.12	−262.9	−173.9	25.34

TABLE 6–1. The selected molecular and chemical constants of hexafluoroethane

Property	Quantity	Property	Quantity
Molecular weight	138.012	Reduced moment of inertia, g cm^2	73.265×10^{-40}
Symmetry number	18	Vibrational fundamentals, cm^{-1}	
Structural parameters [a]		Symmetry species a_{1g}	1228, 807, 348
C—F	1.32	Symmetry species a_{1u}	71 [b]
C—C	1.56	Symmetry species a_{2u}	1117, 714
∠FCF	109.44 [c]	Symmetry species e_g	1250, 619, 372
∠FCC	109.5	Symmetry species e_u	1251, 520, 220
Principal moments of inertia		Barrier height V_3, cal mol^{-1}	4300
$I_A=I_B$, g cm^2	452.82×10^{-40}	Enthalpy of formation	
I_C, g cm^2	176.49×10^{-40}	$\Delta Hf°$ (g, 298.15), kcal mol^{-1}	−320.9

[a] Bond distances in 10^{-8} cm and bond angles in degrees.

[b] Torsional mode.

[c] Calculated value.

7. Hexafluoroethane

The molecular structure of C_2F_6 was studied by electron diffraction techniques [30, 33, 72]. The analysis of the electron diffraction data measured by Swick and Karle [72] with a sector microphotometer was considered to be more reliable and their structural parameters have been selected. The derived principal and reduced moments of inertia are given in table 6–1.

The C_2F_6 molecule belongs to the D_{3d} point group. The Raman spectra of liquid [73] and gas [74] and infrared spectra of the gas [75–79] were investigated. Vibrational assignments, including the calculated torsional fundamental, were given [80] from an analysis of all the reported spectral data. Shimanouchi [14] critically reviewed the specific references [77, 80] together with his earlier theoretical work and selected wavenumbers for the vibrational fundamentals that have been adopted in this work and are given in table 6–1.

As a result of the symmetry of C_2F_6, its torsional mode is inactive. The barrier height to internal rotation has been estimated to be approximately 4000 cal mol^{-1} from electron-diffraction studies [33, 72]. Karle [81] reanalyzed his earlier work [72] and proposed a barrier height of 4300 cal mol^{-1}. In a normal coordinate treatment [80], the torsional mode, $\nu_4 = 68$ cm^{-1}, was calculated from $V_3 = 3920$ cal mol^{-1} which was estimated [77] from spectral data, an assumed structure and a third-law entropy [82]. A torsional fundamental at about 88 cm^{-1} has been estimated from coherent neutron scattering data [61] for the gas but was not considered to be accurate. On the basis of the observed [82] and calculated entropies, we have selected $V_3 = 4300$ cal mol^{-1} and derived $\nu_4 = 71$ cm^{-1} from our adopted structure. Table 6–2 summarizes the values of the torsional fundamental, barrier height and reduced moment.

TABLE 6–2. Reduced moment of inertia, torsional fundamental and barrier height [a] of hexafluoroethane

I_r, g cm$^2\times10^{40}$	Reference	ν_4, cm^{-1}	V_3, cal mol^{-1}	Reference
			~4000	[33]
			~4000	[72]
			4300	[81]
		~88		[61]
		68 [b]		[14, 80]
73.265	This work	71	4300	This work

[a] Values estimated from theoretical and semi-empirical procedures are not included in the table. V_3=4350 cal mol^{-1} was obtained either from spectroscopic and thermodynamic data [82] or from semi-empirical procedures [18, 27]. With spectral data and an assumed molecular structure V_3 = 3920 cal mol^{-1} was obtained [77] from the third-law entropy value [82].

[b] Calculated from a normal coordinate analysis.

Sinke [83] used a platinum-lined combustion bomb to study the reaction (6–1) at 298.15 K.

$$CF_3CF_3\,(g)+2/3\;NF_3\,(g)\rightarrow 2\;CF_4\,(g)+1/3\;N_2\,(g) \qquad (6\text{–}1)$$

The bomb was pre-charged with 99.995 mol percent hydrogen to a pressure of 800 torr and then successively charged with purified CF_3CF_3 to a total pressure of 1270 torr and 99.9 mol percent NF_3 to a total pressure of 2300 torr. No more than 0.05 mol percent of the original CF_3CF_3 and NF_3 in the reaction products was detected with infrared and mass spectroscopy. Experiments were adjusted to yield the same final amount of HF so that the uncertainty in thermochemistry for HF was eliminated. Sinke found the energy change $\Delta Ur°$ (g, 298.15) = − 104.3 ± 1 kcal and the enthalpy change $\Delta Hr°$ (g, 298.15) = − 103.9 ± 1 kcal for the reaction (6–1). Using $\Delta Hf°$ (NF_3, g, 298.15) = −31.43±0.3 kcal mol^{-1} [67] and $\Delta Hf°$(CF_4, g, 298.15) = −223.02±0.2 kcal mol^{-1} [1], a value of $\Delta Hf°$ (CF_3CF_3, g, 298.15) = − 321.2 ± 1.1 kcal mol^{-1} was obtained. From a study of the gas-phase equilibrium

$$CF_3CF_3\,(g)+Br_2\,(g)\rightarrow 2CF_3Br\,(g) \qquad (6\text{–}2)$$

Coomber and Whittle [66] obtained $\Delta Hr°$ (g, 298.15) = 3.66 ± 0.14 kcal using a third-law treatment. They also measured the equilibrium constant for the reaction (6–3) and derived $\Delta Hr°$ (g, 298.15) = − 4.59 ± 0.25 kcal by a third-law treatment:

$$CF_3H\,(g) + Br_2\,(g) \rightarrow CF_3Br\,(g) + HBr\,(g) \qquad (6\text{–}3)$$

Using $\Delta Hf°$ (CF_3H, g, 298.15) = − 165.7 ± 1 kcal mol^{-1} [1] and $\Delta Hf°$ (Br_2, g, 298.15) = −7.39 kcal mol^{-1} and $\Delta Hf°$ (HBr, g, 298.15) = − 8.7 kcal mol^{-1} [53], we have calculated $\Delta Hf°$ (CF_3Br, g, 298.15) = − 154.2 ± 1 kcal mol^{-1}. On the other hand, Ferguson and Whittle [54] studied the kinetic data for the reactions (6–3) and (6–4) to obtain the bond-dissociation energies $D(CF_3H)$ = 106.7 ± 0.5 kcal mol^{-1} and $D(CF_3 - Br)$ = 70.6 ± 1.0 kcal mol^{-1} from which $\Delta Hr°$ (g, 298.15) = 36.1 ± 1.1 kcal was derived for the reaction (6–5).

$$CF_3Br + Br\cdot \rightarrow CF_3\cdot + Br_2 \qquad (6\text{–}4)$$

$$CF_3H + Br\cdot \rightarrow CF_3Br + H\cdot \qquad (6\text{–}5)$$

We have calculated $\Delta Hf°$ (CF_3Br, g, 298.15) = −155.0 ± 1.5 kcal mol^{-1}, using $\Delta Hf°$ (Br ·, g, 298.15) = 26.7 kcal mol^{-1} [68] and $\Delta Hf°$ (H ·, g, 298.15) = 52.095 kcal mol^{-1} [20]. The weighted average of − 154.2 ± 1 and − 155.0 ± 1.5 kcal mol^{-1} gives $\Delta Hf°$ (CF_3Br, g, 298.15) = −154.5 ± 1.2 kcal mol^{-1} and the $\Delta Hr°$ for the reaction (6–2) then leads to $\Delta Hf°$ (CF_3CF_3, g, 298.15) = − 320.1 ± 2.4 kcal mol^{-1}. We have thus selected the weighted average, $\Delta Hf°$ (CF_3CF_3, g, 298.15) = − 320.9 ± 1.5 kcal mol^{-1}. The enthalpy data are shown in table 6–3.

The calculated ideal gas thermodynamic functions have been tabulated in table 6–4. The third-law entropies

TABLE 6–3. Enthalpy of formation data for hexafluoroethane

Primary data		Auxiliary data		
$\Delta Hr°$ in kcal for reaction	Reference	$\Delta Hf°$ (g, 298.15) in kcal mol^{-1}	Reference	$\Delta Hf°$ (g, 298.15) in kcal mol^{-1}
$\Delta Hr°$ (g, 298.15) = −103.9 ± 1 for		$\Delta Hf°$ (NF_3) = −31.43 ± 0.3	[67]	
$CF_3CF_3 + \frac{2}{3} NF_3 \rightarrow 2CF_4 + \frac{1}{3} N_2$	[83]	$\Delta Hf°$ (CF_4) = −223.02 ± 0.2	[1]	$\Delta Hf°$ (CF_3CF_3) = −321.2 ± 1.1
$\Delta Hr°$ (g, 298.15) = −4.59 ± 0.25 for		$\Delta Hf°$ (CF_3H) = −165.7 ± 1	[1]	
$CF_3H + Br_2 \rightarrow CF_3Br + HBr$	[66]	$\Delta Hf°$ (Br_2) = 7.39	[53]	
		$\Delta Hf°$ (HBr) = −8.7	[53]	$\Delta Hf°$ (CF_3Br) = −154.2 ± 1
$\Delta Hr°$ (g, 298.15) = 36.1 ± 1.1 for		D (CF_3—H) = 106.7 ± 0.5	[54]	
$CF_3H + Br \rightarrow CF_3Br + H$	[54]	D (CF_3—Br) = 70.6 ± 1.0	[54]	
		$\Delta Hf°$ (H) = 52.095	[20]	$\Delta Hf°$ (CF_3Br) = −155.0 ± 1.5
		$\Delta Hf°$ (Br) = 26.7	[68]	
$\Delta Hr°$ (g, 298.15) = 3.66 ± 0.14 for		$\Delta Hf°$ (CF_3Br) = −154.5 ± 1.2	−154.2 ± 1 and	
$CF_3CF_3 + Br_2 \rightarrow 2CF_3Br$	[66]	(weighted average)	−155.0 ± 1.5	$\Delta Hf°$ (CF_3CF_3) = −320.1 ± 2.4

Selected value: $\Delta Hf°$ (CF_3CF_3)^{a} = −320.9 ± 1.5

[a] Weighted average of −321.2 ± 1.1 and −320.1 ± 2.4 kcal mol^{-1}.

TABLE 6–4. Ideal gas thermodynamic functions for hexafluoroethane

T	C_p°	$S°$	$-(G°-H_0^\circ)/T$	$H°-H_0^\circ$	$\Delta Hf°$	$\Delta Gf°$	log Kf
K	cal K^{-1}mol^{-1}			kcal mol^{-1}			
0	0	0	0	0	−318.91	−318.91	∞
100.00	12.71	59.32	49.47	0.985	−320.04	−313.71	685.61
150.00	16.30	65.15	53.75	1.711	−320.41	−310.47	452.34
200.00	19.72	70.32	57.26	2.613	−320.67	−307.11	335.59
273.15	24.10	77.13	61.69	4.220	−320.87	−302.11	241.72
298.15	25.43	79.30	63.07	4.839	−320.90	−300.15	220.02
300.00	25.52	79.46	63.17	4.886	−320.90	−300.27	218.74
400.00	30.01	87.45	68.26	7.673	−320.92	−293.38	160.29
500.00	33.29	94.52	72.82	10.847	−320.80	−286.51	125.23
600.00	35.60	100.80	76.97	14.298	−320.60	−279.67	101.87
700.00	37.23	106.42	80.78	17.945	−320.36	−272.87	85.19
800.00	38.40	111.47	84.31	21.729	−320.09	−266.10	72.69
900.00	39.24	116.04	87.59	25.613	−319.81	−259.37	62.98
1000.00	39.87	120.21	90.64	29.570	−319.52	−252.65	55.22
1100.00	40.3	124.0	93.51	33.58	−319.2	−246.0	48.88
1200.00	40.7	127.6	96.20	37.64	−319.0	−239.3	43.59
1300.00	41.0	130.8	98.74	41.72	−318.7	−232.7	39.12
1400.00	41.2	133.9	101.14	45.84	−318.4	−226.1	35.30
1500.00	41.4	136.7	103.42	49.97	−318.2	−219.5	31.98

[82] of S° (g, 176.61) = 67.92 ± 0.20 and S° (g, 194.87) = 69.88 ± 0.20 cal K^{-1} mol^{-1} are within the experimental uncertainty of our calculated values of 67.97 and 69.81 cal K^{-1} mol^{-1}, respectively.

8. Conclusion

The vibrational fundamentals selected by Shimanouchi [14] were adopted for the calculation of thermodynamic properties of C_2H_5F and, except for the torsional mode, of C_2F_6. Whenever possible, fundamental frequencies for the other compounds were based on observed spectral data. Conflicting assignments have been published for CF_3CH_3 and CF_3CFH_2.

The only thermodynamic data available for comparisons are the third-law entropies of CF_3CH_3 of Russell et al. [40] and CF_3CF_3 of Pace and Aston [82]. Our calculated values agree well within experimental uncertainties.

The principal sources of error in the calculated values of the ideal gas heat capacity and related thermodynamic properties at temperatures below about 700 K arise from the uncertainties in the assignments of the low-frequency normal modes of vibration and the potential barriers to internal rotation. Table 7 summarizes the effect of an uncertainty in the potential barrier. It tabulates the change in the various thermodynamic properties which results from a decrease of 200 cal mol^{-1} in the height of the potential barrier. At any given temperature, these effects depend primarily on the height of the barrier. Thus, the effects are similar for the three compounds, fluoroethane, 1,1-difluoroethane, and 1,1,1-trifluoroethane and for the three compounds, 1,1,1,2-tetrafluoroethane, pentafluoroethane, and hexafluoroethane. Average values for these two groups are shown in the table.

As the temperature increases, errors resulting from the assumption of the harmonic-oscillator rigid-rotor model become more important.

TABLE 7. Effect of a decrease of 200 cal mol^{-1} in the potential barriers to internal rotation on the calculated ideal gas thermodynamic properties

T	δC_p°	$\delta(H^\circ - H_0^\circ)$	δS°	$\delta(G^\circ - H_0^\circ)/T$
K	cal K^{-1} mol^{-1}	cal mol^{-1}	cal K^{-1} mol^{-1}	cal K^{-1} mol^{-1}
Fluoroethane, 1,1-difluoroethane, 1,1,1-trifluoroethane				
200	0.045	7.3	0.065	−0.028
400	−0.024	9.5	0.079	−0.055
900	−0.053	−17	0.036	−0.055
1500	−0.027	−41	0.015	−0.042
1,1,1,2-tetrafluoroethane, pentafluoroethane, hexafluoroethane				
200	0.015	3.6	0.050	−0.032
400	0.008	6.9	0.060	−0.043
900	−0.049	−12	0.041	−0.054
1500	−0.031	−38	0.019	−0.044

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