

Pressure-Volume-Temperature Behavior of Carbon Tetrafluoride Using a Variable-Volume Cell of Bellows Design

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This paper presents data observed for the pressure-volume-temperature (P-V-T) behavior of carbon tetrafluoride (CF_4) below room temperature, and uses these data in conjunction with higher temperature data from the literature to evaluate an equation of state. The P-V-T measurements were made via a variable-volume technique without using a confining liquid. The variable-volume design makes it possible to cover a range of specific volumes with a single charge, resulting in an efficient operating procedure.

A unique bellows design with a 14-fold volume variation was developed. The bellows contained the compound under study (CF_4) and was surrounded by a hydraulic liquid whose pressure could be varied causing the bellows to expand or contract. The volume of the bellows was determined by measuring the volume of the hydraulic liquid. Calibrations were made using a gas (CO_2) of known thermodynamic properties. Pressure measurements were made via a differential pressure transducer on three Heise gauges calibrated in place against a Ruska dead-weight tester. The bellows cell was maintained in a well-agitated bath whose temperature was measured by a platinum resistance thermometer.

The data were taken by charging a known amount of the compound into the bellows and observing the pressure-volume relationship at a fixed bath temperature. At the end of a run, the charge was recovered, the amount recovered agreeing within 0.01% with the amount charged.

The observed data were analyzed graphically on pressure-volume, pressure-temperature, and compressibility diagrams. Very good consistency was observed with the higher temperature data from literature. The data were correlated analytically with the Martin equation of state. This equation represents all the data with an average deviation of 0.25%.

Carbon tetrafluoride (sometimes referred to as tetrafluoromethane or Freon 14) belongs to a group of chloro-fluoro compounds that have found considerable use as refrigerants. To facilitate the design of equipment using carbon tetrafluoride, thermodynamic properties such as entropy, enthalpy, and specific volume are needed at various temperatures and pressures. These properties may be evaluated from experimental determinations such as vapor pressure, liquid density, pressure-volume-temperature (P-V-T) behavior, and specific heat. Vapor pressure, liquid density, heat capacity, and P-V-T properties above the ice point have already been reported in literature (1 to 6). One of the purposes of the present program was to observe the P-V-T behavior of carbon tetrafluoride in the low-temperature region extending to about 50°R. below the critical temperature (409.48°R.) with some overlap of the literature data. This would permit, in conjunction with the literature data, to determine an equation of state for carbon tetrafluoride over a wide range of pressure, temperature, and specific volume.

A further objective of the work was to make the P-V-T measurements via a unique bellows-type variable-volume technique without using a confining liquid. The variable-volume design makes it possible to cover a range of specific volumes with a single charge, resulting in an efficient operating procedure.

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LITERATURE SEARCH

Carbon Tetrafluoride

A literature survey of references related to the (P-V-T) behavior of carbon tetrafluoride has shown that the only P-V-T data are reported by Douslin et al. (3, 4) and by MacCormack and Schneider (5, 6).

MacCormack and Schneider (5, 6), of the National Research Council of Canada, have obtained compressibility up to 50 atm. in the temperature range of 0° to 400°C. (491.67° to 1211.67°R.). Douslin et al. (3, 4), at the U.S. Bureau of Mines, have reported complete P-V-T data in the region 0° to 350°C. (491.67° to 1121.67°R.) and 15 to 394 atm. They have been correlated by a Benedict-Webb-Rubin equation with an average deviation of about 0.555% and a maximum deviation of 3.17%.

Other investigators have made measurements on other properties of carbon tetrafluoride. Chari (1) has reported vapor pressure, liquid density, and the critical properties. Martin and Hwang (2) have reported the constant-volume heat capacity.

Equipment and Methods of P-V-T Measurements

A review of literature for equipment for observing P-V-T behavior of fluids shows two basic types of equipment used: constant-volume equipment or variable-volume constant-temperature equipment.

The constant-volume cell usually consists of a fixed-volume vessel in which the (P-V-T) behavior is determined

by measuring pressures for different temperatures to which the constant-volume vessel is exposed (7). In order to cover a range of specific volumes, different masses of the compound are charged to the constant-volume vessel, and this results in gross inefficiency.

A variable-volume equipment requires only a single charge of material to cover a wide range of specific volumes. Numerous investigators, dating back to Amagat's work of 1893 (8), have used variable-volume cells to measure the P-V-T properties of fluids. Beattie (9) has measured the P-V-T behavior of gaseous mixtures using a steel bomb whose volume can be varied by injection of mercury. Several other investigators (10 to 21) have used very similar techniques. Some investigators (5, 6, 22 to 24) have used a technique attributed to Burnett (22) of evaluating behavior of state of a compound which only involves very accurate measurement of the pressure and temperature of the gas. Bridgeman (25, 26) has proposed two other types of variable-volume equipment: piston and bellows. Several investigators have utilized these systems primarily for liquid compressibility measurements (27, 28). For such applications, the expansion (of the bellows or the piston travel) need not be very large (for example, 2 to 1 volume change would be satisfactory). However, literature reports no successful applications of such systems to P-V-T measurements involving the gaseous state (where zero leakage and large volume changes are prime requirements).

EXPERIMENTAL WORK

Equipment

A scheme of the experimental system is shown in Figure 1. Details of the P-V-T cell are shown in Figure 2. The bellows, containing the gas under study, are enclosed in a thick-walled cylindrical shell made of stainless steel.

Details of the bellows are shown in Figure 3. It is made of 316 stainless steel and is capable of expanding from a solid height of 1.26 to about 8.50 in. The minimum volume is about 3.4 cu. in. and maximum volume is about 47 cu. in., a volume change of approximately 14-fold. It should be pointed out that because of the stringent volume expansion and materials requirements the bellows had to be specifically designed (of particular-shaped concentric rings welded at the inner and outer diameters) in consultation with engineers from Belfab Corporation, which also made the final construction.

The expansion and contraction of the bellows is achieved by release or forcing of the hydraulic fluid (propanol in this case) into the space between the bellows and the cylindrical shell via the leak-proof hydraulic system pump. The low-pressure end of the pump is connected to a fluid reservoir and a level-measurement glass gauge, 60 in. high. The level observed is related to the volume occupied by the gas in the bellows. This indication, after suitable calibration, is used for volume measurement.

The pressure measuring system consists of a Pace diaphragm pressure transducer leading to a set (0 to 100, 0 to 500, 0 to 2,000 lb./sq. in.) of very sensitive Heise pressure gauges calibrated by a Ruska dead-weight gauge tester. The diaphragm transducer is of the differential pressure type which indicates pressure imbalance on the two sides of the diaphragm. On one side of the diaphragm is the pressure of the compound in the bellows, and this pressure is balanced by pressure applied on the other side from a cylinder of nitrogen. When the diaphragm gauge indicator shows equalized pressure on both sides, then the pressure of the nitrogen side is measured by the set of accurate Heise gauges; three such gauges are used covering three pressure ranges. These pressure gauges are calibrated in place periodically by means of a Ruska dead-weight gauge tester. The temperature of the bath was measured very accurately with a platinum resistance thermometer in circuit with a Leeds and Northrup potentiometer and a lamp-and-scale galvanometer.

The evacuation and charging system includes a Cenco vacuum pump and a vacuum gauge, together with the large cylinder containing the compound to be charged and a smaller cylinder whose weight can be accurately determined. The compound is loaded into the smaller cylinder (called charge cylinder in Figure 1) prior to charging into the P-V-T cell. Weight measurements of this charge cylinder before and after charging (or recovery) indicate amount of compound charged (or recovered).

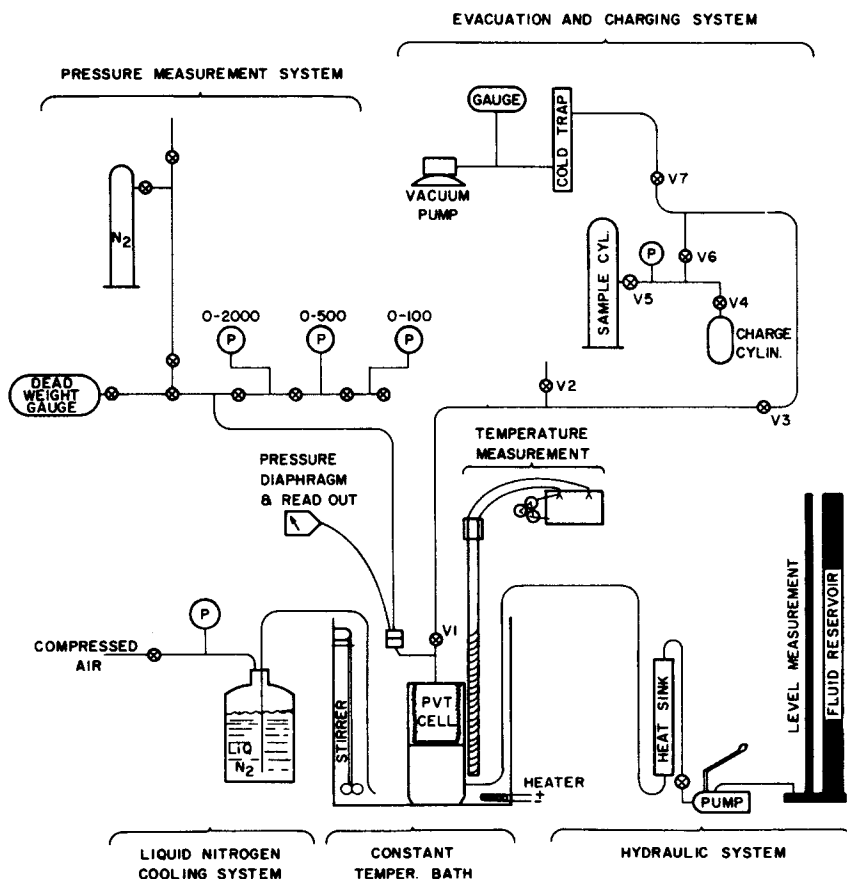


Fig. 1. System for measuring P-V-T behavior.

The P-V-T cell was immersed in a bath filled with normal propanol which could maintain a constant temperature while pressure and volume readings were observed along an isotherm.

Experimental Precision

This section summarizes the estimated errors that might be involved in the measurements and calibrations. Details of this, as

well as other aspects of this paper, have been reported in a University of Michigan dissertation (30).

Pressure testing of the P-V-T cell, at pressures ranging from 100 to 1,500 lb./sq. in. gauge, up to 24 hr. has shown absolutely no pressure drop. Furthermore, the very close check between the amount recovered and the amount charged (± 0.005 g.) indicates that the P-V-T cell has essentially zero leakage.

The Freon-14 charged was specially prepared by the duPont Company for making P-V-T measurements. The compound contains less than 0.004% CClF_3 as impurity.

Errors in pressure, volume, and temperature measurement have been critically reviewed, and the following are the maximum errors expected:

1. Pressure: ± 1 lb./sq. in. above 500 lb./sq. in.
 ± 0.26 lb./sq. in. between 100 to 500 lb./sq. in.
2. Volume: ± 0.06 lb./sq. in. below 100 lb./sq. in.
 $\pm 1.3\%$ at the smallest bellows volume
 $\pm 0.24\%$ at the largest bellows volume
3. Temperature: $\pm 0.084^\circ\text{F}$.

RESULTS

The laboratory data for carbon tetrafluoride, converted to pressure, specific volume, and temperature are reported in the first three columns of Table 1. These have been analyzed graphically as well as algebraically. These analyses have been made in conjunction with the literature reported data of Douslin et al. (3, 4) and of MacCormack and Schneider (5, 6).

Graphical Analysis

The data have been graphically analyzed by construction of a pressure-volume plot, a pressure-temperature plot, and a compressibility chart.

The pressure-volume diagram is shown in Figure 4; the saturation curve is from reference 1. Within the limits of accuracy of the original diagram of Figure 4 (estimated to be $\pm 0.3\%$), the data of this paper show very good agreement with the data of the literature in the regions of overlap. The diagram further illustrates the inflection properties of the isotherms, especially near the critical point.

The pressure-temperature diagram is shown in Figure 5. This illustrates the linearity of the isometrics near the

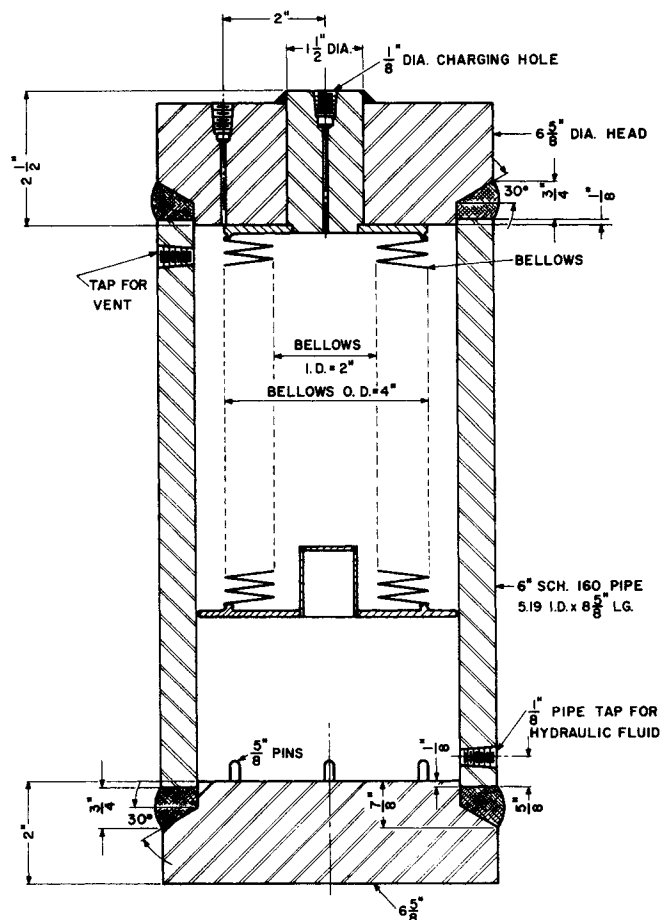


Fig. 2. Details of the P-V-T cell.

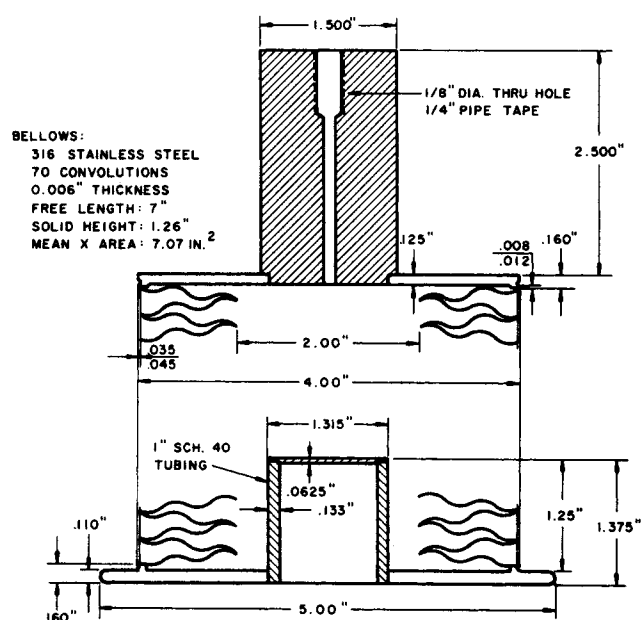


Fig. 3. Details of the bellows.

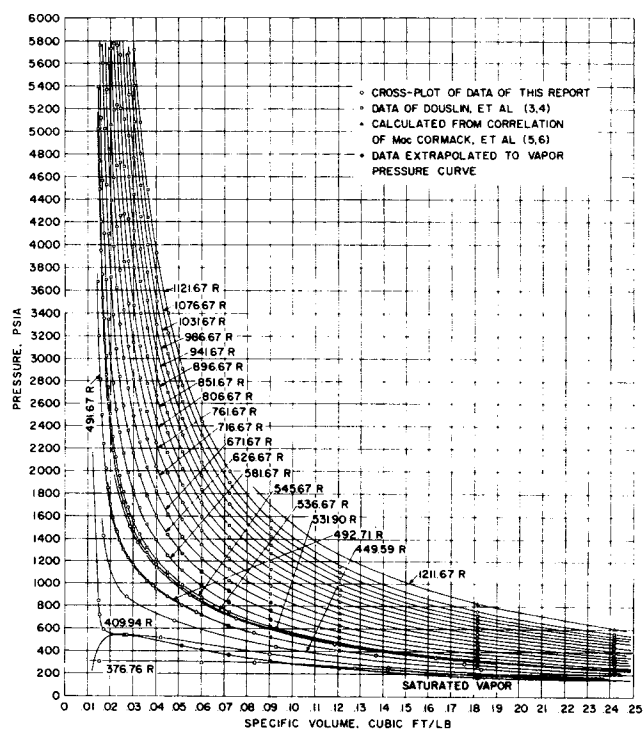


Fig. 4. Pressure-volume diagram for carbon tetrafluoride.

TABLE I. COMPARISON OF THE MARTIN EQUATION OF STATE WITH DATA OF THIS PAPER
FOR CARBON TETRAFLUORIDE

Temp., °R	Specific volume, cu. ft./lb.	Pressure observed, lb./sq.in.abs.	% deviation $\frac{p_{exp} - p_{calc}}{p_{exp}} \times 100$	Reduced properties		
				T_r	P_r	z
531.90	0.16379	359.3	0.004	1.299	0.662	0.907
	0.11929	476.9	0.056		0.878	0.877
	0.07583	699.2	-0.159		1.287	0.817
	0.05549	900.1	0.008		1.657	0.770
	0.04093	1145.4	0.326		2.109	0.723
	0.03243	1378.7	0.030		2.538	0.689
492.71	0.02895	1518.8	-0.300	1.203	2.796	0.678
	0.17619	304.9	0.025		0.561	0.894
	0.13715	379.2	-0.090		0.698	0.866
	0.08378	567.7	-0.292		1.045	0.792
	0.05809	748.8	0.056		1.379	0.724
	0.03907	983.0	0.132		1.810	0.639
449.59	0.2314	1467.6	-0.795	1.0980	2.702	0.565
	0.18388	259.9	0.000		0.479	0.872
	0.09338	448.6	0.198		0.826	0.764
	0.04868	677.5	0.286		1.247	0.602
	0.02762	883.2	-0.689		1.626	0.445
	0.01713	1432.9	0.220		2.638	0.447
409.94	0.14297	278.5	-0.063	1.0011	0.513	0.797
	0.09082	382.4	-0.045		0.704	0.695
	0.04261	527.7	-0.048		0.972	0.450
	0.02776	543.0	-0.752		0.9997	0.302
	0.01523	851.5	-2.548		1.568	0.259
	0.01578	734.5	-3.367		1.334	0.229
376.76	0.01743	596.6	-1.095	0.9201	1.098	0.208
	0.14169	243.8	0.329		0.449	0.752
	0.12809	261.1	0.387		0.4807	0.728
	0.08402	309.1	0.013*		0.570	0.565
	0.06081	309.2	0.016*		0.570	0.409
	0.01580	309.2	0.016*		0.570	0.106

*Calculated from Chari's vapor pressure equation (1) since these points are in the two-phase region.

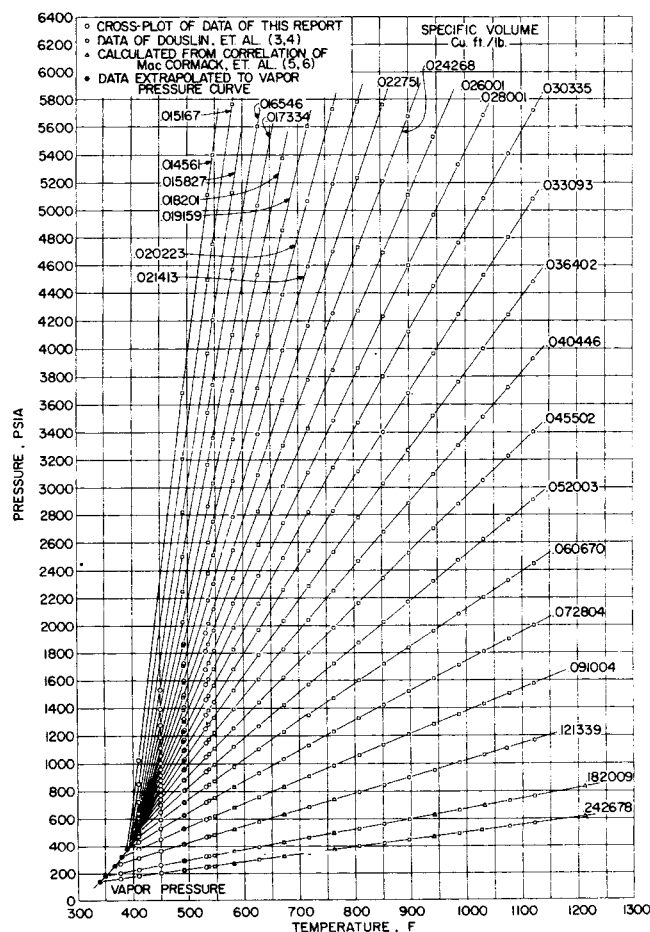


Fig. 5. Pressure-temperature diagram for carbon tetrafluoride.

critical and at the extreme ends, as well as the downward curvature of the isometrics at the intermediate densities. The isometrics have been extended graphically to the vapor pressure curve, and the points of intersection are noted with the dark dots in Figure 5.

To check the generalized trends, the data have been plotted on a compressibility chart as shown in Figure 6. No disagreement is noticed between this compressibility plot and what has been observed from study of many other compounds.

In addition to showing the proper generalized trends, Figures 4, 5, and 6 also show good agreement between the data of this paper with those from the literature (3 to 6) in all regions of overlap.

Algebraic Analysis

Following the graphical analysis of the data, the next step was to analyze the data algebraically with an equation of state. Many equations of state have been proposed in literature. Probably the most exhaustive study on this subject of equations of state was recently reported by Martin (29). A logical interpretation of the various characteristics of P-V-T data has led Martin to the following form of the equation:*

$$p = \frac{RT}{v-b} + \frac{A_2 + B_2T + C_2e^{-kT}}{(v-b)^2} + \frac{A_3 + B_3T + C_3e^{-kT}}{(v-b)^3} + \frac{A_4 + B_4T + C_4e^{-kT}}{(v-b)^4} + \frac{A_5 + B_5T + C_5e^{-kT}}{(v-b)^5} + \frac{A_6 + B_6T + C_6e^{-kT}}{e^{av}(1 + ce^{av})}$$

*This equation will be called the Martin equation of state in this paper.

This equation has built into its form and derivation all the observed properties of the P-V-T behavior. The constants, A_2 , B_2 , etc., ... C_6 , are assigned values dependent on the data of the particular compound under study.

There are 15 constants in the temperature function of the equation of state, exclusive of k , a , b , c , which must be

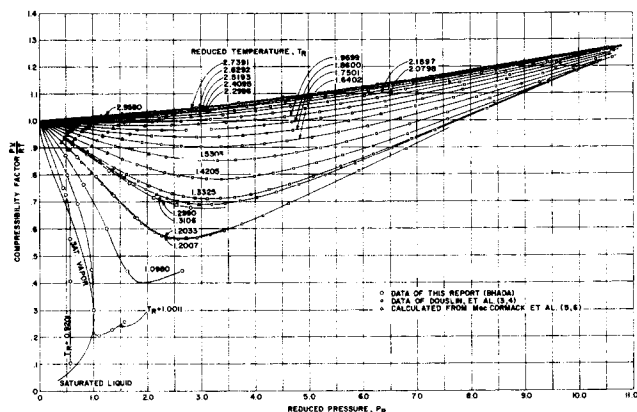


Fig. 6. Compressibility factor of carbon tetrafluoride.

TABLE 2. FINAL INPUT PARAMETERS FOR THE MARTIN EQUATION OF STATE FOR CARBON TETRAFLUORIDE

1. $T_c = 409.48^\circ\text{R.}$, $p_c = 543.16 \text{ lb./sq.in.abs.}$, $v_c = \frac{1}{39.06} = 0.02560163 \text{ cu.ft./lb.}$
2. At T_c , $p = 1,080 \text{ lb./sq.in.abs.}$, $v = 0.0145607 \text{ cu.ft./lb.}$
3. $(dz/dp_r)_{p_r \rightarrow 0} = -0.34$ $T_r = 1$
4. $(dp/dv)_{p_c, T_c} = 0$
5. $(d^2p/dv^2)_{p_c, T_c} = 0$
6. $a = 725.0$, $b = 0.00000$, $c = 5 \times 10^{-7}$
7. $T' = (0.800) T_c$
8. $T_B = 935^\circ\text{R.}$
9. $k = 4.2/T_c$
10. $(d^2p/dT^2) = 0$ $(dp/dT) = 36.55$ } at $v = 0.55 v_c$
11. $(d^2p/dT^2)_{v_c} = 0$ $(dp/dT)_{v_c} = 9.60$
12. $(dp/dT)_{1.5 v_c} = 1.061 (R/v_c)$ $T \rightarrow \infty$
13. $Cr(T_B) = 0.0142$
14. $Cr(T') = 0.050$
15. Selected point $T_{\text{sat}} = 399.53^\circ\text{R.}$ $P_{\text{sat}} = 459.30 \text{ lb./sq.in.abs.}$ $v = 0.01616 \text{ cu. ft./lb.}$

evaluated. Therefore, 15 input parameters (shown in Table 2) have been utilized in the evaluation of these constants. The method of arriving at the numerical values of these parameters for carbon tetrafluoride is similar to that described by Martin (29). The final selected values of these parameters are given in Table 2.

The latest paper by Martin (29) fully describes the logic behind the equation of state and the constants. The form of the equation given is capable of accurate representation of P-V-T behavior at densities as high as 2.5 times the critical. The method of solution for the constants, A_2 , B_2 , C_2 , etc., has been fully covered by Martin (29). The final forms of the constants derived for carbon tetrafluoride are shown in Table 3. It is believed that these constants give the best possible fit of the equation to the experimental data (that is, low deviations and least possible trends for data of this report as well as those from literature). Tables 1, 4, and 5 show the comparison of the experimental data of this paper as well as from literature with the calculated

TABLE 3. CONSTANTS FOR THE MARTIN EQUATION OF STATE FOR CARBON TETRAFLUORIDE

$p = \frac{RT}{(v-b)} + \frac{A_2 + B_2T + C_2e^{-kT}}{(v-b)^2} + \frac{A_3 + B_3T + C_3e^{-kT}}{(v-b)^3}$	
$+ \frac{A_4 + B_4T + C_4e^{-kT}}{(v-b)^4} + \frac{A_5 + B_5T + C_5e^{-kT}}{(v-b)^5}$	
$+ \frac{A_6 + B_6T + C_6e^{-kT}}{e^{aV}(1 + ce^{aV})}$	
where	$A_2 = -2.2937960$ $B_2 = 2.4545836 \times 10^{-3}$ $C_2 = -1.8125736 \times 10^{+1}$ $A_3 = 1.2063702 \times 10^{-2}$ $B_3 = 1.7195172 \times 10^{-6}$ $C_3 = 1.2232951 \times 10^{-1}$ $A_4 = -3.0017046 \times 10^{-4}$ $B_4 = 3.4565907 \times 10^{-7}$ $C_4 = 1.9662646 \times 10^{-2}$ $A_5 = 1.0070856 \times 10^{-6}$ $B_5 = 2.0376194 \times 10^{-9}$ $C_5 = -2.7942103 \times 10^{-4}$ $A_6 = 3.2856989 \times 10^6$ $B_6 = 1.9199674 \times 10^4$ $C_6 = 1.4483858 \times 10^9$ $R = 0.12193362$ $a = 725.0$ $b = 0.00$ $c = 5.0 \times 10^{-7}$ $k = +4.2/T_c$ $T_c = 409.48^\circ\text{R.}$ p , lb./sq.in.abs. T , $^\circ\text{R.}$ v , cu. ft./lb.

TABLE 4. COMPARISON OF EQUATION WITH DATA OF DOUSLIN*

Temp., $^\circ\text{R.}$	Specific volume, cu. ft./lb.	Pressure observed	% deviation		Reduced properties	
			$\frac{p_{\text{exp}} - p_{\text{calc}}}{p_{\text{exp}}} \times 100$		T_r	P_r
491.67	0.242678	227.49	-0.028		1.2007	0.419
	0.121339	419.70	-0.064			0.773
	0.072804	631.54	-0.041			1.163
	0.052003	805.40	0.032			1.483
	0.036402	1024.37	0.068			1.886
	0.028001	1233.04	-0.242			2.270
	0.020223	1713.19	-0.531			3.154
	0.016546	2505.39	0.324			4.613
	0.014561	3689.12	0.254			6.791
						0.896

*Sample data only shown in this table. Complete comparison is given in reference 30 and has also been placed with the ADI. (See footnote on p. 688.)

TABLE 5. COMPARISON OF EQUATION WITH CORRELATION OF MACCORMACK AND SCHNEIDER

Temp., °R.	Specific volume, cu. ft./lb.	Pressure, observed*	lb./sq. in. calc.	% deviation	Reduced properties		
				$\frac{p_{\text{exp}} - p_{\text{calc}}}{p_{\text{exp}}} \times 100$	T_r	P_r	z
491.67	0.242678	227.46	227.55	-0.042	1.2007	0.419	0.921
	0.121339	419.90	419.97	-0.016		0.773	0.849
	0.091004	531.65	531.56	0.017		0.979	0.807
	0.072804	632.00	631.80	0.032		1.164	0.768
	0.060670	722.35	722.42	-0.009		1.330	0.731
671.67	0.242678	327.79	327.14	0.200	1.6402	0.603	0.970
	0.121339	638.60	637.22	0.217		1.176	0.946
761.67	0.242678	376.35	376.31	0.011	1.8600	0.693	0.984
	0.121339	743.99	743.56	0.057		1.370	0.972
941.67	0.242678	474.53	474.39	0.029	2.2996	0.874	1.003
	0.182009	633.87	633.66	0.033		1.167	1.005
1,031.67	0.242678	523.02	523.39	-0.072	2.5194	0.963	1.010
	0.182009	700.03	700.70	-0.095		1.289	1.012
1,211.67	0.242678	620.49	621.38	-0.144	2.9590	1.142	1.019

*A few selected points obtained from correlation of MacCormack and Schneider (5,6).

values from the equation of state.* Also shown in Tables 1, 4, and 5 are the reduced properties P_r and T_r , together with the z values for each data point.

CONCLUSIONS

A variable-volume cell has been designed for observation of the (P-V-T) behavior of gases and liquids which does not use any liquid medium in contact with the compound under observation. The equipment consists of a bellows, in which the gas is confined, enclosed in a cylinder containing a fluid at the same pressure as the gas.

The P-V-T behavior of carbon tetrafluoride has been observed over a temperature range of 376° to 532 R°, a pressure range of 100 to 1,500 lb./sq. in. abs., and a specific volume range of 0.184 to 0.0152 cu. ft./lb. (about 1.66 times the critical density). The data have been correlated by the Martin equation of state, as shown in Table 3. This equation represents the observed data of this paper with an average deviation of 0.411% (average deviation is 0.236% for the literature data of Douslin et al. (3,4)).

It is concluded that data which are internally consistent as well as consistent with data from literature can be observed using the equipment of the study. The P-V-T cell is unique in that it utilizes stainless steel bellows with a 14:1 volume variation and with no liquid medium in contact with the compound under investigation.

NOTATION

- A_2 - A_6 = constants in the Martin equation of state
 a = constant in the Martin equation of state
 B_2 - B_6 = constants in the Martin equation of state
 b = constant in the Martin equation of state
 $Cr(T)$ = reduced third virial coefficient defined as $f_3(T)p^2/R^2T^3$
 C_2 - C_6 = constants in the Martin equation of state
 c = constant in the Martin equation of state
 k = curvature constant in the Martin equation of state
 p = pressure, lb./sq. in. abs.
 p_r = reduced pressure, p/p_c
 p_c = critical pressure, lb./sq. in. abs.
 p_{sat} = pressure along the vapor pressure curve, lb./sq. in. abs.
 R = gas constant
 T = temperature, °R.

*Table 4 shows comparison with the data of Douslin et al. (3,4) for one temperature only; the complete comparison may be found in the original dissertation (30). Table 4 has also been deposited as document No. 01384 with the ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc. 909 Third Ave., New York 10022 and may be obtained for \$2.00 for microfiche or \$5.00 for photocopies.

- T_r = reduced temperature, T/T_c
 T_c = critical temperature, °R.
 T' = temperature at which $B(T')p_c/RT' = z_c - 1$
 T_B = Boyle temperature (at which $B(T_B)p_c/RT_B = 0$)
 T_{sat} = Temperature along the saturation curve, °R.
 v = specific volume, cu.ft./lb.
 v_c = critical specific volume, cu.ft./lb.
 z = compressibility factor, pv/RT

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