Thermodynamic Quantities of Two Halogenated Propanes

C. L. ANGELL
Union Carbide Research Institute, Tarrytown, New York.

Specific heats, enthalpies, entropies, and free energies in the ideal-gas approximation were calculated for the temperature range 200–500° K. for $CH_3CF_2CF_3$ and $Cl(CF_2)_3Cl$ on the basis of assumed molecular dimensions and conformations and of values for the fundamental frequencies of vibration of the molecules as deduced from their infrared and Raman spectra.

1,1,1,2,2-PENTAFLUOROPROPANE (CH_3-CF_2CF_3) and 1,3-dichloro-hexafluoropropane ($ClCF_2CF_2CF_2Cl$) are of interest as refrigerants. For this purpose the thermodynamic properties, especially the gas-phase heat capacities in the temperature range of their proposed use, are needed. These can be obtained from direct *P*-*V*-*T* and heat capacity measurements on the gas phase, but these measurements are involved and time consuming. Another method is to start with the ideal gas heat capacities calculated by statistical mechanical methods. For this all the fundamental modes of vibrations of the molecule are needed as well as the moments of inertia, symmetry, and molecular weight.

Infrared spectra (vapor, from 4000 cm.$^{-1}$ to 150 cm.$^{-1}$) for the first compound and infrared (vapor, 4000 to 300 cm.$^{-1}$) and Raman spectra (liquid, 3600 to 100 cm.$^{-1}$) for the second were determined by V.A. Yarborough and H. F. White of the Union Carbide Technical Center (*14*) and by W.G. Fateley and F.A. Miller of the Mellon Institute (*3*). From these data, and from similar data on related compounds reported in the literature, all the fundamental vibrational frequencies of the two molecules were established. Heat capacity, enthalpy, entropy, and free energy contributions were calculated for the temperature range 200° to 500° K. by standard statistical mechanical methods

Table I. Infrared Spectrum and Assignment of $CH_3CF_2CF_3$

Frequency in cm.$^{-1}$	Intensity[a]	Assignment	
3030[b]	s	ν_2, ν_{15}	CH_3 stretching assym.
2967[b]	w	ν_3	CH_3 stretching sym.
2584	w	$\nu_{22} + \nu_{16} = 2582$	
2415	w	$2 \times \nu_{22} = 2424$	
2320	w	$\nu_6 + \nu_{12} = 2325$	
2160	w	$\nu_6 + \nu_{21} = 2170$	
1980	w	$\nu_{22} + \nu_{21} = 1985$	
1887	w	$\nu_7 + \nu_{12} = 1893$	
1802	w	$\nu_{22} + \nu_{17} = 1809$	
1700	w	$\nu_{12} + \nu_{21} = 1701$	
1567	w	$\nu_{12} + \nu_4 = 1566$	
1527	w	$\nu_{12} + \nu_{17} = 1525$	
1466[b]	s doublet	ν_5, ν_{11}	CH_3 deformation assym.
1397[b]	vs PQR	ν_6	CH_3 deformation sym.
1370[b]	vs	ν_{16}	CF_3 stretching sym.
1280[b]	s	ν_{10}, ν_{23}	CF_3 stretching assym.
1212[b]	vvs	ν_{22}	CF_2 stretching assym.
1129[b]	vs PQR	ν_1	CF_2 stretching sym.
965[b]	vs PQR	ν_7	CH_3 rocking
928[b]	vs PQR	ν_{12}	CH_3 rocking
890[b]	w	ν_8	C—C stretching assym.
773[b]	s PQR	ν_{21}	C—C stretching sym.
668	w sh	$2 \times \nu_{20} = 672$	
638[b]	vs PQR	ν_4	CF_2 deformation
597[b]	m	ν_{17}, ν_{24}	CF_3 deformation assym.
510[b]	vs	ν_{13}	CF_2 twisting
		ν_{18}	CF_3 deformation sym.
447	w		
373			
364[b]	m PQR	ν_{19}, ν_{25}	CF_2 rocking
355			
345			
336[b]	m PQR	ν_{20}, ν_{26}	CF_3 rocking
330			
219[b]	m PQR	ν_{14}	CH_3 torsion

[a] s = strong; m = medium; w = weak. [b] Fundamentals.

(*4*). The harmonic oscillator-rigid rotator approximation was used and the Einstein functions were obtained from a computer program.

By making use of heat capacities of related compounds found in the literature, a principle of homology was also applied to the estimation of the subject heat capacities. The results are in pleasingly satisfactory agreement with the values calculated as above.

ASSIGNMENT OF FUNDAMENTAL VIBRATIONS

A literature search revealed complete assignments of vibrational frequencies for the following compounds: CH_3CF_3 (*11*), CF_3-CF_3 (*8*), CF_2Cl-CF_2Cl (*10*), CF_3CF_2-Cl (*2*, *8*), and CF_3-CF_2CF_3 (*6*). These values were used to estimate frequencies for the two compounds under study.

For compound I ($CH_3CF_2CF_3$) the molecular symmetry is C_s and the expected fundamental vibrations are given in the last column of Table I (numbering corresponds to propane). For compound II ($ClCF_2CF_2CF_2Cl$) a number of rotational isomers are possible. It was felt that of these the gauche-gauche form would be the most stable, and all calculations were carried out for it. The symmetry is C_2 and the fundamental vibrations are given in Table II.

The spectra and assignments are given in Tables I and II. These include all fundamental frequencies with the exception of C-C-C bending and the torsional vibrations. For the first the arbitrary value of 100 cm.$^{-1}$ was used for both compounds. This value is lower than any of the frequencies observed in the spectra; it is also subject to considerable error. For the torsions the following values were arrived at by analogy: methyl torsion 219 cm.$^{-1}$ (from CH_3-CF_3) (*5*), fluoromethyl torsion 70 cm.$^{-1}$ (from CF_3CF_3) (*8*), and CF_2Cl torsion 80 cm.$^{-1}$ (from CF_3-CF_2Cl) (*10*). (Further considerations of the restricted rotation of these groups is given below.)

Products of moments of inertia were calculated using the following bond-lengths:

C-H = 1.085A
C-C = 1.54 A
C-F = 1.33 A
C-Cl = 1.74 A

Table II. Infrared and Raman Spectra and Assignment of $Cl(CF_2)_3Cl$

Raman (Liquid)		Infrared (Vapor)			
Frequency, cm.$^{-1}$	Intensity[a]	Frequency cm.$^{-1}$	Intensity[a]	Assignment	
		2487	w	$\nu_2 + \nu_{22} = 2485$	
		2392	w	$2 \times \nu_{22} = 2406$	
		2325	w		
		2252	w	$\nu_{16} + \nu_1 = 2253$	
		1923	w	$\nu_2 + \nu_4 = 1923$	
		1894	w	$\nu_{15} + \nu_4 = 1889$	
		1862	w	$\nu_{16} + \nu_{10} = 1865$	
		1802	w	$\nu_{22} + \nu_5 = 1803$	
		1782	w	$\nu_3 + \nu_{23} = 1779$	
		1724	w	$\nu_3 + \nu_{10} = 1726$	
		1585	w	$\nu_{19} + \nu_{16} = 1595$	
		1527	w	$2 \times \nu_{23} = 1538$	
		1504	w	$\nu_2 + \nu_{20} = 1509$	
		1422	w	$\nu_1 + \nu_{17} = 1421$	
1287[b]	s	1282[b]	w	ν_2	C—F(CF_2Cl) stretching assym.
1261[b]	s	1258[b]	m	ν_{15}	C—F(CF_2Cl) stretching assym.
1195[b]	m	1203[b]	vvs	ν_{22}	C—F(CF_2) stretching assym.
		1149[b]	vs	ν_{16}	C—F(CF_2Cl) stretching sym.
1102[b]	w	1105[b]	s	ν_1	C—F(CF_2) stretching sym.
		1070	w	$\nu_7 + \nu_4 = 1074$	
1012[b]	m	1010[b]	m	ν_3	C—F(CF_2Cl) stretching sym.
982	w	990	m	$\nu_{19} + \nu_{13} = 991$	
		906	w	$\nu_{10} + \nu_{26} = 907$	
		875	w	$\nu_8 + \nu_{26} = 884$	
844[b]	w	845[b]	vs	ν_{21}	C—C stretching assym.
766[b]	w	769[b]	vvs	ν_{23}	C—Cl stretching
716[b]	vvs			ν_{10}	C—Cl stretching
696[b]	vvs	693[b]	w	ν_8	C—C stretching sym.
684	w			$\nu_5 + \nu_{14} = 684$	
670	w			$\nu_{19} + \nu_{20} = 673$	
641[b]	w	641[b]	s	ν_4	CF_2 deformation
604[b]	w	600[b]	s	ν_5, ν_{11}	$CF_2(CF_2Cl)$ deformation
591	w			$\nu_8 - \nu_9 = 596$	
576	w				
548[b]	m	545[b]	w	ν_{13}	CF_2 twisting
508[b]	w	508[b]	w	ν_6, ν_{18}	$CF_2(CF_2Cl)$ twisting
446[b]	vvvs			ν_{19}, ν_{25}	CF_2 rocking
435[b]	sh	433[b]	m	ν_7, ν_{12}	CF_2 (CF_2Cl) rocking
376	w	376	w	$2 \times \nu_{26} = 382$	
365	w			$\nu_{19} - \nu_{14} = 366$	
338	w			$\nu_{19} - \nu_9 = 346$	
322	sh	321	w	$\nu_{20} + \nu_9 = 327$	
316[b]	vs			ν_{17}	C—Cl in-plane bending
290[b]	w	not measured		ν_{24}	C—Cl in-plane bending
227[b]	vvs	not measured		ν_{20}	C—Cl out-plane bending
191[b]	m	not measured		ν_{26}	C—Cl out-plane bending

[a] s = strong; m = medium; w = weak. [b] Fundamentals.

All angles were assumed to be tetrahedral. The resulting values are:

$I_aI_bI_c = 60{,}429{,}486 \times 10^{-120}$ g.^{3} cm.^{6} for $CH_3CF_2CF_3$ and
$I_aI_bI_c = 851{,}345{,}083 \times 10^{-120}$ g.^{3} cm.^{6} for $ClCF_2CF_2CF_2Cl$.

Table III and IV list, at 10° intervals from 200° to 500° K., the following quantities: heat content, heat capacity, free energy, and entropy.

RESTRICTED ROTATION

In both compounds there is a possiblity of restricted rotation of the end groups. Contributions to various thermodynamic quantities due to these motions can be estimated using tables given by Pitzer and Gwinn (*9*). To use these a number of quantities had to be calculated and these are given in Table V.

From Pitzer and Gwinn's tables the following values were found for the heat capacity contributions:

	CH_3	CF_3	Total for $CH_3CF_2CF_3$
at 200° K.	1.74	2.10	3.84 (3.57)
at 298.15° K.	2.08	2.26	4.34 (3.76)
at 600° K.	2.03	2.16	4.19 (3.92)

	CF_2Cl	Total for $ClCF_2CF_2CF_2Cl$
at 200° K.	2.05	4.10 (3.86)
at 295.15° K.	2.10	4.20 (3.92)
at 600° K.	2.30	4.60 (3.96)

The values in brackets are heat capacity contributions due to the two torsional vibrations as calculated by the Einstein functions for the two molecules. The formulae of Pitzer and Gwinn are strictly true only for two rotating groups with no interaction between them. In the molecules under study this is not very likely; therefore, it is felt that the restricted rotation values serve as estimates for a maximum contribution rather than true contributions to the heat capacities.

ADDITIVITY OF HEAT CAPACITIES

Masi and coworkers (7) have found that in the series CF_4 CF_3-CF_3, CF_3—CF_2—CF_3 there is a nearly constant increment in heat capacity per mole for each added CF_2 group. In the present work an attempt was made to apply the same principle to the molecules under study.

Heat capacities at 25° C., in cal. deg.$^{-1}$ mole^{-1}:

CF_3-CF_3 (*13*)	25.2
CF_3-CF_2-CF_3 (*7*)	35.27
CF_2 increment	35.3–25.2 = 10.1
CH_3CF_3 (*12*)	18.7
$CH_3CF_2CF_3$, by homology	18.7 + 10.1 = 28.8
(Compare Table III	28.71)

A similar argument is used in the case of $Cl(CF_2)_3Cl$:

CF_3-CF_3	25.2
CF_3-CF_2Cl (*1, 8*)	26.34
Increment: Cl substituted for F	1.1
$CF_3CF_2CF_3$	35.27
$CF_2ClCF_2CF_2Cl$, assuming additivity	35.3 + 2 × 1.1 = 37.5
(Compare Table IV	37.28)

While it is realized that these estimates by homology can be only approximate, the good agreement between values obtained by the two methods lends confidence that the tentative heat capacities given in Tables III and IV are not greatly in error. It is felt that the error in the heat capacity values is not more than 0.5 units. The other quantities, however, depend much more on the low frequencies, which are the most likely to be wrong; the following errors are estimated for these quantities: enthalpy 1.0 unit, free energy 2.0 units and entropy 3.0 units. Therefore, it is imperative that direct measurements be made if

Table III. Thermodynamic Functions for $CH_3CF_2CF_3$

(cal. deg.$^{-1}$ mole^{-1})

T, ° K	$(H^\circ - H_0^\circ)/T$ (vib)	C_p°	$-(F^\circ - H_0^\circ)/T$ (vib)	S° (vib)	$(H^\circ - H_0^\circ)/T$	C_p°	$-(F^\circ - H_0^\circ)/T$	S°
200	6.28	13.88	4.49	10.77	14.23	21.83	61.85	76.08
210	6.66	14.63	4.81	11.47	14.61	22.58	62.55	77.16
220	7.04	15.37	5.13	12.17	14.98	23.32	63.24	78.23
230	7.41	16.10	5.45	12.87	15.36	24.05	63.92	79.28
240	7.79	16.82	5.77	13.57	15.74	24.77	64.58	80.32
250	8.17	17.52	6.10	14.27	16.11	25.47	65.23	81.35
260	8.54	18.22	6.42	14.97	16.49	26.17	65.87	82.36
270	8.91	18.90	6.75	15.67	16.86	26.85	66.50	83.36
280	9.28	19.57	7.08	16.37	17.23	27.52	67.12	84.35
290	9.65	20.23	7.42	17.07	17.59	28.18	67.73	85.33
300	10.01	20.88	7.75	17.76	17.96	28.83	68.33	86.29
310	10.37	21.52	8.08	18.46	18.32	29.47	68.93	87.25
320	10.73	22.14	8.42	19.15	18.68	30.09	69.51	88.20
330	11.08	22.76	8.76	19.84	19.03	30.71	70.09	89.13
340	11.44	23.36	9.09	20.53	19.38	31.31	70.67	90.06
350	11.78	23.95	9.43	21.22	19.73	31.90	71.23	90.97
360	12.13	24.53	9.77	21.90	20.08	32.47	71.80	91.88
370	12.47	25.09	10.10	22.58	20.42	33.04	72.35	92.78
380	12.81	25.64	10.44	23.26	20.76	33.59	72.90	93.67
390	13.15	26.18	10.78	23.93	21.10	34.13	73.44	94.55
400	13.48	26.71	11.11	24.60	21.43	34.66	73.98	95.42
410	13.81	27.23	11.45	25.27	21.76	35.18	74.52	96.28
420	14.14	27.73	11.79	25.93	22.08	35.68	75.04	97.13
430	14.46	28.22	12.12	26.59	22.41	36.17	75.57	97.98
440	14.78	28.71	12.46	27.24	22.73	36.65	76.09	98.82
450	15.09	29.17	12.80	27.89	23.04	37.12	76.60	99.65
460	15.40	29.63	13.13	28.54	23.35	37.58	77.11	100.47
470	15.71	30.08	13.47	29.18	23.66	38.03	77.62	101.28
480	16.01	30.51	13.80	29.82	23.96	38.46	78.12	102.08
490	16.31	30.94	14.13	30.45	24.26	38.89	78.61	102.88
500	16.61	31.35	14.47	31.08	24.56	39.30	79.11	103.67
298.15	9.94	20.76	7.69	17.64	17.89	28.71	68.22	86.12

Table IV. Thermodynamic Functions for $Cl(CF_2)_3Cl$

(cal. deg.$^{-1}$ mole^{-1})

T, °K.	$(H^\circ - H_0^\circ)/T$ (vib)	C_p°(vib)	$-(F^\circ - H_0^\circ)/T$ (vib)	S°(vib)	$(H^\circ - H_0^\circ)/T$	C_p°	$-(F^\circ - H_0^\circ)/T$	S°
200	9.31	20.22	6.70	16.01	17.26	28.17	66.80	84.06
210	9.85	21.28	7.16	17.02	17.80	29.23	67.65	85.46
220	10.39	22.30	7.63	18.03	18.34	30.25	68.49	86.84
230	10.93	23.30	8.11	19.05	18.88	31.25	69.32	88.21
240	11.47	24.27	8.59	20.06	19.42	32.22	70.13	89.56
250	12.00	25.21	9.06	21.07	19.95	33.16	70.94	90.89
260	12.53	26.12	9.55	22.08	20.48	34.07	71.73	92.21
270	13.05	27.00	10.03	23.08	21.00	34.95	72.51	93.51
280	13.56	27.86	10.51	24.08	21.51	35.81	73.29	94.80
290	14.07	28.68	11.00	25.07	22.02	36.63	74.05	96.07
300	14.57	29.47	11.48	26.06	22.52	37.42	74.81	97.33
310	15.06	30.24	11.97	27.04	23.01	38.19	75.55	98.57
320	15.55	30.98	12.45	28.01	23.50	38.93	76.29	99.79
330	16.03	31.70	12.94	28.97	23.97	39.65	77.02	101.00
340	16.50	32.39	13.43	29.93	24.45	40.33	77.74	102.19
350	16.96	33.05	13.91	30.88	24.91	41.00	78.46	103.37
360	17.42	33.69	14.40	31.82	25.37	41.64	79.17	104.54
370	17.86	34.31	14.88	32.75	25.81	42.25	79.87	105.69
380	18.30	34.90	15.36	33.67	26.25	42.85	80.56	106.82
390	18.74	35.47	15.84	34.59	26.69	43.42	81.25	107.94
400	19.16	36.02	16.32	35.49	27.11	43.97	81.93	109.05
410	19.58	36.55	16.80	36.39	27.53	14.50	82.61	110.14
420	19.99	37.06	17.28	37.27	27.94	45.01	83.28	111.22
430	20.39	37.56	17.75	38.15	28.34	45.51	83.94	112.29
440	20.79	38.03	18.23	39.02	28.74	45.98	84.59	113.34
450	21.18	38.49	18.70	39.88	29.13	46.44	85.24	114.38
460	21.56	38.93	19.17	40.73	29.51	46.88	85.89	115.40
470	21.93	39.35	19.64	41.57	29.88	47.30	86.53	116.41
480	22.30	39.76	20.10	42.41	30.25	47.71	87.15	117.41
490	22.66	40.15	20.57	43.23	30.61	48.10	87.79	118.40
500	23.01	40.53	21.03	44.05	30.96	48.48	88.41	119.38
298.15	14.48	29.33	11.39	25.87	22.42	37.28	74.67	97.10

Table V. Calculated Quantities for Use with Values from Pitzer and Quinn (9).

Quantity	$CH_3CF_2CF_3$		$ClCF_2CF_2CF_2Cl$
I_x	304.04×10^{-40} g. cm.^{2}		707.44×10^{-40} g. cm.^{2}
I_y	445.30		1104.77
I_z	446.34		1089.28
	CH_3	CF_3	CF_2Cl
V (potential barrier) calories	3660	3900	7000
angle with X axis	66°26′	3°34′	39°30′
angle with Y axis	90°	90°	71°10′
angle with Z axis	23°34′	86°26′	55°
reduced moment I_m	5.21×10^{-40}	76.08×10^{-40}	176.07×10^{-40} g. cm.^{2}

values reliable to within less than the above errors are needed.

In the case of $Cl(CF_2)_3Cl$, the heat capacity and enthalpy are independent of molecular configuration, but the entropy and free energy depend on it significantly (through terms involving symmetry and product of inertia). Experimental measurement of these quantities, therefore, would give useful information about the molecular configuration of this compound.

LITERATURE CITED

(1) Aston, J.G., Wills, P.E., Zolki, T.P., *J. Am. Chem. Soc.* **77**, 3939 (1955).

(2) Barcelo, J.R., *J. Res. Natl. Bur. Std.* **44**, 521 (1950).

(3) Fateley, W.G., Miller, F.A., unpublished work.

(4) Herzberg, G., "Infrared and Raman Spectra of Polyatomic Molecules," Chap. V. 1, D. Van Nostrand, New York, 1945.

(5) Luft, N.W., *J. Phys. Chem.* **59**, 92 (1955).

(6) Mallory, H.D., Ph.D. thesis, State University of Iowa, Iowa City, Iowa, 1950.

(7) Masi, J.F., Flieger, H.W., Wicklund, J.S., *J. Res. Natl. Bur. Std.* **52**, 283 (1954).

(8) Nielsen, J.R., Liang, C.Y., Smith, R.M., Smith, D.C., *J. Chem. Phys.* **21**, 283 (1953).

(9) Pitzer, P.S., Gwinn, W.D., *J. Chem. Phys.* **10**, 428 (1942).

(10) Simpson, D., Plyler, E.K., *J. Res. Natl. Bur. Std.* **50**, 223 (1953).

(11) Smith, D.C., Saunders, R.A., Nielsen, J.R., Ferguson, E.E., *J. Chem. Phys.* **20**, 847 (1952).

(12) Vanderkooi, W.N., De Vries, T., *Ibid.* **60**, 636 (1956).

(13) Wicklund, J.S., Flieger, H.W., Masi, J.F., *J. Res. Natl. Bur. Std.* **51**, 91 (1953).

(14) Yarborough, V.A., White, H.F., unpublished work.

RECEIVED for review February 11, 1964. Accepted April 2, 1964.