1963

A burnett apparatus for the measurements of compressibilities of gases up to pressures of 1000 pounds

Peter Wanser
Lehigh University

CERTIFICATE OF APPROVAL

This research report is accepted and approved in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering.

Sept. 26, 1963
Date

Leonard A. Wenzel
Dr. Leonard A. Wenzel,
Professor in Charge, and
Head, Department of
Chemical Engineering

A BURNETT APPARATUS FOR
THE MEASUREMENTS OF COMPRESSIBILITIES
OF GASES UP TO PRESSURES OF
1000 POUNDS

* * * * * * *

by Peter Wanser

A Research Report

Presented to the Graduate Faculty
of Lehigh University

in partial fulfillment of the
requirements for the
degree of Master of Science

* * * * * * *

Lehigh University
Bethlehem, Pennsylvania

1963

ACKNOWLEDGEMENTS

Many thanks are due Dr. Leonard A. Wenzel whose aid and basic understanding did much to make the work easier.

Thanks are also due Joseph Hosack who particularly helped with many of the pieces of equipment.

The helpful suggestions from many fellow students must certainly be acknowledged.

Last, but certainly not least, for making the work more enjoyable and worthwhile and for aid in typing and proofreading, thanks to my wife, Janet.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

The construction, calibration, and testing of a gaseous compressibility measuring device of the Burnett type is described. The apparatus will operate at pressures up to 1000 pounds and at about room temperature. The apparatus was calibrated using nitrogen and tested using methane.

INTRODUCTION

After consideration of the phase rule, one arrives at the conclusion that for a single component gas or a gas mixture of known composition two conditions determine the pressure-volume-temperature relation of the gas. The most commonly used methods of determining gaseous compressibility data (P-V-T data) do not make use of this fact. All four variables--temperature, pressure, volume, and mass--are normally determined in order to get compressibility data.

In 1936 E. S. Burnett (1) introduced a method for determining compressibility data for gases in which only two variables, temperature and pressure, are measured. The Burnett apparatus consists mainly of two constant volume cells connected through a positive shut-off valve. Provisions are made for evacuation of the cells and for charging and measuring the pressure in the cells. The cells are placed in a constant temperature bath. Both cells are evacuated; then one cell (No. 1) is charged to a high pressure with the gas being studied, and this high pressure is measured. The other cell (No. 2) is evacuated and sealed, after which the valve between the cells is opened. After thermal equilibrium is reached, the new pressure is measured, the valve between the cells shut, and cell No. 2 again evacuated. Again the Cell 1 gas is expanded into Cell 2, and the new pressure read. These evacuations, expansions, and pressure measurements, all at constant temperature, are repeated until the pressure in the cells has dropped below atmospheric. After this procedure is repeated at all the temperatures of interest, the compressibility data is completely obtained.

The Burnett method has several advantages, one being that two rather than four measurements are required. These measurements are relatively easy, i.e., temperature and pressure are much easier to measure accurately than volume and mass. A third advantage is that the apparatus is relatively simple.

The chief disadvantage of the Burnett method can be seen by examining the phase rule again; gas-liquid systems cannot be considered. A minor disadvantage is that one run yields few data points at high pressure and many data points at low pressure.

THEORY

Compressibility data are given in many different forms, for example, tables of compressibility factors, tables of Amagat units, equations of state (Van der Waals, Benedict-Webb-Rubin, virial, etc.) Burnett data can be put into any of the above forms. Kobe, et al. (2) give quite a comprehensive review of ways in which Burnett data have been handled.

Burnett originally developed a graphical method for handling his data. This method will be discussed and has been used in handling the data obtained to date at Lehigh.

The graphical method is developed as follows. Consider

$$N = \frac{V_I + V_{II}}{V_I} \quad (1)$$

where V_I is the volume of the cell No. 1 and V_{II} is the volume of cell No. 2. The number of moles of gas, n_0, in cell No. 1 after charging is:

$$n_0 = \frac{P_0 V_I}{Z_0 RT} \quad (2)$$

where P_0 is the initial pressure, Z_0 is the compressibility at P_0, T is the bath temperature, and R is the universal gas constant. After expansion into cell No. 2 and temperature equilibration, the number of moles of gas, n_0, is:

$$n_0 = \frac{P_1 (V_I + V_{II})}{Z_1 RT} \quad (3)$$

where Z_1 is the compressibility at P_1 and T. Dividing equation (2) by (3), substituting using equation (1), and rearranging yields:

$$\frac{P_0}{P_1} = \frac{Z_0}{Z_1} N \quad (4)$$

One can continue to write equations like this for each successive expansion:

$$\frac{P_1}{P_2} = \frac{Z_1}{Z_2} N \tag{5-1}$$

$$\frac{P_2}{P_3} = \frac{Z_2}{Z_3} N \tag{5-2}$$

$$\vdots$$

$$\frac{P_{P-1}}{P_P} = \frac{Z_{P-1}}{Z_P} N \tag{5-P}$$

$$\vdots$$

$$\frac{P_{R-1}}{P_R} = \frac{Z_{R-1}}{Z_R} N \tag{5-R}$$

As the gas pressure gets lower and lower, the gas behaves more and more like an ideal gas; therefore, the ratio Z_{R-1}/Z_R approaches unity. In other words,

$$\lim_{p \to 0} \frac{P_{R-1}}{P_R} = N \tag{6}$$

It is possible, therefore, to determine the apparatus constant, N, at any one temperature by extrapolating a plot of P_{R-1}/P_R vs. P to zero pressure. This extrapolation is made easier if Z is a linear function of P at constant temperature because then P_{R-1}/P_R vs. P is a straight line.

Using equations (4) and (5-1) and making the proper rearrangements and substitutions, one gets

$$\frac{P_o}{Z_o} = \frac{P_2}{Z_2} N^2 \tag{7}$$

Making similar rearrangements and substitutions using equations (5-2) through (5-R), one obtains:

$$\frac{P_o}{Z_o} = \frac{P_R}{Z_R} N^R \quad \text{or} \quad P_R N^R = \frac{P_o}{Z_o} Z_R \tag{8}$$

Again, making use of the fact that Z_R approaches unity as P_R approaches zero, one can see that

$$\lim_{P \to 0} P_R N^R = \frac{P_O}{Z_O} \tag{9}$$

Therefore, for each set of expansions a plot of $P_R N^R$ vs. P can be extrapolated to yield the run constant P_o/Z_o. Then, using equation (8), the value of Z can be calculated for each P.

APPARATUS CONSTRUCTION

The two constant volume cells, the basis of the Burnett apparatus, are constructed from a single piece of two-inch diameter cylindrical brass rod. The cells were made by drilling out 5/8-inch diameter cavities, one in each end of the cylinder, and sealing the ends with caps made from the same brass bar stock (see Figure 1). Ports were drilled in the sides of the cylinder to allow for filling and evacuating the cells. Ports were also made so the cells could be connected and the pressure measured. Thermocouple glands were put in the caps that sealed the cells. The temperatures in the cells are measured with copper-constantan thermocouples used in conjunction with a Leeds-Northrup potentiometer which can read to a tenth of a micro-volt. Figure 2 is a diagram of the thermocouple circuit.

The vacuum system consists of a mechanical, oil vacuum pump and a McLeod gauge. It is possible to evacuate the cells to 5 microns. A cold trap was purchased for the system but was not used, since the gases used to date couldn't damage the pump or the oil.

At present the temperature range in which the apparatus can be operated is very limited. The constant temperature bath consists of a water-filled metal tank equipped with an electrical immersion heater and a stirrer for circulation. The power to the heater is controlled by a Bailey temperature controller. With this system it is possible to maintain

FIGURE I
CONTANT VOLUME PRESSURE CELLS

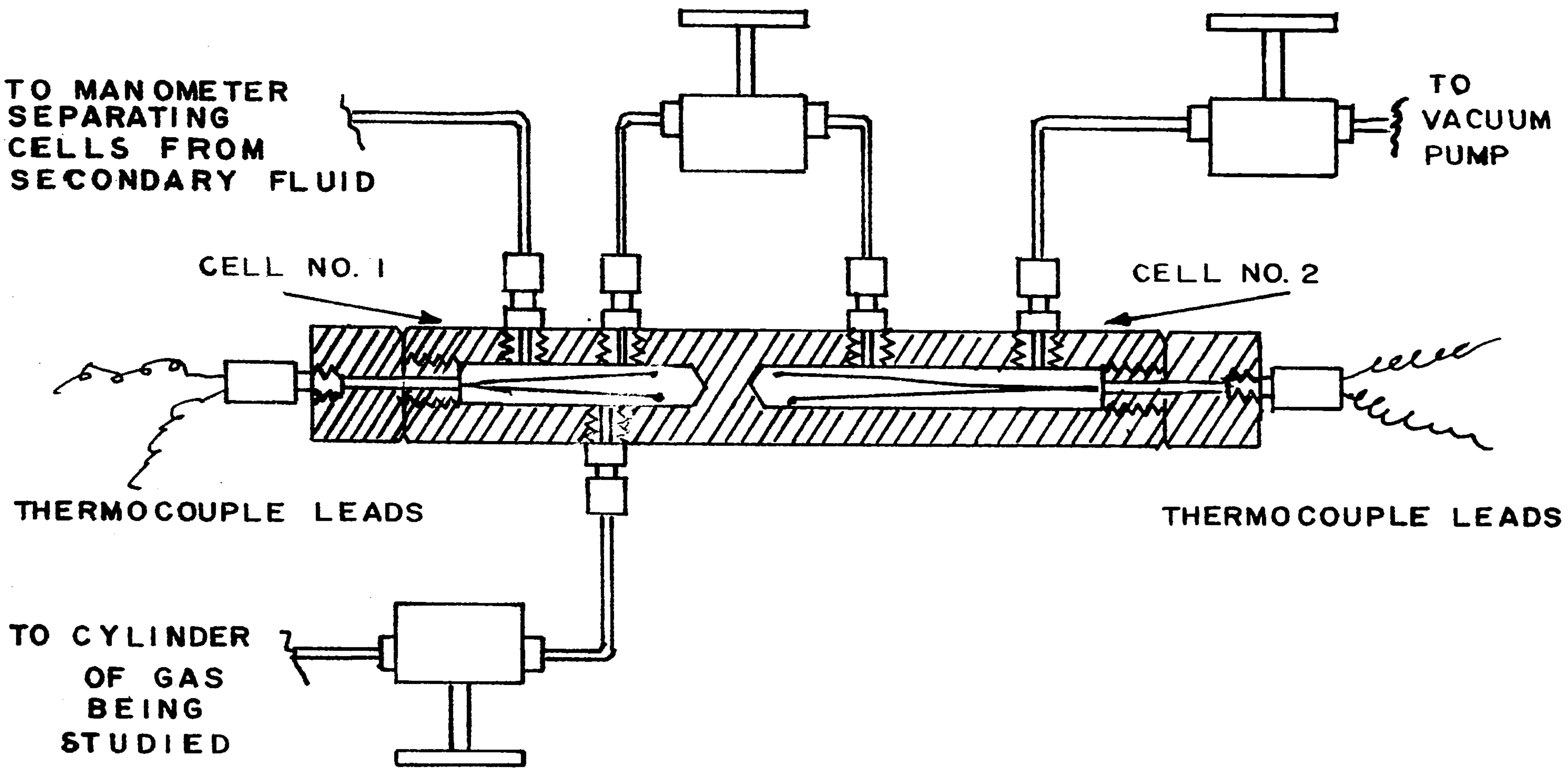


FIGURE 2
THERMOCOUPLE CIRCUIT

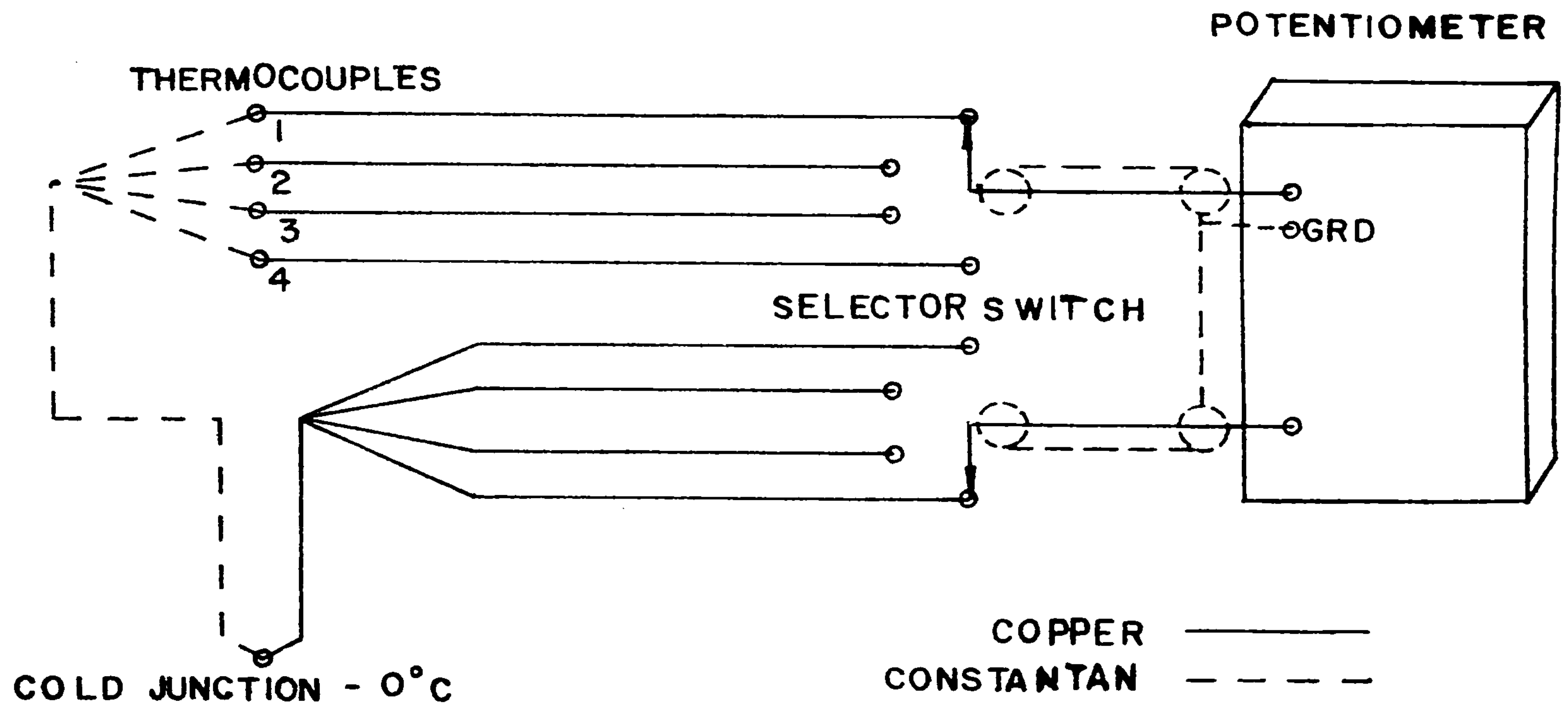
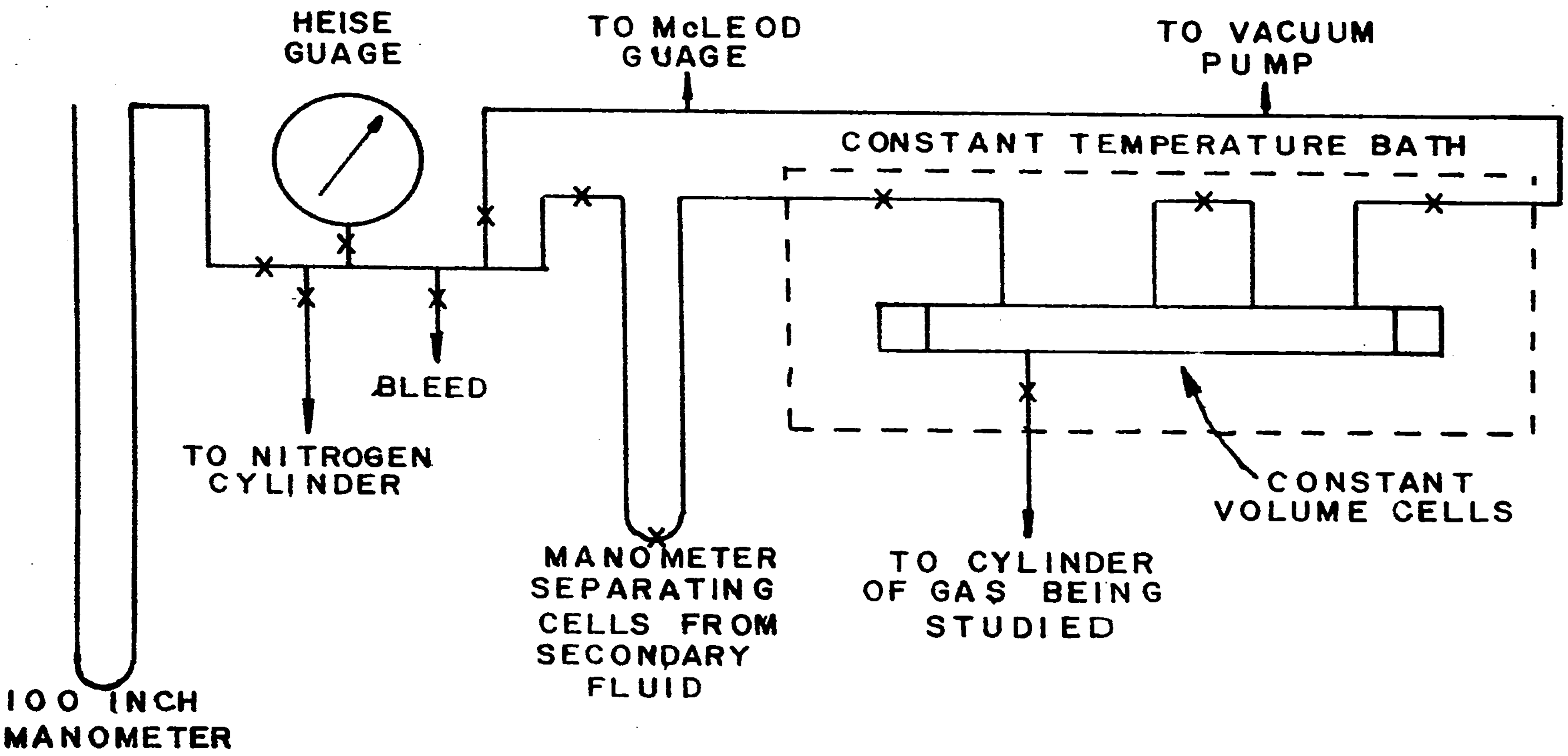


FIGURE 3
SCHEMATIC REPRESENTATION OF APPARATUS



temperatures slightly above room temperature to within a tenth of a degree centigrade.

From the previous analysis it can be seen that it is desirable that the volume and temperatures of the cells remain constant. This is commonly achieved in the Burnett apparatus by measuring the pressure indirectly. The pressure of a secondary fluid, either gas or liquid, is measured. The secondary fluid is separated from the Burnett cells by a metal diaphram or a U-tube of mercury. Prior to reading a pressure, the position of the diaphram or mercury is adjusted to achieve the desired cell volume. In the present situation the secondary fluid is nitrogen, which is separated from the cells by a U-tube of mercury. The U-tube is constructed of thick-walled nylon tubing which has a bursting pressure of 2500 psi. The nylon is transparent enough to see the level of the mercury; this makes it easy to adjust the mercury level to maintain the cell volume constant.

The pressures from 60-1000 psia are measured with a Heise Bourdon type pressure gauge which is accurate to 0.5 psi. Pressures below 60 psia were read on a large U-tube mercury manometer.

The apparatus as assembled is shown in Figure 3. All connections were made with thick wall (.065 in) copper tubing.

CALIBRATION OF APPARATUS

The copper-constantan thermocouples were calibrated using the sublimation point of carbon dioxide.* The procedure is described by Scott (5). The calibration showed that at 194.36°K, the carbon dioxide sublimation point, the thermocouples read within 4 microvolts (.13°K) of each other and an average of 8.5 microvolts (.28°K) below the EMF corresponding to 194.36°K given in the Air Products and Chemicals Company Data Book.

The apparatus constant, N, (see Theory section) was obtained by a series of isothermal expansions of nitrogen. Linde high purity dry nitrogen was used. This data appears in Table 1 and Figure 4. It can be seen that the average per cent variation in N is small, 0.146 per cent. This variation is well within the reading errors of the pressure measuring equipment. The Bourdon gauge can be read to 0.005% at 1000 psig but only 1.0% at 50 psig. The manometer could be read to .02% at 50 psig but only 1.0% at 1 psig.

The manometer separating the cells from the secondary measuring fluid was not in the constant temperature bath, and therefore part of the gas is not at the temperature of

---

*The original calibrated thermocouples became inoperative when another graduate student was using the apparatus. He put in new thermocouples but failed to calibrate them. For this reason the original thermocouple calibration data does not appear in this report. All data in this report was obtained using the second set of thermocouples. It was assumed that these thermocouples followed the EMF-temperature relationship given for copper-constantan thermocouples in the Air Products and Chemicals Company Data Book.

TABLE 1

Calibration Run Data

Pressure (psia)	1/N
913.5	
	.3967
362.4	
	.3971
143.9	
	.3961
57.0	
	.3967
22.61	
	.3985
9.01	

Expansion made later as check

Pressure (psia)	1/N
310.2	
	.3988
123.6	

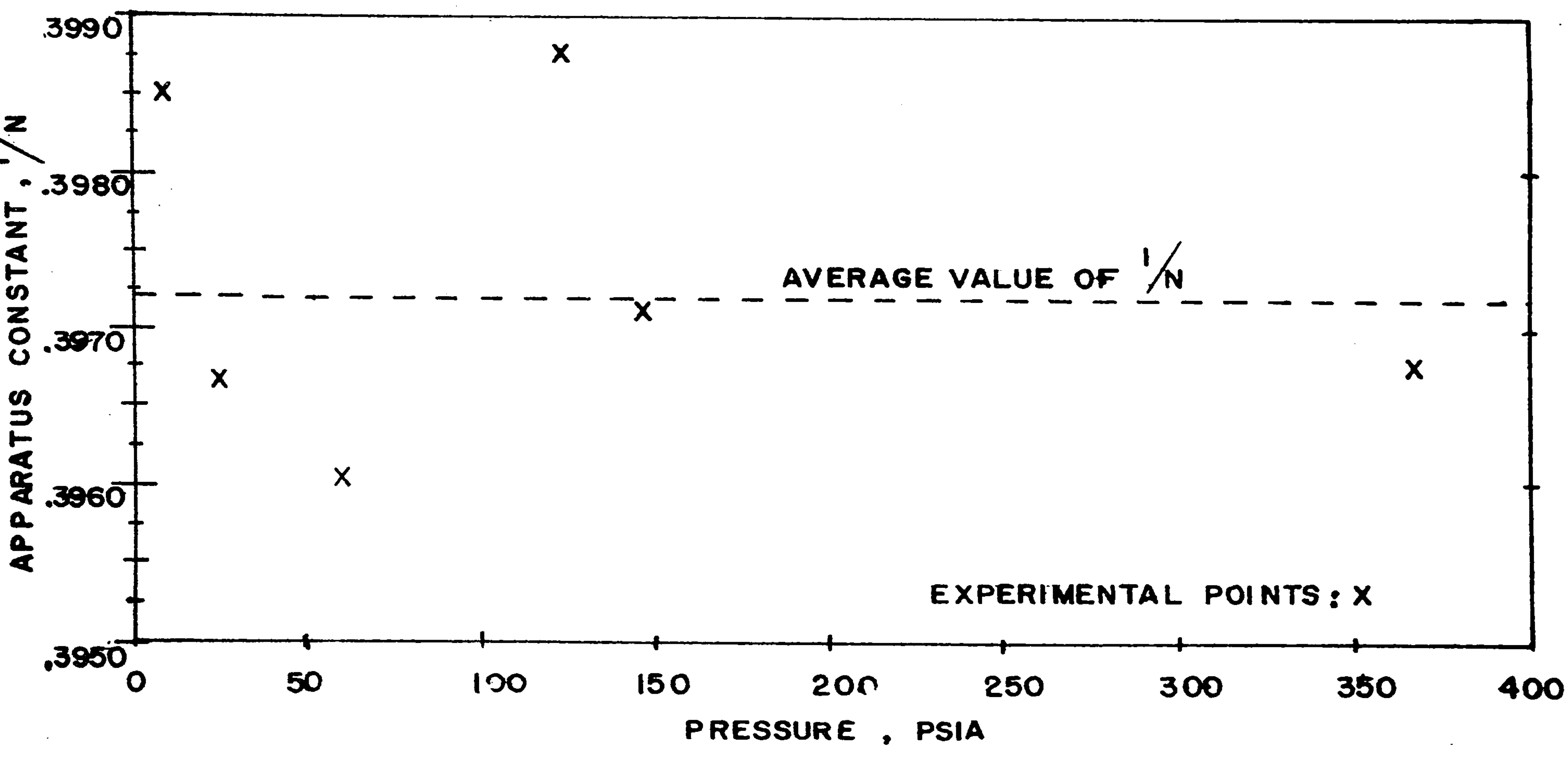
Average 1/N = .3972

N = 2.518

Average Per Cent Variation of 1/N = 0.146

Run Temperature = 299.0 $\pm$ 0.08°K

FIGURE 4
CALIBRATION DATA : APPARATUS CONSTANT, 1/N, VS PRESSURE



the bath. The question arises as to how much error this causes. Schneider (4) has derived an expression for a correction to be used to correct the value of any pressure reading used in Burnett-type calculations when a small part of one of the cells is not at the desired temperature. If P_e is the measured pressure and F the correction factor, then P_f, the corrected pressure, is given by

$$P_f = FP_e \tag{1}$$

The gas at P_e is contained in a volume, V, which is subdivided into subdivisions, v_i, all of which can be at different temperatures, t_i, i.e.

$$V = \Sigma\, v_i \tag{2}$$

If the temperatures t_i are not too different from the desired cell temperature, T, one can get a sufficiently accurate value of F using the perfect gas law. Therefore:

$$\frac{P_f\, \Sigma\, v_i}{T} = P_e\, \Sigma(v_i/t_i) \tag{3}$$

Thus:

$$F = \frac{T\, \Sigma(v_i/t_i)}{V} \tag{4}$$

In order to get some idea of the size of the correction, the following numbers which closely approximate the case in question are substituted:

t_1 = T = 298°K (Cells' temperature)

t_2 = 296°K (Manometer temperature)

V = 12 cu in (Total Volume)

v_1 = 11.816 cu in (Volume of cells)

v_2 = .184 cu in (Volume of gas in manometer)

Substitution yields F equal to 1.000025. This correction is insignificant in comparison to the reading error associated with the pressure measuring apparatus. Therefore, as long as measurements are made within a few degrees of room temperature, the separating manometer can remain outside the constant temperature bath.

APPARATUS TESTING

The apparatus was tested using methane. Matheson C. P. grade methane was used without further purification.

The data obtained appears in Table 2. The values of $P_R N^R$ that appear in the table are plotted against P_R in Figure 5. From this plot the value of P_o/Z_o is obtained. The values of Z_R were calculated using Formula 8 in the Theory section. The data has been compared with the methane compressibility data of Mathew and Hurd (3). The per cent difference between the Mathew-Hurd data and the data obtained with the Burnett apparatus is given. This is within the reading accuracy of the pressure measuring equipment except for the point at the lowest pressure. Figure 6 is a plot of compressibility vs. pressure and shows both the Mathew-Hurd data and the Burnett apparatus data.

TABLE 2

Test Data: COMPRESSIBILITY OF METHANE DETERMINED WITH BURNETT APPARATUS COMPARED TO DATA OF MATHEW AND HURD (3)

Burnett Apparatus Temperature: 299.0°K
Mathew and Hurd Data Temperature: 299.8°K

P_R (psia)	$P_R N^R$	Z_R Burnett Apparatus	Z Mathew and Hurd	Per Cent Difference*
941.9	------	.9035	.8969	0.74
397.5	1000.9	.9601	.9539	0.64
162.2	1028.2	.9863	.9806	0.58
64.8	1034.2	.9920	.9920	0.00
25.91	1041.3	.9988	.9970	0.18
10.26	1038.0	.9957	.9994	- 0.37
4.11	1062.0	1.0187	.9997	1.90

P_o/Z_o (Determined from Figure 5) = 1042.5

*Per Cent Difference = $\frac{\text{Burnett}}{\text{Mathew-Hurd}}(100)$

FIGURE 5

TEST DATA : $P_R N^R$ VS PRESSURE

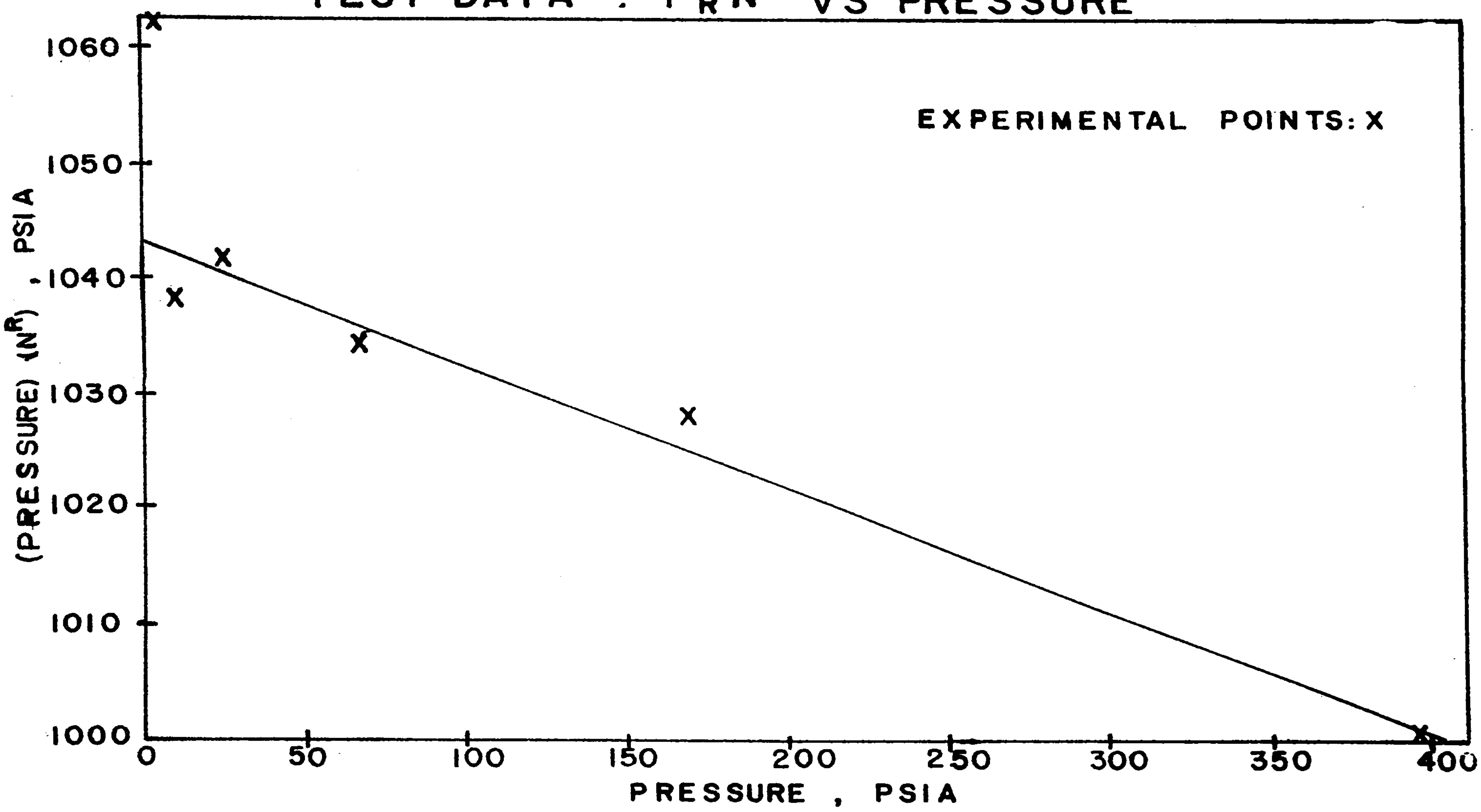
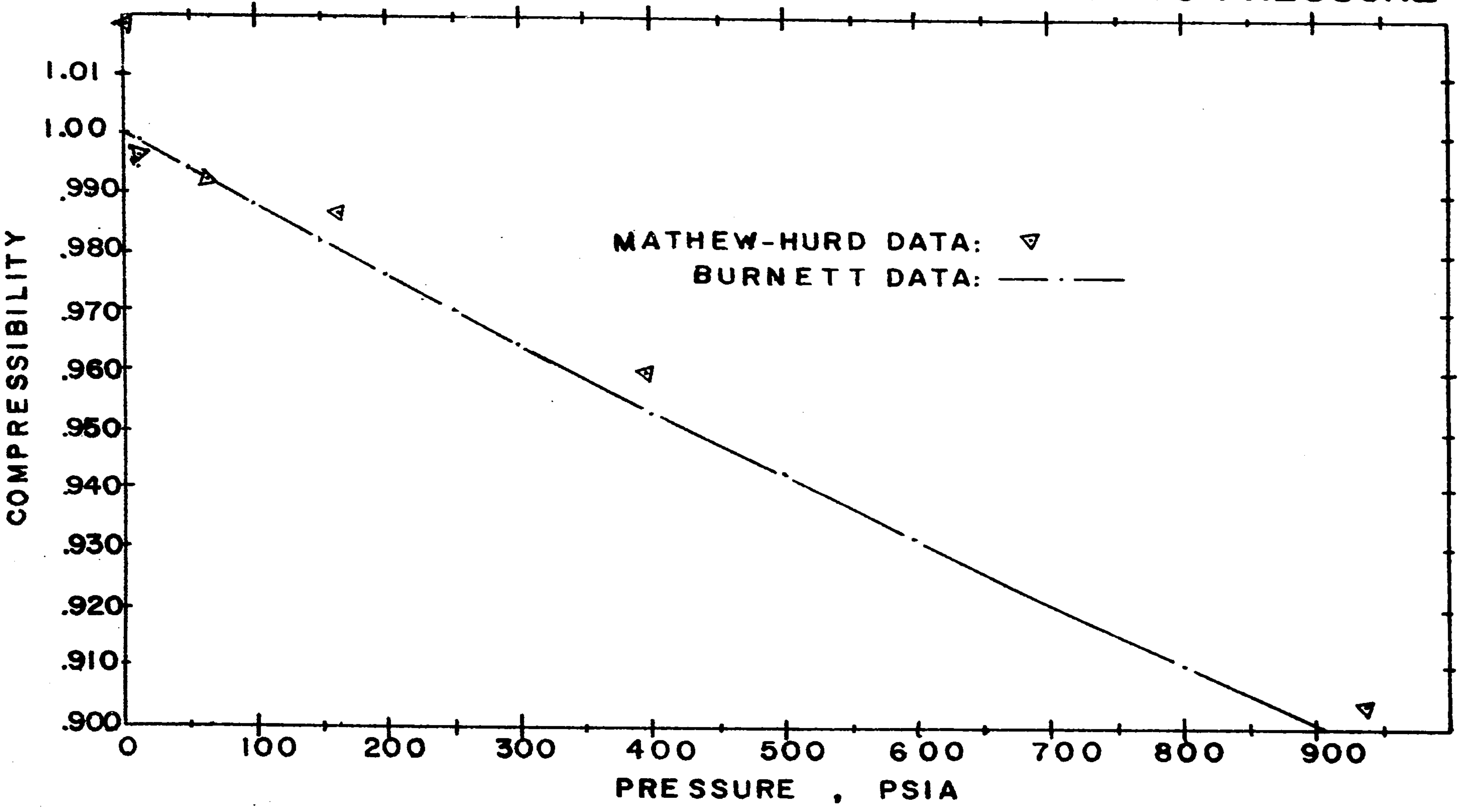


FIGURE 6

TEST DATA: COMPRESSIBILITY OF METHANE VS PRESSURE



BIBLIOGRAPHY

(1) Burnett, E.S., J. of Applied Mechanics, 58-A, 136-140, (1936)

(2) Kobe, K.A., et al, J. of Chem. and Eng. Data, 4, 314-323, (1959)

(3) Mathew, C.S., and Hurd, C.O., Trans. of the A.I.Ch.E., 42, 55-78, (1946)

(4) Schneider, W.G., Canadian J. of Research, 27-B, 339-352, (1949)

(5) Scott, R.B., "The Calibration of Thermocouples at Low Temperatures," Temperature: Its Measurement and Control in Science and Industry, Reinhold Publishing Co. New York, Vol. I, p. 206, (1941)

APPENDIX I

PARTIAL MATHEW AND HURD METHANE COMPRESSIBILITY DATA

Temperature: 299.8°K

Pressure (psia)	Specific Volume (cu ft/lb)	Compressibility
10	36.10	.9994
15	25.02	.9987
20	18.02	.9977
25	14.41	.9973
30	12.00	.9966
40	8.99	.9955
50	7.18	.9938
60	5.98	.9933
80	4.47	.9899
100	3.569	.9880
150	2.364	.9816
200	1.762	.9756
250	1.402	.9702
300	1.161	.9642
400	.861	.9534
500	.681	.9426
600	.561	.9318
800	.411	.9102
1000	.3217	.8906

APPENDIX II

Equipment Specifications

1. Potentiometer
   Leeds and Northrop Company
   444 North Sixteenth Street
   Philadelphia 30, Pennsylvania
   Model K-3
   Cat. No. 7553-5

2. Standard Cell
   Eppley Laboratories, Inc.
   Newport, Rhode Island
   Cat. No. 100

3. Battery
   The Willard Storage Battery Company
   Cleveland, Ohio
   Model DD-S-1

4. Selector Switch
   Centralab; Division of Globe-Union, Inc.
   900 East Keefe
   Milwaukee 1, Wisconsin

5. Copper-Constantan Thermocouple Wire
   Leeds and Northrop Company
   444 North Sixteenth Street
   Philadelphia 30, Pennsylvania
   Cat. No. 24-55-15

6. Temperature Controller
   Bailey Instrument Company
   Danville, California
   Model 237
   Range: -200°C to +100°C
   Control: -0.1°C

7. Immersion Heater
   Fisher Scientific Company
   Gulph Road (Route 23)
   King of Prussia, Pennsylvania
   Cat. No. 11-463-5V4

8. Thermocouple Glands
   Conax Corporation
   2300 Walden Avenue
   Buffalo, New York

9. **Manometer**
   Meriam Instrument Company
   10920 Madison Avenue
   Cleveland 2, Ohio
   Doubleheader Model B-1114
   Range: 100 inches Hg

10. **Pressure Gauge**
   Heise Bourdon Tube Company, Inc.
   Newtown, Connecticut
   Heise Gauge No. 2696 4 R
   Range: 0-1000 psi

11. McLeod Gauge
   The Vir-Tis Company, Inc.
   Gardiner, New York
   Model No. 10-22
   Range: 5mm to 5 microns

12. Nylon Pressure Tubing
   Plastics Supply Corporation
   75 Cliff Street
   New York 38, New York

13. Vacuum Pump
   W. M. Welch Manufacturing Company
   Chicago, Illinois
   Serial No. 8733-5

14. Temperature Bath Stirrer
   Mixing Equipment Company, Inc.
   135 Mt. Read Boulevard
   Rochester 11, New York
   "Lightnin" Mixer Model F

15. Valves
   (a) Whitey Research Tool Company
   5525 Marshall Street
   Oakland 8, California
   Cat. No. 21RS4

   (b) Nuclear Products Company
   15635 Saranac Road
   Cleveland 10, Ohio
   Cat. No. B-4M

   (c) Auto Clave Engineers, Inc.
   P. O. Box 4007
   Erie, Pennsylvania

16. Fittings
    Crawford Fitting Company
    884 East 140 Street
    Cleveland, Ohio
    "Swagelok" Fittings

17. Copper Tubing
    Chase Copper and Brass Company
    Collingdale, Pennsylvania
    O.D. 0.250 in, Wall 0.065 in

18. Nitrogen
    The Linde Air Products Company
    Division of Union Carbide Corporation
    270 Park Avenue
    New York 17, New York
    High Purity Dry- 99.999% N_2

19. Methane
    The Matheson Company, Inc.
    East Rutherford, New Jersey
    C. P. Grade