tert-butyl ether by any of a variety of conventional techniques is well established (22).

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LITERATURE CITED

- (1)Barr-David, F.H., Dodge, B.F., J. Chem. Eng. Data 4, 107 (1959).
- Berman, N.S., McKetta, J.J., J. Phys. Chem. 66, 1444 (1962). (2)
- Beynon, E.T., Jr., McKetta, J.J., Ibid., 67, 2761 (1963). (3)
- (4)Buckley, E., Herington, E.F.G., Trans. Faraday Soc. 61, 1618 (1965)
- Cope, C.S., A.I.Ch.E.J. 10, 277 (1964). (5)
- Cope, C.S., Dodge, B.F., Ibid., 5, 10 (1959). (6)
- Dodge, B.F., "Chemical Engineering Thermodynamics," (7)Chap. 11, McGraw-Hill, New York, 1944. Eberz, W.F., Lucas, H.J., J. Am. Chem. Soc. 56, 1230 (1934).
- (8)
- (9) Green, J.H.S., Trans. Faraday Soc. 59, 1559 (1963).
- (10)
- Green, J.H.S., Quart. Revs. (London) 15, 125 (1961). Janz, G. J., "Estimation of Thermodynamic Properties of (11)
- Organic Compounds," Academic Press, New York, 1958.
- Majewski, F.M., Marek, L.F., Ind. Eng. Chem. 30, 203 (1938). (12)
- (13)(14)
- Nicolini, E., Laffitte, P., Compt. rend. 229, pp.757, 935 (1939). Parks, G.S., Huffman, H.M., "The Free Energies of Some Organic Compounds," A.C.S. Monograph No. 60, p. 124, The Chemical Catalog Co., Inc., New York, 1932.
- Tetrafluoromethane

Thermodynamic Properties of the Real Gas

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The thermodynamic properties, $H = H^{\circ}$, $S = S^{\circ}$, and $G = G^{\circ}$, of tetrafluoromethane were determined as functions of temperatures (0° to $350^\circ\,C.)\,$ and molal density (0.75 to 11.0 gram-moles per liter) over a pressure range of 0 to 400 atm. The analytical and graphical correlating techniques described have produced results that reflect all of the inherent accuracy of the basic data used, and in this sense the values given are useful as comparison standards.

THE thermodynamic properties of compressed gaseous tetrafluoromethane were determined at the Bureau of Mines as part of a larger program (8, 9) to evaluate P-V-T and intermolecular potential energy relationships as well as chemical thermodynamic properties for hydrocarbons, fluorocarbons, and mixtures of hydrocarbons and fluorocarbons

The quantities presented in this paper are the contributions that originated in the intermolecular phenomenon or nonideality of the gas. Thus, to obtain thermodynamic properties for the total or real gas, one must add to the present values the contributions for the ideal gas at the same temperature and at 1-atm. pressure. Spectroscopically based values of the ideal gas have been reported by Nagarajan (13) and by McBride and coauthors (12).

In addition to providing useful information for various direct engineering applications, the present values will qualify, when required, as standards in the sense that they reflect faithfully all of the trends that appear in the experimental data from which they were derived. Because the computations are based directly on unsmoothed experimental compressibility values (8) measured at even temperatures and densities, the introduction of spurious trends from arbitrary smoothing of the basic data was prevented.

- (15) Parks, G.S., Huffman, H.M., Barmore, M., J. Am. Chem. Soc. 55, 2733 (1933).
- Parks, G.S., Manchester, K.E., Thermochem. Bull. I.U.P.A.C. (16)No. 2, 8 (1956).
- Pilcher, G., Pell, A.S., Coleman, D.J., Trans. Faraday Soc. (17)60, 499 (1964).
- Rossini, F.D., et al., U. S. Natl. Bur. Standards Circ. 461, (18)1947.
- Ibid., No. 500 (1952). (19)
- Rossini, F.D., et al., "Selected Values of Physical and Thermo-dynamic Properties of Hydrocarbons and Related (20)Compounds,"(and supplements), A.P.I. Research Project 44, Carnegie Press, Pittsburgh, Pa., 1953.
- Shiffler, W.H., Holm, M.M., Brooke, L.F., Ind. Eng. Chem. (21)31, 1099 (1939).
- (22)Smutny, E.J., Bondi, A.A., J. Phys. Chem. 65, 546 (1961). (23)Stanley, H.M., Youell, J.E., Dymock, J.B., J. Soc. Chem.
- Ind. (London) 53, 205T (1934). Taft, R.W., Jr., Riesz, P., J. Am. Chem. Soc. 77, 902 (1955). (24)

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Many of the numerical calculations were performed on a digital computer; however, a combination of analytical and graphical correlational methods was adopted to ensure full utilization of the inherent accuracy and precision of the experimental results.

Briefly, the approach to the correlations was as follows: First, the temperature-dependent slopes of the experimental isometric lines $(\partial P/\partial T)_{\rho}$, which appear in the integrands for enthalpy and entropy (Equations 1 and 2), were evaluated by fitting analytical functions to them, differentiating the analytic functions with respect to temperature, and adding graphically determined residuals. The integrals that contained $(\partial P / \partial T)$, were then evaluated graphically. Location of the zero density intercepts of the integrals, which usually presents a problem, was accurately placed by a method based on independently derived values of the second virial coefficients and their first derivatives with respect to temperature.

Recently, Chari (7) calculated thermodynamic properties for the saturated liquid and gas, and the superheated gas. However, his calculations for the super-heated gas were based on unpublished values of the P-V-T properties, and it seemed best, therefore, not to make a serious attempt at comparing those results with the currently derived ones.

THERMODYNAMIC RELATIONS

For ease in evaluating thermodynamic properties from isometric data, the functions given for the real gas (1, 4)were converted into forms having density ρ , as the primary variable; thus,

$$H - H^{\circ} = \int_{0}^{\rho} \frac{\left[P - T(\partial P / \partial T)\rho\right] d\rho}{\rho^{2}} + P/\rho - RT$$
(1)

$$S - S^{\circ} = \int_{\tau}^{\rho} \frac{\left[R\rho - (\partial P/\partial T)\rho\right] d\rho}{\rho^2} - R \ln R T\rho$$
(2)

and

$$G - G^{\circ} = \int_{T}^{\rho} \frac{P - RT\rho}{\rho^{2}} \, \mathrm{d}\rho + P/\rho - RT + RT \ln RT\rho \qquad (3)$$

The standard state value indicated by the superscript degree mark as in H° , S° , or G° is for the ideal gas at 1 atm. and is, therefore, a function only of temperature and substance. It is identical to the standard state used by the American Petroleum Institute Research Project 44 on $P \cdot V \cdot T$ Properties (6).

Experimental values of P, T, and ρ used in evaluating the thermodynamic functions were taken from Table I (8). Although the derived values of the functions are tabulated at even values of the Celsius temperature scale, t, °C., all calculations were made with the thermodynamic temperature scale T (2), since thermodynamic derivatives were shown (10) to have small but significant error when computed on the Celsius scale. The most recent definition 0°C. = 273.15° K. was not used because much of the correlational work was already completed on the basis of the older definition (15). The effect on the slope of the isometric lines is very small, about 0.006%, and can, therefore, be neglected for most purposes.

The slopes, $(\partial P/\partial T)_{\rho}$, of the isometric lines appearing in the integrands of the enthalpy and entropy functions were derived from the data by a technique that utilizes the isometric representation of Beattie and Bridgeman (3). The isometric representation was adapted, previously, to our correlation of the thermodynamic properties of perfluorocyclobutane (9). Some variations, described below, were necessary to provide a more precise representation of the tetrafluoromethane results. Following this method, one first "straightens" the isometric lines (Figure 1) by adding to the measured pressure, P, a quantity $c(\Delta p'/\Delta T)_{\rho}/VT^{k}$ in which the best values of c and k are determined for each isometric by an iterative trial-and-error calculation. Differences in



Figure 1. Schematic representation of original and "straightened" isometric

50.00° C.	$G - G^{\circ}$	cal.	1855.2	2019.6	2241.3	2390.1	2500.1	2586.8	2658.1	2718.9	2772.5	2821.2	2866.4	2909.5	2951.5	2993.6	3036.1	3080.4	3126.8	3176.3	3230.0	3288.8	3353.6	3495 E
	$(-(S - S^{\circ}))$	cal./deg.	6.1472	6.7869	7.7281	8.4346	9.0123	9.5084	9.9483	10.3472	10.7154	11.0597	11.3853	11.6963	11.9957	12.2862	12.5698	12.8485	13.1241	13.3982	13.6719	13.9465	14.2229	14 5090
	$(\circ H - H)$ -	cal.	131.2	173.6	256.1	335.6	412.2	485.9	556.7	624.8	690.2	752.8	812.7	870.1	924.9	976.7	1025.8	1071.6	1114.2	1153.3	1188.1	1218.1	1242.5	1960.0
	P,	atm.	18.898	24.792	36.057	46.720	56.893	66.701	76.251	85.656	95.045	104.587	114.393	124.621	135.468	147.186	159.922	174.093	189.908	207.791	228.320	251.970	279.425	311 330
	G – G,	cal.	1689.5	1839.8	2039.9	2171.8	2267.5	2341.6	2401.3	2451.5	2494.9	2533.8	2569.5	2603.1	2635.7	2668.2	2701.1	2735.5	2771.6	2810.5	2853.2	2900.3	2952.9	3019-0
۵C.	$(-(S - S^{\circ}))$	cal./deg.	6.0331	6.6768	7.6254	8.3387	8.9225	9.4243	9.8693	10.2727	10.6446	10.9920	11.3199	11.6325	11.9330	12.2241	12.5080	12.7868	13.0620	13.3354	13.6084	13.8825	14.1587	14 4381
30.00	$-(H - H^{\circ})$	cal.	139.4	184.3	271.8	356.1	437.3	515.4	590.6	662.7	732.0	798.5	862.2	923.3	981.8	1037.5	1090.7	1140.9	1188.2	1232.2	1272.2	1308.2	1339.3	136/ 0
	Ъ,	atm.	17.538	22.923	33.087	42.538	51.387	59.764	67.756	75.520	83.129	90.736	98.470	106.456	114.879	123.929	133.791	144.774	157.077	171.140	187.469	206.428	228.708	954 030
	$G - G^{\circ}$,	cal.	1648.4	1795.1	1989.8	2117.5	2209.6	2280.4	2337.3	2384.8	2425.7	2462.0	2495.3	2526.7	2557.0	2587.1	2617.6	2649.5	2683.1	2719.5	2759.5	2803.6	2853.2	0000
c.	$-(S - S^{\circ}),$	cal./deg.	6.0039	6.6487	7.5996	8.3149	8.9006	9.4040	9.8504	10.2551	10.6281	10.9763	11.3050	11.6182	11.9190	12.2102	12,4942	12.7728	13.0479	13.3211	13.5938	13.8677	14.1438	0201 11
25.00	$-(H - H^{\circ})$,	cal.	141.7	187.3	276.1	361.7	444.2	523.4	599.6	672.8	743.1	810.6	875.3	937.3	996.7	1053.4	1107.6	1158.8	1207.2	1252.3	1293.6	1331.1	1363.8	1201 0
	Ρ,	atm.	17.194	22.453	32.339	41.486	50.000	58.012	65.628	72.967	80.130	87.251	94.473	101.908	109.726	118.131	127.244	137.455	148.916	162.056	177.339	195.101	216.126	941 054
	G – G°,	cal.	1444.8	1573.3	1740.4	1846.4	1920.3	1974.9	2017.2	2051.1	2079.2	2103.4	2124.9	2144.6	2163.4	2182.0	2200.7	2220.3	2241.4	2264.8	2290.9	2320.4	2354.5	0.004 1
0.00° C.	$-(S - S^\circ)$,	cal./deg.	5.8527	6.5046	7.4685	8.1957	8.7923	9.3056	9.7609	10.1735	10.5532	10.9070	11.2399	11.5561	11.8589	12.1512	12.4357	12.7145	12.9893	13.2617	13.5334	13.8063	14.0822	14 2692
	-((<i>H</i> - <i>H</i>)).	cal.	153.9	203.5	299.7	392.4	481.4	567.0	649.1	727.9	803.5	876.0	945.4	1012.0	1075.9	1137.3	1196.2	1252.8	1306.7	1357.8	1405.9	1450.9	1492.2	1590 1
	Ρ,	atm.	15.480	20.086	28.559	36.149	42.974	49.150	54.804	60.039	64.967	69.704	74.369	79.050	83.903	89.061	94.676	100.961	108.149	116.575	126.561	138.458	152.884	170 481
Density.	GMole	Liter	0.75	1.0	51	2.0	2.5	3.0	3.5	4.0	4.5	5.0	5.5	6.0	6.5	7.0	7.5	8.0	8.5	0.6	9.5	10.0	10.5	11.0

Table 1. Gram-Molal Thermodynamic Properties

	$\begin{array}{c} 2713.3\\ 2947.4\\ 3274.4\\ 3274.4\\ 3585.2\\ 3686.6\\ 4074.3\\ 3882.6\\ 4178.2\\ 4178.2\\ 4178.2\\ 4178.2\\ 4178.2\\ 4178.2\\ 4178.9\\$		3614.8 3917.0 4346.9 4346.9 4904.5 5112.8 52915.6 55615.6 55615.6 5761.4 5761.4 5761.4 5761.4 5761.4 5761.4 6314.4 6314.4		4552.3 4922.0 5453.4 55453.4 6156.4 6412.8 6461.2 6661.2 6878.1 7281.1 7274.6 7261.2 7462.2 7465.9
150.00° C.	$\begin{array}{c} 6.6479\\ 7.2766\\ 8.1968\\ 8.1968\\ 9.4439\\ 9.9242\\ 10.7371\\ 10.7371\\ 11.4056\\ 11.4096\\ 11.4096\\ 11.4096\\ 11.4096\\ 11.2348\\ 12.3482\\ 12.3482\\ 11.2348\\ 12.3482\\ 12.3482\\ 11.2348\\ 12.34641\\ 13.7357\\ 13.7557\\ 13.7557\\ 13.7557\\ 13.7557\\ 13.7557\\ 13.7557\\ 13.7557\\ 13.7557\\ 13.7557\\ 13.7557\\ 13.7557\\ 13.7557\\ 13.7557\\ 13.7557\\ 13.7557\\ 1$	250.00° C.	$\begin{array}{c} 7.0554\\ 7.6795\\ 8.5910\\ 9.2699\\ 9.8222\\ 10.29553\\ 10.2147\\ 11.0954\\ 11.4475\\ 11.0954\\ 11.776\\ 11.0954\\ 11.2.9910\\ 12.3912\\ 12.639\\ 12.639\end{array}$	°C.	$\begin{array}{c} 7.3959\\ 8.0178\\ 8.9249\\ 9.59595\\ 10.1478\\ 10.1478\\ 10.6171\\ 11.0328\\ 11.4100\\ 11.7586\\ 11.0328\\ 12.0354\\ 12.3954\\ 12.6921 \end{array}$
	$\begin{array}{c} 99.9\\ 132.0\\ 132.0\\ 132.0\\ 254.3\\ 367.1\\ 367.1\\ 367.1\\ 367.1\\ 367.1\\ 367.1\\ 708.1\\ 775.8\\ 775.8\\ 775.8\\ 775.8\\ 7788.5\\ 78$		$\begin{array}{c} 76.9\\ 101.3\\ 193.0\\ 193.0\\ 234.9\\ 234.9\\ 234.9\\ 310.6\\ 310.6\\ 34.1\\ 374.3\\ 374.3\\ 374.3\\ 401.2\\ 401.2\\ 401.2\\ 458.4\\ 458.4\\ 458.9\end{array}$	350.00	$\begin{array}{c} 57.5\\ 75.4\\ 109.4\\ 1109.4\\ 1140.5\\ 1160.7\\ 1180.7\\ 233.6\\ 233.6\\ 248.0\\ 253.8\\ 265.0\\ 265.0\\ 265.0\\ \end{array}$
	25.625 34.021 50.671 67.233 83.30 100.617 117.715 117.		$\begin{array}{c} 32.289\\ 43.132\\ 65.034\\ 87.334\\ 110.200\\ 113.307\\ 153.307\\ 158.373\\ 183.973\\ 183.973\\ 183.973\\ 3250.100\\ 302.842\\ 333.173\\ 376.424\\ 338.173\\ 376.424\\ \end{array}$		38.921 52.187 79.273 107.240 1107.240 1136.267 1166.267 198.378 198.378 305.438 305.438 305.438 305.660
125.00° C.	$\begin{array}{c} 2494.5\\ 2711.2\\ 2711.2\\ 33012.3\\ 3322.8\\ 3322.8\\ 3518.1\\ 3631.8\\ 3631.8\\ 3631.8\\ 36324.0\\ 33990.6\\ 4147.0\\ 4385.5\\ 4470.2\\ 4559.6\\ 4470.2\\ 4559.6\\ 662.6\\ 455.0\\ 662.6\\ 66$	225.00° C.	3385.8 3671.0 4075.3 4075.3 4596.1 4596.3 4596.3 4596.3 5111.7 5515.7 5515.7 5516.8 5516.8 5516.8 5516.8 5516.8 5516.8 6021.0		4314.9 4667.6 55173.8 5543.6 5543.6 6093.3 6317.0 6521.1 6521.1 6521.1 6692.7 7069.2 7242.3
	6.5328 7.1634 8.7777 9.8.7777 9.8.7777 9.8.7777 9.8.237 9.8237 10.6410 11.3006 11.3006 11.3006 11.3006 11.3006 11.3006 11.3006 11.3006 11.30510 13.3786 13.1047 13.37866 13.37866 13.37866 13.37866 13.37866 13.37866		$\begin{array}{c} 6.9606\\ 7.5855\\ 8.4986\\ 9.1789\\ 9.7326\\ 10.2071\\ 10.2077\\ 11.0098\\ 11.6093\\ 11.6093\\ 11.6093\\ 11.6093\\ 11.6093\\ 12.0093\\ 12.8010\\ 12.8059\\ 1$	325.00° C.	$\begin{array}{c} 7.3159\\ 7.9382\\ 8.8462\\ 9.5217\\ 10.0708\\ 10.5708\\ 10.5477\\ 10.9570\\ 11.3347\\ 11.6338\\ 12.0110\\ 12.3214\\ 12.6186\\ 12.6186\end{array}$
	$\begin{array}{c} 106.7\\ 141.1\\ 141.1\\ 207.8\\ 272.2\\ 272.2\\ 233.4.0\\ 333.4.0\\ 556.1\\ 651.1\\ 734.3\\ 770.1\\ 734.3\\ 770.1\\ 883.7\\ 883.7\\ 888.7$		$\begin{array}{c} 82.2\\ 159.0\\ 159.0\\ 159.0\\ 207.2\\ 207.2\\ 207.2\\ 207.2\\ 207.2\\ 336.2\\ 336.2\\ 336.2\\ 336.2\\ 336.2\\ 336.2\\ 337.2\\ 537.7\\ 537$		$\begin{array}{c} 62.1\\ 81.7\\ 81.7\\ 153.1\\ 153.1\\ 153.1\\ 153.1\\ 213.1\\ 213.1\\ 226.3\\ 223.3\\ 223.3\\ 223.3\\ 302.5\\ 307.2\\ 307.2\\ \end{array}$
	$\begin{array}{c} 23,952\\ 31,725\\ 47.047\\ 62,155\\ 77.175\\ 92,224\\ 107.462\\ 155,832\\ 173,413\\ 107.462\\ 155,832\\ 173,413\\ 192.127\\ 173,413\\ 192.127\\ 2312.147\\ 2312.147\\ 2312.493\\ 3312.493\\ 3312.493\\ 3312.493\\ 3312.441\\ $		30.627 40.860 61.455 82.331 103.639 125.550 1148.22 114.872 136.686 138.696 348.121 386.496 348.121 386.496		37.266 49.924 75.723 1102.278 1189.773 1188.385 219.957 219.957 219.957 219.957 219.957 219.957 219.957 219.957 219.957 219.957 219.353 327.091 368.163
100.00° C.	$\begin{array}{c} 2278.4\\ 2477.8\\ 2477.8\\ 2942.8\\ 3097.9\\ 3395.2\\ 3305.2\\$	200.00° C.	$\begin{array}{c} 3159.2\\ 3427.3\\ 3427.3\\ 3806.0\\ 4076.9\\ 4763.0\\ 5131.7\\ 5131.7\\ 5131.7\\ 5538.8\\ 5538.8\\ 5707.6\\ 5707.6 \end{array}$	300.00° C.	4079.4 4415.3 5246.2 5764.2 5764.7 6344.7 6514.2 6514.2 6514.2 6514.2 6519.3 659.3
	$\begin{array}{c} 6.4113\\7.0726\\7.9726\\9.2340\\9.72340\\9.72340\\9.72340\\10.5430\\10.5430\\11.2439\\11.5654\\11.2439\\11.5654\\11.8731\\11.8731\\11.8731\\11.8731\\11.8731\\11.5654\\11.7406\\11.$		$\begin{array}{c} 6.8614\\ 7.4874\\ 7.4874\\ 9.0846\\ 9.0846\\ 10.5384\\ 10.5384\\ 11.2768\\ 11.2768\\ 11.2768\\ 11.2283\\ 11.2283\\ 11.28657\\ 11.3639\\ 11.3639\\ 13.3583\\ $		$\begin{array}{c} 7.2326\\ 7.8554\\ 7.8554\\ 9.4407\\ 9.4407\\ 9.4407\\ 10.4614\\ 10.8785\\ 11.2571\\ 11.2571\\ 11.2571\\ 11.2571\\ 11.2571\\ 11.2571\\ 11.2571\\ 11.2571\\ 11.2571\\ 11.2571\\ 11.2571\\ 11.2571\\ 11.2571\\ 11.2571\\ 11.2571\\ 12.5464\\ 12$
	$\begin{array}{c} 114.0\\ 150.8\\ 222.3\\ 222.3\\ 257.6\\ 551.4\\ 421.7\\ 701.7\\ 701.7\\ 701.7\\ 701.7\\ 701.7\\ 909.3\\ 909.3\\ 906.1\\ 1000.3\\ 1000.3\\ \end{array}$		87.7 115.8 115.8 170.2 3318.5 362.1 540.4 550.4 566.5 566.5 566.5 566.5 566.7 6602.7 613.7		$\begin{array}{c} 66.8\\ 88.0\\ 1165.9\\ 2200.7\\ 2200.7\\ 2201.7\\ 226$
	$\begin{array}{c} 22.275\\ 29.426\\ 57.049\\ 57.049\\ 70.48\\ 83.789\\ 97.142\\ 110.662\\ 110.662\\ 110.662\\ 110.662\\ 123.853\\ 109.728\\ 169.728\\ 169.728\\ 169.728\\ 169.728\\ 169.728\\ 169.728\\ 169.728\\ 330.330\\ 365.751\\ 365.$		$\begin{array}{c} 28.964\\ 38.585\\ 57.868\\ 77.316\\ 97.066\\ 1117.270\\ 1317.270\\ 1317.270\\ 1317.270\\ 1317.270\\ 1317.270\\ 1317.259\\ 231.582\\ 231.582\\ 231.582\\ 319.607\\ 354.291\\ 319.607\\ 354.291\\ 322.333\\ 319.607\\ 352.333\\ 322.332\\ 322$		$\begin{array}{c} 35.609\\ 47.661\\ 72.165\\ 97.306\\ 123.266\\ 1502.12\\ 178.382\\ 178.382\\ 178.382\\ 207.995\\ 207.995\\ 207.995\\ 308.116\\ 308.116\\ 387.599\end{array}$
75.00° C.	$\begin{array}{c} 2265.3\\ 2245.7\\ 2495.7\\ 2495.7\\ 2665.2\\ 2665.2\\ 2980.6\\ 3054.8\\ 3054.8\\ 3121.1\\$	175.00° C.	$\begin{array}{c} 22334.9\\ 3186.0\\ 3538.9\\ 3538.9\\ 33789.8\\ 33986.3\\ 33986.3\\ 33986.3\\ 34149.6\\ 44149.6\\ 44149.6\\ 44149.5\\ 44149.5\\ 4534.8\\ 4534.8\\ 5158.3\\ 5158.$	275.00° C.	3846.0 4165.0 4950.7 54314.4 5431.4 5634.4 5813.0 6139.0 6289.5 6439.0 6587.1 6587.1
	$\begin{array}{c} 6.2829\\ 6.9188\\ 7.8528\\ 9.1242\\ 9.6147\\ 10.0497\\ 10.0497\\ 10.0497\\ 10.0497\\ 10.0497\\ 11.609\\ 11.1783\\ 11.4739\\ 11.7733\\ 11$		$\begin{array}{c} 6.7573\\ 7.3845\\ 8.3019\\ 8.3019\\ 9.5438\\ 9.5438\\ 9.5438\\ 10.4219\\ 10.4219\\ 10.4219\\ 10.4219\\ 10.6310\\ 11.1873\\ 11.5215\\ 11.1873\\ 11.5215\\ 11.1873\\ 11.5215\\ 11.3385\\ 11.2335\\ 11.2335\\ 11.2335\\ 11.3385\\ 11.3385\\ 11.3385\\ 11.3385\\ 11.3385\\ 11.3385\\ 11.3385\\ 11.3385\\ 11.3385\\ 11.3385\\ 11.3385\\ 11.3385\\ 11.3385\\ 11.3385\\ 11.3385\\ 11.3385\\ 12.3479\\ 13.5756\\ 13.$		$\begin{array}{c} 7.1458\\ 7.7692\\ 8.6792\\ 8.6792\\ 9.3677\\ 9.3796\\ 10.7978\\ 11.1773\\ 11.1773\\ 11.1572\\ 11.1572\\ 11.16572\\ 11.16572\\ 11.16572\\ 11.16572\\ 112.1693\\ 12.1683\\ 12.7570\\ 12.7570\end{array}$
	$\begin{array}{c} 122.1\\ 161.5\\ 312.4\\ 312.4\\ 332.7\\ 332.7\\ 533.7\\ 533.7\\ 551.4\\ 551.4\\ 551.4\\ 700.1\\ 755.4\\ 858.0\\ 969.3\\ 9858.0\\ 949.0\\ 949.0\\ 949.0\\ 949.0\\ 949.0\\ 949.0\\ 949.0\\ 10055.6\\ 11085.8\\ 11085$		93.7 123.7 123.7 182.0 237.8 291.2 291.2 330.6 436.5 556.5 556.5 556.5 556.5 556.5 556.5 556.5 556.5 630.1 636.7 688.3 687.1		$\begin{array}{c} 71.8\\ 94.5\\ 94.5\\ 179.2\\ 217.6\\ 2235.6\\ 315.1\\ 382.5\\ 382.5\\ 336.9\\ 382.5\\ 382.$
	20.591 27.116 39.749 63.709 63.709 63.709 86.735 86.735 121.755 121.755 124.178 192.825 134.178 192.482 192.482 192.482 192.482 192.482 192.482 192.482 192.482 192.482 192.482 192.482 192.482 192.440 342.440 381.498		27.296 36.304 54.274 72.282 90.460 108.963 1127.937 1127.937 1127.937 1127.533 168.020 1189.528 189.528 236.618 232.764 2312.777 232.043 336.107 333.701		33.949 45.398 68.596 92.326 92.326 116.738 116.014 116.014 116.014 116.014 138.145 225.145 225.145 225.145 225.145 225.145 225.165 236.161 324.652 324.652 362.875
	$\begin{array}{c} 0.75\\ 1.0\\ 1.0\\ 10.0\\ 1$		8.7.7.6.6.9.9.6.4.8.3.9.9.0.5 8.0.9.0.9.0.9.4.9.5 9.0.9.0.9.0.9.0.9.0.9.0.9.0.5 9.0.9.0.9.0.9.0.9.0.9.0.9.0.5 9.0.9.0.0.9.0.0.9.0.0.9.0.0.5 9.0.0.0.0.0.0.0.0.0.0.0.0.0.0.0.0.0.0.0		6.5 5.5 5.5 5.5 5.5 5.5 5.5 5.5 5.5 5.5

pressure and temperature over the extremes of an iterated isometric line are represented by $\Delta p'$ and ΔT , respectively. Any difference between the pressure denoted by a "straightened" isometric and a straight line represented by q is carried as a residual pressure, r. For tetrafluoromethane, minimum values of the residual pressures were obtained for all isometrics when k = 1.5. Thus, differentiation of the relationship

$$P = q + r - c(\Delta p' / \Delta T)_{\rho} / VT^{1.5}$$
⁽⁴⁾

yielded an exact expression for the slope of the isometric line at any data point,

$$(\partial P/\partial T)_{\rho} = (\partial q/\partial T)_{\rho} + (\partial r/\partial T)_{\rho} + 1.5c(\Delta p'/\Delta T)_{\rho}/VT^{25}$$
(5)

Since the first and third terms on the right of Equation 5 were evaluated analytically, all errors arising strictly from imperfection in the analytical representation of the isometric data accumulated in the residual terms and were finally accounted for in a graphical evaluation of $(\partial r/\partial T)_{\rho}$. Consequently, the estimated percentage error in $(\partial P/\partial T)_{\rho}$ will be equal to the estimated percentage error in $(\partial r/\partial T)_{\rho}$ multiplied by the ratio $(\partial r/\partial T)_{\rho}/(\partial P/\partial T)_{\rho}$.

By far the most difficult areas for determining $(\partial r/\partial T)_{\rho}$ are at the temperature extremities of the isometrics and are, therefore, the areas where the largest purely correlational errors are introduced. Thus, at both 0° and 350° C. the probable correlational error in $(\partial P/\partial T)_{\rho}$ varies from <0.1% at the lowest and highest densities to 0.3 to 0.4% at medium densities. For all densities at intermediate temperatures the correlational errors in $(\partial P/\partial T)_{\rho}$ are considerably less than 0.1%.

A comprehensive analysis of the way small experimental and correlational errors are translated to the final thermodynamic function is involved and generally impossible to give in numerical terms; but in some areas at least, one can reasonably expect them to be magnified when reckoned on a percentage basis. In the integrand of $H - H^{\circ}$, Equation 1, for example, the situation becomes most critical when the magnitude of the product $T(\partial P/\partial T)_{e}$ approaches that of the pressure. Near this point, the error in the integrand may be an order of magnitude greater than the error in $(\partial P/\partial T)$, itself. Fortunately, the integration over density takes advantage of the cancellation of errors having opposite sign, a likely occurrence when the residual quantities are taken into account. On the other hand, large systematic errors are possible when thermodynamic functions are calculated by analytical methods only, based on closed equations of state that deviate consistently in one direction from the true slope $(\partial P/\partial T)_{\rho}$ over fairly wide ranges of density.

INTEGRATION OF FUNCTIONS

The integrals in Equations 1, 2, and 3 were determined by graphical integration with little or no introduction of spurious errors from this operation. However, the entropy values tabulated were obtained from $(G - G^{\circ}) = (H - H^{\circ}) - T(S - S^{\circ})$ rather than from Equation 2 in order to preserve numerical consistency between the values for $(S - S^{\circ})$, $(H - H^{\circ})$, and $(G - G^{\circ})$. To make certain that no significant errors were introduced by the correlating techniques themselves, comparisons were made of the entropies, $(S - S^{\circ})$'s,



Figure 2. Integrand from enthalpy function at 75° C.



Figure 3. Integrand from entropy function at 75° C.



Figure 4. Integrand from Gibbs energy function at 75° C.

calculated by the two methods. The greatest percentage deviation, 0.01%, was found for some points on the 0°, 25°, and 30° isotherms. Results of a comparison for integer values of the density on the 75° isotherm, given in Table II, are typical of most isotherms.

Characteristic behaviors of the integrands are illustrated for a single temperature, 75° C. (Figures 2, 3, and 4) by solid lines drawn through points calculated from experimental values of P, T, ρ , and derived values of $(\partial P/\partial T)_{o}$. These lines terminate on the zero density intercepts at points calculated from the second virial coefficients and/or their first derivatives with respect to temperature.

Approximate values of the integrands, shown as dashed lines, relate them to the virial equation of state,

$$P = RT_{\rho}(1 + B_{\rho} + C_{\rho}^{2} + D_{\rho}^{3} + \dots)$$
(6)

in which B, C, and D are the temperature-dependent second, third, and fourth virial coefficients, respectively. At zero density, the integrands reduce to exact functions of the second virial coefficients and their derivatives with respect to temperature; at densities above zero the integrands are functions of an infinite series of virial coefficients and their temperature derivatives. Successive approximations through the fourth virial coefficient were calculated and plotted to illustrate the various degrees of approximations that can be expected from terminated virial expansions.

Table II.	$-(S - S^{\circ})$	for the 75°	lsotherm
Density, G. Moles/	$\frac{(G - G^\circ) - (H - H^\circ)}{T}$	Eq. 2	Dev %
1	6.9188	6.9188	0
2	8.5526	8.5526	0
3	9.6148	9.6147	0.001
4	10.4445	10.4444	0.001
5	11.1505	11.1505	0
6	11.7833	11.7833	0
7	12.3712	12.3710	0.002
8	12.9326	12.9324	0.002
9	13.4820	13.4817	0.002
10	14.0298	14.0295	0.002
11	14.5843	14.5841	0.001

For these calculations, numerical values of B, C, and D were taken from a previous publications (8).

The first derivatives of the second virial coefficients with respect to temperature, dB/dT, were calculated from the differentiated equation of the Lennard-Jones [n,m] (11) statistical mechanical expression fitted to experimental Bvalues. Correlation of the second virial coefficient of tetrafluoromethane by the Lennard-Jones [n,m] potential with n = 500 and m = 6 will appear in a separate publication. To these calculated derivatives were added small graphically determined temperature derivatives of the differences between observed and calculated values of the second virial coefficients according to the [500,6] potential. Values for the derivatives of the third and fourth virial coefficients with respect to temperature, dC/dT and dD/dT, were determined by graphical differentiation of experimental values of the third and fourth virial coefficients, respectively.

Closed equations of state applied without the aid of a residual term are notoriously unreliable for estimating thermodynamic properties, particularly when a derivative quantity is involved. For comparison with results obtained by the present method, the enthalpies of tetrafluoromethane were also calculated at 20 selected points based on the Redlich-Kwong (14) and the Benedict-Webb-Rubin (5, 8)





equations of state. In general, the results indicated that a closed equation of state that had the ability to represent the P-V-T data over a given range of variables with an average deviation of less than 1%, would often, because of large percentage errors in $(\partial P/\partial T)_{\rho}$, produce numbers for the enthalpy that deviated an order of magnitude greater over the same range of variables. Some individual points were off by as much as 27%.

Values for the thermodynamic properties, $P, H - H^{\circ}$, $S - S^{\circ}$, and $G - G^{\circ}$, are presented in Table I, tabulated at the even densities and temperatures corresponding to the original experimental data (8). In some cases the values are given to an extra significant figure to minimize uncertainties in any subsequent calculations rather than to indicate this degree of accuracy.

As previously discussed, the methods have introduced small uncertainties from $(\partial P/\partial T)_{\rho}$, dB/dT, and the graphical integrations. These uncertainties apply largely to the enthalpy and entropy functions because the free energy functions are independent of $(\partial P/\partial T)_{\rho}$ and dB/dT. However, all calculations are dependent on the original data whose estimated maximum uncertainty is 0.03% at the lowest temperature and pressure and 0.3% at the highest temperature and pressure. As noted in the original publication (8), the values of "observed pressure" were corrected for the partial pressure of mercury vapor adjusted at each pressure for the Poynting effect. The correction did not include the van der Waals interaction of mercury vapor with tetrafluoromethane, but the inaccuracy introduced is probably within the range of the stated over-all uncertainty of the P-V-T data. Thus, the thermodynamic properties are, possibly, subject to small but significant corrections due to the van der Waals interaction.

The enthalpy and entropy data in Table I have been plotted in Figures 5 and 6 to illustrate the internal consistency of the derived values.

Values of the thermodynamic properties $(H - H^{\circ})/T$, $(S_p - S_{p, \text{ideal}}), (S_v - S_{v, \text{ideal}}), (G_p - G_{p, \text{ideal}}), (G_v - G_{v, \text{ideal}}), (G - G^{\circ}/T, \text{and activity coefficient } \gamma, \text{ were tabulated also,}$ and can be made available to interested parties upon request.

NOMENCLATURE

- B = second virial coefficient, cm.³/mole
- a parameter с
- C third virial coefficient, cm.⁶/mole² =
- D = fourth virial coefficient, cm.⁹/mole³
- G = molal Gibbs energy, cal./mole
- H =molal enthalpy, cal./mole k
- a parameter =
- value of attractive exponent in Lennard-Jones potential т = function
- value of repulsive exponent in Lennard-Jones potential n Ξ function
- Ρ pressure, atm.
- "corrected" pressure, atm. $P + c(\Delta p'/\Delta T)_{\rho}/VT^{*} r$ p' =
- q =
- residual pressure, atm. =
- gas constant = 0.0820544 liter atm./mole deg. R Ξ
- S molal entropy, cal./deg. mole =
- thermodynamic temperature = 273.16 + (0.04106 7.363)T= $\times 10^{-5}t$) (t/100) (t/100 - 1)
- ۰C. International Celsius temperature Ξ
- V molal volume, liter/g.-mole =
- activity coefficient = exp. $[(G G^{\circ})/RT]/P$ = γ
- molal density, g.-mole/liter 4.12917 × 10^{-2} liter atm. = 4.1840 joules = ø
- cal. =
- = superscript indicating standard state
- ideal = subscript indicating ideal gas state

LITERATURE CITED

- (1)Beattie, J.A., Chem. Revs. 44, No. 1, 141 (1949).
- Beattie, J.A., "Temperature, Its Measurement and Control (2)Science and Industry," Vol. II, Chap. 5, p. 93, Reinhold, New York, 1955.
- Beattie, J.A., Bridgeman, O.C., Proc. Am. Acad. Arts Sci. 63, (3)229 (1928).
- Beattie, J.A., Stockmayer, W.H., "Treatise on Physical (4)Chemistry," Vol. II, Chap. 2, H.S. Taylor and S. Glasstone, eds., Van Nostrand, New York, 1951.
- Benedict, M., Webb, G.B., Rubin, L.C., J. Chem. Phys. 8, (5)334(1940)
- Canjar, L.N., Rossini, F.D., "Work of American Petroleum (6)Institute Research Project 44 on P-V-T Properties," Conf. on Thermodynamic and Transport Properties of Fluids, sponsored jointly by British Institute of Mechanical Engineers and International Union of Pure and Applied Chemistry, London, England, July 1957.
- Chari, N.C.S., Sc. D. dissertation, University of Michigan, (7)1960.
- Douslin, D.R., Harrison, R.H., Moore, R.T., McCullough, (8)J.P., J. Chem. Phys. 35, 1357 (1961).
- "Perfluorocyclobutane. (9) Harrison, R.H., Douslin, D.R., Thermodynamic Properties of the Real Gas," U. S. Bur. Mines Rept. Invest. 6475 (1964).
- Keyes, F.G., J. Chem. Phys. 15, 602 (1947). (10)
- Lennard-Jones, J.E., Proc. Roy. Soc. (London), Ser. A 106, (11)463 (1924)
- McBride, B.J., Heimel, S., Ehlers, J.G., Gordon, S., "Thermo-(12)dynamic Properties to 6000° K. for 210 Substances Involving the First 18 Elements," NASA, SP-3001, 156 (1963).
- Nagarajan, G., Australian J. Chem. 15, 566 (1962) (13)
- Redlich, O., Kwong, J.N.S., Chem. Revs. 44, 233 (1949). (14)
- (15) Stimson, H.F., Am. J. Phys. 23, 614 (1955).

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