

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

ACKNOWLEDGMENT

The author thanks B.F. Dodge of Yale University, New Haven, Conn., and W.M.D. Bryant of E. I. du Pont de Nemours and Co., Inc., Wilmington, Del., for their suggestions.

LITERATURE CITED

- (1) Barr-David, F.H., Dodge, B.F., *J. Chem. Eng. Data* **4**, 107 (1959).
- (2) Berman, N.S., McKetta, J.J., *J. Phys. Chem.* **66**, 1444 (1962).
- (3) Beynon, E.T., Jr., McKetta, J.J., *Ibid.*, **67**, 2761 (1963).
- (4) Buckley, E., Herington, E.F.G., *Trans. Faraday Soc.* **61**, 1618 (1965).
- (5) Cope, C.S., *A.I.Ch.E.J.* **10**, 277 (1964).
- (6) Cope, C.S., Dodge, B.F., *Ibid.*, **5**, 10 (1959).
- (7) Dodge, B.F., "Chemical Engineering Thermodynamics," Chap. 11, McGraw-Hill, New York, 1944.
- (8) Eberz, W.F., Lucas, H.J., *J. Am. Chem. Soc.* **56**, 1230 (1934).
- (9) Green, J.H.S., *Trans. Faraday Soc.* **59**, 1559 (1963).
- (10) Green, J.H.S., *Quart. Revs. (London)* **15**, 125 (1961).
- (11) Janz, G. J., "Estimation of Thermodynamic Properties of Organic Compounds," Academic Press, New York, 1958.
- (12) Majewski, F.M., Marek, L.F., *Ind. Eng. Chem.* **30**, 203 (1938).
- (13) Nicolini, E., Laffitte, P., *Compt. rend.* **229**, pp.757, 935 (1949).
- (14) 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.
- (15) Parks, G.S., Huffman, H.M., Barmore, M., *J. Am. Chem. Soc.* **55**, 2733 (1933).
- (16) Parks, G.S., Manchester, K.E., *Thermochem. Bull. I.U.P.A.C. No. 2*, 8 (1956).
- (17) Pilcher, G., Pell, A.S., Coleman, D.J., *Trans. Faraday Soc.* **60**, 499 (1964).
- (18) Rossini, F.D., *et al.*, *U. S. Natl. Bur. Standards Circ.* **461**, 1947.
- (19) *Ibid.*, No. **500** (1952).
- (20) Rossini, F.D., *et al.*, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," (and supplements), A.P.I. Research Project 44, Carnegie Press, Pittsburgh, Pa., 1953.
- (21) Shiffier, W.H., Holm, M.M., Brooke, L.F., *Ind. Eng. Chem.* **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).
- (24) Taft, R.W., Jr., Riesz, P., *J. Am. Chem. Soc.* **77**, 902 (1955).

RECEIVED for review September 24, 1965. Accepted April 6, 1966. Material supplementary to this article has been deposited as Document number 8959 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting \$1.25 for photoprints, or \$1.25 for 35 mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

Tetrafluoromethane

Thermodynamic Properties of the Real Gas

ROLAND H. HARRISON and DONALD R. DOUSLIN

Petroleum Research Center, Bureau of Mines, U. S. Department of the Interior, Bartlesville, Okla.

The thermodynamic properties, $H - H^\circ$, $S - S^\circ$, and $G - G^\circ$, of tetrafluoromethane were determined as functions of temperatures (0° to 350° 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.

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 $(\partial P/\partial T)_\rho$ 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,

$$H - H^\circ = \int_{\tau} \int_0^{\rho} \frac{[P - T(\partial P/\partial T)_\rho]}{\rho^2} d\rho + P/\rho - RT \quad (1)$$

$$S - S^\circ = \int_{\tau} \int_0^{\rho} \frac{[R\rho - (\partial P/\partial T)_\rho]}{\rho^2} d\rho - R \ln RT\rho \quad (2)$$

and

$$G - G^\circ = \int_{\tau} \int_0^{\rho} \frac{P - RT\rho}{\rho^2} d\rho + P/\rho - RT + RT \ln RT\rho \quad (3)$$

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 - V - 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

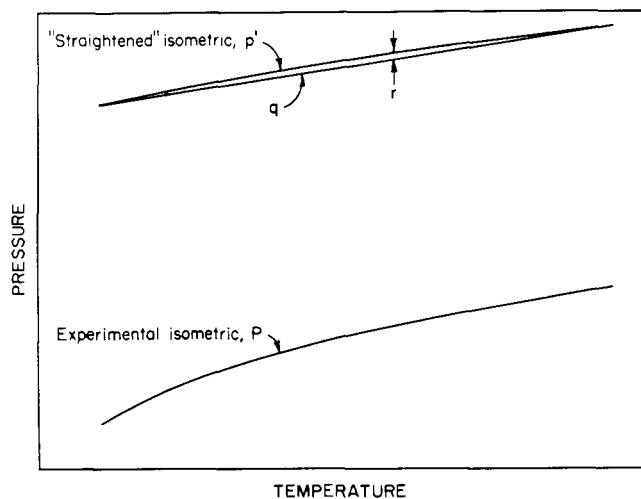


Figure 1. Schematic representation of original and "straightened" isometric

Table I. Gram-Molal Thermodynamic Properties

Density, G./Mole Liter	0.00° C.			25.00° C.			30.00° C.			50.00° C.		
	P , atm.	$-(H - H^\circ)_\rho, - (S - S^\circ)_\rho$, cal./deg.	$G - G^\circ$, cal.	P , atm.	$-(H - H^\circ)_\rho, - (S - S^\circ)_\rho$, cal./deg.	$G - G^\circ$, cal.	P , atm.	$-(H - H^\circ)_\rho, - (S - S^\circ)_\rho$, cal./deg.	$G - G^\circ$, cal.	P , atm.	$-(H - H^\circ)_\rho, - (S - S^\circ)_\rho$, cal./deg.	$G - G^\circ$, cal.
0.75	15.480	153.9	5.8527	17.194	141.7	6.0039	17.538	139.4	6.0331	18.898	131.2	6.1472
1.0	20.086	203.5	6.5046	22.453	187.3	6.6487	22.923	184.3	6.6768	24.792	173.6	6.7869
1.5	28.559	299.7	7.4685	32.339	276.1	7.5996	33.087	271.8	7.6254	36.057	256.1	7.7281
2.0	36.149	392.4	8.1957	41.486	361.7	8.3149	42.538	356.1	8.3387	46.720	335.6	8.4346
2.5	42.974	481.4	8.7923	50.000	444.2	8.9006	51.387	437.3	8.9225	56.893	412.2	9.0123
3.0	49.150	567.0	9.3056	58.012	523.4	9.4040	59.764	515.4	9.4243	66.701	485.9	9.5084
3.5	54.804	649.1	9.7609	65.628	599.6	9.8504	67.556	590.6	9.8693	76.251	556.7	9.9483
4.0	60.039	727.9	10.1735	72.967	672.8	10.2551	75.520	662.7	10.2727	85.656	624.8	10.3472
4.5	64.967	803.5	10.5532	80.130	743.1	10.6281	83.129	732.0	10.6446	95.045	690.2	10.7154
5.0	69.704	876.0	10.9070	87.251	810.6	10.9763	90.736	798.5	10.9920	104.587	752.8	11.0597
5.5	74.369	945.4	11.2399	94.473	875.3	11.3050	98.470	862.2	11.3199	114.393	812.7	11.3853
6.0	79.050	1012.0	11.5561	101.908	937.3	11.6182	106.456	926.3	11.6325	124.621	870.1	11.6963
6.5	83.903	1075.9	11.8589	109.726	996.7	11.9190	114.879	981.8	11.9330	135.468	924.9	11.9957
7.0	89.061	1137.3	12.1512	118.131	1053.4	12.2102	123.929	1037.5	12.2241	147.186	976.7	12.2862
7.5	94.676	1196.2	12.4357	127.244	1107.6	12.4942	133.791	1090.7	12.5080	159.922	1025.8	12.5698
8.0	100.961	1252.8	12.7145	137.455	1158.8	12.7728	144.774	1140.9	12.7868	174.093	1071.6	12.8485
8.5	108.149	1306.7	12.9893	148.916	1207.2	13.0479	157.077	1188.2	13.0620	189.908	1114.2	13.1241
9.0	116.575	1357.8	13.2617	162.056	1252.3	13.3211	171.140	1232.2	13.3354	207.791	1153.3	13.3982
9.5	126.561	1405.9	13.5384	177.339	1293.6	13.5938	187.469	1272.2	13.6084	228.320	1188.1	13.6719
10.0	138.458	1450.9	13.8063	195.101	1331.1	13.8677	206.428	1308.2	13.8825	251.970	1218.1	13.9465
10.5	152.884	1492.2	14.0822	216.126	1363.8	14.1438	228.708	1339.3	14.1587	279.425	1242.5	14.2229
11.0	170.481	1529.1	14.3623	241.054	1391.0	14.4232	254.939	1364.9	14.4381	311.330	1260.9	14.5020

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

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

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

$$(\partial P / \partial T)_\rho = (\partial q / \partial T)_\rho + (\partial r / \partial T)_\rho + 1.5c(\Delta p' / \Delta T)_\rho / VT^{2.5} \quad (5)$$

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%.

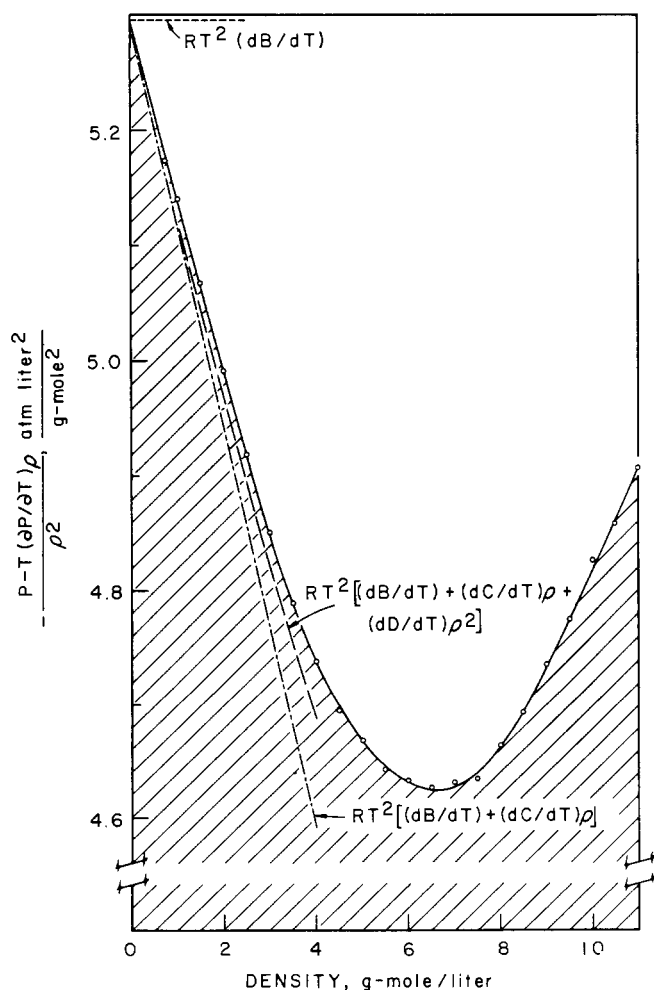


Figure 2. Integrand from enthalpy function at 75° C.

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 $T(\partial P / \partial T)_\rho$ approaches that of the pressure. Near this point, the error in the integrand may be an order of magnitude greater than the error in $(\partial P / \partial T)_\rho$ 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,

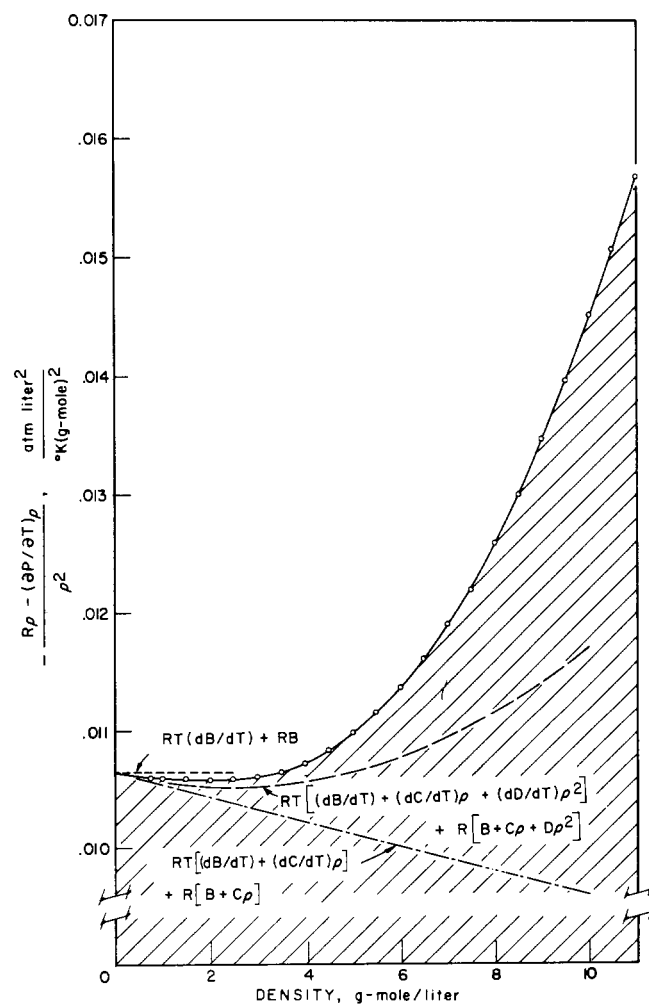


Figure 3. Integrand from entropy function at 75° C.

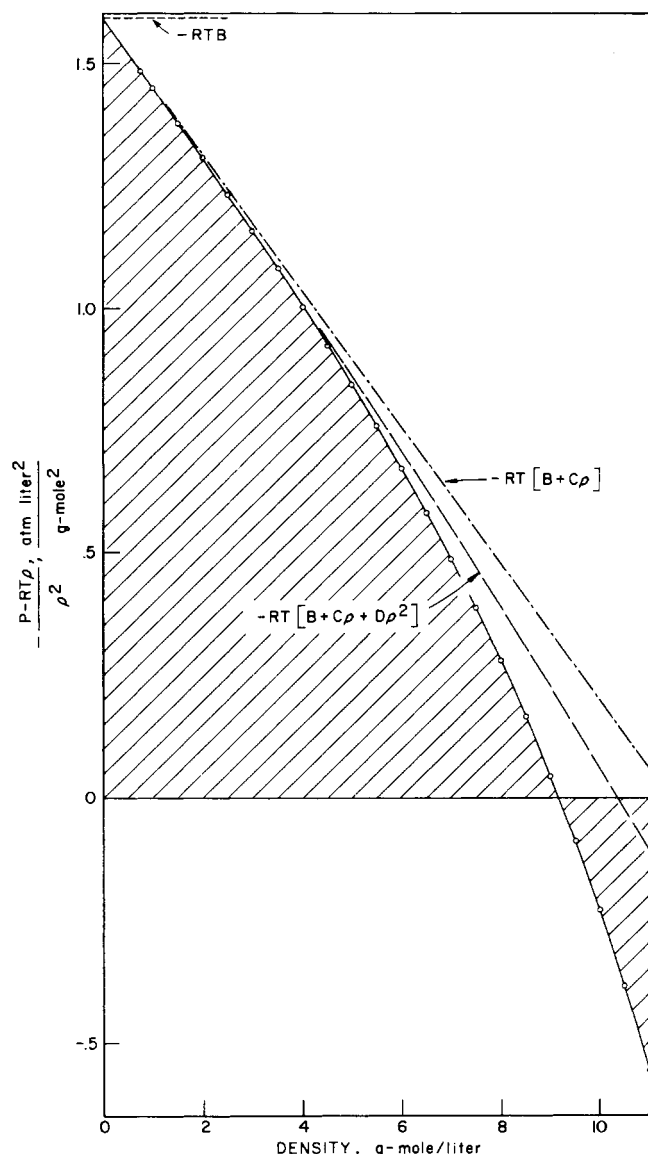


Figure 4. Integrand from Gibbs energy function at 75° C.

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 $(\partial P / \partial T)_\rho$. 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,

$$P = RT\rho(1 + B\rho + C\rho^2 + D\rho^3 + \dots) \quad (6)$$

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° Isotherm

Density, G. Moles/ Liter	$(G - G^\circ) -$ $(H - H^\circ)/T$	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 B values. 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)

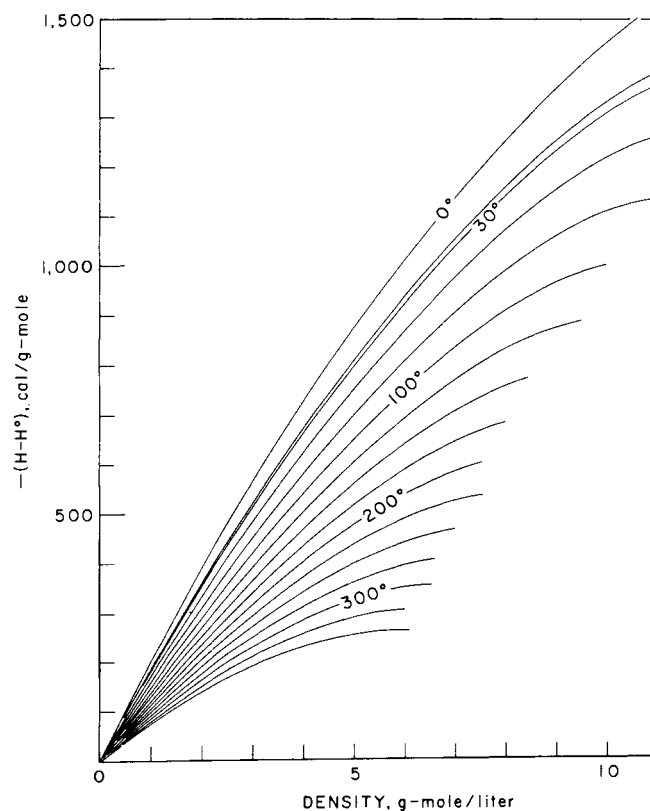


Figure 5. Enthalpy, $-(H - H^\circ)$

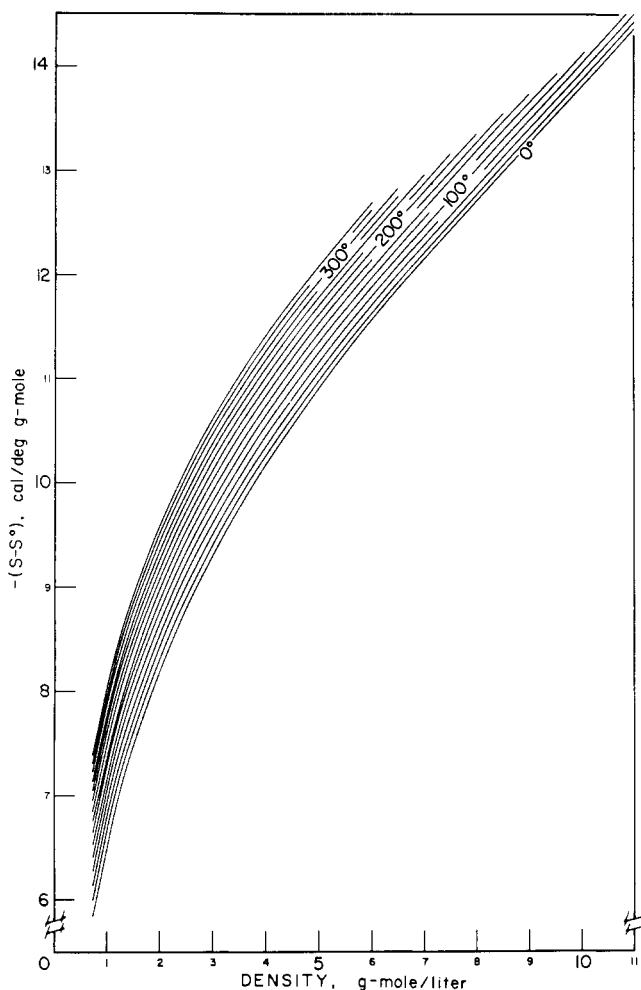


Figure 6. Entropy, $-(S - S^\circ)$

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 $(\partial P/\partial T)_p$, 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 $(\partial P/\partial T)_p$, dB/dT , and the graphical integrations. These uncertainties apply largely to the enthalpy and entropy functions because the free energy functions are independent of $(\partial P/\partial T)_p$ 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 $(H - H^\circ)/T$, $(S_p - S_{p,ideal})$, $(S_v - S_{v,ideal})$, $(G_p - G_{p,ideal})$, $(G_v - G_{v,ideal})$, $(G - G^\circ)/T$, and activity coefficient γ , were tabulated also, and can be made available to interested parties upon request.

NOMENCLATURE

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

LITERATURE CITED

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

RECEIVED for review October 4, 1965. Accepted March 14, 1966. Work conducted in part under an Interservice Support Agreement between the Air Force Office of Scientific Research, Office of Aerospace Research, U. S. Air Force, Project No. 9713, Task No. 9713-02, and the Bureau of Mines, U. S. Department of the Interior. Contribution 143 from the Thermodynamics Laboratory, Bartlesville Petroleum Research Center, Bureau of Mines.