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# Volumetric Properties of Gas Mixtures at Low Temperatures and High Pressures by the Burnett Method: the Hydrogen-Methane System

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**A Burnett type of apparatus for the study of the volumetric behavior of gases at low temperatures and high pressures was constructed. The apparatus was used to study the volumetric behavior of methane and four mixtures of hydrogen and methane from +50° to —200°F. and pressures as high as 7,000 lb./sq. in.**

**The experimental data were used to obtain the second virial coefficients for pure methane and for the mixtures. The results of approximately 600 experimental points were used to obtain a table of compressibility factors for methane and the mixtures at even increments of pressure and temperature.**

## HISTORICAL BACKGROUND

In 1936 E. S. Burnett introduced a method for determining compressibility factors without directly measuring either volume or mass (*3*). The apparatus as described was to be applied to a homogeneous gaseous phase only. Following the introduction of this apparatus by Burnett many investigators have applied the apparatus to study the compressibility of gases. The wide range of conditions over which the Burnett apparatus has been applied to obtain compressibility factors attests to the versatility of the method (*2, 12, 5, 8, 14, 15, 18, 4, 16, 17*).

## ADVANTAGES AND DISADVANTAGES OF THE BURNETT METHOD

In the most commonly used experimental techniques for Z value measurement it is necessary to determine temperature and pressure for a fixed amount of gas in a measured volume. Accurate volume measurements may be made with high accuracy and precision at low pressures, but high-pressure measurements become much less certain. It is also necessary in these techniques to know the mass of the sample under observation; this is determined either directly by differential weighings of a sample bomb before and after material has been removed, or by measuring the gas volume at a low pressure where the compressibility of the material studied is accurately

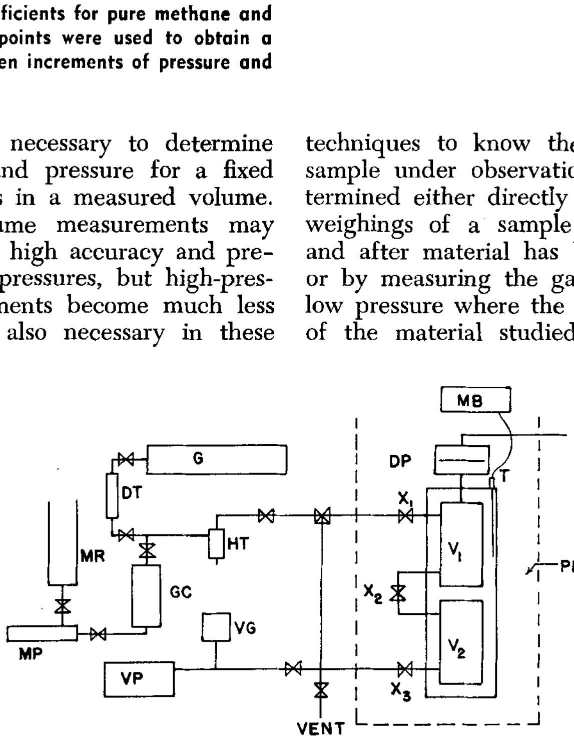

Fig. 1. Charge and expansion sections.

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known. In the latter case the resulting compressibility-factor data are usually given in Amagat unit. Amagat units are the ratio of the pressure times the volume of the gas at experimental conditions to the pressure volume product of the gas at 1 atm. pressure at 0°C. Kobe (*7*) discusses the conversion of Amagat units to compressibility factors which are more commonly used in engineering practices.

In contrast the Burnett method yields compressibility data from determinations of pressure under isothermal conditions. The volumes need not be known, nor is any measure of mass required. These measurements are more easily made to higher accuracy than are measurements of mass and volume. Furthermore the necessity of using mercury as a confining fluid is eliminated, making measurements possible at low temperatures.

There are however some disadvantages in using the Burnett method. Only a single phase gaseous system may be studied in the equipment. For this reason studies at low temperatures on systems for which no phase-equilibrium data are available would be difficult. When the equipment is used to study gases which are not easily liquefied, material must be either vented to the atmosphere, requiring large amounts of pure gases, or allowed to flow into a relatively large volume followed by recompression.

Another disadvantage is the wide spacing of data at high pressures and the relatively close spacing at low pressures. In order to overcome this effect several runs must be made for each set of conditions starting at different initial pressures.

## BASIC EQUATIONS

The basic equations for the evaluation of the apparatus constant, the ratio of pressure to compressibility factor at the highest pressure under consideration, and the compressibility factor corresponding to each expansion have been derived (*3*, *16*, *17*). The general equation relating the pressure after *j* expansion to the apparatus constant *N* and the ratio of the highest pressures under consideration to the corresponding compressibility factor is given by

$$P_j N^j = Z_j \frac{P_o}{Z_o} \qquad (1)$$

where $P_o/Z_o$ is the ratio of highest pressure under consideration to the corresponding compressibility factor. When $P_jN^j$ is plotted against $P_j$ and the resulting curve is extrapolated to

TABLE 1. EXPERIMENTAL GAS COMPOSITIONS

| Mole % | $CH_4$ | A | B | C | D |
|---|---|---|---|---|---|
| $CH_4$ | 99.7 | 79.4 | 64.5 | 43.1 | 21.7 |
| $H_2$ | 0.0 | 20.2 | 35.1 | 56.5 | 78.0 |
| $N_2$ | 0.2 | 0.3 | 0.3 | 0.2 | 0.2 |
| Others | 0.1 | 0.1 | 0.1 | 0.2 | 0.1 |

TABLE 2. SMOOTHED COMPRESSIBILITY FACTORS

50°F.

| Pressure, lb./sq. in. abs. | $CH_4$ | Mixtures | | | |
|---|---|---|---|---|---|
| | | A | B | C | D |
| 200 | 0.9706 | 0.9835 | 0.9916 | 0.9995 | 1.0050 |
| 400 | 0.9434 | 0.9679 | 0.9837 | 0.9994 | 1.0105 |
| 600 | 0.9160 | 0.9531 | 0.9765 | 1.0000 | 1.0163 |
| 800 | 0.8891 | 0.9394 | 0.9706 | 1.0004 | 1.0224 |
| 1,000 | 0.8639 | 0.9271 | 0.9660 | 1.0019 | 1.0287 |
| 1,400 | 0.8200 | 0.9072 | 0.9595 | 1.0102 | 1.0425 |
| 1,800 | 0.7881 | 0.8946 | 0.9580 | 1.0193 | 1.0574 |
| 2,200 | 0.7763 | 0.8897 | 0.9611 | 1.0300 | 1.0733 |
| 2,600 | 0.7781 | 0.8924 | 0.9684 | 1.0429 | 1.0900 |
| 3,000 | 0.7923 | 0.9024 | 0.9798 | 1.0577 | 1.1074 |
| 3,400 | 0.8137 | 0.9186 | 0.9961 | 1.0743 | 1.1252 |
| 3,800 | 0.8430 | 0.9415 | 1.0139 | 1.0923 | 1.1436 |
| 4,200 | 0.8779 | 0.9678 | 1.0331 | 1.1117 | 1.1609 |
| 4,600 | 0.9163 | 0.9959 | 1.0550 | 1.1331 | 1.1810 |
| 5,000 | 0.9560 | 1.0258 | 1.0796 | 1.1557 | 1.2024 |
| 5,400 | 0.9950 | 1.0571 | 1.1052 | 1.1782 | 1.2250 |
| 5,800 | 1.0323 | 1.0902 | 1.1326 | 1.2004 | 1.2471 |
| 6,200 | 1.0690 | 1.1236 | 1.1620 | 1.2226 | 1.2687 |
| 6,600 | 1.1063 | 1.1580 | 1.1929 | 1.2450 | 1.2901 |
| 7,000 | 1.1450 | 1.1940 | 1.2247 | 1.2680 | 1.3118 |

0°F.

| Pressure, lb./sq. in. abs. | $CH_4$ | Mixtures | | | |
|---|---|---|---|---|---|
| | | A | B | C | D |
| 200 | 0.9581 | 0.9757 | 0.9858 | 0.9960 | 1.0046 |
| 400 | 0.9162 | 0.9512 | 0.9722 | 0.9933 | 1.0095 |
| 600 | 0.8751 | 0.9285 | 0.9598 | 0.9914 | 1.0143 |
| 800 | 0.8323 | 0.9070 | 0.9486 | 0.9905 | 1.0196 |
| 1,000 | 0.7908 | 0.8867 | 0.9390 | 0.9905 | 1.0258 |
| 1,400 | 0.7152 | 0.8525 | 0.9248 | 0.9933 | 1.0392 |
| 1,800 | 0.6725 | 0.8312 | 0.9177 | 0.9996 | 1.0543 |
| 2,200 | 0.6673 | 0.8229 | 0.9178 | 1.0091 | 1.0710 |
| 2,600 | 0.6844 | 0.8277 | 0.9249 | 1.0216 | 1.0889 |
| 3,000 | 0.7150 | 0.8425 | 0.9376 | 1.0368 | 1.1068 |
| 3,400 | 0.7548 | 0.8653 | 0.9567 | 1.0546 | 1.1252 |
| 3,800 | 0.7992 | 0.8945 | 0.9788 | 1.0747 | 1.1450 |
| 4,200 | 0.8453 | 0.9279 | 1.0042 | 1.0972 | 1.1648 |
| 4,600 | 0.8913 | 0.9652 | 1.0323 | 1.1217 | 1.1856 |
| 5,000 | 0.9380 | 1.0031 | 1.0634 | 1.1482 | 1.2080 |
| 5,400 | 0.9879 | | 1.0961 | | 1.2324 |
| 5,800 | | | 1.1295 | | 1.2568 |

—50°F.

| Pressure, lb./sq. in. abs. | $CH_4$ | Mixtures | | | |
|---|---|---|---|---|---|
| | | A | B | C | D |
| 200 | 0.9395 | 0.9627 | 0.9771 | 0.9928 | 1.0029 |
| 400 | 0.8760 | 0.9251 | 0.9547 | 0.9859 | 1.0065 |
| 600 | 0.8091 | 0.8872 | 0.9334 | 0.9802 | 1.0107 |
| 800 | 0.7352 | 0.8505 | 0.9138 | 0.9758 | 1.0155 |
| 1,000 | 0.6593 | 0.8165 | 0.8965 | 0.9727 | 1.0209 |
| 1,400 | 0.5378 | 0.7612 | 0.8692 | 0.9703 | 1.0335 |
| 1,800 | 0.5237 | 0.7300 | 0.8546 | 0.9733 | 1.0482 |
| 2,200 | 0.5662 | 0.7254 | 0.8533 | 0.9815 | 1.0657 |
| 2,600 | 0.6147 | 0.7390 | 0.8621 | 0.9947 | 1.0848 |
| 3,000 | 0.6640 | 0.7669 | 0.8805 | 1.0123 | 1.1045 |
| 3,400 | 0.7156 | 0.8053 | 0.9058 | 1.0329 | 1.1249 |
| 3,800 | 0.7690 | 0.8489 | 0.9360 | 1.0560 | 1.1470 |
| 4,200 | 0.8246 | 0.8937 | 0.9703 | 1.0809 | 1.1693 |
| 4,600 | 0.8820 | 0.9382 | 1.0070 | 1.1071 | 1.1926 |
| 5,000 | 0.9422 | 0.9880 | 1.0453 | 1.1373 | 1.2189 |
| 5,400 | 1.0043 | | 1.0851 | 1.1706 | 1.2483 |
| 5,800 | 1.0683 | | 1.1259 | | |

—100°F.

| Pressure, lb./sq. in. abs. | $CH_4$ | Mixtures | | | |
|---|---|---|---|---|---|
| | | A | B | C | D |
| 200 | 0.9076 | 0.9426 | 0.9621 | 0.9863 | 1.0006 |
| 400 | 0.7996 | 0.8819 | 0.9251 | 0.9721 | 1.0018 |
| 600 | 0.6627 | 0.8183 | 0.8897 | 0.9590 | 1.0038 |
| 800 | 0.4416 | 0.7550 | 0.8553 | 0.9483 | 1.0068 |
| 1,000 | 0.3017 | 0.6931 | 0.8239 | 0.9396 | 1.0107 |
| 1,400 | 0.3646 | 0.6072 | 0.7758 | 0.9273 | 1.0216 |
| 1,800 | 0.4325 | 0.5939 | 0.7536 | 0.9275 | 1.0362 |
| 2,200 | 0.4998 | 0.6247 | 0.7583 | 0.9352 | 1.0538 |
| 2,600 | 0.5667 | 0.6656 | 0.7800 | 0.9502 | 1.0740 |
| 3,000 | 0.6331 | 0.7159 | 0.8107 | 0.9718 | 1.0964 |
| 3,400 | 0.7006 | 0.7732 | 0.8506 | 0.9988 | 1.1209 |
| 3,800 | 0.7682 | 0.8331 | 0.8952 | 1.0296 | 1.1473 |
| 4,200 | 0.8254 | 0.8923 | 0.9431 | 1.0626 | 1.1758 |
| 4,600 | 0.9021 | 0.9502 | 0.9909 | 1.0980 | 1.2059 |
| 5,000 | 0.9704 | 1.0075 | 1.0391 | 1.1332 | 1.2366 |
| 5,400 | | 1.0651 | 1.0850 | 1.1708 | 1.2655 |
| 5,800 | | 1.1227 | 1.1356 | | |

—150°F.

| Pressure, lb./sq. in. abs. | $CH_4$ | Mixtures | | | |
|---|---|---|---|---|---|
| | | A | B | C | D |
| 100 | 0.9278 | 0.9521 | 0.9679 | 0.9868 | 0.9992 |
| 200 | 0.8415 | 0.9024 | 0.9353 | 0.9737 | 0.9981 |
| 300 | 0.7438 | 0.8465 | 0.9026 | 0.9621 | 0.9973 |
| 400 | | 0.7890 | 0.8694 | 0.9517 | 0.9968 |
| 500 | | | 0.8354 | 0.9437 | 0.9974 |
| 600 | | | 0.8004 | 0.9354 | 0.9978 |
| 700 | | | 0.7642 | 0.9280 | 0.9982 |
| 800 | | | | 0.9208 | 0.9995 |
| 1,000 | | | | 0.9088 | 1.0024 |
| 1,400 | | | | 0.8949 | 1.0138 |
| 1,800 | | | | 0.8962 | 1.0293 |
| 2,200 | | | | 0.9113 | 1.0482 |
| 2,600 | | | | 0.9340 | 1.0714 |
| 3,000 | | | | 0.9631 | 1.0966 |
| 3,400 | | | | | 1.1243 |
| 3,800 | | | | | 1.1552 |
| 4,200 | | | | | 1.1913 |
| 4,600 | | | | | 1.2320 |
| 5,000 | | | | | 1.2746 |

—200°F.

| Pressure, lb./sq. in. abs. | $CH_4$ | Mixtures | | | |
|---|---|---|---|---|---|
| | | A | B | C | D |
| 40 | 0.9483 | | | | |
| 60 | 0.9229 | 0.9485 | | | |
| 80 | 0.8965 | 0.9313 | 0.9556 | | |
| 100 | 0.8686 | 0.9136 | 0.9446 | 0.9745 | 0.9971 |
| 120 | | 0.8957 | 0.9342 | | |
| 160 | | | 0.9097 | | |
| 200 | | | 0.8486 | 0.9489 | 0.9946 |
| 300 | | | | 0.9232 | 0.9923 |
| 400 | | | | 0.8972 | 0.9908 |
| 500 | | | | | 0.9901 |
| 600 | | | | | 0.9906 |
| 800 | | | | | 0.9929 |
| 1,000 | | | | | 0.9968 |
| 1,600 | | | | | 1.0193 |
| 2,200 | | | | | 1.0572 |
| 2,800 | | | | | 1.1061 |
| 3,400 | | | | | 1.1673 |
| 4,000 | | | | | 1.2360 |

zero pressure, $Z_j$ approaches unity as pressure decreases, and the intercept of the curve at zero pressure is $P_o/Z_o$. After the value of $P_o/Z_o$ is known, substitution into Equation (1) yields compressibility factors at any of the intermediate pressures.

The apparatus constant may be evaluated by rewriting Equation (1) for successive expansions:

$$\frac{P_i}{P_{i-1}} N = \frac{Z_i}{Z_{i-1}} \qquad (2)$$

Rearranging the terms one gets

$$\frac{P_{i-1}}{P_i} = N \frac{Z_{i-1}}{Z_i} \qquad (3)$$

The pressure ratio $P_{i-1}/P_i$ is plotted against $P_i$, and the resulting curve is extrapolated to zero pressure. The compressibility factors $Z_i$ and $Z_{i-1}$ go to unity as the pressure decreases to zero, and the intercept gives the value of $N$.

It should be noted that the value of $N$ obtained in this manner applies to the apparatus at zero pressure only. For high pressure operation the effect on $N$ caused by elastic deformation of the volumes must be included.

When one uses the Lamé formula for the elastic deformation of a thick-walled cylinder, the relative change in the volume of a cylinder at a pressure is given by the following equation:

$$\frac{\Delta V}{V_o} = \frac{P}{E} \left[ 2 \left\{ \left( \frac{b^2 + a^2}{b^2 - a^2} \right) + \mu \right\} + \frac{a^2 (1 - 2\mu)}{b^2 - a^2} \right] \qquad (4)$$

In terms of this relative change in volume the true volume ratio between pressures $P_{i-1}$ and $P_i$ *is*

$$N = \frac{(V_1 + V_2)_o}{(V_1)_o} \frac{\left(1 + \frac{\Delta V}{V_o}\right)_{P_i}}{\left(1 + \frac{\Delta V}{V_o}\right)_{P_{i-1}}} \qquad (5)$$

This makes the apparatus constant a function of two pressures $P_{i-1}$ and $P_i$. The constant used in calculation is defined by Equation (5) and is expressed by the following equation:

$$N = N\ (P_i, P_{i-1}) \qquad (6)$$

For the dimensions of this apparatus the numerical value of $V/V_o$ from Equation (4) at a pressure $P$ is 1.27 x $10^{-7}$ $P$.

The equation used in this work for calculating compressibility factors, including the pressure effect on $N$, is

$$P_j \prod_{i=1}^{j} N\ (P_i, P_{i-1}) = Z_j \frac{P_o}{Z_o} \qquad (7)$$

## SYSTEM STUDIED

The gases studied in this investigation were methane and four mixtures of hydrogen and methane whose compositions are given in Table 1. This particular binary system was chosen because one of the components, hydrogen, exhibits quantum deviation (6) at low temperatures and because of

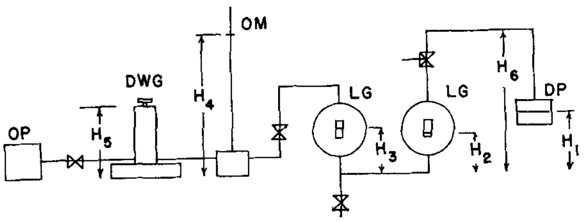

Fig. 2. Pressure-measurement section.

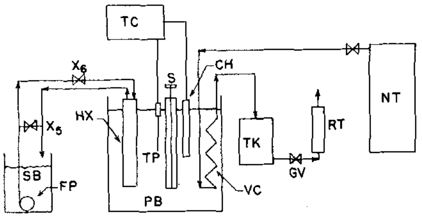

Fig. 3. Temperature control.

the practical interest in such mixtures. Also dew-point data on the mixtures were available (*1*).

The gas mixtures studied were mixed and stored in 220 st. cu. ft. cylinders. In each case hydrogen was added to the cylinder after methane. Before addition the hydrogen was passed through a coil of heavy walled copper tubing containing activated charcoal and magnesium perchlorate. The coil was immersed in liquid nitrogen during the transfer. The mixtures were made up to pressures above 1,000 lb./sq. in. abs. so that all runs could be made with the same gas composition. After addition of the hydrogen the gases were allowed to mix for ten days before use. Heat lamps were directed to the bottom of the cylinder providing a temperature gradient to promote mixing. The samples were analyzed with a mass spectrometer.

After all experimental work was completed, one gas mixture was reanalyzed to check for a possible change in composition. Exactly the same results were reported as in the earlier analysis. Duplicate samples were run in each case, and no component varied by more than 0.1 mole % between different samples of the same gas mixture. The results are probably good to 0.1 mole %.

The phase behavior of the hydrogen-methane system has been studied by Benham and Katz (*1*). They investigated vapor-liquid equilibrium compositions at —150°, —200°, —250°, and —297°F. Their dew-point values were used to set the maximum pressures on runs with mixtures below their critical temperatures.

## EXPERIMENTAL EQUIPMENT

The apparatus may be separated into six functional groups: expansion section, pressure measurement, temperature measurement, temperature control, charging system, and vacuum system.

### Expansion Section (Figure 1)

The basic piece of equipment in a Burnett apparatus is the high-pressure cell containing two gas volumes $V_1$ and $V_2$. The cell is a cylinder 15¼ in. long and 4½ in. O.D. The internal chambers are 2 in. in diameter and 6 in. long containing nearly equal volumes (approximately 23 cu. in.). Three 1½-in. diameter type 303 stainless steel spheres were introduced into $V_2$ to reduce the value of the apparatus constant. This allows a larger number of expansions from a given initial pressure.

The expansion, exhaust, and charging valves are mounted in the constant temperature bath to insure a constant gas temperature. These valves must operate at the bath temperature and not be subject to volume changes with pressure. Bellows type of valves could not be used for this reason. A stainless steel needle valve with a small diameter stem (⅛ in.) and Teflon packing gave excellent results at —200°F. Solid graphite packing allowed operation even in liquid nitrogen.

### Pressure Measurement Section (Figure 2)

All pressures were measured with a piston or dead-weight gauge (*DWG*). Two separate piston-gauge assemblies were used in the experimental work as the pressure range was too extensive for the low-range piston. The low-range gauge is capable of measuring pressures from 5 to 2300 lb./sq. in. gauge and the high range from 30 to 12,000 lb./sq. in. gauge. The low-range gauge was used whenever possible for better sensitivity. With a pressure of approximately 2,000 lb./sq. in. abs. the values given by the two piston assemblies agree to within 0.1 lb./sq. in. abs.

All weights used were calibrated and corrected for the effects of local gravity and air buoyancy. A diaphragm differential pressure indicator was used to separate the gas in the cell from the fluid in the pressure transmission system and to indicate equality between the pressures in the two systems.

The liquid used in the differential-pressure indicator must have a boiling point above room temperature and a freezing point below the lowest temperature investigated. Methylcyclopentane, with a boiling point of 161°F. and a freezing point of —224°F. (*11*), was selected for this purpose. This material remains very fluid down to its freezing point and is commercially available. Methylcyclopentane however did not have sufficient viscosity at room temperature for use in the dead-weight gauge. To overcome this difficulty a mercury *U* tube was used to separate the gauge fluid from the indicator fluid.

Two high-pressure liquid-level indicators form the two legs of the mercury *U* tube which separates the oil from the methyl cyclopentane. The visual section of the glass window is 2 in. long and ¼ in. wide with a rectangular cavity behind the window ¼ in. wide and 1 in. deep.

The mercury levels were measured with a cathetometer to the nearest hundredth of a millimeter. The cathetometer telescope was rotated in a horizontal plane to read each leg without moving the base. To insure a reproducible base height the adjusting screw legs of the cathetometer were machined to points on the ends and were locked in place. The leg points fit into tapered sockets in a steel plate attached to the lab bench.

A hydraulic head correction must be made to each pressure reading because pressure must be transmitted from the base of the piston to the diaphragm. The problem is somewhat complicated because three fluids are involved, not all at the same temperature.

Pressure determinations require all of the following measurements, and each is a source of error: barometric pressure, weight calibration, hydraulic head correction, zero correction, effective piston area, and zero reading. The barometric pressure was read on a recently calibrated mercury barometer with an estimated accuracy of ± 0.004 in. of mercury.

At each temperature the pressure required to make the differential pressure indicator denote balance with atmospheric temperature in the cell must be measured. This value must be subtracted from all measurements and is called *zero correction*. The uncertainty in this value based on reproduceability is ± 0.005 lb./sq. in. abs.; the hydraulic head uncertainty is ± 0.002 lb./sq. in. abs.; the zero reading uncertainty is ± 0.005 lb./sq. in. abs. with the low pressure assembly. This value corresponds to the sensitivity of the differential pressure indicator. The relative error from these sources is 0.028% at 50 lb./sq. abs.; the error decreases rapidly as pressure increases. The calibrated weights are probably accurate to ± 0.001% at all pressures. The pistons are made from carefully honed and polished materials with a diameter tolerance of ± 0.000005 in. according to the manufacturer. The cylinders were similarly checked by the manufacturer for diameter with plug gauges in steps of 0.000020 in. with tolerances of ± 0.000005 in. The diameters were estimated to be correct to the nearest ± 0.000005 in. The uncertainty in area would be double the uncertainty in diameter, and if the diameter is taken to be accurate to ± 0.000010 in. the corresponding area uncertainties are ± 0.010% for the low-range gauge. The area used for the piston gauge is the geometric mean between the piston and the cylinder. The area is corrected for the effect of pressure and temperature variations.

The uncertainties from all these sources, if they are all in the same direction, sum to ± 0.039% at 50 lb./sq. in. abs. and decrease to ± 0.011% at 2,000 lb./sq.

in. abs. The probable error in pressure measurements therefore does not exceed ± 0.040% at any pressure.

### Temperature Measurement and Control (Figure 3)

The temperature of the gas in the cell was taken from a calibrated platinum resistance thermometer ($T$) inserted in a thermometer well in the wall of the expansion cell. The thermometer is surrounded in the well with the bath fluid in use at any particular temperature.

Resistances were measured with calibrated Mueller bridge ($MB$). Temperatures could be measured to the nearest 0.001°K., but since bath temperatures were not sufficiently close to warrant this accuracy, readings were made to the closest 0.01°K.

Refrigeration was required at all temperatures of operation. In all cases slightly more coolant than necessary was supplied, and accurate control of the temperature was effected by heating. The bath fluids used were as follows:

| | |
|---|---|
| 32°F. and above | —water |
| —100°, —50°, 0°F. | —ethyl alcohol |
| —150°, —200°F. | —50-50 mixture of isopentane and *n*-pentane |

The bath fluid was stirred by an air-driven stirrer ($S$). Temperature probes throughout the bath indicated thermal variation of less than 0.05°C. For operation at —50°F. and above cooling fluid was pumped through a brass heat exchanger ($HX$) from an external bath ($SB$). A carbon bearing gear pump ($FP$), for coolant circulation, was mounted in the bottom of the tank. Coolant flow rate was controlled by suitable adjustments of the bypass feed valves ($X_5$, $X_6$). At —100°F. dry ice was added directly to the primary bath with excellent results.

For temperatures below —100°F. liquid nitrogen was supplied to a copper vaporization coil ($VC$) from 110 liter liquid nitrogen tanks ($NT$). After vaporizing in the bath the nitrogen passed through a surge tank ($TK$) and finally through a rotameter ($RT$). The flow rate of the nitrogen was controlled by the gate valve ($GV$).

Fine temperature control was maintained at all experimental temperatures with an electronic temperature controller ($TC$) with a temperature sensing element ($TP$). With the arrangement discussed the temperature in the Burnett cell may be held within ± 0.01°C. at all temperatures of operation.

### Charging System (Figure 1)

The diagram of the charging system is included in Figure 1. The gas compression cylinder ($GC$) was used to charge the Burnett Cell ($V_1$) in all cases where the desired initial pressure of operation was higher than the tank pressure. Any gas fed to the compression cylinder was previously passed through drying tube ($DT$) which was filled with magnesium perchlorate, activated charcoal, and asbestos impregnated with sodium hydroxide. Mercury is supplied to the compression cylinder from a mercury vessel, while ($HT$) is a high pressure mercury trap.

### Vacuum System (Figure 1)

A vacuum pump ($VP$) with a pressure rating of 0.05 $\mu$ was used to evacuate the system, including chamber $V_2$ of the cell. The vacuum was indicated on a gauge ($VG$).

## EXPERIMENTAL PROCEDURE

An experimental run consisted of the following operational steps: evacuation and charging, adjustment of bath temperature, attainment of thermal equilibrium, and conduction of expansion sequence. From 15 to 40 min. were required for equilibrium to be reached. The equilibrium pressures were determined with the expansion valve closed because the apparatus constant was determined with this valve closed. Between expansions the volume $V_2$ was evacuated to a pressure below 50 $\mu$. The effectiveness of the expansion valve was checked continually by checking the constancy of the pressure on the vacuum side. Approximately ten expansions were made for each isothermal expansion sequence.

## EXPERIMENTAL RESULTS

### Hydrogen Calibration

The Burnett apparatus constant $N$ was determined with hydrogen at 0°C. Hydrogen was used for two reasons: first, it is at a high reduced temperature at 0°C. and only the second virial coefficient is important at low pressures.

A plot of $P_j \prod_{i=1}^{j} N(P_i, P_{i-1})$ vs. $P_j$ is therefore linear at fairly high pressures which facilitates extrapolation to zero pressure. Second, accurate data are available in the literature for volumetric properties of this gas, allowing a check on the accuracy of the method. Four runs were made for the calibration. The average value of $N$ was used. The resulting cell constant at zero pressure is $N = 1.49740$. The average deviation of the values from this result is ± 0.00010 corresponding to a relative deviation of ± 0.007%.

The resulting second virial coefficient for hydrogen at 0°C. is + 0.000044 ± 0.000001 lb./sq. in. abs.$^{-1}$. As a comparison the data of Michels (*10*) yield a value of + 0.0000425 lb./sq. in. abs.$^{-1}$ at the same temperature. A plot of the compressibility factors of hydrogen determined from these calibration runs show no deviation greater than ± 0.03% from the data of Michels (*10*).

### Experimental Data

Compressibility factor isotherms for methane and for each gas mixture were determined from + 50° to —200°F. at 50°F. intervals. Experimental pressures ranged to 7,000 lb./sq. in. abs. In order to obtain more readings, especially at the high pressures, two runs were made with different starting pressures to establish each isotherm. The experimental data were treated graphically, as described earlier, on a large-scale plot allowing the intercept to be read to ± 0.01%. Deviation of individual points from the smooth curves is less than ± 0.1% in all cases. In all work with data the hydrogen analysis was taken as correct and the remainder of the gas was considered to be methane.

Smoothed values of compressibility factors for the gas mixtures at even increments of pressure are given in Table 2. Smoothing was accomplished by a combination of least mean square curve fitting over short pressure ranges and graphical interpolation.

### Accuracy

Errors in compressibility factors arise from the following sources: errors in temperature, errors in $N$ at zero pressure, uncertainty in the intercept $P_o/Z_o$, and errors in pressure. Errors in the temperature are approximately ± 0.01°K. which corresponds to a relative error of ± 0.01% at the greatest. The effect of errors in the cell constant is more pronounced. Let the relative error in the cell constant $N$ at zero pressure be defined as $E_N$. The true cell constant is then

$$N_T = N_M\ (1 + E_N) \qquad (8)$$

When Equation (8) is substituted into Equation (7) the resulting expression is

TABLE 3. SECOND VIRIAL COEFFICIENTS (BERLIN)

| Gas | 50°F. | 0°F. | —50°F. | —100°F. | —150°F. | —200°F. |
|---|---|---|---|---|---|---|
| | | | $B \times 10^6$ lb./sq. in. abs.$^{-1}$ | | | |
| Pure $CH_4$ | —145±5 | —207±3 | —300±4 | —451±8 | —745±8 | —1280±10 |
| Mixture A | —82±3 | —120±3 | —188±2 | —287±5 | —483±5 | —863±8 |
| Mixture B | —46±2 | —71±1 | —114±2 | —185±2 | —327±3 | —558±8 |
| Mixture C | —3±.5 | —22±1 | —32±2 | —72±2 | —135±2 | —261±5 |
| Mixture D | +25±1 | +22±1 | +14±1 | +3±.5 | —9±.5 | —29±2 |
| Pure $H_2$* | +41±.4 | +42±.4 | +45±.4 | +46±.4 | +43±.4 | +37±.4 |

* Calculated from data published by Michels (*10*).

$$\frac{P_o}{Z_o} Z_j = P_j \prod_{i=1}^{j} (1 + E_N)\, N\, (P_i, P_{i-1}) \qquad (9)$$

When one expands the right side of Equation (6) and neglects all error terms above first order, the relative error is approximately $jE_n$. Thus the relative error in $P_o/Z_o$ from this source after $n$ expansion is $nE_N$. The relative error in compressibility factors at intermediate pressures is then approximately $(n-j)E_N$ because this error in any individual $Z$ value is caused only by the effect of the $N$ error on the subsequent expansions. For ten expansions the error from this source would thus be ± 0.07% at the initial pressure, since the relative deviation in the $N$ value is ± 0.007%. At most only the last few values of $P_j \prod_{i=1}^{j} N(P_i, P_{i-1})$ become linear at any temperature, and at the lowest temperatures there is still slight curvature even at low pressures. As a result of this effect and because of scatter in the points uncertainties are produced in the extrapolated intercept to the extent of ± 0.03% maximum.

Errors in pressure have been discussed in the section on pressure measurements. When one considers all of the possible errors, the Z values determined are probably accurate to ± 0.13%.

## EVALUATION OF VIRIAL COEFFICIENTS

### Virial Coefficients

Second virial coefficients were determined by extrapolating residual volumes to zero pressure. The residual volume is defined as the difference between the actual gas volume at a particular temperature and pressure and the volume which would be occupied by an ideal gas at the same temperature and pressure:

$$\alpha = \frac{ZnRT}{P} - \frac{nRT}{P} \qquad (10)$$

The compressibility factor at a fixed temperature may be expanded as a power series in pressure. This is the Berlin expansion:

$$Z = 1 + BP + CP^2 + \ldots \qquad (11)$$

Equation (10) may be simplified as follows:

$$\frac{\alpha}{RT} = \frac{Z-1}{P} \qquad (12)$$

defined as

$$\alpha' = \frac{\alpha}{RT} = \frac{Z-1}{P} \qquad (13)$$

TABLE 4. INTERACTION SECOND VIRIAL COEFFICIENTS

| Temp, °F. | $B_{12} \times 10^6$ lb./sq. in. abs.$^{-1}$ |
|---|---|
| 50 | 22 |
| 0 | 16 |
| −50 | 10 |
| −100 | −2 |
| −150 | −22 |
| −200 | −56 |

Substituting Equation (11) into Equation (13) one obtains

$$\alpha' = B + CP + DP^2 + \ldots \qquad (14)$$

Values of $\alpha$ were calculated from low-pressure data for each composition at each temperature. The results were plotted as a function of pressure, and the intercept at zero pressure gives the second virial coefficient for the mixture. The compressibility at a fixed temperature may also be expanded as a power series in volume known as the *Leiden expansion*:

$$Z = 1 + \frac{B'}{V} + \frac{C'}{V^2} + \ldots \qquad (15)$$

The second virial coefficients $B$ and $B'$ are related by

$$B = \frac{B'}{RT} \qquad (16)$$

The calculated second virial coefficients $B$ are tabulated in Table 3. The second virial coefficient for hydrogen was calculated from data published by Michels (*10*).

The difference found in the second virial coefficients for methane obtained from literature values (*9, 13*) and this study are less than the experimental errors expected in the virials calculated from this work. The interaction virial coefficients $B_{12}$ were calculated at each temperature by trial to fit

$$x_1^2 B_{11} + 2x_1 x_2 B_{12} + x_2^2 B_{22} = B_M \qquad (17)$$

to the experimental isotherms. The resulting $B_{12}$ virial coefficients are presented in Table 4.

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## NOTATION

$a$ = inner radius
$b$ = outer radius
$B$ = second virial coefficient
$C$ = third virial coefficient
$D$ = fourth virial coefficient
$E$ = elastic modulus
$E_N$ = relative error in $N$
$n$ = number of moles
$N$ = apparatus constant, $(V_1 + V_2)/V_1$
$P$ = pressure, lb./sq. in.
$P_j$ = absolute pressure after $j$ expansions
$R$ = gas law constant
$T$ = absolute temperature
$V$ = volume
$V_1$ = volume of chamber 1
$V_2$ = volume of chamber into which gas is expanded from $V_1$
$x$ = mole fraction
$Z$ = compressibility factor
$Z_j$ = compressibility factor of gas after $j$ expansion
$\alpha$ = residual volume
$\Delta$ = incremental change
$\prod_{i=1}^{j}$ = product of factors from $i$ = 1 to $i$ = $j$.

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