Part III

Thermodynamic Functions for Freon 113

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Thermodynamic functions, C_p^0, S_t^0, $(H^0 - H_0^0)/T$, $-(F^0 - H_0^0)/T$, have been calculated for Freon 113 in the ideal gas state at 1 atm. pressure. The internal rotational contribution has been treated in two ways: by the Lielmezs-Bondi approximate method and with Pitzer-Gwinn's computed value of internal rotational partition function. The agreement between the computed results and the few available experimental vapor state heat capacity values, is satisfactory.

RECENT AVAILABILITY of molecular structural (*4, 6, 10*) and spectrographic (*4, 6*) data has made possible the calculation of thermodynamic functions, C_p^0, S_t^0, $(H^0 - H_0^0)/T$, and $-(F^0 - H_0^0)/T$ for Freon 113 (1,1,2 trifluoro - 1,2,2-trichloroethane equilibrium mixture of trans and skew form isomers) in the ideal gas state at 1 atm. pressure.

Table I presents the thermodynamic functions calculated by two methods: the Lielmezs-Bondi approximate method (*7*) and Pitzer and Gwinn's (*8*) computed values of internal rotation partition functions.

To obtain the tabulated thermodynamic function values, a digital computer program was written (*5*) for use of the Lielmezs and Bondi method as well as for the calculation of Planck-Einstein functions coupled with the classical translational and rotational degrees of freedom.

The results presented in Table I, calculated by the Lielmezs-Bondi approximate method, are correlated into Equation 1:

$$\Lambda = a + bT + cT^2 + dT^3 + eT^4 \qquad (1)$$

where Λ is the thermodynamic function and T the temperature in °K. The constants, a, b, c, d, e, associated with Equation 1, were evaluated by means of a digital computer program based upon least squares curve-fitting methods (*5*) and are given in Table II.

The use of Equation 1 can cause a maximum deviation of $\pm 0.03\%$ in the C_p^0 value, and a $\pm 0.005\%$ change in the free energy, enthalpy, and entropy functions from those shown in Table I, calculated by means of the Lielmezs-Bondi method.

Table III gives molecular parameters used in the above thermodynamic function calculations. The value of the reduced moment of inertia, I_{red}, appearing in Table III, was calculated from Equation 2 (*2, 10*).

$$I_{\text{red}} = I_m\left[1 - \sum_{i=1}^{3} \frac{\alpha_i^2 I_m}{I_i}\right]_{(i = A,B,C)} \qquad (2)$$

where $I_m = I_{\text{CF}_2\text{Cl}} = 26.91 \times 10^{-39}$ gram cm.^{2}, the moment of inertia of the rotating top; and where [compare with (*6*)] the principal moments of inertia:

$$I_A = 6.067 \times 10^{-38} \text{ gram cm.}^2$$
$$I_B = 7.690 \times 10^{-38} \text{ gram cm.}^2$$
$$I_C = 8.112 \times 10^{-38} \text{ gram cm.}^2$$

with the following values of α_i^2, the square of the directional cosine:

$$\alpha_A^2 = 0.9820, \qquad \alpha_B^2 = 0, \qquad \alpha_C^2 = 0.018$$

The harmonic oscillator approximation—i.e., Equation 3:

$$\nu_{\text{torsional}} = \frac{n_m}{2\pi}\left(\frac{V_0}{2I_{\text{red}}}\right)^{1/2} \qquad (3)$$

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Table I. Freon 113 (CCl_2F-CF_2Cl) Thermodynamic Functions

Temperature, ° K.	C_p^0, Cal./Mole – ° K.		$(H^\circ - H_0^0)/T$ Cal./Mole – ° K.		$-(F - H_0^0)/T$ Cal./Mole – ° K.		S_t^0, E.U.	
	L-B[a]	P-G[b]	L-B[a]	P-G[b]	L-B[a]	P-G[b]	L-B[a]	P-G[b]
298.16	30.29	30.23	19.87	19.49	72.90	73.19	92.78	92.68
400	34.14	34.22	23.06	22.80	79.20	79.38	102.26	102.18
500	36.67	36.87	25.55	25.30	84.63	84.82	110.18	110.12
600	38.88	38.64	27.56	27.46	89.47	89.61	117.03	117.07
700	39.57	39.83	29.20	29.11	93.84	93.93	123.04	123.04
800	40.42	40.72	30.55	30.48	97.84	97.96	128.34	128.44
900	41.04	41.37	31.68	31.61	101.50	101.65	133.18	133.26
1000	41.50	41.84	32.64	32.58	104.89	105.09	137.53	137.67

[a] L-B, Lielmezs-Bondi approximate method (*7*). [b] P-G, Pitzer and Gwinn's tables (*8*), corrected for the asymmetrical top contribution (*3*).

Table II. Calculated Constants

Function	a	$b \times 10^1$	$c \times 10^4$	$d \times 10^7$	$e \times 10^{11}$
C_p^0	6.591519	1.231554	−1.823443	1.313835	−3.728515
$\frac{H - H_0^0}{T}$	5.089414	0.673871	−0.711699	0.416322	−1.029523
$-\frac{F^0 - H_0^0}{T}$	48.094506	1.037721	−0.820581	0.475549	−1.247483
S_t^0	53.153489	1.713581	−1.536518	0.895449	−2.287244

Table III. Molecular Parameters

Frequencies in wave numbers, ν(cm.$^{-1}$) (*4, 6*)

Trans form:

80[a], 183, 203, 251, 288, 314, 350, 373, 392, 437, 460, 507, 651, 816, 909[b], 1041, 1114, 1179

Skew form:

80[a], 168, 203, 240, 288, 309, 350, 373, 391, 442, 460, 531, 631, 816, 927[b], 1047, 1119, 1212

Moment of inertia product:

Skew form:

$I_A I_B I_C = 391{,}933 \times 10^{-117}$ gram^3 cm.^{6} (footnote *c*)

Trans form:

$I_A I_B I_C = 378{,}512 \times 10^{-117}$ gram^3 cm.^{6} (footnote *c*)

Reduced moment of inertia:

$I_{\text{red}} = 150.3 \times 10^{-40}$ gram cm.^{2}

Isomerization energy:

$\Delta E_{\text{iso}} = 350$ cal./mole (*4*)

Estimated energy of internal rotational barrier:

$V_0 = 10.9$ kcal./mole

Symmetry number:

$\sigma = 1$

Number of rotational minima:

$n_m = 3$ (assumed threefold internal rotational barrier)

Molecular weight:

187.375 grams/mole

Physical constants: reference (*9*)

[a] Torsional frequency, see (*4, 6*). [b] Frequency values suggested by Hallam and Ray (*4*). [c] These moment of inertia product values were calculated using Sutton's proposed structural data (*10*). See also (*6*).

assuming that n_m = 3 (threefold rotational barrier), yields the height of the internal rotational barrier as 10.9 kcal./mole. This approximate value of the relatively high potential energy to the internal rotation is indirectly supported through the recent work by Ward (*11*) on the internal rotational barrier for CF_3CH_2X (X = H,F,Cl,Br,I) molecules.

Comparing the calculated (ideal gas, C_p^0) and the observed (at 85.8 and 134.2° C., vapor, C_p) heat capacity values (*1*), the measured values are lower than the calculated ones, the maximum deviation being 5%. This deviation, however, appears to be within the given calorimetric data accuracy (*1*).

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LITERATURE CITED

(1) Benning, A.F., McHarness, R.C., Markwood, W.H., Jr., Smith, W.J., *Ind. Eng. Chem.* **32**, 976 (1940).

(2) Crawford, B.L., Jr., *J. Chem. Phys.* 8, 273 (1940).

(3) Godnev, I.N., "Calculation of Thermodynamic Functions from Molecular Data," Chapter X, *U.S. At. Energy Comm. Rept.* **AEC-tr-3855**, 1959.

(4) Hallam, H.E., Ray, T.C., *J. Mol. Spectry.* **12**, 69 (1964).

(5) Higgins, E.R., B.A.Sc. thesis, University of British Columbia, Vancouver, 1964.

(6) Klaboe, P., Nielsen, J.R., *J. Mol. Spectry.* **6**, 379 (1961).

(7) Lielmezs, J., Bondi, A.A., "Rotational Isomers in Thermodynamic Calculations," Shell Development Co. Tech. Rept., No. **208-58-R**, 1958.

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

(9) Rossini, F.D., Gucker, F.T., Jr., Johnston, H.L., Pauling, L., Vinal, G.W., *J. Am. Chem. Soc.* 74, 2699 (1952).

(10) "Tables of Interatomic Distances and Configuration in Molecules and Ions," L.E. Sutton, Ed., The Chemical Society, London, 1958.

(11) Ward, C.R., Ward, C.H., *J. Mol. Spectry.* **12**, 289 (1964).

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