NOMENCLATURE

$A_0, B_0, C_0, a, b, c, \alpha, \gamma$ = Benedict-Webb-Rubin constants
P = pressure
R = gas constant
T = temperature
Z = compressibility factor
ρ = density
ρ_c = critical density

LITERATURE CITED

(1) Bartlett, E.P., Cupples, H.L., Tremearne, T.H., *J. Am. Chem. Soc.* **50**, 1275 (1928).
(2) Bartlett, E.P., Hetherington, H.C., Kvalnes, H.M., Tremearne, T.H., *Ibid.*, **52**, 1363 (1930).
(3) Benedict, M., Webb, G.B., Rubin, L.C., *J. Chem. Phys.* **8**, 334 (1940); **10**, 747 (1942).
(4) Benedict, M., Webb, G.B., Rubin, L.C., *Chem. Eng. Prog., Symp. Ser.* **47**, 419 (1951).
(5) Canfield, F.B., Leland, T.W., Kobayashi, R., *Advan. Cryog. Eng.* **8**, 146 (1963).
(6) Crain, R.W., Jr., Sonntag, R.E., *Ibid.*, **11**, 379 (1966).
(7) Friedman, A.S., Ph.D. thesis, Ohio State University, Columbus, Ohio, 1950.
(8) Hirschfelder, J.O., Curtiss, C.F., Bird, R.B., "Molecular Theory of Gases and Liquids," Wiley, New York, 1954.
(9) Lin, M.S., Naphtali, L., *A.I.Ch.E. J.* **9**, 580 (1963).
(10) Michels, A., Wouters, H., De Boer, J., *Physica* **3**, 585 (1936).
(11) Schiller, F.C., Canjar, L.N., *Chem. Eng. Progr., Symp. Ser.* **49**, 67 (1953).
(12) Smith, G.E., Sonntag, R.E., Van Wylen, G.J., *Advan. Cryog. Eng.* **8**, 162 (1963); **9**, 197 (1964).
(13) Stottler, H.H., Benedict, M., *Chem. Eng. Progr., Symp. Ser.* **49**, 25 (1953).
(14) Zudkevitch, D., Kaufmann, T.G., *A.I.Ch.E. J.* **12**, 577 (1966).

RECEIVED for review April 21, 1966. Accepted July 29, 1966.

Thermodynamic Functions for 1,2-Dichloro-1,1-difluoroethane

J. B. CROSS[1] and J. LIELMEZS
Department of Chemical Engineering, The University of British Columbia, Vancouver, B. C., Canada

Thermodynamic functions C_p°, S_T°, $(H^\circ - H_0^\circ)/T$, $-(F^\circ - H_0^\circ)/T$ have been computed for 1,2-dichloro-1,1-difluoroethane in the ideal gas state from 250° to 750° K. at 1 atm. pressure. The restricted internal rotational contribution has been treated in two ways: by the Lielmezs-Bondi approximate method and the conventional treatment of Pitzer and Gwinn. The agreement between the calculated results by both methods is satisfactory.

THE RECENT availability of spectroscopic data for 1,2-dichloro-1,1-difluoroethane (*1, 5, 8*) has made it possible to estimate the thermodynamic functions—heat capacity, enthalpy, entropy, and free energy—for the equilibrium mixture of trans and skew form isomers of this compound in the ideal gas state at 1 atm. pressure. Table I gives the thermodynamic functions calculated by both the Lielmezs-Bondi approximate method (*3, 7, 9, 10*) and the Pitzer and Gwinn (*11, 12*) method corrected for the asymmetrical top contribution (*4*).

To compute the tabulated thermodynamic function values, a digital computer (IBM-7040) program has been coded (*3*) evaluating the reduced moment of inertia (Equation 1), the two Pitzer and Gwinn parameters, V_0/RT and $1/Q_f$,

$$Q_f = \frac{2.7935}{n_m}(I_{\text{red}}10^{38}T)^{1/2},$$

Table I. 1,2-Dichloro-1,1-difluoroethane Thermodynamic Functions

Temperature,	C_p° Cal./Mole – °K.		S_T°, E.U.		$(H^\circ - H_0^\circ)/T$ Cal./Mole – °K.		$-(F^\circ - H_0^\circ)/T$ Cal./Mole – °K.	
°K.	L-B[a]	P-G[b]	L-B[a]	P-G[b]	L-B[a]	P-G[b]	L-B[a]	P-G[b]
250	21.32	...	79.70	...	14.96	...	64.74	...
298.15	23.40	...	83.64	...	16.16	...	67.48	...
350	25.47	25.25	87.56	87.64	17.39	16.74	70.16	70.91
400	27.25	27.10	91.08	91.14	18.52	17.92	72.56	73.22
450	28.81	28.72	94.38	94.43	19.58	19.03	74.80	75.40
500	30.18	30.13	97.49	97.53	20.57	20.07	76.92	77.46
550	31.36	31.36	100.43	100.46	21.50	21.04	78.92	79.42
600	32.40	32.44	103.20	103.24	22.37	21.95	80.83	81.29
650	33.31	33.38	105.83	105.87	23.18	22.79	82.65	83.08
700	34.12	34.22	108.33	108.38	23.93	23.58	84.40	84.79
750	34.83	34.96	110.71	110.76	24.64	24.31	86.08	86.45

[a] L-B, Lielmezs-Bondi approximate method (*9, 10*). [b] P-G, Pitzer and Gwinn tables (*11, 12*) corrected for asymmetrical top contribution (*4*).

---

[1] Present address: Cominco Ltd., Trail, B. C.

Table II. Molecular Parameters

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

Trans form:

126, 177, 195, 284, 325, 423, 560, 761, 785, 855, 891, 968, 1103, 1235, 1303, 1431, 2989, 3036.

Skew form:

126, 177, 195, 284, 314, 430, 578, 661, 768, 819, 891, 1029, 1109, 1250, 1303, 1431, 2979, 3036.

Principal moments of inertia:[a,b]

$I_A = 18.53 \times 10^{-39}$ g. cm.^{2}

$I_B = 64.27 \times 10^{-39}$ g. cm.^{2}

$I_C = 66.49 \times 10^{-39}$ g. cm.^{2}

Moment of inertia product:[a,c]

Trans form:

$I_{ABC} = 79189 \times 10^{-117}$g.^{3} cm.^{6}

Skew form:

$I_{ABC} = 74988 \times 10^{-117}$g.^{3} cm.^{6}

Square of the direction cosine:[a,d]

$\alpha_A^2 = 0.4658$
$\alpha_B^2 = 0$
$\alpha_C^2 = 0.5342$

Moment of inertia of rotating top:[a]

$I_m = I_{\text{ClH}_2} = 16.74 \times 10^{-39}$ g. cm.^{2}

Reduced moment of inertia:[a]

$I_{\text{red}} = 7.44 \times 10^{-39}$ g. cm.^{2}

Isomerization energy:

$\Delta E_{\text{iso}} = 430$ cal./mole (*1, 3*)

Estimated energy of internal rotational barrier (Equation 2):[e]

$V_0 = 13.4$ Kcal./mole

Molecular shape factor:

$\sigma = 1$ (*6*)
$n_m = 3$ (assumed threefold internal rotational barrier)

Physical constants: (*13*).

[a] The following bond lengths were used for calculation: C – C = 1.54A., C – H = 1.09A., C – F = 1.37A., C – Cl = 1.77A. Tetrahedral angles assumed. [b] $I_A = 19.1 \times 10^{-39}$ g. cm.^{2}, $I_B = 64.2 \times 10^{-39}$ g. cm.^{2}, $I_C = 65.9 \times 10^{-39}$ g. cm.^{2}, obtained by Bucker and Nielsen (*1*) from microwave data. [c] Trans form: $I_{ABC} = 80{,}809 \times 10^{-117}$ g.^{3} cm.^{6}, obtained by Bucker and Nielsen (*1*), microwave data. [d] $\alpha_A^2 = 0.453$, $\alpha_B^2 = 0$, $\alpha_C^2 = 0.547$, obtained from microwave data by Bucker and Nielsen (*1*). [e] This value is indirectly supported by Ward and Ward (*14*).

the values of the Planck-Einstein functions coupled with the classical translational, vibrational, and rotational degrees of freedom and the contribution owing to the internal restricted rotation by means of the Lielmezs-Bondi method.

Table II presents molecular parameters used in these thermodynamic function calculations. The value of the reduced moment of inertia, I_{red}, appearing in this table, was calculated from Equation 1 (*2, 4*)

$$I_{\text{red}} = I_m \left[\frac{1 - \sum_i \alpha_i^2 I_m}{I_i} \right]_{i = A, B, C} \tag{1}$$

where I_m is the moment of inertia of the rotating top about the rotational axis, I_A, I_B, I_C are the principal moments of inertia, and α_A, α_B, α_C, are the corresponding directional cosines.

The torsional harmonic oscillator approximation:

$$\nu \text{ torsional} = \frac{n_m}{2\pi} \left(\frac{V_o}{2I_{\text{red}}} \right)^{1/2} \tag{2}$$

yielded the height of the restricted internal rotational barrier as 13.4 kcal. per mole (Table II). This value of the relatively high potential energy barrier height is indirectly supported through recent work by Ward and Ward (*14*). Although there are no available calorimetric data, the over-all agreement of the calculated thermodynamic function properties by two methods suggests that the presented values (Table I) may well be within the bounds of the experimental accuracy.

ACKNOWLEDGMENT

The financial assistance of the National Research Council of Canada is gratefully acknowledged.

LITERATURE CITED

(1) Bucker, H.P., Nielsen, J.R., *J. Mol. Spectry.* **11**, 47 (1963).
(2) Crawford, B.L., Jr., *J. Chem. Phys.* **8**, 273 (1940).
(3) Cross, J.B., unpublished thesis, University of British Columbia, 1966.
(4) Godnev, I.N., "Calculation of Thermodynamic Functions from Molecular Data," Chapter X, *U. S. Atomic Energy Comm. Rept.* **AEC-tr-3855** (1959).
(5) Hallam, H.E., Ray, T.C., *J. Mol. Spectry.* **12**, 69 (1964).
(6) Herzberg, G., "Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, New York (1945).
(7) Higgins, E.R., unpublished thesis, University of British Columbia, 1964.
(8) Klaboe, P., Nielsen, J.R., *J. Mol. Spectry.* **6**, 379, 1961.
(9) Lielmezs, J., Bondi, A.A., "Rotational Isomers in Thermodynamic Calculations," Shell Development Co. Tech. Rept. No. **208-58-R** (1958).
(10) Lielmezs, J., Bondi, A.A., *Chem. Eng. Sci.* **20**, 706 (1965).
(11) Pitzer, K.S., *J. Chem. Phys.* **14**, 239 (1946).
(12) Pitzer, K.S., Gwinn, W.D., *Ibid.*, **10**, 428 (1942).
(13) Rossini, F.D., Gucker, F.T., Jr., Johnston, H.L., Pauling, L., Vinal, G.W., *J. Am. Chem. Soc.* **74**, 2699 (1952).
(14) Ward, C.R., Ward, C.H., *J. Mol. Spectry.* **12**, 289 (1964).

RECEIVED for review May 23, 1966. Accepted October 27, 1966. Presented at the 16th Canadian Chemical Engineering Conference of the Chemical Institute of Canada, October 1966, Windsor, Ontario, Canada.