$$-\frac{U^2}{b(x)}\frac{db(x)}{dx}ff_{\eta\eta}=\frac{K}{\rho}n\frac{U^{2n+1}}{b(x)^{n+1}}\;f_{\eta\eta}{}^{n-1}f_{\eta\eta\eta} \qquad (A6)$$

Equation (A6) indicates the existence of a similar solution if

$$\frac{U^2}{b(x)}\frac{db(x)}{dx}=C_1\frac{K}{\rho}n\frac{U^{2n+1}}{b(x)^{n+1}} \qquad (A7)$$

in which C_1 is an arbitrary constant. Rewriting Equation (A7) in the form

$$b^n(x)\frac{db(x)}{dx}=C_1\frac{K}{\rho}n\,U^{2n-1}$$

and integrating once yields

$$b(x)=\left[\,C_1\frac{K}{\rho}n(n+1)\,U^{2n-1}x\,\right]^{\frac{1}{n+1}} \qquad (A8)$$

For the case when $x \neq 0$, the substitution of Equation (A8) into Equation (A6) yields

$$\frac{1}{C_1}f_{\eta\eta\eta}f_{\eta\eta}{}^{n-1}+ff_{\eta\eta}=0 \qquad (A9)$$

Furthermore, this equation can be written as

$$f_{\eta\eta\eta}+C_1 ff_{\eta\eta}{}^{2-n}=0 \qquad (A10)$$

Without loss of generality the arbitrary constant, C_1, can be set equal to one. Then, the substitution of Equation (A8) into Equation (A4) with the relation, Equation (A5), gives the similarity transformation, Equation (7), and Equation (A10) becomes Equation (8). Similarly, the transformed boundary conditions for Equations (A2) and (A3) are those given in Equations (9) and (10).

The Experimental Determination of the Volumetric Properties and Virial Coefficients of the Methane-Ethylene System

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An apparatus was constructed for making isochoric measurements of P-V-T properties. Experimental compressibility factors were obtained and are presented for methane, ethylene, and four intermediate mixtures at 60, 40, and 20°F., with pressures from 260 to 2,220 lb./sq.in.abs. Second and third virial coefficients and interaction virial coefficients were determined from the data. The compressibility factors and the virial coefficients are compared with the Benedict-Webb-Rubin equation of state, applied in its original form and in a recent generalized form.

Volumetric (or compressibility factor) data are of industrial interest in process design calculations. The data are also of value in the calculation of derived thermodynamic quantities and in the further development of generalized methods for estimating thermodynamic properties from a minimum of direct data.

In the past, several experimental facilities have been developed for determining compressibility factors of mixtures or pure components along isochoric (constant density) paths. The apparatus of Goodwin (*7*), Michels (*16*, *20*), and Solbrig and Ellington (*28*) are of the isochoric type. In principle the compressibility factors for a constant composition system become established with the simultaneous knowledge of the three quantities pressure, temperature, and density. At selected points along an isochoric path the pressure and temperature are directly measured, and the data thus consist of a series of *P-T* points at constant density. The value of the density may be determined by separate measurement of the mass and volume quantities or, alternately, the density may be determined from the previously measured compressibility factors of the sample at a reference temperature.

In the apparatus described herein, the density of the sample is determined from the compressibility factors along the reference isotherm (77°F.). The isotherm is independently determined using a Burnett type of apparatus (*3*).

The methane-ethylene binary system was selected for this study. The compressibility factors of the methane system have been extensively reported from −274 to 650°F. and at pressures as high as 1,000 atm. (*4*, *10*, *13*, *19*, *21* to *23*, *27*, *30*). By far the largest portion of the experimental data is reported above the critical temperature

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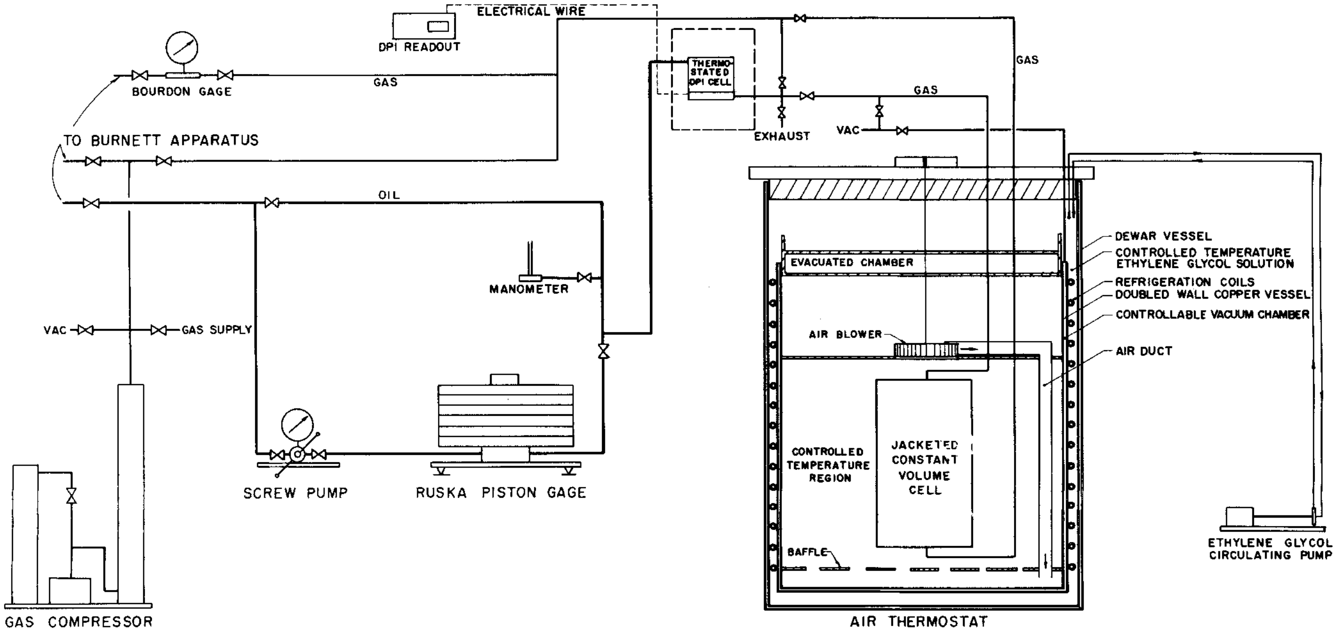

Fig. 1. Schematic diagram of apparatus for isochoric heating and cooling.

(−115.8°F.). The ethylene system has been adequately studied (*10, 12, 18, 31, 32*) above its critical temperature (49.8°F.); no significant amount of data, however, except at or near atmospheric pressure, has been taken for ethylene below 32°F. No vapor phase P-V-T data for the methane-ethylene system are reported in the literature.

EXPERIMENTAL APPARATUS

Cryostat

The cryostat (or air thermostat), illustrated schematically in Figure 1, consists of a double-walled copper vessel containing a jacketed constant volume sample bomb. The surfaces of the annular space between the walls are nickel plated and polished, and the annulus is maintained under vacuum.

An evacuated upper chamber is fitted into the mouth of the double-walled cans. This insulating chamber is also nickel plated and polished, and is sealed under vacuum.

Twenty turns of ½ in. O.D. copper tubing are concentrically wrapped and soldered on the outer surface of the outside wall of the vessel. These coils serve as the evaporator for a Freon-12 refrigeration system. The entire double-walled copper vessel is placed inside a stainless steel dewar. The space between the outside wall of the double-walled vessel and the inner wall of the dewar is filled with ethylene glycol solution, which is circulated by a centrifugal pump. To further minimize heat transfer, the outer wall of the steel dewar is wrapped with a layer of fiberglass material, and a 4 in. thick section of styrofoam is fitted into the top of the dewar.

The air in the cryostat is continuously circulated by a 100 cu. ft./min. air blower supported on a mounting plate approximately 3 in. above the top of the bomb. Air circulation is via a 2 in. I.D. aluminum air duct. The return air is distributed over a baffle located in the bottom part of the controlled temperature region; the distributing baffle promotes uniformity of temperature. The driving motor for the blower is placed outside the cryostat, to remove the effect of the dissipated heat on the temperature control.

Temperature Control

The optimum control of temperature is achieved by removing only a small amount of heat from the cryostat via the ethylene glycol solution and by adding a corresponding small amount of heat through a temperature controller. The control heater consists of approximately 45 ft. of nichrome wire having an electrical resistance of 20 ohms. This control wire is supported in the main circulating air stream by vertical glass rods (not shown in Figure 1). The rods are arranged concentrically at a horizontal distance of approximately 3½ in. from the bomb.

A thermocouple serves as the sensing element for the temperature controller. The thermocouple is located midway in the vertical section of the return air duct. The temperature controller is a Leeds and Northrup series 60 current adjusting type model, with proportional reset and rate control modes.

With this arrangement the apparatus may be satisfactorily operated down to a temperature of 20°F. The temperature of the cryostat could be controlled to 0.03 or 0.04°F, for 4 to 6 hr.

Temperature Measurement

For the determination of the temperature in the bomb, a calibrated copper-constantan thermocouple is fastened midway

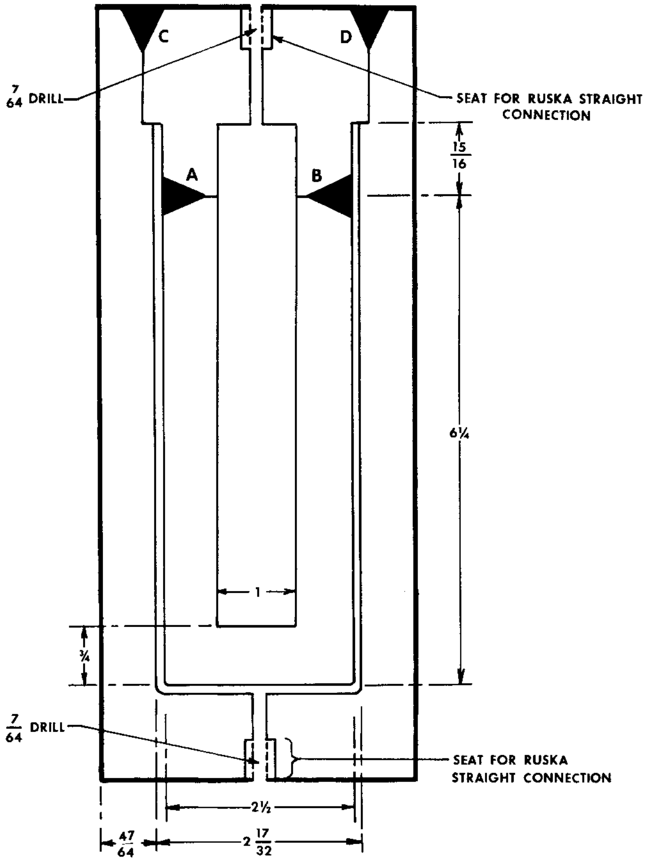

Fig. 2. Jacketed bomb assembly (circular cross section). Material: type 303 stainless steel. All dimensions are in inches.

on its outer vertical surface. The thermocouple output voltage, with reference to an ice bath, is measured by means of a Leeds and Northrup type K-3 potentiometer. The thermocouple was calibrated over the temperature range —40 to 95°F. vs. a Leeds and Northrup model 8163 platinum resistance thermometer. The accuracy of the calibration is estimated to be 0.03 to 0.04°F., which is equivalent to the accuracy of the potentiometer in this range.

Jacketed Bomb

The high pressure bomb (Figure 2) is constructed of Type 303 stainless steel. The bomb assembly is circular in cross section and is formed from three parts: a lower part, an upper part, and the jacket. The upper and lower parts were welded together at A and B, and the welds were machined flush to the cylinder walls. The inner portion of the bomb was then inserted into the pressure jacket and was welded at C and D. Seats for Ruska connections are provided for both inner bomb volume and jacket volume.

Provision is made for connecting the bomb to the vacuum system. All high pressure valves in the gas portion of the system are ⅛ in. Ermeto-type valves. Throughout the system, ⅛ in. stainless steel tubing (1/16 in. I.D.) is used. The gas compressor is a 15,000 lb./sq. in. hand operated piston type pump. This unit is used both for charging the sample into the bomb and for injecting gas into the jacket. The gas sample is injected into the inner chamber of the bomb through the line shown leading into the top of the bomb (Figure 1).

The elastic distortion of the bomb was offset by maintaining the proper value of pressure in the surrounding jacket. The inner chamber of the bomb is assumed to be a cylinder with radius a containing a gas at pressure P_i lb./sq. in. abs. The bomb is surrounded by a thin cylindrically shaped jacket with inner radius b, and confining a gas at pressure P_o lb./sq. in. abs. The radial deformation u of the cylinder, at radius r, due to radial and hoop stresses is given by (*15*)

$$u = \frac{1-\mu}{E}\left(\frac{a^2P_i - b^2P_o}{b^2-a^2}\right) r + \left(\frac{1+u}{E}\right)\frac{a^2b^2(P_i - P_o)}{b^2-a^2}\cdot\frac{1}{r} \qquad (1)$$

Similarly the deformation u_L due to axial stresses is given by

$$u_L = -\frac{\mu}{E}\,\frac{P_ia^2 - P_ob^2}{(b^2-a^2)}\, r \qquad (2)$$

The total deformation is obtained by adding the contributions from both equations. Adding the two equations and recalling that the total deformation must vanish when the inner radius $r = a$, there results

$$P_o = \frac{a^2\,(1-2\mu) + b^2\,(1+u)}{b^2\,(2-\mu)}\cdot P_i \qquad (3)$$

For all measurements the jacket pressure was maintained at the proper value, given above. This pressure was measured with a calibrated Bourdon gauge.

In the derivation of the above equations the following effects were not considered; the distortion of the upper capillary inlet, the volume compression of the inner bomb metal, the lack of balance of the end force on the inner bomb, and the weight of the bomb. At the maximum pressure reported herein (2,200 lb./sq. in.) the calculated total effect of all of the above factors is less than the estimated accuracy of the resultant compressibility factors (0.18%) by at least an order of magnitude.

The effect of temperature on the volume of the bomb was determined by calibration. This procedure is described as follows. Existing methane data from the literature (*21*) were cross plotted to obtain compressibility factor isotherms at 77, 60, 40, and 20°F. These data were then combined with experimentally measured (*15*) pressure changes with temperature (approximate isochors) for the jacketed bomb to determine the volume change. In this case Equations (5) and (6) (the characterizing equations for the apparatus) were used, recalling the V_{BT}/V_B is unity by definition at 77°F. The resultant bomb volume ratios were then expressed by the empirical relationship

$$\frac{V_{BT}}{V_B} = [1 + 0.000025\,(T-77)]^3 \qquad (4)$$

where V_{BT}/V_B is the ratio of the volume at temperature T to the volume at 77°F.

Measurement of Pressure

The pressure of the sample is determined by means of the Ruska model 2400 HL dual range piston gauge. The pressure of the oil is generated by the screw pump, and the oil is separated from the gas sample by the Ruska differential pressure (DPI) cell. This cell consists of two chambers, separated by a flexible metal diaphragm, the zero position of which is detected electronically and indicated by the DPI readout. The DPI cell is placed in an outer thermostat maintained slightly above room temperature. The temperature of the sample in the DPI cell is measured with a calibrated thermocouple.

In order to obtain pressure measurements accurate to one part in 10,000, the effects of pressure and temperature on the area of the piston were taken into account. An additional correction is necessary for the head of gas (at varying temperatures and densities) between the DPI cell and bomb. This head correction is determined by an iterative procedure, and the error associated with the correction is significantly less than the accuracy of the pressure measurements. The barometric pressure is measured with a Texas Instruments Model 141 A servo-nulling pressure gauge.

Corrections for Capillary Lines

The high pressure bomb and DPI cell are connected by insulated ⅛ in. O.D. stainless steel tubing. A small correction is required by the amount of sample mass contained within this tubing. For this purpose the average temperatures of different vertical sections of the tubing are required. These temperatures are determined by thermocouples fastened to the outer wall of the tubing.

PROCEDURE AND CHARACTERIZING EQUATIONS

Charging Procedure

Prior to charging the system, the gas compressor was rinsed, evacuated, and filled with the sample from the gas supply bottles. The entire gaseous portion of the system was then rinsed and evacuated, and the cryostat temperature was adjusted to the reference temperature (77°F.). The bomb was then filled to the desired pressure.

The six gas samples were blended and analyzed by Phillips Petroleum Company, Bartlesville, Oklahoma. The Phillips analyses were performed by mass spectrometry and were reported to the nearest 0.1 mole %. The methane sample contained 0.8% impurities as nitrogen and carbon dioxide, with 0.1% each of ethane and propane. For the preparation of the mixtures a purer source of methane was used. Random samples were selected for independent analysis by gas chromatography. For each of the components in these samples the results of the different analyses agreed to within 0.1 mole %. Results of the entire mass spectrometry analysis are given in Table 1.

Table 1. Composition Analysis of Mixtures

	Sample Identification					
		Mol %				
Mol % Component	CH_4	78.8% CH_4	57.2% CH_4	38.4% CH_4	18.4% CH_4	C_2H_4
CH_4	99.0	78.8	57.2	38.4	18.4	—
C_2H_4	—	20.7	42.4	61.4	81.6	99.9+
C_2H_6	0.1	0.1	0.1	—	—	—
C_3H_8	0.1	0.4	0.3	0.2	—	—
N_2	0.6					
CO_2	0.2					

Determination of Isochoric Run Constant

After the sample had attained equilibrium, the sample pressure and the exact value of temperature were measured. The isochoric run constant n/V_B was then determined from the following equation.

$$\frac{n}{V_B} = \left(\frac{P}{ZRT}\right)_{BT} \left[\frac{V_{BT}}{V_B} + \frac{V_a}{V_B}\right] + K \qquad (5)$$

n/V_B represents the total moles of sample (including capillary lines and DPI cell) divided by the volume of the bomb only. Equation (5) follows directly from a mass balance of the entire sample in the bomb, the capillary lines, the valves, and the DPI cell. The determination of this quantity is described below.

V_a is the volume of the portion of the capillary tubing (6½ in. in length) in the controlled temperature region of the cryostat. The ratio V_a/V_B was determined from scale drawings of the apparatus to be 0.003868. The quantity K represents the entire correction for the sample contained in the length of capillary line and DPI cell. The determination of this quantity will be described below.

The compressibility factor Z in Equation (5) was determined from the independently established reference isotherm at 77°F. This isotherm had been previously determined (*10*) for a sample from the same gas cylinder using the interrelated Burnett apparatus (Figure 1). The Burnett apparatus data were handled graphically to facilitate determination of the compressibility factors (*15*). Common values of R [10.731496 (lb./sq.in.-cu.ft.)/(lb. mole.- °R.)] and absolute temperature conversion T_o (459.670) were used for both Burnett and isochoric data. All data are based on the Carbon 12 International Scale.

Compressibility Factors at Lower Temperatures

After determination of the quantity n/V_B the temperature of the bomb was lowered to the next desired level of temperature and allowed to reach equilibrium. The pressure and the exact value of temperature were measured, and the experimental compressibility factor Z_{BT} was determined from the following rearrangement of Equation (5).

$$Z_{BT} = \left(\frac{P}{RT}\right)_{BT} \left[\frac{\frac{V_{BT}}{V_B} + 0.003868}{n/V_B - K}\right] \qquad (6)$$

The procedure was repeated, until measurements had been taken at all desired temperatures on the isochor.

Measurements at Other Isochors

After all points on the isochor had been taken, the entire procedure was repeated at lower density isochors. The experimental density for the next isochor was obtained by venting a small portion of the sample via the exhaust valve. For each successive isochor the same series of temperatures was selected so that the data could be presented in isothermal, as well as isochoric, form.

Exact Isotherms and Isochors

The temperatures along each isochor were maintained as closely as possible to the pre-selected even values of temperature. Corrections to exact isotherms were normally 0.1 to 0.2°F. The compressibility factors Z_{P,T_o} at pressure P and exact temperature T_o were determined from the corresponding compressibility factors at pressure P and experimental temperature T_x by the expression

$$Z_{P,T_o} = Z_{P,T_x} + \int_{T_x}^{T_o} \left(\frac{\partial Z}{\partial T}\right)_{P,T_x} dT \qquad (7)$$

The term $(\partial Z/\partial T)_{P,T_x}$ was evaluated graphically from the data.

Due to the effect of the sample in the capillary line and DPI cell, the experimental data do not follow an exact isochor. The compressibility factors were corrected to exact isochors by Equation (8). The integral was evaluated graphically by a procedure similar to that used for the temperature correction, Equation (7).

$$Z_{T_o,\rho} = Z_{T_o,\rho x} + \int_{\rho_x}^{\rho} \left(\frac{\partial Z}{\partial \rho}\right)_{T_o,\rho x} d\rho \qquad (8)$$

Determination of K

The quantity K in Equation (5) is given by the expression

$$K = \rho_D \left(\frac{V_D}{V_B}\right) + \rho_5 \left(\frac{V_5}{V_B}\right) + \rho_4 \left(\frac{V_4}{V_B}\right) + \rho_3 \left(\frac{V_3}{V_B}\right) + \rho_2 \left(\frac{V_2}{V_B}\right) + \rho_1 \left(\frac{V_1}{V_B}\right) \qquad (9)$$

The ρ_i are densities of the sample at different vertical sections of the capillary. V_D represents the gas-side volume of the DPI cell, and the terms V_5, .., V_1 represent volumes of the valves and vertical sections of the capillary (with lengths of 25½, 22⅝, 6⅜, 6⅜, and 5½ in., respectively) corresponding to the ρ_i. The capillary was divided into separate sections, as differences in temperature existed along the entire length. The volume ratios were determined by direct measurement and from drawings of the apparatus. The resulting values are given in Table 2.

TABLE 2. VOLUME RATIOS FOR DETERMINATION OF K

V_D/V_B	V_5/V_B	V_4/V_B	V_3/V_B	V_2/V_B	V_1/V_B
0.01263	0.01537	0.01511	0.003794	0.003794	0.003273

K is not a constant but must be determined at each point on the isochor, since the capillary densities ρ_i decrease with the lowering of the temperature of the bomb. The volume ratios are constant; thus K is determined by knowing the densities ρ_i. As these densities involve the unknown compressibility factors at the temperatures and pressures within the capillary, K was first approximated by using the ideal gas law. From this assumption the approximate values of the compressibility factors at each temperature along the isochor were determined. These approximated values were then crossplotted to obtain more accurate values of the compressibility factors of the sample within the capillary, and the above calculational procedure was repeated. Due to the relatively small size of K only one iteration was normally required for convergence. The pressure corrections for vertical height of each section of capillary tubing were determined as part of the above iterative procedure.

Advantages and Disadvantages of the Apparatus

In attaining thermal equilibrium after changing to a lower temperature, a relatively long period of time is required. This undesirable feature is due primarily to the low heat transfer coefficient between the circulating air and the bomb and also to the insulating effect of the surrounding pressure jacket. As the data are taken isochorically only one point is taken between temperature changes, which causes the experimental work to proceed slowly.

The chief advantage of the apparatus is that, given the compressibility factors of the sample along the reference isotherm, the compressibility factors at lower temperatures may be determined solely from the measurement of pressure and temperature. The measurement of these two quantities may generally be accomplished with less difficulty than the determination of either of the quantities mass or volume.

The bomb was satisfactorily tested to 12,000 lb./sq.in.

Experimental data were not taken at these higher pressures, as the data in the lower pressure region are more important in the determination of virial coefficients. The cryostat is designed so as to be operational at lower temperatures. Experimental isochors could be extended to considerably lower temperatures by the use of a different refrigerant, such as liquid nitrogen, in the space between the copper vessel and the dewar.

EXPERIMENTAL ERRORS

Estimates of the experimental error in the compressibility factors were made from estimated errors in each of the quantities in Equations (5) and (6). Estimated errors in the measured quantities are given in Table 3. The resultant estimated error in the compressibility factor was 0.13%. This error was attributed equally to errors in the reference isotherm and to errors in the correction for the sample in the capillary line, valves, and DPI cell. Errors caused by the sample correction were due to errors in the associated volumes. These volume errors were predominantly due to uncertainties in direct measurement, with the volume change due to elastic distortion contributing only a minor amount.

The accuracy of the 77°F. reference isotherm (0.10%) was determined (*10*) for pressures up to 2,200 lb./sq.in. The Burnett data (at temperatures of 77°F. and higher) will be published separately. The errors in the remaining quantities (such as pressure and bomb temperature) have only a small effect here.

TABLE 3. ESTIMATED ERRORS

Reference isotherm compressibility factors	0.10%
Pressure in bomb	0.01%
Bomb temperature	0.03 to 0.04°F.
Temperature of capillary line within cryostat	0.10°F.
Temperature of exposed capillary volumes	1.0°F.
Thermal expansion constant for bomb	2.5×10^{-6}/°F.
Volume ratios for capillary sections (avg.)	2.3%
Pressure in jacket	10.0 lb./sq.in.

In addition to the above calculated error, the error due to graphically correcting the experimental compressibility factors to exact isochors and even values of temperature must be considered. This error is estimated as 0.05%. Considering these effects the compressibility factors are accurate to approximately 0.18%.

EXPERIMENTAL DATA

The resultant compressibility factors for methane, ethylene, and the four intermediate mixtures are presented in Table 4. The experimental data are for the temperatures 60, 40, and 20°F.; the reference isotherm compressibility factors at 77°F. are also shown. The densities (determined from the reference isotherm) are reported to five significant figures in order to retain all possible precision in the determination of virial coefficients.

TABLE 4. EXPERIMENTAL COMPRESSIBILITY FACTORS

		Temperature, °F.			
1/V		77*	60	40	20
lb. moles/cu.ft.	System: methane		Compressibility factor Z		
0.05312		0.9656 (295.41)†	0.9627 (285.19)	0.9582 (272.94)	0.9517 (260.25)
0.12123		0.9255 (646.20)	0.9191 (621.37)	0.9100 (591.58)	0.8988 (560.90)
0.17881		0.8971 (923.83)	0.8891 (886.61)	0.8763 (840.25)	0.8610 (792.45)
0.24734		0.8689 (1237.71)	0.8566 (1181.50)	0.8393 (1113.12)	0.8196 (1043.53)
0.31315		0.8465 (1526.72)	0.8304 (1450.26)	0.8094 (1359.10)	0.7854 (1266.04)
0.37480		0.8306 (1792.98)	0.8117 (1696.56)	0.7870 (1581.69)	0.7591 (1464.60)
0.44789		0.8196 (2114.08)	0.7975 (1992.06)	0.7690 (1846.87)	0.7368 (1698.84)
0.50260		0.8162 (2362.49)	0.7921 (2220.15)	0.7610 (2050.90)	0.7255 (1876.94)
	System: 78.8% methane				
0.05849		0.9509 (320.32)	0.9477 (309.12)	0.9413 (295.22)	0.9332 (280.96)
0.13542		0.8934 (696.80)	0.8857 (668.87)	0.8730 (633.90)	0.8581 (598.19)
0.19841		0.8528 (974.53)	0.8411 (930.73)	0.8240 (876.68)	0.8040 (821.08)
0.26394		0.8174 (1242.58)	0.8023 (1180.91)	0.7807 (1104.99)	0.7555 (1026.41)
0.33082		0.7877 (1500.87)	0.7691 (1419.00)	0.7432 (1318.37)	0.7130 (1214.27)
0.39944		0.7650 (1759.91)	0.7428 (1654.70)	0.7126 (1526.27)	0.6780 (1393.97)
0.46528		0.7511 (2012.63)	0.7257 (1882.97)	0.6911 (1724.29)	0.6522 (1562.11)
0.54018		0.7455 (2319.31)	0.7175 (2161.47)	0.6780 (1963.82)	0.6336 (1761.76)

(*Continued*)

	Temperature, °F.			
1/V lb. moles/cu.ft.	77[*]	60	40	20
	Compressibility factor Z			
System: 57.2% methane				
0.06614	0.9273 (353.24)	0.9217 (339.96)	0.9127 (323.70)	0.9020 (307.07)
0.13826	0.8566 (682.09)	0.8457 (652.08)	0.8300 (615.31)	0.8115 (577.55)
0.21999	0.7902 (1001.11)	0.7737 (949.19)	0.7507 (885.50)	0.7240 (819.83)
0.29116	0.7417 (1243.76)	0.7209 (1170.50)	0.6930 (1081.87)	0.6597 (988.77)
0.39188	0.6903 (1558.04)	0.6643 (1451.79)	0.6281 (1319.84)	0.5880 (1186.07)
0.45251	0.6699 (1745.85)	0.6399 (1614.88)	0.6006 (1457.37)	0.5554 (1293.65)
0.52597	0.6570 (1990.10)	0.6232 (1827.86)	0.5778 (1629.59)	0.5275 (1428.09)
0.60428	0.6563 (2284.13)	0.6154 (2073.99)	0.5653 (1831.85)	0.5094 (1584.51)
System: 38.4% methane				
0.08163	0.8878 (417.38)	0.8792 (400.25)	0.8667 (379.38)	0.8525 (358.21)
0.16409	0.7908 (747.29)	0.7751 (709.25)	0.7541 (663.50)	0.7288 (615.59)
0.25318	0.7048 (1027.74)	0.6833 (964.80)	0.6532 (886.74)	0.6183 (805.82)
0.32863	0.6498 (1229.82)	0.6220 (1139.87)	0.5851 (1031.04)	0.5437 (919.73)
0.44220	0.5881 (1497.62)	0.5540 (1366.21)	0.5091 (1207.41)	0.4597 (1046.38)
0.46090	0.5811 (1542.37)	0.5470 (1405.90)	0.5007 (1237.55)	0.4489 (1065.10)
0.63084	0.5609 (2037.70)	0.5141 (1808.48)	0.4544 (1537.20)	0.3901 (1266.78)
0.67458	0.5682 (2207.36)	0.5201 (1956.55)	0.4557 (1648.49)	0.3870 (1343.92)
System: 18.4% methane				
0.09556	0.8358 (460.00)[†]	0.8231 (438.64)	0.8046 (412.27)	0.7832 (385.23)
0.19124	0.7018 (772.99)	0.6821 (727.45)	0.6500 (666.60)	0.6139 (604.36)
0.34990	0.5427 (1093.71)	0.5066 (988.51)	0.4581 (859.44)	0.3970 (715.11)
0.40255	0.5065 (1174.36)	0.4685 (1051.82)	0.4175 (901.25)	0.3583 (742.45)
0.49363	0.4621 (1313.61)	0.4192 (1154.02)	0.3615 (956.75)	0.3036 (771.33)
0.63410	0.4326 (1579.73)	0.3836 (1356.44)	0.3199 (1087.83)	0.2534 (827.23)
0.79393	0.4374 (2000.21)	0.3789 (1677.51)	0.3073 (1308.31)	0.2292 (936.59)
System: ethylene				
0.10366	0.7861 (469.31)	0.7711 (445.79)	0.7497 (416.69)	0.7264 (386.28)
0.21940	0.5961 (753.21)	0.5678 (694.73)	0.5288 (622.06)	
0.36612	0.4390 (925.66)	0.4036 (824.03)		
0.53576	0.3361 (1037.05)	0.2911 (869.61)		
0.68094	0.3210 (1258.87)	0.2584 (981.17)		
0.78671	0.3686 (1670.07)	0.2943 (1291.39)		

[*] reference isotherm data (*10*).

[†] values in parentheses represent corresponding pressure, lb./sq.in.abs.

The experimental data were compared vs. the eight-constant Benedict-Webb-Rubin (BWR) equation (*2*) and the Edmister et al. (*6*) generalized BWR equation. The equation was used in the form

$$Z = 1 + \left(B_o - \frac{A_o}{RT} - \frac{C_o}{RT^3} \right) d + \left(b - \frac{a}{RT} \right) d^2 + \frac{a\alpha}{RT} d^5 + \frac{cd^2}{RT^3} (1 - \alpha d^2) \exp(-\alpha d^2) \qquad (10)$$

For the original equation the constants as tabulated in Table 5 were used. For the generalized equation eight dimensionless reduced constants, given below, were defined in terms of the specific constants and the criticals plus the gas constant.

$$B_o' = \frac{B_o P_c}{R\,T_c}$$

$$A_o' = \frac{A_o P_c}{R^2 T_c^2}$$

$$C_o' = \frac{C_o P_c}{R^2 T_c^4}$$

$$b' = \frac{b\,P_c^2}{R^2 T_c^2}$$

$$a' = \frac{a\,P_c^2}{R^3 T_c^3}$$

$$c' = \frac{c\,P_c^2}{R^3 T_c^5}$$

$$\alpha' = \frac{\alpha\,P_c^3}{R^3 T_c^3}$$

$$\gamma' = \frac{\gamma\,P_c^2}{R^2 T_c^2} \qquad (11)$$

The reduced constants were computed from the above definitions, using the values of the specific constants obtained by Benedict, et al. (*1*) for twelve hydrocarbons. The reduced constants were then determined to be the following functions of acentric factor.

$$B_o' = 0.113747 + 0.127349\,\omega - 0.243280\,\omega^2$$
$$A_o' = 0.343258 - 0.127521\,\omega - 0.509131\,\omega^2$$
$$C_o' = 0.098224 + 0.401236\,\omega - 0.0397267\,\omega^2$$
$$b' = 0.0275404 + 0.131009\,\omega - 0.134924\,\omega^2$$
$$a' = 0.0235866 + 0.290284\,\omega - 0.295413\,\omega^2$$
$$c' = 0.035694 + 0.185297\,\omega - 0.230125\,\omega^2$$
$$\alpha' a' = 0.0000875$$
$$\gamma' = 0.052058 - 0.09064\,\alpha + 0.10506\,\omega^2 \qquad (12)$$

With the exception of ethylene the acentric factors for all components were available in the literature (*24*). The acentric factor for ethylene was determined from published vapor pressure data (*32*) to be +0.087. For the mixtures the linear combining rule was used for the constant B_o, with the usual BWR combining rules being used for the seven remaining constants.

The standard deviations in compressibility factor (BWR — exp) are summarized in Table 4A. The fit of the original equation to the pure component data is satisfactory. The standard deviations in compressibility factors were 0.003 for methane (32 data points) and 0.005 for ethylene (15 data points). Although the generalized equation does not fit the pure component data as well as does the original equation the fit is considered satisfactory for a generalized relationship. For the intermediate mixtures the standard deviations are somewhat larger, especially for the original equation. This effect is expected from the semi-empirical nature of the mixing rules (*2*). An improved fit to the mixture data could likely be obtained by refinements in the form of these rules.

TABLE 5. CONSTANTS OF THE BENEDICT-WEBB-RUBIN EQUATION OF STATE USED IN THIS WORK
Units: sq.ft./lb. mole, lb./sq.in.abs., or = °F. + 459.63°, R = 10.7335

Component	methane	ethylene	ethane	propane	carbon dioxide	nitrogen*
B_o	0.682401	0.891980	1.00554	1.55884	0.542935	0.0458000
A_o	6995.25	12593.6	15670.7	25915.4	7450.19	1.19250
$C_o \times 10^{-6}$	275.763	1602.28	2194.27	6209.93	950.623	0.00588907
b	0.867325	2.20678	2.85393	5.77355	1.352840	0.00198154
a	2984.12	15645.5	20850.2	57248.0	10571.60	0.0149000
$c \times 10^{-6}$	498.106	4133.60	6413.14	25247.8	1915.750	0.000548064
$\alpha \times 10^3$	511.172	731.661	1000.44	2495.77	287.143	0.291545
$\gamma \times 10^2$	153.961	236.844	302.790	564.524	118.1840	0.750000
reference	*1*	*1*	*1*	*1*	5	29

* Metric units.

Virial Coefficients

The Leiden virial equation may be given in the form

TABLE 4A. EQUATION OF STATE COMPARISONS STANDARD DEVIATION FOR ALL TEMPERATURES

	System						
Equation	methane	78.8% methane	57.2% methane	38.4% methane	18.4% methane	ethylene	overall
Orig. BWR	0.003	0.014	0.020	0.019	0.019	0.005	0.015
Gen. BWR	0.008	0.016	0.016	0.010	0.028	0.022	0.017
No. of Points:	32	32	32	32	28	15	171

$$(Z-1)V = B(T) + C(T)/V + D(T)/V^2 + \ldots \quad (13)$$

For a pure component the coefficients $B(T)$, $C(T)$, $D(T)$, ..., are the second, third, fourth, ..., etc., virial coefficients, which are functions of temperature only for a constant composition system. The virial equation is of fundamental significance and may be derived from first principles using the formulations of statistical mechanics (*9*).

For a mixture the coefficients are functions of both temperature and composition. The expression for the second virial coefficients of a mixture of N components is given by Mayer (*14*) as

$$B_m(T) = \sum_{i}^{N} \sum_{j}^{N} B_{ij}(T)\, X_i X_j \quad (14)$$

Here the interaction coefficients $B_{ij}(T)$ characterize the interaction between species i and j and also are functions of temperature only.

Equation (13), truncated after the third virial coefficient term, was fitted to the isothermal data from Table 4 (at 60, 40, and 20°F.) by a least squares technique. This procedure was justified by the fact that plots of $(Z-1)V$ vs. $1/V$ were linear up to pressures of about 2,400 lb./sq.in. and this technique removes operator bias. The virial coefficients for the reference isotherm compressibility factors were not determined. These coefficients at 77°F. are being determined as part of a related investigation presently in progress (*10*); the results will be published separately.

The second virial coefficients from the above least squares fit were used for the determination of interaction coefficients B_{12}, as is discussed below.

The effect of impurities on the second virial coefficients was accounted for by using Equation (14), expanded to include all components as listed in Table 1. For this calculation the interaction coefficients between the principle components (that is, methane and ethylene) and the impurities were required. The interaction coefficients were taken from available tabulations where possible: methane-ethane (*8*), methane-propane (*8*), and methane-carbon dioxide (*11*). Values not available (ethylene-propane, ethylene-ethane, and methane-nitrogen) were estimated using the method of Prausnitz (*25, 26*). All corrections were positive and generally tended to decrease with increasing temperature and with increasing ethylene composition. The maximum value of the correction was +1.70 cc./g. mole for the 78.8% methane system at 20°F. The corrected values of the second virial coefficients, converted to units of cc./g. mole, are given in Table 6. A sufficient number of data points was not available from this work to determine the virial coefficients for ethylene at 40 and 20°F. The values shown in Table 6 were determined graphically from virial coefficient data published by Michels (*18*). The errors introduced by the graphical procedure were estimated as 0.1 cc./g. mole.

For the binary system, Equation (14) takes the form

$$B_m(T) = X_1^2 B_{11}(T) + 2X_1X_2\, B_{12}(T) + X_2^2 B_{22}(T) \quad (15)$$

Based on Equation (15) and the virial coefficients from Table 6 the methane-ethylene interaction coefficients B_{12} were determined at each temperature by least squares. The results are shown in Table 6.

The third virial coefficients from the least squares fit are given in Table 7. These coefficients were not corrected for the effect of impurities, due to the general nonavailability of the required interaction third virial coefficients.

TABLE 6. SECOND VIRIAL COEFFICIENTS FOR THE METHANE-ETHYLENE SYSTEM

Temperature °F.	60	40	20
	B(mixture), cc./g. mole		
System			
CH_4	−46.07	−51.16	−57.06
79.2% CH_4	−57.78	−64.17	−72.09
57.4% CH_4	−77.04	−84.99	−94.51
38.5% CH_4	−97.91	−106.97	−117.67
18.4% CH_4	−121.29	−133.18	−147.01
C_2H_4	−148.41	−162.58*	−175.95*
	B_{12} (interaction), cc./g. mole		
	−71.5	−78.6	−89.8

* Determined graphically from data of Michels (*18*).

TABLE 7. THIRD VIRIAL COEFFICIENTS FOR THE METHANE-ETHYLENE SYSTEM

Temperature °F.	60	40	20
	C(mixture), cm.^{6}/g. mole^2, $\times 10^{-2}$		
System			
CH_4	25.0	26.7	28.7
78.8% CH_4	30.1	32.8	36.7
57.2% CH_4	39.8	43.1	47.7
38.4% CH_4	50.3	53.7	58.3
18.4% CH_4	57.7	62.8	69.1
C_2H_4	74.5		

Errors in the second virial coefficients were estimated from the calculated accuracy of the compressibility factors. A systematic error of 0.18% in the compressibility factors was assumed; introducing this error, the second virial coefficients were recalculated from the truncated form of Equation (13). This assumed error produced an error ranging from 0.5 to 1.3 cc./g. mole (depending on temperature and composition) in the second virial coefficients. Calculations based on systematic errors in the compressibility factors, however, give maximum calculated errors in the virial coefficients. Random errors in the compressibility factors would cause smaller errors, but the exact effect of these random errors is difficult to characterize. Considering the correction due to composition, the probable accuracy of the coefficients is 0.4 to 0.8 cc./g. mole. This error is largest for the samples with high percentages of methane.

The methane virial coefficients were plotted vs. temperature, and a value of −53.45 cc./g. mole at 32°F. was interpolated. This value compares quite well with the value of −53.35 cc./g. mole determined by Douslin (*4*).

The ethylene virial coefficients of Michels (*18*) were plotted vs. temperature, and a value of −149.95 cc./g. mole at 60°F. was determined. The corresponding value from this investigation is −148.41 cc./g. mole, which is higher by approximately 1.5 cc./g. mole. This difference is thought to be due to the differences in the methods used. The Michels' coefficients were based upon a different mathematical model, and were determined over a range of data different from the range of data of this investigation.

The methane compressibility factors (Table 4) were crossplotted for a direct comparison with the data of Douslin (*4*) at 32°F. Isotherms of Z vs. P were constructed, and values of Z were read off at values of P corresponding to the experimental pressures of Douslin. These compressibility factors were then plotted vs. T at constant P and values were read off at 32°F. The maximum error in the graphical procedure was estimated as 0.10%. Comparisons were made vs. ten data points ranging in pressure from approximately 237 and 2,191 lb./sq.in.abs.

The standard deviation from the ten data points was 0.11%, with the maximum deviation being 0.19%. The stated accuracy of Douslin's data in this region is 0.03%.

The ethylene data at the lower density isochors were compared at 60, 40, and 20°F. vs. the literature values of Walters, et al. (*31*) and York and White (*32*). An accuracy of 0.25 to 0.30% is claimed by both investigators. The York and White values corresponding to the higher density isochors were not used in the comparison, as these data below 77°F. represent an extrapolation by York and White of the data of Michels (*17*). The standard deviations from both of the above sources are given as Walters, et al. (0.30%) and York and White (0.20%), with a total standard deviation from both investigators of 0.26%.

The differences between the compressibility factors of this investigation and the data of the above literature sources are explainable by the combined errors from each source.

Ideally, a closed-form equation of state would accurately predict the second, third (and possibly higher ordered) virial coefficients. By comparing experimental virial coefficients vs. calculated values, the need for further work on the form of equations of state is emphasized. The second and third virial coefficients for the pure components and mixtures were compared vs. both forms of the BWR equation. The virial coefficients as given by the BWR equation are of the form

$$B(T) = B_o - \frac{A_o}{RT} - \frac{C_o}{RT^3} \tag{16}$$

$$C(T) = b - \frac{a}{RT} + \frac{c}{RT^3} \tag{17}$$

For the second virial coefficients the differences (BWR − exp) generally were negative, and were larger than the estimated error of the experimental coefficients. For all points the differences ranged from + 0.85 to − 6.84 cc./g. mole. For the third virial coefficients the differences (BWR − exp) ranged from + 13.5 to − 1.1 $\text{cm}^6/\text{g. mole}^2 \times 10^{-2}$ and tended to increase with decreasing methane composition. In this case the differences between the experimental coefficients and the calculated values are explained by the fact that the original BWR constants were determined by a fit to volumetric data rather than virial coefficients.

ACKNOWLEDGMENT

This work was supported by grants from the National Science Foundation and the Petroleum Research Fund of ACS. The gas samples were supplied by Phillips Petroleum Company.

NOTATION

$a, A_o, b, B_o, c, C_o, a', A_o', b', B_o', c', C_o'$ = constants in equations of state
$B(T), C(T)$ = second, third, etc., virial coefficients
$B_{ij}(T)$ = interaction second virial coefficient
d = density
E = modulus of elasticity
K = capillary correction
n = number of moles
r = bomb radius
u, u_L = cylinder deformations
$V_a, V_1, \ldots, V_5$ = capillary volumes
Z = compressibility factor, PV/RT
$\alpha, \alpha', \gamma, \gamma'$ = constants in equations of state
μ = Poisson's ratio
ρ = density, P/ZRT
ω = acentric factor

Subscripts

B = bomb at 77°F.
BT = bomb at T°F.
D = DPI cell
i = vertical section of interconnecting capillary
= component of a mixture
j = component of a mixture
m = mixture
o = exact level of temperature

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Manuscript received November 17, 1967; revision received March 8, 1968; paper accepted March 11, 1968.