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BUREAU OF MINES  
HELIUM ACTIVITY  
HELIUM RESEARCH CENTER  
INTERNAL REPORT

COMPRESSIBILITY DATA FOR HELIUM AT

0° C AND PRESSURES TO 800 ATMOSPHERES

BY

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BRANCH

Fundamental Research

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ILLUSTRATIONS

Branch of Fundamental Research

Project 6905

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## CONTENTS

	<u>Page</u>
Abstract . . . . .	5
Introduction . . . . .	6
Acknowledgment . . . . .	7
Experimental apparatus and experimental procedure . . . . .	8
Calculation of absolute pressures from the experimental observations . . . . .	12
Experimental results . . . . .	16
Treatment of the experimental data . . . . .	20
Comparison of our results with the work of previous investigators . . . . .	53
Discussion of results . . . . .	63
References . . . . .	68
Appendix A . . . . .	77
Appendix B . . . . .	88

## ILLUSTRATIONS

Fig.

1. Gas pressure system of the high-pressure compressibility apparatus . . . . .	9
2. Oil pressure system of the high-pressure compressibility apparatus . . . . .	10
3. Constant temperature bath system and some of the major components of the high-pressure compressibility apparatus . . . . .	11
4. $\frac{W_r (\delta P_r)^2}{a}$ as a function of $P_r$ . . . . .	35

CONTENTS

Page

Abstract . . . . . 3

Introduction . . . . . 6

Acknowledgment . . . . . 7

Experimental apparatus and experimental procedure . . . . . 8

Calculation of absolute pressure from experimental observations . . . . . 12

Experimental results . . . . . 18

Treatment of the experimental data . . . . . 20

Comparison of our results with the work of previous investigators . . . . . 23

Discussion of results . . . . . 63

References . . . . . 68

Appendix A . . . . . 73

Appendix B . . . . . 85

ILLUSTRATIONS

vii

1. Gas pressure system of the high-pressure compressibility apparatus . . . . . 9

2. Oil pressure system of the high-pressure compressibility apparatus . . . . . 10

3. Constant temperature bath system and some of the major components of the high-pressure compressibility apparatus . . . . . 11

4.  $\frac{W_2(P_2)^2}{P_1}$  as a function of  $P_1$  . . . . . 32

## TABLES

	<u>Page</u>
1. Analysis of vent samples, parts per million mole fraction impurities in helium . . . . .	18
2. Helium cylinder analysis, parts per million mole fraction impurities in helium . . . . .	21
3. Helium cylinders used to supply sample gas for the 22 compressibility runs . . . . .	21
4. Compressibility bath temperatures . . . . .	22
5. Experimental pressures . . . . .	23
6. Summary of average quantities obtained from the nonlinear least-squares treatment of the experimental compressibility measurements on helium at 0° C, treating each run separately . . . . .	30
7. Summary of the results obtained from the nonlinear least-squares treatment of the experimental compressibility measurements on helium at 0° C, treating all runs simultaneously . . . . .	32
8. Least-squares values of a, b, and b/a calculated for the equation $W_r (\delta P_r)^2 = a + bP_r$ , assuming $Z_r = 1 + BP_r + CP_r^2 + DP_r^3 + EP_r^4$ . . . . .	34
9. Pressure residuals, in atm, for a quartic fit in P to represent Z, treating all runs simultaneously, weighting factor $P_{sub r}$ to the $-3/4$ . . . . .	37
10. Mean pressure residual as a function of expansion number and pressure . . . . .	44
11. Experimental and calculated pressures, in atm, parameters, standard errors, variances and covariances, treating all runs simultaneously, weighting factor $P_{sub r}$ to the $-3/4$ . . . . .	46
12. Variances and covariances for integral pressures, treating all runs simultaneously, weighting factor $P_{sub r}$ to the $-3/4$ . . . . .	51

TABLES

1	Analysis of test samples, parts per billion moist fraction reported in helium	10
2	Helium cylinder analysis, parts per billion moist fraction reported in helium	11
3	Helium cylinders used as supply source for the 12 compressibility runs	11
4	Compressibility bath temperature	12
5	Experimental procedure	12
6	Summary of average quantities obtained from the analysis least squares treatment of the experimental compressibility measurements on helium at 0° C, treating each run separately	13
7	Summary of the results obtained from the nonlinear least-squares treatment of the experimental compressibility measurements on helium at 0° C, treating all runs simultaneously	13
8	Least-squares values of $\alpha$ , $\beta$ , and $\gamma$ calculated for the equation $\ln \frac{P}{P_0} = \alpha + \beta P + \gamma P^2$ , assuming $\ln \frac{P}{P_0} = 1 + \beta P + \gamma P^2$	14
9	Pressure residuals, in atm, for a constant fit in P to equation 8, including all runs simultaneously; weighting factor P and $\gamma$ to the $1/P^2$	17
10	Mean pressure residual as a function of degassing number and pressure	18
11	Experimental and calculated pressure, in atm, parameters, standard errors, variances and covariances, treating all runs simultaneously; weighting factor P and $\gamma$ to the $1/P^2$	18
12	Variances and covariances for the final pressure, treating all runs simultaneously, weighting factor P and $\gamma$ to the $1/P^2$	21



	<u>Page</u>
13. Compressibility factors and standard errors for integral pressures, treating all runs simultaneously, weighting factor $P \text{ sub } r$ to the $-3/4$ . . . . .	52
14. Comparison of results obtained from the separate and simultaneous methods . . . . .	54
15. Comparison of the second virial coefficient of helium at $0^\circ \text{ C}$ obtained in this work with the value obtained by various other investigators . . . . .	55
16. Comparison of values of the compressibility factor of helium at $0^\circ \text{ C}$ obtained in this study with values obtained by various other investigators (expressed in terms of a percentage relative difference) . . . . .	56

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23

13. Comparison of factors and standard errors for internal pressure, treated all time, static pressure, weighting factor 2 and 3 to the 1/2

24

14. Comparison of results obtained from the separate and combined methods

27

15. Comparison of the second virtual coefficient of failure at 0.2 obtained in this work with the value obtained by various other investigators

29

16. Comparison of values of the compressibility factor at failure at 0.2 obtained in this work with values obtained by various other investigators reported in terms of a percentage relative difference

17

COMPRESSIBILITY DATA FOR HELIUM AT 0° C AND PRESSURES  
TO 800 ATMOSPHERES

by

Ted C. Briggs,<sup>1/</sup> B. J. Dalton,<sup>1/</sup> and Robert E. Barieau<sup>2/</sup>

ABSTRACT

Twenty-two compressibility runs were made with helium at 0° C and pressures to 800 atmospheres by using a Burnett-type apparatus.

The purpose of making multiple runs at one temperature was to statistically determine an adequate functional form for representing the data, and to then present precise new data.

The work is part of a broad program for the experimental determination of data for the evaluations of the thermodynamic properties of helium and helium-containing mixtures.

Data from the 22 runs were treated simultaneously and as separate runs while different functional forms and weighting factors were used. A summary of the results is included.

---

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COMPRESSIBILITY DATA FOR HELIUM AT 0° C AND PRESSURES  
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L. C. BRIDGE,<sup>1</sup> R. S. BRIDGES,<sup>2</sup> and Robert S. BRIDGES<sup>2</sup>

ABSTRACT

Twenty-two compressibility runs were made with helium at 0° C and pressures to 800 atmospheres by using a Burnett-type apparatus. The purpose of making multiple runs at one temperature was to statistically determine an adequate functional form for representing the data, and to then present precise new data. The work is part of a broad program for the experimental determination of data for the evaluation of the thermodynamic properties of helium and helium-containing mixtures. Data from the 22 runs were treated simultaneously and as separate runs while different functional forms and weighting factors were used. A summary of the results is included.

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<sup>1</sup> Research chemist, Helium Research Center, Bureau of Mines, Annapolis, Tex.  
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A fourth degree polynomial equation in the pressure gives a statistically satisfactory representation of the compressibility factor when the data are treated simultaneously and a weighting factor of  $P_r^{-3/4}$  is used.

The second virial coefficient of helium at 0° C from this investigation is  $11.997 \pm 0.015 \text{ cm}^3 \text{ mole}^{-1}$ . The stated uncertainty is the random error standard deviation. Compressibility factors determined by this investigation are precise to better than 0.01 percent and are believed to be accurate to better than 0.02 percent.

#### INTRODUCTION

Accurate experimental compressibility data for helium and helium-containing mixtures are of importance to the Bureau of Mines helium conservation program. These data are needed for calculations of the amount of helium transported through the various pipelines, of the amount stored in the conservation fields, and of the amount ultimately delivered to the user. Thermodynamic properties, computed from the compressibility data, can be used to design improved process and separation cycles for the extraction, concentration, and purification of helium.

Extensive and accurate compressibility data over wide temperature and pressure ranges are required for the development of an accurate equation of state. These data will contribute toward planning and coordinating the utilization of the nation's helium resources, and will aid in the future development of new uses for helium.

A fourth degree polynomial equation in the pressure gives a statistically satisfactory representation of the compressibility factor when the data are treated simultaneously and a weighting factor of  $P^{-1}$  is used.

The second virial coefficient of helium at 0° C from this investigation is  $11.99 \pm 0.03$  cm<sup>3</sup> mole<sup>-1</sup>. The stated uncertainty is the random error standard deviation. Compressibility factors determined by this investigation are precise to better than 0.5 percent and are believed to be accurate to better than 0.5 percent.

### INTRODUCTION

Accurate experimental compressibility data for helium and helium containing mixtures are of importance to the Bureau of Mines helium conservation program. These data are needed for calculations of the amount of helium transported through the various pipelines, of the energy stored in the conservation fields, and of the amount ultimately delivered to the user. Thermodynamic properties, computed from the compressibility data, can be used to design improved process and separation cycles for the extraction, liquefaction, and purification of helium.

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The Burnett compressibility method (12)<sup>3/</sup> was selected for the

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<sup>3/</sup> Underlined numbers in parentheses refer to items in the list of references preceding the appendices.

---

experimental measurements. This method does not require volume calibrations, nor is it necessary to know the number of moles of sample. Very precise experimental observations can be made with this method.

One objection to the Burnett method is that it does not yield an experimental compressibility factor directly. A functional form must be assumed before the compressibility factor can be derived from the experimental observations, or the data must be reduced graphically.

We feel that a generally acceptable treatment of Burnett data, free from esoteric manipulations, will be required to obtain agreement among investigators consistent with the experimental precision. Criteria must be developed for the selection of a functional form to represent the data and for the choice of a weighting factor.

It is toward these goals that this work is directed.

#### ACKNOWLEDGMENT

The authors thank the staff of the Branch of Automatic Data Processing for their valuable aid.

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The authors thank the staff of the Branch of Automatic Data

Processing for their valuable aid.



## EXPERIMENTAL APPARATUS AND EXPERIMENTAL PROCEDURE

The apparatus used in this investigation was a conventional Burnett compressibility apparatus (12). A Burnett apparatus basically consists of two volumes designated as  $V_1$  and  $V_2$ , equipment to measure the pressure of a gas sample confined in volume  $V_1$  or  $(V_1 + V_2)$ , and equipment to control and measure the temperature of  $V_1$  and  $V_2$ .

An unscaled diagram of the gas pressure system of our apparatus is designated figure 1. Figure 2 is a drawing of the oil pressure

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FIGURE 1. - Gas Pressure System of the High-Pressure Compressibility Apparatus.

FIGURE 2. - Oil Pressure System of the High-Pressure Compressibility Apparatus.

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system. Figure 3 shows the constant temperature bath along with

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FIGURE 3. - Constant Temperature Bath System and Some of the Major Components of the High-Pressure Compressibility Apparatus.

---

some major apparatus components.

Some of the equipment incorporated into the present apparatus has been described in the literature (14, 29, 36, 38, 47). A detailed description of the component parts of our apparatus is contained in appendix A.

EXPERIMENTAL APPARATUS AND EXPERIMENTAL PROCEDURE

The apparatus used in this investigation was a conventional piston compressibility apparatus (12). A detailed apparatus sketch consists of two volumes designated as  $V_1$  and  $V_2$ , adjustment to measure the pressure of a gas sample confined in volume  $V_1$  or  $(V_1 + V_2)$ , and equipment to control and measure the temperature of  $V_1$  and  $V_2$ . An unclassified diagram of the gas pressure system of our apparatus is designated figure 1. Figure 2 is a drawing of the oil pressure

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FIGURE 1 - Gas Pressure System of the High-Pressure Compressibility

Apparatus.

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FIGURE 2 - Oil Pressure System of the High-Pressure Compressibility

Apparatus.

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FIGURE 3 - Constant Temperature Bath System and Some of the Major

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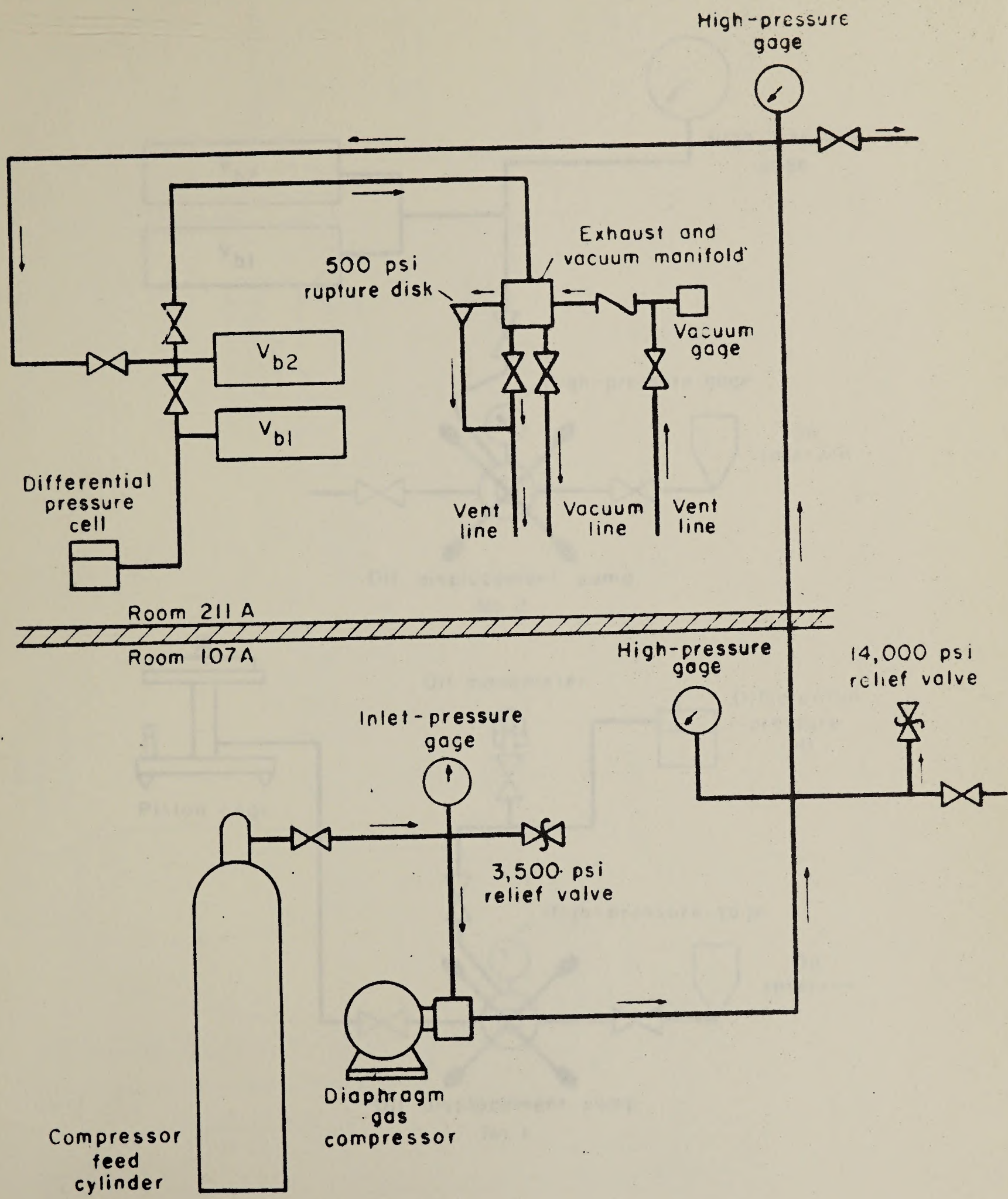
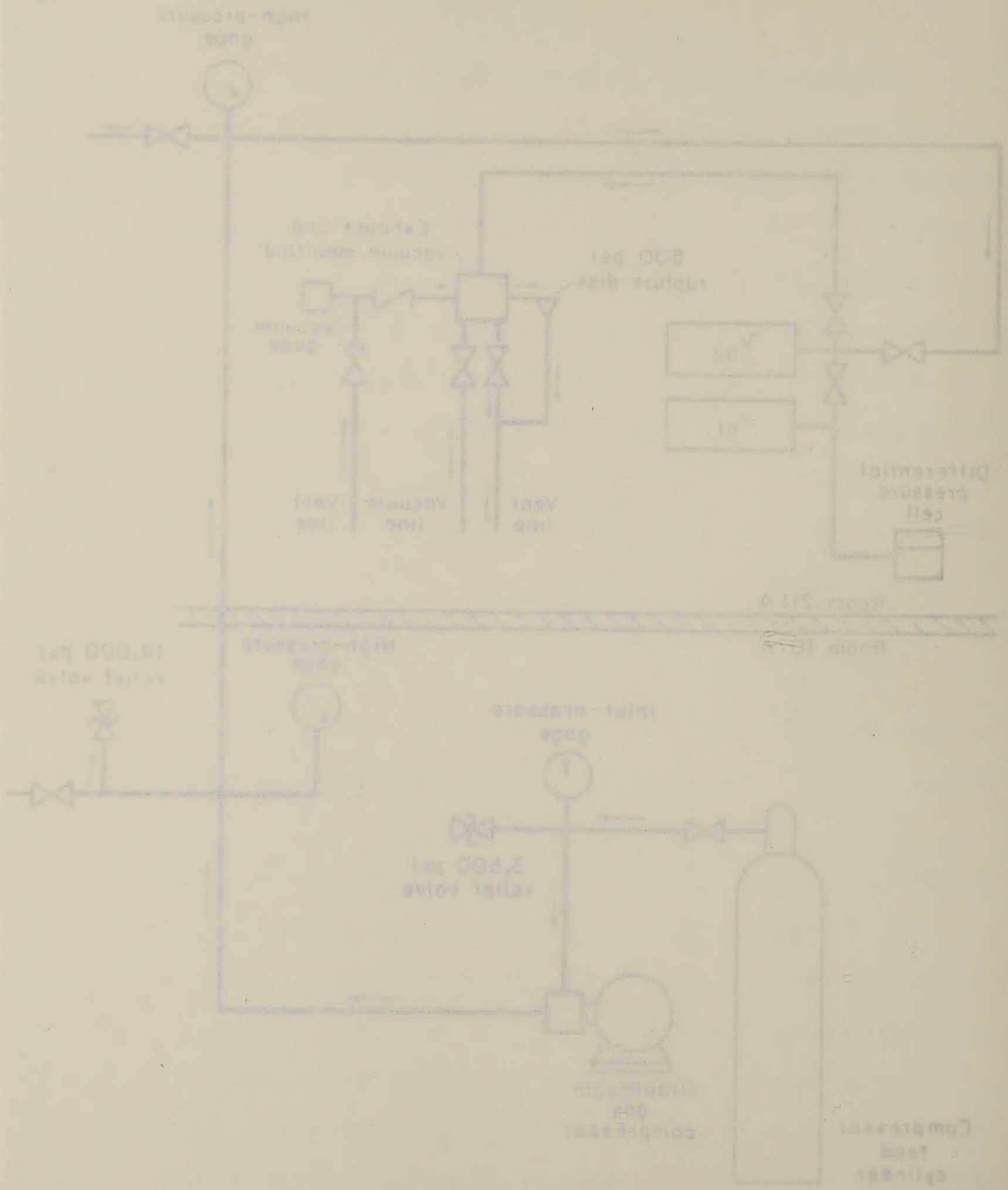


FIGURE I. - Gas Pressure System of the High-Pressure Compressibility Apparatus.

FIGURE 1 - Gas Pressure System of the High-Pressure Compressibility Apparatus



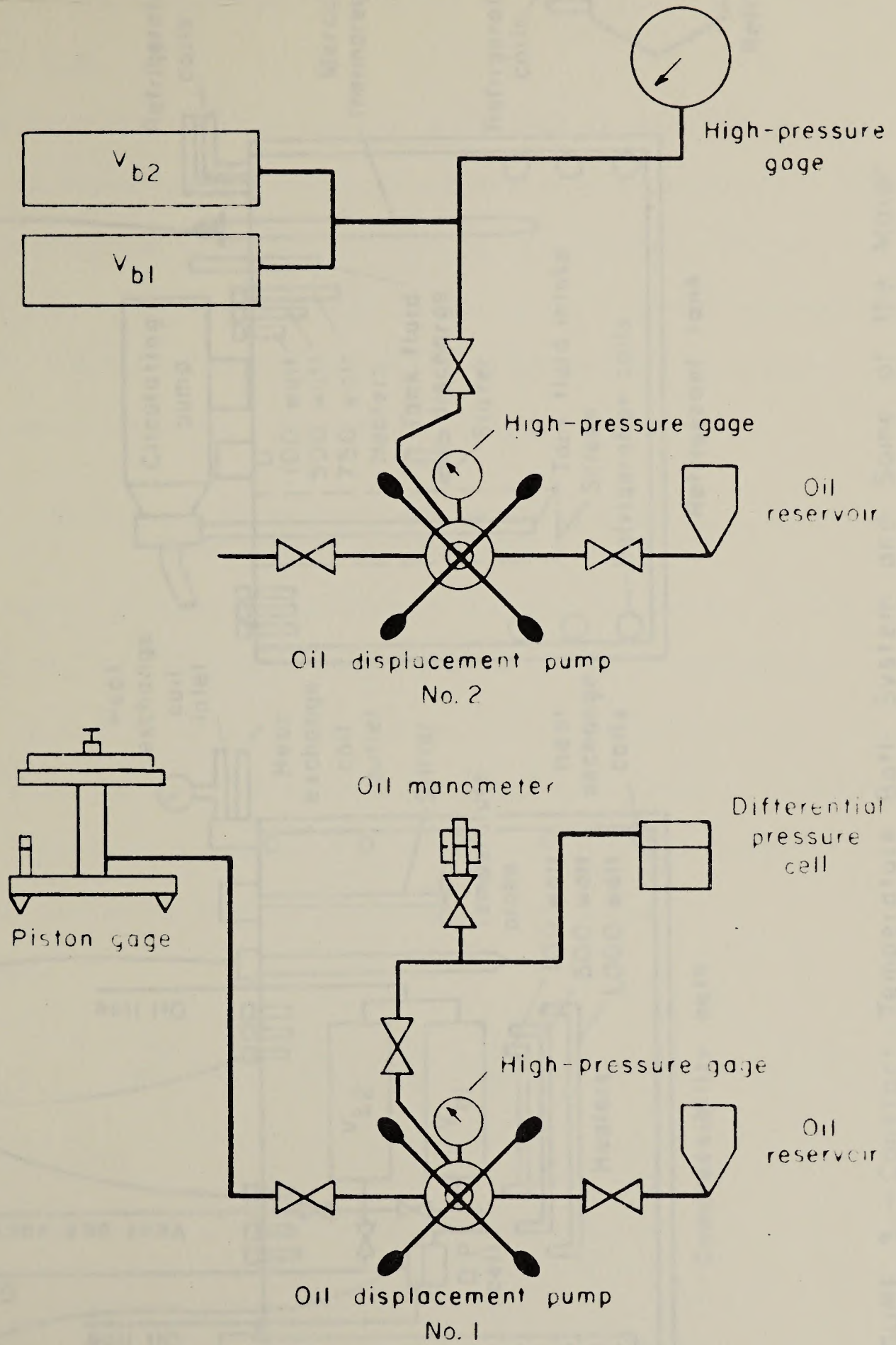


FIGURE 2 - Oil Pressure System of the High-Pressure Compressibility Apparatus.



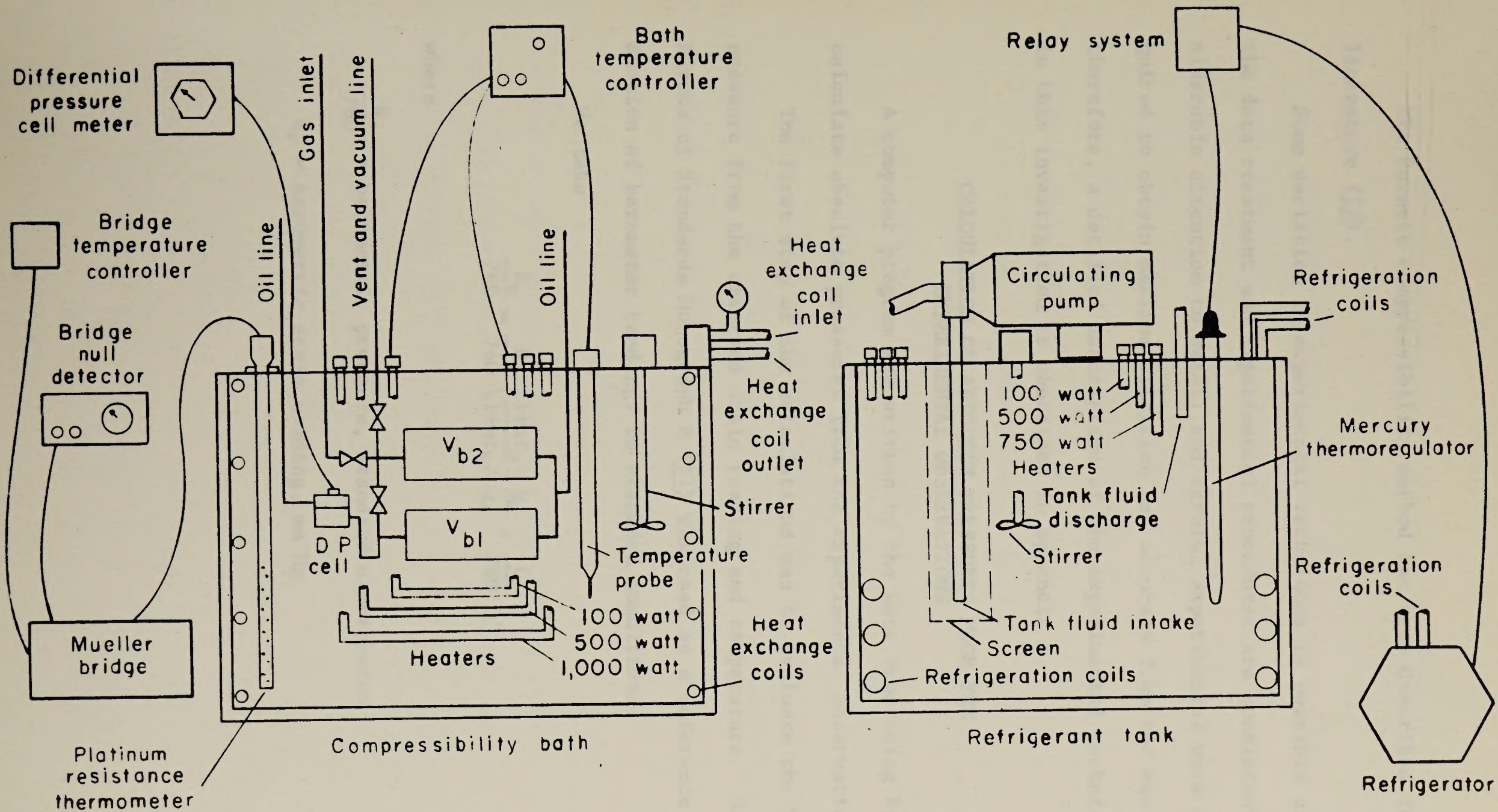
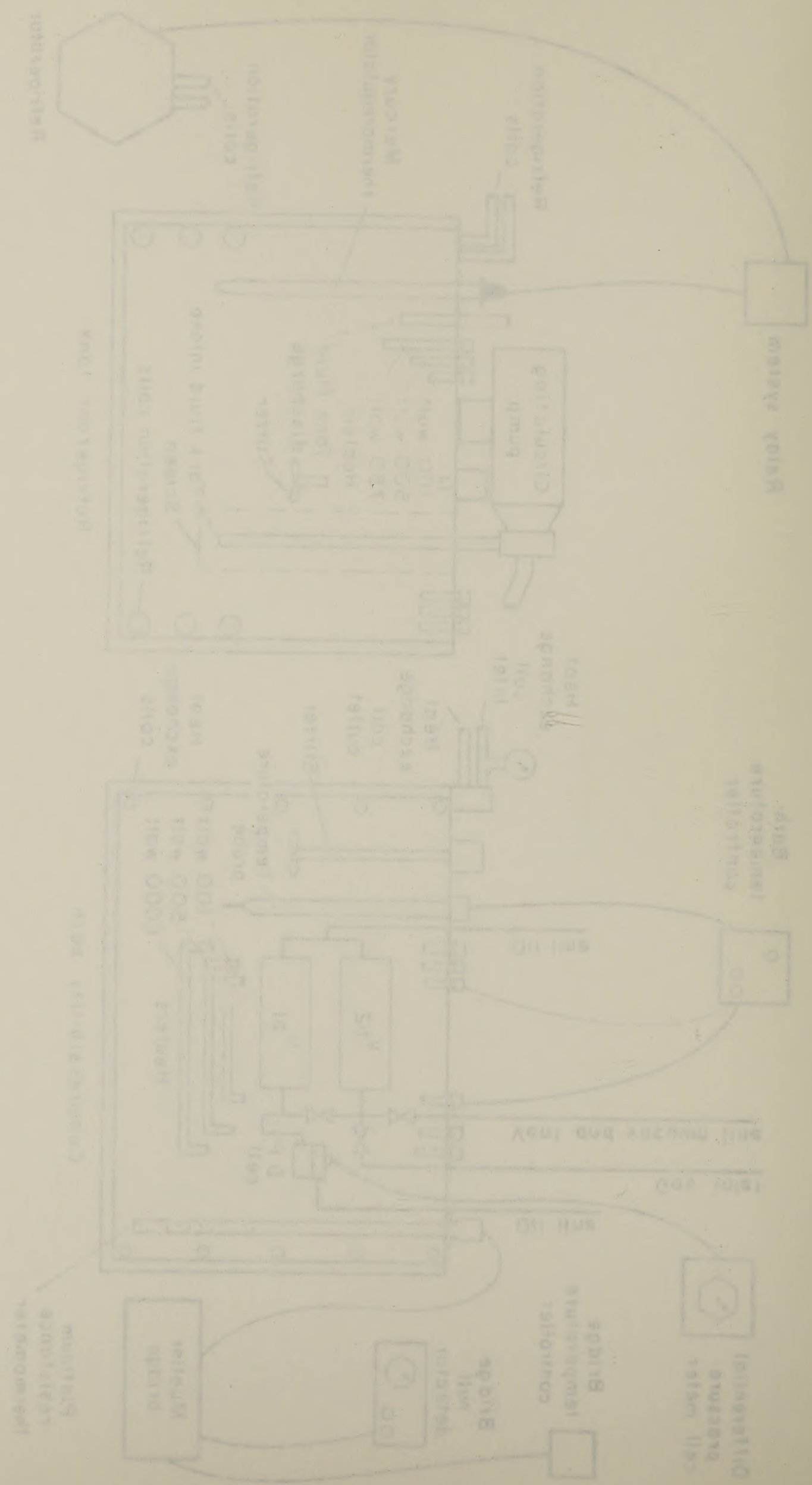


FIGURE 3.—Constant Temperature Bath System and Some of the Major Components of the High-Pressure Compressibility Apparatus.

Σχήμα 2 - Σύστημα μεταφοράς υγρών από τον αεριοποιητή στον αεριοποιητή.





The Burnett compressibility method has been described in the literature (12).

Some variation in experimental techniques is possible as long as the data treatment and experimental procedures are consistent. Considerable attention to detail and careful experimental work are required to obtain maximum precision and accuracy from the equipment; therefore, a detailed description of the experimental techniques used in this investigation is contained in appendix B.

#### CALCULATION OF ABSOLUTE PRESSURES FROM THE EXPERIMENTAL OBSERVATIONS

A computer program was written by the Data Processing Branch to calculate absolute pressures from the experimental observations.

The first step of the calculations was to evaluate the barometric pressure from the observed scale reading and temperature. National Bureau of Standards Monograph 8 (11) was used as a reference for reduction of barometer readings to standard conditions.

We take

$$\frac{R_c}{760} = \frac{R_s}{760} \left( \frac{1+st_b}{1+mt_b} \right) \frac{g_1}{g_s} + \frac{C_c}{760} \quad (1)$$

where

$\frac{R_c}{760}$  = barometric pressure, standard atmospheres

$R_s$  = barometric scale reading, mm Hg

The Burnett compressibility method has been described in the

Literature (15).

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CALCULATION OF ABSOLUTE PRESSURES FROM THE EXPERIMENTAL OBSERVATIONS

A computer program was written by the Data Processing Branch to calculate absolute pressures from the experimental observations. The first step of the calculation was to evaluate the barometric pressure from the observed scale reading and temperature. Bureau of Standards Monograph 5 (11) was used as a reference for the location of barometric readings to standard conditions.

We have

$$(1) \quad \frac{P_s}{760} = \frac{P_r}{760} \left( \frac{273.15}{273.15 + t_r} \right)^{5.426} + \frac{C}{760}$$

where

$\frac{P_s}{760}$  = barometric pressure, standard atmosphere

$P_r$  = barometric scale reading, mm Hg

$s$  = coefficient of linear expansion of barometer scale,  
 $18.4 \times 10^{-6}$ ,  $^{\circ}\text{C}^{-1}$ , (11, page 28)

$m$  = mean cubical coefficient of thermal expansion of  
 mercury

$$m \times 10^8 = 18144.01 + 0.7016t_b + 0.0028625t_b^2 + 0.000002617t_b^3,$$

$^{\circ}\text{C}^{-1}$ , (11, page 4)

$t_b$  = barometer and/or room temperature,  $^{\circ}\text{C}$

$g_1$  = acceleration due to gravity at the barometer  
 location,  $979.4091 \text{ cm sec}^{-2}$ , (18)

$g_s$  = standard acceleration due to gravity,  $980.665 \text{ cm sec}^{-2}$

$C_c$  = calibration correction provided by the National Bureau  
 of Standards for serial No. 13346 barometer,  $+0.06 \text{ mm Hg}$

Next, a piston gage pressure was computed from the experimental observations. National Bureau of Standards Monograph 65 (17) was used as a reference for reduction of piston gage data. Equation 2,

$$P_g = \frac{M_a (1 - \rho_a / \rho_b) g_1 / g_s}{A_o (1 + bP_g) [1 + c(t_g - 25)]} + C_d, \quad (2)$$

was used to calculate gage pressures for the data recorded in this report. Calibration constants and data for piston gage, serial No. 9274 were provided by Ruska Instrument Corporation.

In equation 2,

$P_g$  = gage pressure, psig

coefficient of linear expansion of barometer scale,

$$18.2 \times 10^{-6} \text{ } ^\circ\text{C}^{-1} \text{ (Eq. (1), page 10)}$$

m = mean vertical coefficient of thermal expansion of

mercury

$$18.1 \times 10^{-6} = 18.1 \times 10^{-6} + 0.170 \times 10^{-6} + 0.0225 \times 10^{-6} + 0.00003 - 17.5 \times 10^{-6}$$

$$^\circ\text{C}^{-1} \text{ (Eq. (1), page 10)}$$

$\Delta$  = barometer height from temperature,  $^\circ\text{C}$

$g$  = acceleration due to gravity at the barometer

$$\text{location, } 9.78 \text{ m/sec}^2 \text{ (Eq. (18))}$$

$g_s$  = standard acceleration due to gravity, 9.80665 m/sec<sup>2</sup>

$C_1$  = calibration correction provided by the National Bureau

of Standards for serial No. 15548 barometer, 10.00 mm Hg

Next, a piston gage pressure was computed from the experimental

observations. National Bureau of Standards Monograph 55 (11) was

used as a reference for reduction of piston gage data. Equation 2,

$$P_1 = \frac{W_1 (1 + \alpha_1 \Delta_1) + W_2 (1 + \alpha_2 \Delta_2)}{A (1 + \beta \Delta)} \quad (2)$$

was used to calculate gage pressure for the data recorded in this

report. Calibration constants and data for piston gage, serial No.

9374 were provided by Fiske Instrument Corporation.

In equation 2,

$P_1$  = gage pressure, psig

$M_a$  = mass of the piston gage load<sup>4/</sup>, lbs

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<sup>4/</sup> The calibrated piston gage weights were reported by Ruska Instrument Corporation as apparent mass in air against brass standards; therefore, the standard brass density of 8.4 grams  $\text{cm}^{-3}$  was used in equation 2 rather than the actual density of the weights, (17, page 3).

---

$\rho_a$  = density of air, grams  $\text{cm}^{-3}$

$\rho_b$  = density of brass standards, 8.4 grams  $\text{cm}^{-3}$

$g_1$  = acceleration due to gravity at the piston gage location, 979.4091  $\text{cm sec}^{-2}$ , (18)

$g_s$  = standard acceleration due to gravity, 980.665  $\text{cm sec}^{-2}$

$A_o$  = piston gage No. 9274 effective area at 25° C and atmospheric pressure, 0.0260416  $\text{in}^2$

$b$  = piston gage No. 9274 effective area pressure distortion coefficient,  $-3.5 \times 10^{-8}$   $\text{psi}^{-1}$

$c$  = piston gage No. 9274 effective area temperature distortion coefficient,  $1.7 \times 10^{-5}$   $^{\circ}\text{C}^{-1}$

$t_g$  = piston gage temperature,  $^{\circ}\text{C}$

$C_d$  = differential pressure cell correction,  $1.85 \times 10^{-6}$   $P_g$ .

Barieau (1) derived equations 3 and 4 for the calculation of the density of moist air in grams  $\text{liter}^{-1}$ :

$M_2$  = mass of the piston gas loss

The calibrated piston gas weights were reported by Bureau Instrument Corporation as apparent mass in air against brass standards; therefore, the standard brass density of 8.4 grams  $cm^{-3}$  was used in equation 2 rather than the actual density of the weights. (11, page 31)

- A = density of air, grams  $cm^{-3}$
  - B = density of brass standards, 8.4 grams  $cm^{-3}$
  - C = acceleration due to gravity at the piston gas location, 979.001  $cm\ sec^{-2}$  (12)
  - D = standard acceleration due to gravity, 980.665  $cm\ sec^{-2}$
  - E = piston gas No. 9278 effective area at 25° C and atmospheric pressure, 0.0160416  $in^2$
  - F = piston gas No. 9278 effective area pressure correction coefficient,  $-3.32 \times 10^{-6}\ gal^{-1}$
  - G = piston gas No. 9278 effective area temperature distortion coefficient,  $1.1910 \times 10^{-6}\ in^2\ ^\circ C^{-1}$
  - H = piston gas temperature, °C
  - I = differential pressure cell correction,  $1.82 \times 10^{-6}\ in^2$
- Equation (1) derived equations 2 and 3 for the calculation of the density of moist air in grams  $liter^{-1}$ .

$$\rho_a = 1.2932 \frac{T_o}{T} \frac{R_c}{760} (1 - 0.37807y) \frac{Z_o}{Z} , \quad (3)$$

$$\frac{Z_o}{Z} = 1 - 0.000602 \left( \frac{R_c}{760} - 1 \right) + (0.00254y + 0.0758y^2) \frac{R_c}{760} \\ - (0.0000105 + 0.0000131y + 0.00131y^2) t_b \frac{R_c}{760} , \quad (4)$$

where

$\rho_a$  = density of moist air

$T$  = absolute temperature,  $273.15 + t_b$ , °K,

$T_o$  = absolute temperature at the ice point,  $273.15^\circ$  K,

and

$y$  = mole fraction of water vapor.

Equation 5 was assumed to be valid for the air density calculations of this work:

$$y = \frac{P_s \cdot 760 \cdot H}{R_c} , \quad (5)$$

where

$P_s$  = vapor pressure of liquid water, atm, and

$H$  = relative humidity expressed as a decimal fraction.

Osborne, Stimson, and Ginnings (42) presented the following equation for the calculation of the vapor pressure of water.

$$\log_{10} P_s = -3.142305 \left( \frac{10^3}{T'} - \frac{10^3}{373.16} \right) + 8.2 \log_{10} \left( \frac{373.16}{T'} \right) \\ - 0.0024804 (373.16 - T') , \quad (6)$$

where  $T' = (273.16 + t_b)$ , °K.

$$(3) \quad p_a = 1.1922 \frac{p}{T} - \frac{p}{180} (1 - 0.37607y) \frac{p}{T}$$

$$\frac{p}{T} = 1 - 0.00602 \left( \frac{p}{T} - 1 \right) + (0.00124y + 0.0728y^2) \frac{p}{T}$$

$$(4) \quad -10.000192 + 0.000121y + 0.00121y^2 \frac{p}{T}$$

where

$p_a$  = density of moist air

$T$  = absolute temperature,  $273.15 + t$ , °K

$T_0$  = absolute temperature at the ice point, 273.15° K

and

$y$  = mole fraction of water vapor

Equation 2 was assumed to be valid for the air density calculations

of this work.

$$(5) \quad y = \frac{p_a - p_{H_2O}}{p}$$

where

$p_a$  = vapor pressure of liquid water, air, and

$H$  = relative humidity expressed as a decimal fraction

Gaborn, Stinson, and Gintling (23) presented the following

equation for the calculation of the vapor pressure of water.

$$\log_{10} p_a = -3.142302 \left( \frac{10^4}{T} - \frac{10^4}{373.16} \right) + 8.2 \log_{10} \left( \frac{373.16}{T} \right)$$

$$(6) \quad -0.0024804 (373.16 - T)$$

where  $T = (273.16 + t)$ , °K



The density of air was calculated by using equations 3, 4, 5, and 6, the barometer or room temperature, barometric pressure, and relative humidity.

Piston gage pressures in psig were calculated from equation 2 by using an iterative procedure which continued until the change in the computed gage pressure was less than 0.0001 psig. Calibration data for piston gage No. 9274 along with the experimental observations were used as input data for the calculations.

Defined values used by Ruska Instrument Corporation in the calibration of piston gage No. 9274 were:

1 in. = 2.54 cm exactly

1 lb. = 453.5924 grams.

An atmosphere in terms of the constants supplied by Ruska Instrument Corporation is:

$$1 \text{ atm} = \frac{1.013250 \cdot 10^6 \cdot (2.54)^2}{453.5924 \cdot 980.665} = 14.69594780 \text{ psi} .$$

Ruska piston gage pressure in psig was divided by 14.69594780 to obtain gage pressure in atmospheres. Absolute pressure in atmospheres was obtained by adding the barometric pressure in atmospheres to the piston gage pressure in atmospheres.

#### EXPERIMENTAL RESULTS

An experiment was run to determine if any impurities were introduced into the test gas while filling the compressibility volumes to

The density of air was calculated by using equations 1, 2, 3, and 4, the barometer at room temperature, barometric pressure, and relative humidity.

Piston gage pressure in psg were calculated from equation 1 by using an iterative procedure which continued until the change in the computed gage pressure was less than 0.0001 psg. Calibration data for piston gage No. 9154 along with the experimental observations were used as input data for the calculations.

Defined values used by Ruska Instrument Corporation in the calibration of piston gage No. 9154 were:

$$1 \text{ in.} = 2.54 \text{ cm exactly}$$
$$1 \text{ lb.} = 453.5926 \text{ grams}$$

An atmosphere in terms of the constant supplied by Ruska Instrument Corporation is:

$$1 \text{ atm} = \frac{1.01325 \times 10^5 \text{ Pa}}{101325 \text{ Pa}} = 1.01325 \text{ bar}$$

Ruska piston gage pressure in psg was derived by 14.6959 psg of absolute pressure in atmosphere. Absolute pressure in atmosphere was obtained by adding the barometric pressure in atmosphere to the piston gage pressure in atmosphere.

### EXPERIMENTAL RESULTS

An experiment was run to determine if any significant change occurred into the test gas while filling the compressibility volume in

the initial high-pressure. An analyzed<sup>5/</sup> cylinder of grade A helium

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<sup>5/</sup> All composition analyses were performed by the Branch of Laboratory Services, Bureau of Mines, Helium Research Center.

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was attached to the inlet of the gas compressor. The gas system was evacuated and purged with test gas. Then the pressure containers were filled to an initial pressure of about 700 atmospheres. Filling of the pressure containers was carried out exactly as it would be done for a compressibility run. Gas was vented from the pressure containers, and a sample of the test gas was trapped for analysis. The compressibility volumes were filled three times to pressures of about 700 atmospheres, and three samples were trapped for analysis. A sample taken directly from the supply cylinder and the three vent samples were analyzed by high-pressure mass spectrometry (48). The results of these analyses are recorded in table 1 of this report. Examination of the data of table 1 indicates a slight increase in the nitrogen and oxygen content of the vent samples over that of the cylinder sample; however, the increase in total sample impurities is considered negligible and probably occurred during the sampling procedure rather than during the bomb filling procedure.

An experiment was conducted to determine if any errors were introduced into the compressibility pressure measurements due to differences in the density of oil in the line to the differential

The initial high-pressure gas cylinder in Figure 4 and

All composition analyses were performed by the Bureau of  
Laboratory Services, Bureau of Mines, Belmont Research Center.

was attached to the inlet of the gas component. The gas system was  
evacuated and purged with inert gas. Then the pressure transducer

was fitted with an initial pressure of about 100 atmospheres. With  
the pressure transducer was carried out during the work.

When the temperature was constant, the gas was vented from the pressure  
transducer, and a sample of the test gas was trapped for analysis.

The composition of the gas was determined by means of a pressure of  
about 100 atmospheres, and then trapped with a pressure transducer.

A sample of the gas was taken from the system cylinder and the gas was  
sampled with a pressure transducer with a pressure of 100.

Results of these analyses are recorded in Table 1 of this report.  
The composition of the gas in Table 1 indicates a slight increase in the

nitrogen and water content of the gas during the test of the cell.  
These results, however, are believed to be due to analytical error.

considered negligible in the present context. The results are  
shown rather than during the test of the cell.

An experiment was conducted to determine if any errors were in-  
cluded into the compositionally measured measurements due to dif-

ferences in the density of oil in the line to the differential

TABLE 1. - Analysis of vent samples, parts per million mole fraction impurities in helium

Sample	H <sub>2</sub>	CH <sub>4</sub>	Ne	N <sub>2</sub>	O <sub>2</sub>	Ar	CO <sub>2</sub>
Sample direct from cylinder No. 25598...	0.9	0.2	20.0	3.5	0.7	0.1	0.2
Vent sample No. 1.....	1.2	.3	17.8	18.5	6.9	.2	.2
Vent sample No. 2.....	1.3	.4	16.8	9.7	1.8	.1	.3
Vent sample No. 3.....	.9	.5	19.4	12.3	2.1	.1	.4



pressure cell. Part of the vertical portion of the oil line was at ambient temperature while another vertical portion of the oil line was at the bath temperature. This situation existed because the oil line entered the constant temperature bath over the edge of the bath rather than directly through the bath wall.

A heat exchanger was placed around the vertical part of the oil line located outside of the constant temperature bath. Bath fluid could be circulated through the heat exchanger so pressure measurements could be made with the outside vertical part of the oil line at room temperature or at approximately the bath temperature.

Measurements were made with both sides of the differential pressure cell open to atmospheric pressure, with and without cooling in the heat exchanger. A measurable difference in pressure due to oil density changes was observed. This effect was completely compensated for at atmospheric pressure by setting the meter of the differential pressure cell on zero at the start of a compressibility run while atmospheric pressure was applied to both sides of the differential pressure cell diaphragm.

Next, pressure measurements were made at about 365 atmospheres and at about 700 atmospheres with and without cooling in the heat exchanger. There were no measurable differences in the observed pressures when cooling was applied to the oil line or when the line was at ambient temperature.

pressure cell. Part of the vertical portion of the oil line was at ambient temperature while another vertical portion of the oil line was at the bath temperature. This situation existed because the oil line entered the constant temperature bath over the edge of the bath rather than directly through the bath wall.

A heat exchanger was placed around the vertical part of the oil line located outside of the constant temperature bath. Bath fluid could be circulated through the heat exchanger so pressure measurements could be made with the outside vertical part of the oil line at some temperature or at approximately the bath temperature.

Measurements were made with both ends of the differential pressure cell open to atmosphere, with and without cooling in the heat exchanger. A noticeable difference in pressure due to oil density change was observed. This effect was completely compensated for an atmospheric pressure by setting the ratio of the differential pressure cell on each side of the cell at a compressibility ratio while atmospheric pressure was applied to both sides of the differential pressure cell diagram.

Heat pressure measurements were made at about 100 atmospheres and at about 700 atmospheres with and without cooling in the heat exchanger. There was no noticeable difference in the observed pressure when cooling was applied to the oil line or when the line was at ambient temperature.



We conclude that any errors in our pressure measurements due to density gradients in vertically displaced tubing lines in inhomogeneous temperature environments are completely negligible.

A total of 22 compressibility runs were made with helium at 0° C. Three helium cylinders were used to supply sample gas for the runs. Analyses of impurities of each cylinder are recorded in table 2. The particular cylinder used for each run is listed in table 3 of this report.

A platinum resistance thermometer was mounted in the compressibility bath and was used to measure the temperature of the bath fluid (9). The average bath temperature for a complete run was assumed to be representative of the actual sample temperature. The average measured bath temperature and the standard error of the average measured bath temperature are recorded in table 4 for each of the 22 runs. Temperatures are in terms of the International Practical Temperature Scale (IPTS).

Experimental gage pressures, barometric pressures, and experimental absolute pressures are listed in table 5 for each run.

#### TREATMENT OF THE EXPERIMENTAL DATA

The data treatments are based on the mathematical formulas developed by Barieau and Dalton (2) which are specific applications of their general nonlinear least-squares techniques (3). Two computer programs, written by Douglas and Moffitt (19) and by Grout (22), were used in the data treatments.

We conclude that any errors in our pressure measurements due to density gradients in vertically displaced tubing lines in inhomogeneous temperature environments are completely negligible.

A total of 25 compressibility runs were made with helium at 0° C. Three helium cylinders were used to supply sample gas for the runs. Analyses of samples of each cylinder are recorded in Table 3. The particular cylinder used for each run is listed in Table 2 of this report.

A platinum resistance thermometer was mounted in the compressibility bath and was used to measure the temperature of the bath fluid. The average bath temperature for a complete run was assumed to be representative of the actual sample temperature. The average measured bath temperature and the standard error of the average measured bath temperature are recorded in Table 4 for each of the 25 runs. Parameters are in terms of the International Practical Temperature Scale (IPTS).

Experimental gas pressures, thermometric pressures, and experimental absolute pressures are listed in Table 5 for each run.

### TREATMENT OF THE EXPERIMENTAL DATA

The data treatment is based on the statistical formulas developed by Barrow and Helton (5) which are specific applications of their general nonlinear least-squares technique (3). The computer program, written by Douglas and Kottitt (12) and by Gross (13), was used in the data treatment.

TABLE 2. - Helium cylinder analysis, parts per million mole fraction impurities in helium

Cylinder number	H <sub>2</sub>	CH <sub>4</sub>	H <sub>2</sub> O	Ne	N <sub>2</sub>	O <sub>2</sub>	Ar	CO <sub>2</sub>	Total
H-135022	0.4	0.0	0.7	15.2	1.4	0.3	0.0	0.0	18.0
AEC107250	.0	.0	.8	11.8	2.5	.6	Tr. <sup>1/</sup>	Tr.	15.7
AEC103941	.3	.0	.9	11.7	.6	.1	.0	.1	13.7

<sup>1/</sup> Tr. indicates less than 0.05 parts per million.

TABLE 3. - Helium cylinders used to supply sample gas for the 22 compressibility runs

Run No.	Cylinder No.	Run No.	Cylinder No.
HE-0-1	H-135022	HE-0-12	AEC107250
HE-0-2	H-135022	HE-0-13	AEC107250
HE-0-3	H-135022	HE-0-14	AEC107250
HE-0-4	H-135022	HE-0-15	AEC107250
HE-0-5	H-135022	HE-0-16	AEC107250
HE-0-6	H-135022	HE-0-17	AEC107250
HE-0-7	H-135022	HE-0-18	AEC107250
HE-0-8	H-135022	HE-0-19	AEC107250
HE-0-9	AEC107250	HE-0-20	AEC103941
HE-0-10	AEC107250	HE-0-21	AEC103941
HE-0-11	AEC107250	HE-0-22	AEC103941

TABLE 2 - Helium cylinder analysis, parts per million mole fraction impurities in helium

Cylinder number	H <sub>2</sub>	CH <sub>4</sub>	N <sub>2</sub>	O <sub>2</sub>	Ar	CO <sub>2</sub>	Total
H-133025	0.0	0.0	0.7	12.2	1.4	0.3	16.6
AC107250	0	0	8	11.6	2.2	7.2	25.7
AC103941	2	0	8	11.1	1	1	23.2

T<sub>2</sub> indicates less than 0.02 parts per million

TABLE 3 - Helium cylinder used to supply sample gas for the isotope ratio mass spectrometer

Run No.	Cylinder No.	Run No.	Cylinder No.
HE-0-1	H-133025	HE-0-12	H-133025
HE-0-2	H-133025	HE-0-13	H-133025
HE-0-3	H-133025	HE-0-14	H-133025
HE-0-4	H-133025	HE-0-15	H-133025
HE-0-5	H-133025	HE-0-16	H-133025
HE-0-6	H-133025	HE-0-17	H-133025
HE-0-7	H-133025	HE-0-18	H-133025
HE-0-8	H-133025	HE-0-19	H-133025
HE-0-9	AC107250	HE-0-20	AC107250
HE-0-10	AC107250	HE-0-21	AC107250
HE-0-11	AC107250	HE-0-22	AC107250

TABLE 4. - Compressibility bath temperatures

Run No.	t, °C (IPTS)	Run No.	t, °C (IPTS)
HE-0-1	-0.006 $\pm$ 0.001	HE-0-12	+0.003 $\pm$ 0.000
HE-0-2	+0.002 $\pm$ 0.001	HE-0-13	+0.002 $\pm$ 0.001
HE-0-3	-0.001 $\pm$ 0.001	HE-0-14	+0.003 $\pm$ 0.001
HE-0-4	-0.001 $\pm$ 0.000	HE-0-15	+0.002 $\pm$ 0.000
HE-0-5	+0.001 $\pm$ 0.001	HE-0-16	+0.003 $\pm$ 0.001
HE-0-6	+0.003 $\pm$ 0.001	HE-0-17	-0.001 $\pm$ 0.001
HE-0-7	+0.002 $\pm$ 0.001	HE-0-18	+0.002 $\pm$ 0.001
HE-0-8	+0.004 $\pm$ 0.001	HE-0-19	-0.001 $\pm$ 0.001
HE-0-9	+0.003 $\pm$ 0.001	HE-0-20	.000 $\pm$ 0.001
HE-0-10	+0.002 $\pm$ 0.001	HE-0-21	+0.002 $\pm$ 0.001
HE-0-11	+0.001 $\pm$ 0.001	HE-0-22	.000 $\pm$ 0.001

TABLA 4 - Compressibilidad de vapor de agua

Run No.	$\epsilon, ^\circ C$ (PTS)	Run No.	$\epsilon, ^\circ C$ (PTS)	Run No.	$\epsilon, ^\circ C$ (PTS)
RS-0-1	+0.001 ± 0.001	RS-0-13	+0.003 ± 0.003	RS-0-25	+0.000 ± 0.001
RS-0-2	+0.002 ± 0.001	RS-0-14	+0.002 ± 0.001	RS-0-26	+0.002 ± 0.001
RS-0-3	+0.001 ± 0.001	RS-0-15	+0.003 ± 0.003	RS-0-27	+0.002 ± 0.001
RS-0-4	+0.001 ± 0.001	RS-0-16	+0.002 ± 0.001	RS-0-28	+0.002 ± 0.001
RS-0-5	+0.001 ± 0.001	RS-0-17	+0.001 ± 0.001	RS-0-29	+0.002 ± 0.001
RS-0-6	+0.002 ± 0.001	RS-0-18	+0.002 ± 0.001	RS-0-30	+0.002 ± 0.001
RS-0-7	+0.002 ± 0.001	RS-0-19	+0.001 ± 0.001	RS-0-31	+0.002 ± 0.001
RS-0-8	+0.004 ± 0.001	RS-0-20	+0.001 ± 0.001	RS-0-32	+0.002 ± 0.001
RS-0-9	+0.003 ± 0.001	RS-0-21	+0.002 ± 0.001		
RS-0-10	+0.002 ± 0.001				
RS-0-11	+0.001 ± 0.001				

TABLE 5. - Experimental pressures

R	Gage pressure, atm	Barometric pressure, atm	Absolute pressure, atm
Run No. HE-0-1			
0	646.4120277069	0.8769311813517	647.2889588883
1	280.3759539201	.8769454385195	281.2528993587
2	130.8076096956	.8770905151851	131.6847002107
3	62.97670429211	.8768062323970	63.85351052451
4	30.61519494207	.8764649185141	31.49165986059
5	14.78507020371	.8762032717097	15.66127347542
6	6.946035181388	.8756657411545	7.821700922543
7	3.039906680540	.8752078666919	3.915114547232
Run No. HE-0-2			
0	689.5170315508	0.8762738697152	690.3933054205
1	296.7309855857	.8763450974200	297.6073306831
2	137.9581306295	.8760239146634	138.8341545442
3	66.32798378899	.8750997728367	67.20308356183
4	32.24010065330	.8747869576745	33.11488761097
5	15.58767440123	.8745395418001	16.46221394303
6	7.345869800917	.8738342433041	8.219704044221
7	3.240439740641	.8735213919652	4.113961132606
Run No. HE-0-3			
0	700.4084415110	0.8739253759817	701.2823668870
1	300.8341453471	.8738514027795	301.7079967498
2	139.7399746708	.8737916238975	140.6137662947
3	67.16019770479	.8733621694687	68.03355987426
4	32.64421980891	.8731005311728	33.51732034008
5	15.78791517340	.8726568518288	16.66057202523
6	7.446612599290	.8719885684152	8.318601167705
7	3.292375244210	.8716102816285	4.163985525839
Run No. HE-0-4			
0	704.8641147696	0.8810867121807	705.7452014818
1	302.4895877704	.8817856682931	303.3713734387
2	140.4576848864	.8818367398739	141.3395216263
3	67.49191770212	.8817345949371	68.37365229705
4	32.80078704206	.8813483717485	33.68213541380
5	15.86074344101	.8810642718613	16.74180771287
6	7.477834751585	.8812318696604	8.359066621246
7	3.301370424995	.8812686284498	4.182639053445
Run No. HE-0-5			
0	696.9955688057	0.8839887329134	697.8795575386
1	299.5308764732	.8838435598045	300.4147200330
2	139.1709653445	.8834511534051	140.0544164979
3	66.88916039177	.8830077009650	67.77216809273
4	32.50828178547	.8819102020566	33.39019198753
5	15.71605782455	.8812561701240	16.59731399467
6	7.406375775771	.8804488692424	8.286824645014
7	3.268308619611	.8796332827422	4.147941902353

TABLE 2 - Experimental procedure

Run No.	Gas Pressure, atm	Barometric Pressure, atm	Absolute Pressure, atm
0	0.00000000	0.75200000	0.75200000
1	0.00000000	0.75200000	0.75200000
2	0.00000000	0.75200000	0.75200000
3	0.00000000	0.75200000	0.75200000
4	0.00000000	0.75200000	0.75200000
5	0.00000000	0.75200000	0.75200000
6	0.00000000	0.75200000	0.75200000
7	0.00000000	0.75200000	0.75200000
Run No. 10-0-1			
0	0.00000000	0.75200000	0.75200000
1	0.00000000	0.75200000	0.75200000
2	0.00000000	0.75200000	0.75200000
3	0.00000000	0.75200000	0.75200000
4	0.00000000	0.75200000	0.75200000
5	0.00000000	0.75200000	0.75200000
6	0.00000000	0.75200000	0.75200000
7	0.00000000	0.75200000	0.75200000
Run No. 10-0-2			
0	0.00000000	0.75200000	0.75200000
1	0.00000000	0.75200000	0.75200000
2	0.00000000	0.75200000	0.75200000
3	0.00000000	0.75200000	0.75200000
4	0.00000000	0.75200000	0.75200000
5	0.00000000	0.75200000	0.75200000
6	0.00000000	0.75200000	0.75200000
7	0.00000000	0.75200000	0.75200000
Run No. 10-0-3			
0	0.00000000	0.75200000	0.75200000
1	0.00000000	0.75200000	0.75200000
2	0.00000000	0.75200000	0.75200000
3	0.00000000	0.75200000	0.75200000
4	0.00000000	0.75200000	0.75200000
5	0.00000000	0.75200000	0.75200000
6	0.00000000	0.75200000	0.75200000
7	0.00000000	0.75200000	0.75200000
Run No. 10-0-4			
0	0.00000000	0.75200000	0.75200000
1	0.00000000	0.75200000	0.75200000
2	0.00000000	0.75200000	0.75200000
3	0.00000000	0.75200000	0.75200000
4	0.00000000	0.75200000	0.75200000
5	0.00000000	0.75200000	0.75200000
6	0.00000000	0.75200000	0.75200000
7	0.00000000	0.75200000	0.75200000
Run No. 10-0-5			
0	0.00000000	0.75200000	0.75200000
1	0.00000000	0.75200000	0.75200000
2	0.00000000	0.75200000	0.75200000
3	0.00000000	0.75200000	0.75200000
4	0.00000000	0.75200000	0.75200000
5	0.00000000	0.75200000	0.75200000
6	0.00000000	0.75200000	0.75200000
7	0.00000000	0.75200000	0.75200000



TABLE 5. - Experimental pressures--Continued

R	Gage pressure, atm	Barometric pressure, atm	Absolute pressure, atm
Run No. HE-0-6			
0	702.1184744399	0.8702066886767	702.9886811286
1	301.4683901262	.8700616745118	302.3384518007
2	140.0183182667	.8700333791464	140.8883516458
3	67.29454910138	.8691492883398	68.16369838972
4	32.71106911175	.8687656722470	33.57983478400
5	15.82199250306	.8687887124937	16.69078121556
6	7.465224361390	.8682371602237	8.333461521614
7	3.302930725135	.8680691486822	4.170999873817
Run No. HE-0-7			
0	701.2180830037	0.8687210533628	702.0868040570
1	301.1394439427	.8686824068501	302.0081263496
2	139.8803547994	.8685233086120	140.7488781080
3	67.22943089199	.8684065799029	68.09783747189
4	32.68057988169	.8674251969547	33.54800507864
5	15.80835835797	.8666259990989	16.67498435707
6	7.458410384007	.8664156377437	8.324826021751
7	3.300149583854	.8657473267522	4.165896910606
Run No. HE-0-8			
0	699.7285681673	0.8827347709460	700.6113029383
1	300.5655371206	.8829246892377	301.4484618098
2	139.6251276605	.8831145738312	140.5082422344
3	67.10290632809	.8825912546956	67.98549758279
4	32.61143324705	.8826199551148	33.49405320216
5	15.76649427462	.8823009046303	16.64879517925
6	7.430836014840	.8815383662152	8.312374381055
7	3.278450102214	.8813788877451	4.159828989959
Run No. HE-0-9			
0	683.7113986306	0.8633966156373	684.5747952462
1	294.5442035018	.8635507333729	295.4077542352
2	137.0068278494	.8636442251013	137.8704720745
3	65.88969973099	.8632890950770	66.75298882607
4	32.03333637603	.8632236855030	32.89656006153
5	15.48782008142	.8627658184852	16.35058589990
6	7.300724831583	.8622285236672	8.162953355250
7	3.223765520253	.8618734563292	4.085638976582
Run No. HE-0-10			
0	706.4006329458	0.8749632389877	707.2755961848
1	303.0742241189	.8756968986971	303.9499210176
2	140.7169389485	.8757396096306	141.5926785581
3	67.61494253624	.8759785524275	68.49092108867
4	32.86278893303	.8761890262546	33.73897795929
5	15.89149483270	.8760070366065	16.76750186931
6	7.495482000912	.8757453898021	8.371227390714
7	3.312819082249	.8754837429978	4.188302825247

TABLE 2 - Experimental Results - Continued

Run No.	Gas Pressure, atm	Barometric Pressure, atm	Absolute Pressure, atm
Run No. 18-0-6			
0	701.1254128	0.00000000	701.08881280
1	701.1254128	0.00000000	701.08881280
2	701.1254128	0.00000000	701.08881280
3	701.1254128	0.00000000	701.08881280
4	701.1254128	0.00000000	701.08881280
5	701.1254128	0.00000000	701.08881280
6	701.1254128	0.00000000	701.08881280
7	701.1254128	0.00000000	701.08881280
Run No. 18-0-7			
0	701.1254128	0.00000000	701.08881280
1	701.1254128	0.00000000	701.08881280
2	701.1254128	0.00000000	701.08881280
3	701.1254128	0.00000000	701.08881280
4	701.1254128	0.00000000	701.08881280
5	701.1254128	0.00000000	701.08881280
6	701.1254128	0.00000000	701.08881280
7	701.1254128	0.00000000	701.08881280
Run No. 18-0-8			
0	701.1254128	0.00000000	701.08881280
1	701.1254128	0.00000000	701.08881280
2	701.1254128	0.00000000	701.08881280
3	701.1254128	0.00000000	701.08881280
4	701.1254128	0.00000000	701.08881280
5	701.1254128	0.00000000	701.08881280
6	701.1254128	0.00000000	701.08881280
7	701.1254128	0.00000000	701.08881280
Run No. 18-0-9			
0	701.1254128	0.00000000	701.08881280
1	701.1254128	0.00000000	701.08881280
2	701.1254128	0.00000000	701.08881280
3	701.1254128	0.00000000	701.08881280
4	701.1254128	0.00000000	701.08881280
5	701.1254128	0.00000000	701.08881280
6	701.1254128	0.00000000	701.08881280
7	701.1254128	0.00000000	701.08881280
Run No. 18-0-10			
0	701.1254128	0.00000000	701.08881280
1	701.1254128	0.00000000	701.08881280
2	701.1254128	0.00000000	701.08881280
3	701.1254128	0.00000000	701.08881280
4	701.1254128	0.00000000	701.08881280
5	701.1254128	0.00000000	701.08881280
6	701.1254128	0.00000000	701.08881280
7	701.1254128	0.00000000	701.08881280

TABLE 5. - Experimental pressures--Continued

R	Gage pressure, atm	Barometric pressure, atm	Absolute pressure, atm
Run No. HE-0-11			
0	702.5241244213	0.8794799381871	703.4036043594
1	301.6190721062	.8796925959585	302.4987647022
2	140.0822349999	.8795617789376	140.9617967788
3	67.31701389271	.8793798502741	68.19639374298
4	32.71699099093	.8785723770434	33.59556336798
5	15.81999675572	.8779182493966	16.69791500511
6	7.460373454598	.8766099941030	8.336983448702
7	3.294951232367	.8763995068130	4.171350739181
Run No. HE-0-12			
0	698.1774194280	0.8758277050837	699.0532471331
1	299.9914171748	.8753698827309	300.8667870575
2	139.3770283460	.8750713191034	140.2520996651
3	66.99035375297	.8750201394122	67.86537389239
4	32.56209784277	.8736750129967	33.43577285577
5	15.74527942310	.8731005311728	16.61837995427
6	7.424333849166	.8725772545810	8.296911103747
7	3.279510932827	.8723668427877	4.15187775614
Run No. HE-0-13			
0	710.1568450183	0.8676085841898	711.0244536025
1	304.4851924201	.8671403682317	305.3523327883
2	141.2684818409	.8669672182456	142.1354490591
3	67.91060783425	.8668081781562	68.77741601241
4	33.01103192882	.8661026033712	33.87713453219
5	15.97185770344	.8654997101146	16.83735741355
6	7.541110926879	.8648454760937	8.405956402972
7	3.342758393301	.8648314140170	4.207589807318
Run No. HE-0-14			
0	697.6627960235	0.8761605363940	698.5389565599
1	299.7995950705	.8760808845412	300.6756759550
2	139.2935027453	.8760297193731	140.1695324647
3	66.95088667224	.8759785524275	67.82686522467
4	32.54100831655	.8753386879669	33.41634700452
5	15.73488840020	.8750912727913	16.60997967299
6	7.418015287165	.8746988025848	8.292714089749
7	3.275455464607	.8745821983979	4.150037663005
Run No. HE-0-15			
0	706.3718540013	0.8821074330062	707.2539614343
1	303.0579222501	.8818250796224	303.9397473297
2	140.7030908260	.8817820635829	141.5848728896
3	67.60547615335	.8816225369381	68.48709869029
4	32.85474805965	.8812299837589	33.73597804341
5	15.88603113031	.8807576837478	16.76678881405
6	7.490382185862	.8803508223873	8.370733008250
7	3.308926021058	.8799582819748	4.188884303033

TABLE 2 - Experimental procedure - Continued

K	Gage pressure, atm	Barometric pressure, atm	Absolute pressure, atm
Exp No. H-0-11			
0	702.5241244513	0.878475281871	703.402602246
1	301.619072104	.87852525282	302.487647022
2	140.08222999	.87857522378	140.967387388
3	67.317072221	.87862519471	68.196324198
4	32.718999077	.87867516574	33.525262898
5	15.81897222	.87872513678	16.827190011
6	7.40973222	.87877510781	8.3388248702
7	3.70486222	.87882507885	4.11390222
Exp No. H-0-12			
0	699.17479280	0.87887504989	699.052271331
1	299.0917728	.87892502092	300.8678072
2	139.37082280	.87897500006	140.2209867
3	66.90932227	.87902497920	67.882378029
4	32.56902227	.87907495834	33.422718227
5	15.78272222	.87912493748	16.43819222
6	7.89136222	.87917491662	8.39611022
7	3.94568222	.87922489576	4.13187222
Exp No. H-0-13			
0	710.159222	0.87927487490	711.024222
1	302.427222	.87932485404	303.252222
2	141.268222	.87937483318	142.132222
3	67.816222	.87942481232	68.732222
4	33.812222	.87947479146	34.812222
5	17.412222	.87952477060	18.872222
6	8.702222	.87957474974	9.402222
7	4.352222	.87962472888	4.502222
Exp No. H-0-14			
0	697.602222	0.87967470802	698.332222
1	297.192222	.87972468716	300.622222
2	139.222222	.87977466630	140.192222
3	69.908222	.87982464544	71.822222
4	35.812222	.87987462458	37.422222
5	17.722222	.87992460372	19.022222
6	8.812222	.87997458286	9.522222
7	4.402222	.88002456200	4.722222
Exp No. H-0-15			
0	706.212222	0.88007454114	707.222222
1	303.022222	.88012452028	304.922222
2	140.702222	.88017449942	141.282222
3	67.802222	.88022447856	68.482222
4	34.802222	.88027445770	35.722222
5	17.802222	.88032443684	18.722222
6	8.902222	.88037441598	9.722222
7	4.452222	.88042439512	4.822222

TABLE 5. - Experimental pressures--Continued

R	Gage pressure, atm	Barometric pressure, atm	Absolute pressure, atm
Run No. HE-0-16			
0	704.8780447545	0.8743716205323	705.7524163750
1	302.5013284971	.8744598322460	303.3757883294
2	140.4678649356	.8741184531733	141.3419833888
3	67.50087124635	.8733418957295	68.37421314208
4	32.80882900305	.8724629627553	33.68129196580
5	15.86828180075	.8717661818688	16.74004798261
6	7.485697576303	.8713082255012	8.357005801804
7	3.310740668733	.8705744244341	4.181315093167
Run No. HE-0-17			
0	698.2372753729	0.8750600359184	699.1123354089
1	300.0107262375	.8752220961934	300.8859483337
2	139.3833027406	.8753102257581	140.2586129663
3	66.99246918307	.8750201394122	67.86748932249
4	32.56161610313	.8745054240785	33.43612152721
5	15.74537885842	.8736779874653	16.61905684589
6	7.423746309458	.8731406014611	8.296886910919
7	3.278175151165	.8728364413387	4.151011592503
Run No. HE-0-18			
0	704.1153690775	0.8726024839403	704.9879715614
1	302.2189970017	.8726710398511	303.0916680416
2	140.3451528107	.8730863364027	141.2182391471
3	67.44352544444	.8730067345339	68.31653217897
4	32.78196173269	.8712265691693	33.65318830186
5	15.85640853209	.8697363621858	16.72614489428
6	7.480714618288	.8694093249510	8.350123943239
7	3.306957570342	.8692926427963	4.176250213138
Run No. HE-0-19			
0	694.9865344622	0.8758770341266	695.8624114964
1	298.7833283840	.8753618584328	299.6586902425
2	138.8467393769	.8756748981965	139.7224142751
3	66.73951310222	.8759736808505	67.61548678307
4	32.43839773162	.8757630779786	33.31416080960
5	15.68246073581	.8762808882956	16.55874162411
6	7.390886624099	.8759109191181	8.266797543218
7	3.260606042031	.8762238875722	4.136829929603
Run No. HE-0-20			
0	685.3298625462	0.8756664095909	686.2055289558
1	295.1451253806	.8756976258424	296.0208230064
2	137.2620746086	.8760475950205	138.1381222036
3	65.99994771761	.8754158428421	66.87536356045
4	32.08007116705	.8751910392938	32.95526220635
5	15.50704145733	.8747414747694	16.38178293210
6	7.305086175129	.8742037435632	8.179289918692
7	3.218774229971	.8737969042076	4.092571134179

TABLE 2 - Experimental results - Continued

R	Gage pressure, atm	Automatic pressure, atm	Abalone pressure, atm
Run No. 18-10			
0	104.870000000	0.871160000	105.320000000
1	103.501380000	0.871160000	103.320000000
2	100.461000000	0.871160000	101.320000000
3	97.500000000	0.871160000	98.320000000
4	93.800000000	0.871160000	94.320000000
5	89.800000000	0.871160000	90.320000000
6	85.800000000	0.871160000	86.320000000
7	81.800000000	0.871160000	82.320000000
Run No. 18-11			
0	104.870000000	0.871160000	105.320000000
1	103.501380000	0.871160000	103.320000000
2	100.461000000	0.871160000	101.320000000
3	97.500000000	0.871160000	98.320000000
4	93.800000000	0.871160000	94.320000000
5	89.800000000	0.871160000	90.320000000
6	85.800000000	0.871160000	86.320000000
7	81.800000000	0.871160000	82.320000000
Run No. 18-12			
0	104.870000000	0.871160000	105.320000000
1	103.501380000	0.871160000	103.320000000
2	100.461000000	0.871160000	101.320000000
3	97.500000000	0.871160000	98.320000000
4	93.800000000	0.871160000	94.320000000
5	89.800000000	0.871160000	90.320000000
6	85.800000000	0.871160000	86.320000000
7	81.800000000	0.871160000	82.320000000
Run No. 18-13			
0	104.870000000	0.871160000	105.320000000
1	103.501380000	0.871160000	103.320000000
2	100.461000000	0.871160000	101.320000000
3	97.500000000	0.871160000	98.320000000
4	93.800000000	0.871160000	94.320000000
5	89.800000000	0.871160000	90.320000000
6	85.800000000	0.871160000	86.320000000
7	81.800000000	0.871160000	82.320000000
Run No. 18-14			
0	104.870000000	0.871160000	105.320000000
1	103.501380000	0.871160000	103.320000000
2	100.461000000	0.871160000	101.320000000
3	97.500000000	0.871160000	98.320000000
4	93.800000000	0.871160000	94.320000000
5	89.800000000	0.871160000	90.320000000
6	85.800000000	0.871160000	86.320000000
7	81.800000000	0.871160000	82.320000000

TABLE 5. - Experimental pressures--Continued

R	Gage pressure, atm	Barometric pressure, atm	Absolute pressure, atm
Run No. HE-0-21			
0	773.4792447485	0.8746931169914	774.3539378655
1	327.9503923646	.8746817427037	328.8250741073
2	151.4663134605	.8743119936602	152.3406254541
3	72.62586671643	.8737460381948	73.49961275463
4	35.28527915768	.8731289217587	36.15840807944
5	17.08701089108	.8725118450070	17.95952273609
6	8.091134431307	.8721564377234	8.963290869031
7	3.612440477369	.8717498202373	4.484190297606
Run No. HE-0-22			
0	581.3092872243	0.8766132786184	582.1859005029
1	255.2070832114	.8764908416644	256.0835740531
2	119.7052428099	.8765361723173	120.5817789822
3	57.75117285393	.8766099941030	58.62778284803
4	28.07558827206	.8763198475297	28.95190811959
5	13.53087369724	.8759643108626	14.40683800810
6	6.320927090012	.8758704223976	7.196797512410
7	2.726188056005	.8756457310696	3.601833787075

TABLE 1. - Experimental procedure - Continued

Run	Cage pressure, atm	Barometric pressure, atm	Absolute pressure, atm
Run No. 10-9-51			
0	1.00	1.00	1.00
1	1.00	1.00	1.00
2	1.00	1.00	1.00
3	1.00	1.00	1.00
4	1.00	1.00	1.00
5	1.00	1.00	1.00
6	1.00	1.00	1.00
7	1.00	1.00	1.00
Run No. 10-9-52			
0	1.00	1.00	1.00
1	1.00	1.00	1.00
2	1.00	1.00	1.00
3	1.00	1.00	1.00
4	1.00	1.00	1.00
5	1.00	1.00	1.00
6	1.00	1.00	1.00
7	1.00	1.00	1.00

9



Data from the 22 runs were treated in different ways. First, each run was treated separately. Values for the parameters and compressibility factors were evaluated for each run when the data were fitted to the equations;

$$Z_r = 1 + BP_r + CP_r^2 = \frac{Z_0}{P_0} f_r N^r P_r, \quad (7)$$

$$Z_r = 1 + BP_r + CP_r^2 + DP_r^3 = \frac{Z_0}{P_0} f_r N^r P_r, \quad (8)$$

and

$$Z_r = 1 + BP_r + CP_r^2 + DP_r^3 + EP_r^4 = \frac{Z_0}{P_0} f_r N^r P_r, \quad (9)$$

where

$Z_r$  = compressibility factor at  $P_r$ ,

$B$  = parameter evaluated from the experimental pressures,

$C$  = parameter evaluated from the experimental pressures,

$D$  = parameter evaluated from the experimental pressures,

$E$  = parameter evaluated from the experimental pressures,

$P_r$  = pressure after the  $r$  th expansion,

$P_0$  = pressure before the first expansion,

$Z_0$  = compressibility factor at  $P_0$ ,

$r = R$  = expansion number,

$f_r$  = factor to correct for elastic pressure distortion

(2, page 5), and

$N$  = isothermal zero pressure volume ratio.



Weighting factors of  $P_r$ , 1,  $P_r^{-3/4}$ ,  $P_r^{-1}$ , and  $P_r^{-2}$  were used when the data were fitted to equations 7 through 9. A summary of the results is presented in table 6. Details of the calculations are on file at the Bureau of Mines Helium Research Center. Data for run No. HE-0-13 were not consistent with the data of the other runs and were not included in the calculations.

We decided upon the following criteria for an acceptable data treatment:

1. The solution should give pressure residuals that appear to be consistent with our assumption of a normally distributed random variable with a mean of zero.

2. The solution should give values of  $W_r (\delta P_r)^2$  which are the same for different expansion numbers except for statistical variations, where

$W_r$  = weighting factor,

$\delta P_r$  = standard error of a single pressure residual.

None of the solutions met these criteria when the data were treated as separate runs.

Next a method was developed to treat all of the data simultaneously.

The function

$$R' = \sum_{i=1}^M \left[ \sum_{r=1}^{n_i} W_r (\Delta P_r)^2 \right]_i \quad (10)$$



TABLE 6. - Summary of average quantities obtained from the nonlinear least-squares treatment of the experimental compressibility measurements on helium at 0° C, treating each run separately

Weighting factor	Z(1 atm)	Z(700 atm)	N	B·10 <sup>4</sup> , atm <sup>-1</sup>	C·10 <sup>7</sup> , atm <sup>-2</sup>	D·10 <sup>10</sup> , atm <sup>-3</sup>	E·10 <sup>13</sup> , atm <sup>-4</sup>
$Z_r = 1 + BP_r + CP_r^2 + DP_r^3 + EP_r^4 = Z_0 P_0^{-1} f_r N^r P_r$							
P <sub>r</sub>	1.000536309 ±0.000001334	1.347589 ±0.000183	1.994197 ±0.000052	5.36388 ±0.01341	-0.7832 ±0.0697	0.508 ±0.172	-0.288 ±0.135
1	1.000538871 ±.000001226	1.347832 ±.000179	1.994121 ±.000048	5.38965 ±.01233	-.9331 ±.0650	.897 ±.163	-.604 ±.129
P <sub>r</sub> <sup>-3/4</sup>	1.000541274 ±.000001513	1.348033 ±.000211	1.994059 ±.000053	5.41382 ±.01521	-1.0835 ±.0862	1.299 ±.223	-.933 ±.180
P <sub>r</sub> <sup>-1</sup>	1.000542158 ±.000001698	1.348100 ±.000228	1.994038 ±.000056	5.42272 ±.01708	-1.1416 ±.0996	1.457 ±.261	-1.064 ±.212
P <sub>r</sub> <sup>-2</sup>	1.000546131 ±.000002860	1.348353 ±.000325	1.993961 ±.000076	5.46273 ±.02879	-1.4245 ±.1858	2.253 ±.506	-1.730 ±.418
$Z_r = 1 + BP_r + CP_r^2 + DP_r^3 = Z_0 P_0^{-1} f_r N^r P_r$							
P <sub>r</sub>	1.000533759 ±0.000000336	1.347259 ±0.000072	1.994277 ±0.000023	5.33823 ±0.00337	-0.63860 ±0.00796	0.1421 ±0.0066	
1	1.000534337 ±.000000389	1.347385 ±.000086	1.994239 ±.000028	5.34402 ±.00390	-.65164 ±.00895	.1526 ±.0074	
P <sub>r</sub> <sup>-1</sup>	1.000535614 ±.000000518	1.347633 ±.000112	1.994171 ±.000035	5.35682 ±.00519	-.68357 ±.01192	.1793 ±.0098	
P <sub>r</sub> <sup>-2</sup>	1.000537852 ±.000000930	1.347992 ±.000174	1.994087 ±.000049	5.37926 ±.00932	-.74848 ±.02420	.2367 ±.0207	
$Z_r = 1 + BP_r + CP_r^2 = Z_0 P_0^{-1} f_r N^r P_r$							
P <sub>r</sub>	1.000525873 ±0.000000138	1.345515 ±0.000044	1.994812 ±0.000019	5.25919 ±0.00129	-0.46180 ±0.00136		
1	1.000526830 ±.000000179	1.345888 ±.000056	1.994659 ±.000022	5.26877 ±.00149	-.46789 ±.00137		
P <sub>r</sub> <sup>-1</sup>	1.000528390 ±.000000221	1.346442 ±.000064	1.994459 ±.000021	5.28438 ±.00199	-.47887 ±.00161		
P <sub>r</sub> <sup>-2</sup>	1.000530567 ±.000000314	1.347075 ±.000099	1.994276 ±.000034	5.30616 ±.00314	-.49706 ±.00288		



is minimized in the simultaneous treatment of the data,

where

$R'$  = the sum of the weighted squares of the residuals of  $P_r$ ,

$M$  = number of sets of data,

$n_i$  = number of expansions,

$$\Delta P_r = P_r - p_r,$$

where

$P_r$  = observed pressure, and

$p_r$  = calculated pressure.

Each element of the coefficient matrix is calculated for each run, just as in the separate method (2), then the contributions from each run are added together to obtain the coefficient matrix for the simultaneous data treatment. Once this coefficient matrix has been obtained, then the rest of the calculation is the same as that used to treat the data as separate runs.

Data from 21 runs<sup>6/</sup> were fitted to equations 7 through 9 with

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<sup>6/</sup> Data from run No. HE-0-13 were not included in the calculations.

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the method developed to treat data simultaneously. Weighting factors of 1,  $P_r^{-1/2}$ ,  $P_r^{-3/4}$ ,  $P_r^{-1}$ , and  $P_r^{-2}$  were used. A summary of the results is included in table 7. Details of the calculations are on file at the Bureau of Mines Helium Research Center.





TABLE 7. - Summary of the results obtained from the nonlinear least-squares treatment of the experimental compressibility measurements on helium at 0° C, treating all runs simultaneously

Weighting factor	Z(1 atm)	Z(700 atm)	N	$B \cdot 10^4, \text{atm}^{-1}$	$C \cdot 10^8, \text{atm}^{-2}$	$D \cdot 10^{11}, \text{atm}^{-3}$	$E \cdot 10^{15}, \text{atm}^{-4}$
$Z_r = 1 + BP_r + CP_r^2 + DP_r^3 + EP_r^4 = Z_0 P_0^{-1} f_r N^r P_r$							
1	1.000533574 ±0.000000851	1.347212 ±0.000154	1.994285 ±0.000046	5.33638 ±0.00807	-6.4129 ±0.2473	1.717 ±0.372	-3.33 ±2.00
$P_r^{-1/2}$	1.000534673 ±.000000701	1.347421 ±.000108	1.994225 ±.000033	5.34740 ±.00674	-6.7415 ±.2226	2.197 ±.348	-5.83 ±1.93
$P_r^{-3/4}$	1.000535209 ±.000000696	1.347517 ±.000112	1.994199 ±.000030	5.35278 ±.00672	-6.9099 ±.2316	2.448 ±.371	-7.15 ±2.09
$P_r^{-1}$	1.000535750 ±.000000741	1.347610 ±.000114	1.994174 ±.000029	5.35820 ±.00720	-7.0848 ±.2592	2.711 ±.425	-8.53 ±2.44
$P_r^{-2}$	1.000537856 ±.000001518	1.347944 ±.000185	1.994092 ±.000041	5.37934 ±.01499	-7.7698 ±.6517	3.708 ±1.170	-13.56 ±7.09
$Z_r = 1 + BP_r + CP_r^2 + DP_r^3 = Z_0 P_0^{-1} f_r N^r P_r$							
1	1.000532301 ±0.000000288	1.346984 ±0.000072	1.994349 ±0.000025	5.32361 ±0.00258	-6.0067 ±0.0446	1.0972 ±0.0322	
$P_r^{-1/2}$	1.000532779 ±.000000272	1.347114 ±.000062	1.994305 ±.000020	5.32839 ±.00251	-6.0838 ±.0500	1.1480 ±.0385	
$P_r^{-3/4}$	1.000533097 ±.000000291	1.347195 ±.000063	1.994279 ±.000019	5.33159 ±.00272	-6.1400 ±.0580	1.1867 ±.0459	
$P_r^{-1}$	1.000533470 ±.000000331	1.347284 ±.000068	1.994253 ±.000020	5.33532 ±.00313	-6.2096 ±.0710	1.2357 ±.0576	
$P_r^{-2}$	1.000535361 ±.000000751	1.347680 ±.000124	1.994148 ±.000030	5.35427 ±.00734	-6.5791 ±.1941	1.4922 ±.1663	
$Z_r = 1 + BP_r + CP_r^2 = Z_0 P_0^{-1} f_r N^r P_r$							
1	1.000524535 ±0.000000433	1.345098 ±0.000137	1.994946 ±0.000055	5.24580 ±0.00360	-4.5120 ±0.0240		
$P_r^{-1/2}$	1.000526112 ±.000000351	1.345707 ±.000108	1.994708 ±.000040	5.26158 ±.00302	-4.6130 ±.0218		
$P_r^{-3/4}$	1.000526792 ±.000000323	1.345959 ±.000098	1.994616 ±.000034	5.26839 ±.00284	-4.6588 ±.0214		
$P_r^{-1}$	1.000527421 ±.000000309	1.346184 ±.000091	1.994537 ±.000030	5.27468 ±.00277	-4.7027 ±.0219		
$P_r^{-2}$	1.000529564 ±.000000449	1.346900 ±.000110	1.994321 ±.000028	5.29613 ±.00430	-4.8631 ±.0413		

$L_2$	$F_1(0,0,0) = 0$	$F_1(1,0,0) = 0$	$F_1(0,1,0) = 0$	$F_1(0,0,1) = 0$	$F_1(1,1,0) = 0$	$F_1(0,1,1) = 0$	$F_1(1,0,1) = 0$	$F_1(1,1,1) = 0$
$L_3$	$F_2(0,0,0) = 0$	$F_2(1,0,0) = 0$	$F_2(0,1,0) = 0$	$F_2(0,0,1) = 0$	$F_2(1,1,0) = 0$	$F_2(0,1,1) = 0$	$F_2(1,0,1) = 0$	$F_2(1,1,1) = 0$
$L_4$	$F_3(0,0,0) = 0$	$F_3(1,0,0) = 0$	$F_3(0,1,0) = 0$	$F_3(0,0,1) = 0$	$F_3(1,1,0) = 0$	$F_3(0,1,1) = 0$	$F_3(1,0,1) = 0$	$F_3(1,1,1) = 0$
$L_5$	$F_4(0,0,0) = 0$	$F_4(1,0,0) = 0$	$F_4(0,1,0) = 0$	$F_4(0,0,1) = 0$	$F_4(1,1,0) = 0$	$F_4(0,1,1) = 0$	$F_4(1,0,1) = 0$	$F_4(1,1,1) = 0$

$$F = 1 + 2x^2 + 3x^3 + 4x^4 + 5x^5$$

$L_2$	$F_1(0,0,0) = 0$	$F_1(1,0,0) = 0$	$F_1(0,1,0) = 0$	$F_1(0,0,1) = 0$	$F_1(1,1,0) = 0$	$F_1(0,1,1) = 0$	$F_1(1,0,1) = 0$	$F_1(1,1,1) = 0$
$L_3$	$F_2(0,0,0) = 0$	$F_2(1,0,0) = 0$	$F_2(0,1,0) = 0$	$F_2(0,0,1) = 0$	$F_2(1,1,0) = 0$	$F_2(0,1,1) = 0$	$F_2(1,0,1) = 0$	$F_2(1,1,1) = 0$
$L_4$	$F_3(0,0,0) = 0$	$F_3(1,0,0) = 0$	$F_3(0,1,0) = 0$	$F_3(0,0,1) = 0$	$F_3(1,1,0) = 0$	$F_3(0,1,1) = 0$	$F_3(1,0,1) = 0$	$F_3(1,1,1) = 0$
$L_5$	$F_4(0,0,0) = 0$	$F_4(1,0,0) = 0$	$F_4(0,1,0) = 0$	$F_4(0,0,1) = 0$	$F_4(1,1,0) = 0$	$F_4(0,1,1) = 0$	$F_4(1,0,1) = 0$	$F_4(1,1,1) = 0$

$$F = 1 + 2x^2 + 3x^3 + 4x^4 + 5x^5$$

$L_2$	$F_1(0,0,0) = 0$	$F_1(1,0,0) = 0$	$F_1(0,1,0) = 0$	$F_1(0,0,1) = 0$	$F_1(1,1,0) = 0$	$F_1(0,1,1) = 0$	$F_1(1,0,1) = 0$	$F_1(1,1,1) = 0$
$L_3$	$F_2(0,0,0) = 0$	$F_2(1,0,0) = 0$	$F_2(0,1,0) = 0$	$F_2(0,0,1) = 0$	$F_2(1,1,0) = 0$	$F_2(0,1,1) = 0$	$F_2(1,0,1) = 0$	$F_2(1,1,1) = 0$
$L_4$	$F_3(0,0,0) = 0$	$F_3(1,0,0) = 0$	$F_3(0,1,0) = 0$	$F_3(0,0,1) = 0$	$F_3(1,1,0) = 0$	$F_3(0,1,1) = 0$	$F_3(1,0,1) = 0$	$F_3(1,1,1) = 0$
$L_5$	$F_4(0,0,0) = 0$	$F_4(1,0,0) = 0$	$F_4(0,1,0) = 0$	$F_4(0,0,1) = 0$	$F_4(1,1,0) = 0$	$F_4(0,1,1) = 0$	$F_4(1,0,1) = 0$	$F_4(1,1,1) = 0$

$$F = 1 + 2x^2 + 3x^3 + 4x^4 + 5x^5$$

$L_2$	$F_1(0,0,0) = 0$	$F_1(1,0,0) = 0$	$F_1(0,1,0) = 0$	$F_1(0,0,1) = 0$	$F_1(1,1,0) = 0$	$F_1(0,1,1) = 0$	$F_1(1,0,1) = 0$	$F_1(1,1,1) = 0$
$L_3$	$F_2(0,0,0) = 0$	$F_2(1,0,0) = 0$	$F_2(0,1,0) = 0$	$F_2(0,0,1) = 0$	$F_2(1,1,0) = 0$	$F_2(0,1,1) = 0$	$F_2(1,0,1) = 0$	$F_2(1,1,1) = 0$
$L_4$	$F_3(0,0,0) = 0$	$F_3(1,0,0) = 0$	$F_3(0,1,0) = 0$	$F_3(0,0,1) = 0$	$F_3(1,1,0) = 0$	$F_3(0,1,1) = 0$	$F_3(1,0,1) = 0$	$F_3(1,1,1) = 0$
$L_5$	$F_4(0,0,0) = 0$	$F_4(1,0,0) = 0$	$F_4(0,1,0) = 0$	$F_4(0,0,1) = 0$	$F_4(1,1,0) = 0$	$F_4(0,1,1) = 0$	$F_4(1,0,1) = 0$	$F_4(1,1,1) = 0$

TABLE 1: Results of the algorithm for the computation of the coefficients of the characteristic polynomial of the matrix  $A$ .

The functional form of  $Z_r$  selected as best representing the experimental data, treating all runs simultaneously, is a fourth degree polynomial in  $P_r$ . This particular functional form was the lowest degree polynomial for which there appeared to be random scattering of the calculated pressure residuals. Higher order polynomials in the pressure were investigated; however, no significant improvement in the randomness of the pressure residuals resulted from this work.

The weighting factor was selected as follows.

The product  $W_r (\delta P_r)^2$  was examined for each fourth degree polynomial fit in the pressure to determine if  $W_r (\delta P_r)^2$  was a constant independent of pressure. Standard errors of the single pressure residuals were fitted to the equation.

$$W_r (\delta P_r)^2 = a + bP_r \quad (11)$$

by using a least-squares method. Values of  $a$ ,  $b$ , and  $b/a$ , along with their standard errors are listed in table 8. The calculated curves for

$$\frac{W_r (\delta P_r)^2}{a} = 1 + \frac{b}{a} P_r \quad (12)$$

are illustrated in figure 4. From table 8 and figure 4, we see that

---

FIGURE 4. -  $\frac{W_r (\delta P_r)^2}{a}$  as a Function of  $P_r$ .

---

the most horizontal curve is that obtained when a weighting factor of  $P_r^{-3/4}$  was used.

The functional form of  $F_1$  selected as best representing the experimental data, treating all runs simultaneously, is a fourth degree polynomial in  $P_1$ . This particular functional form was the lowest degree polynomial for which there appeared to be random scattering in the calculated pressure residuals. Higher order polynomials in the pressure were investigated; however, no significant improvement in the randomness of the pressure residuals resulted from this work.

The weighting factor was selected as follows.

The product  $W_1(\delta P_1)^2$  was examined for each fourth degree poly-

nomial fit to the pressure to determine if  $W_1(\delta P_1)^2$  was a constant

independent of pressure. Standard errors of the single pressure resid-

uals were fitted to the equation.

$$W_1(\delta P_1)^2 = a + bP_1 \quad (11)$$

by using a least-squares method. Values of  $a$ ,  $b$ , and  $b/a$ , along with

their standard errors are listed in Table 8. The calculated curves

for

$$\frac{W_1(\delta P_1)^2}{a} = 1 + \frac{b}{a} P_1 \quad (12)$$

are illustrated in Figure 5. From Table 8 and Figure 5, we see that

---

FIGURE 5.  $\frac{W_1(\delta P_1)^2}{a}$  as a function of  $P_1$ .

---

The most satisfactory curve is that obtained when a weighting factor of

$F_1^{-2}$  was used.

TABLE 8. - Least-squares values of a, b, and b/a calculated for the equation

$$W_r (\delta P_r)^2 = a + bP_r, \text{ assuming}$$

$$Z_r = 1 + BP_r + CP_r^2 + DP_r^3 + EP_r^4$$

$W_r$	$a \cdot 10^7$	$b \cdot 10^8$	$\left(\frac{b}{a}\right) \cdot 10^1$
1	6.360 $\pm$ 4.552	5.764 $\pm$ 0.355	0.9064 $\pm$ 0.6854
$P_r^{-1/2}$	3.942 $\pm$ .708	.231 $\pm$ .055	.0585 $\pm$ .0222
$P_r^{-3/4}$	2.320 $\pm$ .487	.003 $\pm$ .038	.0014 $\pm$ .0166
$P_r^{-1}$	1.372 $\pm$ .399	-.034 $\pm$ .031	-.0244 $\pm$ .0190
$P_r^{-2}$	.218 $\pm$ .123	-.010 $\pm$ .009	-.0463 $\pm$ .0342

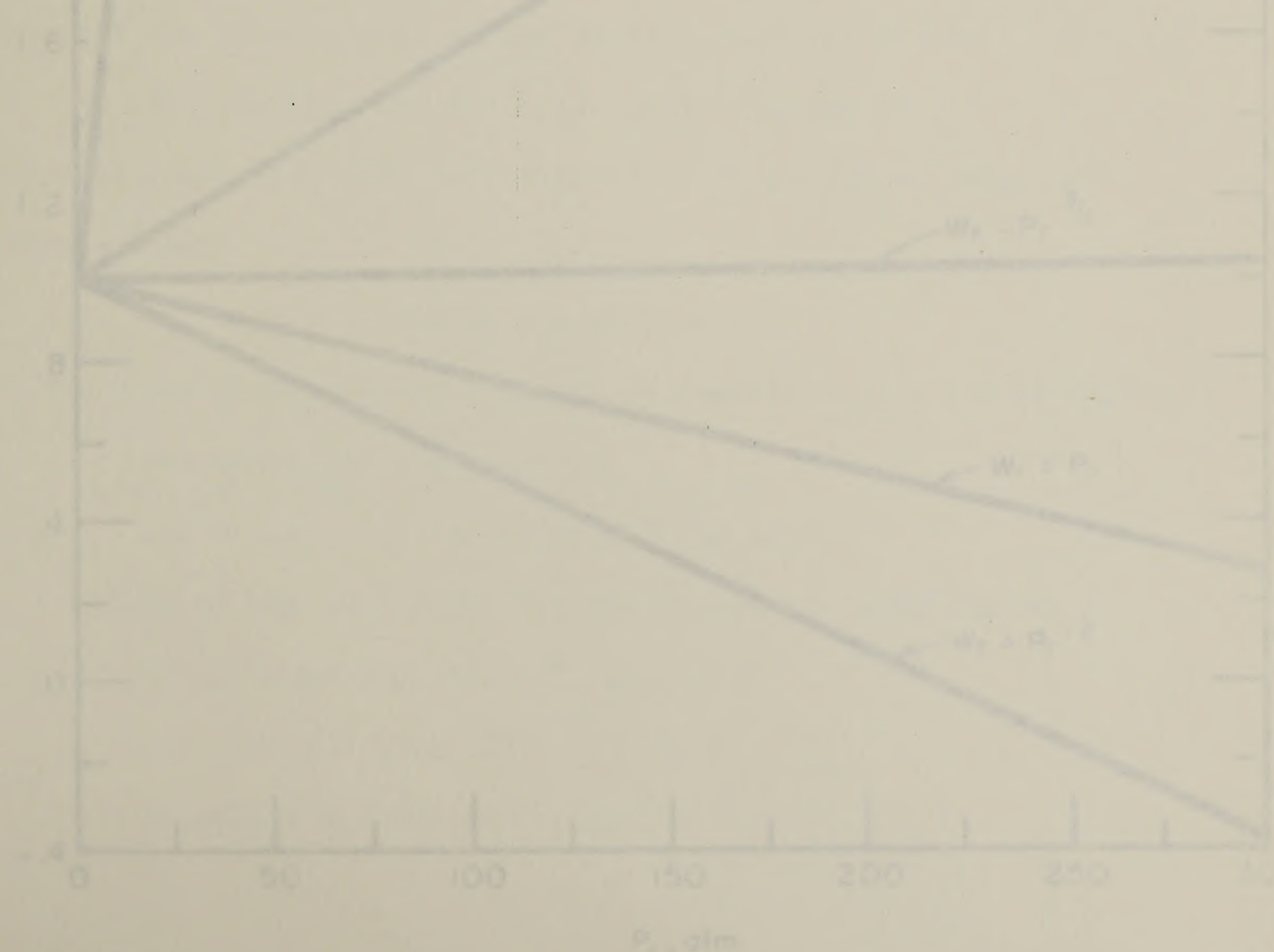


FIGURE 4. -  $\frac{W_r (\delta P_r)^2}{a}$  as a Function of  $P_r$

TABLA 8 - Least-squares values of  $a$ ,  $b$ , and  $c$  calculated for the equation

$$W_i(t_i)^2 = a + b t_i^2 + c t_i^4$$

$$E_i = 1 + B_i^2 + C_i^2 + D_i^2 + E_i^2$$

$W_i$	$a \cdot 10^7$	$b \cdot 10^6$	$\left(\frac{b}{a}\right) \cdot 10^7$
1	0.369 ± 0.252	2.704 ± 0.222	0.906 ± 0.824
$K_{1/2}$	2.942 ± 0.708	.321 ± 0.222	.078 ± 0.222
$K_{1/3}$	2.320 ± 0.482	.003 ± 0.038	0.010 ± 0.166
$K_{1/4}$	1.225 ± 0.180	-.024 ± 0.021	-.026 ± 0.130
$K_{1/5}$	-.228 ± 0.123	-.010 ± 0.009	-.046 ± 0.142

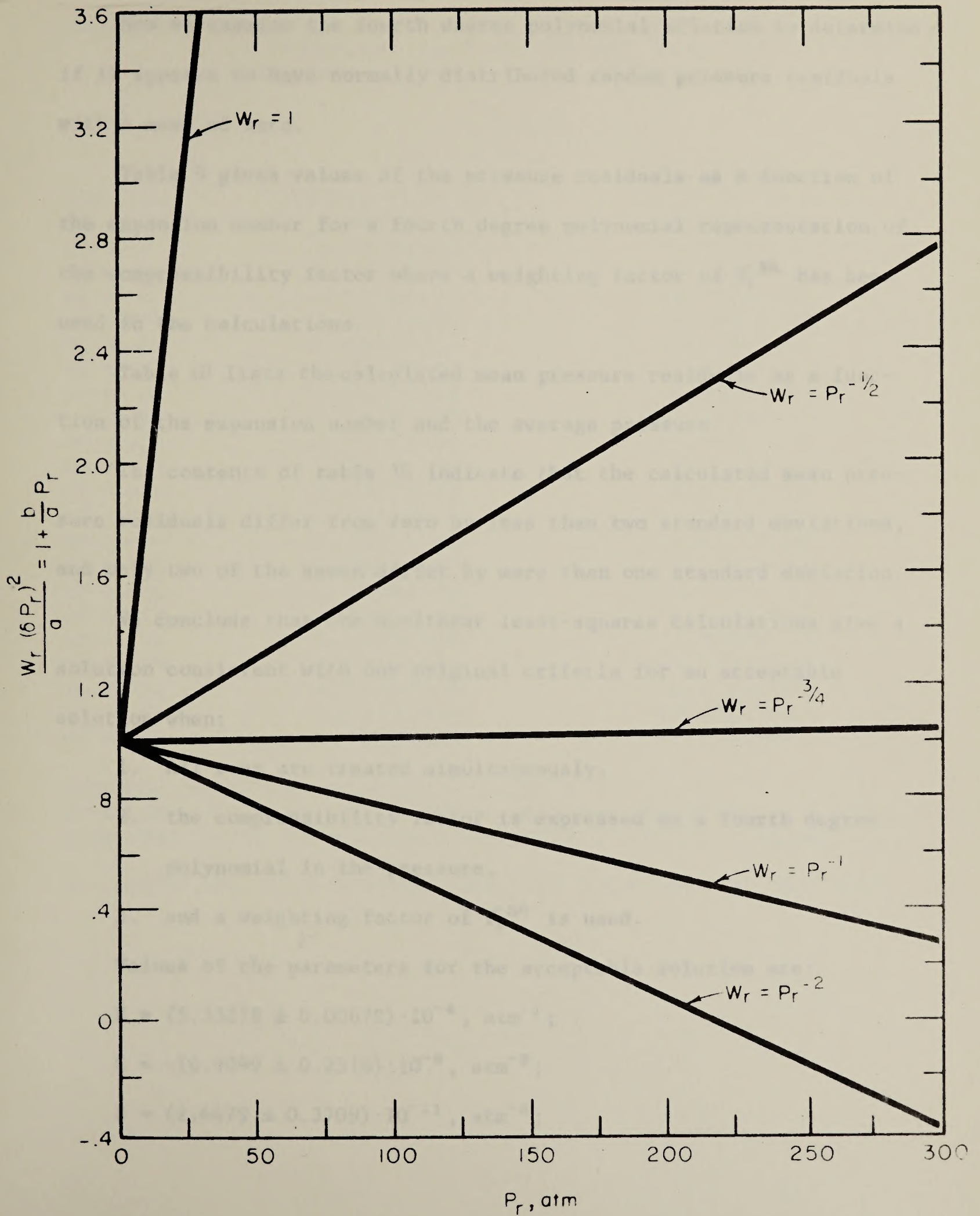


FIGURE 4. -  $\frac{W_r (\delta P_r)^2}{a}$  as a Function of  $P_r$ .

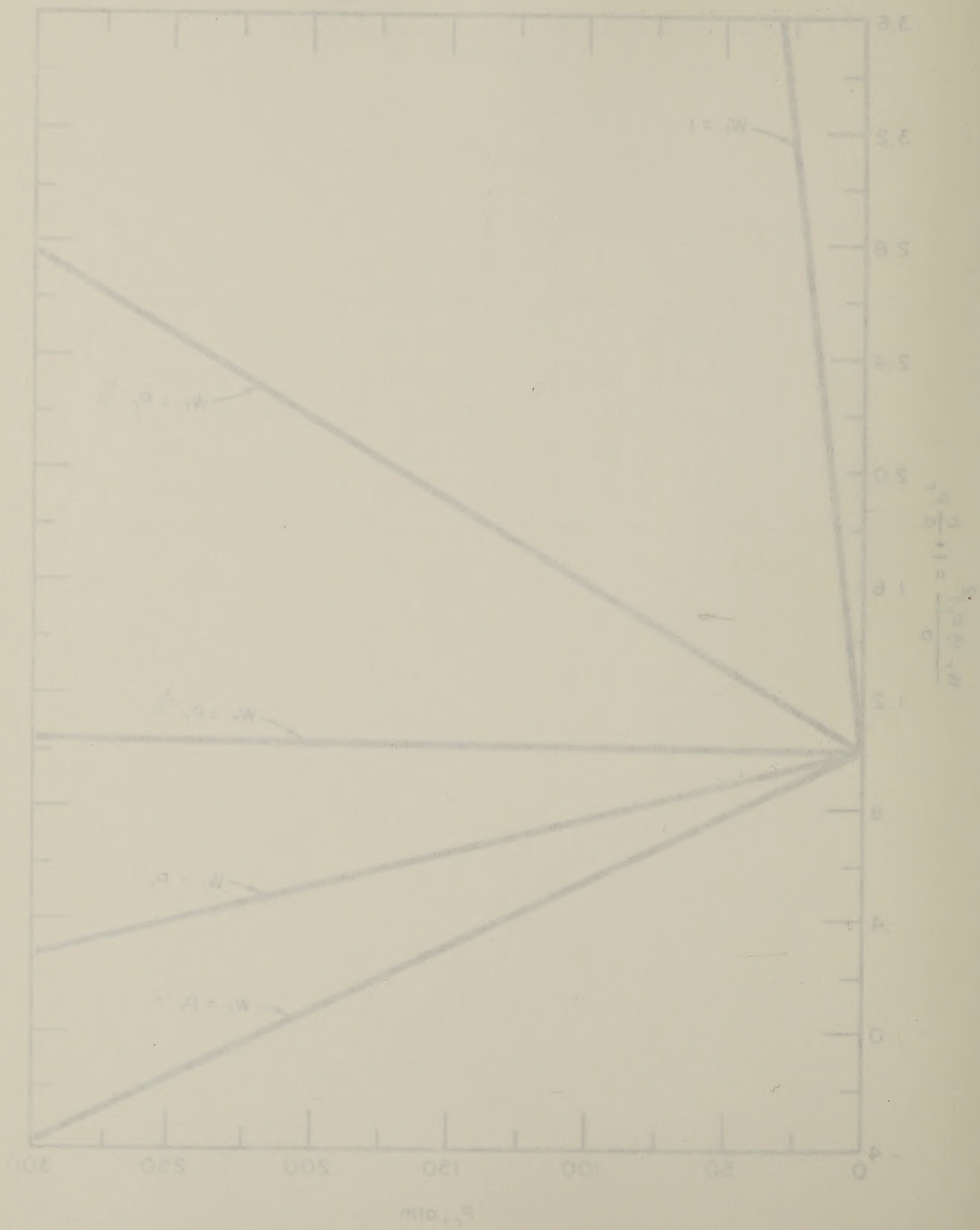


FIGURE 4 -  $\frac{S_1(8P_1)S}{1000 \cdot W}$  as a function of  $P_1$



Now we examine the fourth degree polynomial solution to determine if it appears to have normally distributed random pressure residuals with a mean of zero.

Table 9 gives values of the pressure residuals as a function of the expansion number for a fourth degree polynomial representation of the compressibility factor where a weighting factor of  $P_r^{-3/4}$  has been used in the calculations.

Table 10 lists the calculated mean pressure residuals as a function of the expansion number and the average pressure.

The contents of table 10 indicate that the calculated mean pressure residuals differ from zero by less than two standard deviations, and only two of the seven differ by more than one standard deviation.

We conclude that the nonlinear least-squares calculations give a solution consistent with our original criteria for an acceptable solution when:

1. All runs are treated simultaneously,
2. the compressibility factor is expressed as a fourth degree polynomial in the pressure,
3. and a weighting factor of  $P_r^{-3/4}$  is used.

Values of the parameters for the acceptable solution are:

$$B = (5.35278 \pm 0.00672) \cdot 10^{-4}, \text{ atm}^{-1};$$

$$C = -(6.9099 \pm 0.2316) \cdot 10^{-8}, \text{ atm}^{-2};$$

$$D = (2.4479 \pm 0.3709) \cdot 10^{-11}, \text{ atm}^{-3};$$

Now we examine the fourth degree polynomial solution to determine if it appears to have normally distributed random pressure residuals with a mean of zero.

Table 9 gives values of the pressure residuals as a function of the expansion number for a fourth degree polynomial representation of the compressibility factor where a weighting factor of  $K_{20}^{-0.2}$  has been used in the calculations.

Table 10 lists the calculated mean pressure residuals as a function of the expansion number and the average pressure.

The contents of Table 10 indicate that the calculated mean pressure residuals differ from zero by less than two standard deviations, and only two of the seven differ by more than one standard deviation. We conclude that the nonlinear least-squares calculations give a solution consistent with our original criteria for an acceptable

solution when:

1. All runs are treated simultaneously.
2. The compressibility factor is expressed as a fourth degree polynomial in the pressure.
3. and a weighting factor of  $K_{20}^{-0.2}$  is used.

Values of the parameters for the acceptable solution are:

$$B = (2.35278 \pm 0.00672) \cdot 10^{-2}, \text{ atm}^{-1};$$

$$C = -(6.9089 \pm 0.2316) \cdot 10^{-4}, \text{ atm}^{-2};$$

$$D = (2.4479 \pm 0.3709) \cdot 10^{-2}, \text{ atm}^{-3};$$

TABLE 9. - PRESSURE RESIDUALS, IN ATM, FOR A QUARTIC FIT IN P TO REPRESENT Z, TREATING ALL RUNS SIMULTANEOUSLY, WEIGHTING FACTOR P SUB R TO THE  $-3/4$

R=1

RUN NO.	(P, OBS. - P, CAL.)	DEV. FROM AVG. PRESSURE RESIDUAL
HE-0-1	5.4355E-03	5.7576E-03
HE-0-2	2.6220E-03	2.9442E-03
HE-0-3	7.2385E-03	7.5606E-03
HE-0-4	-4.0043E-03	-3.6822E-03
HE-0-5	-7.5702E-03	-7.2481E-03
HE-0-6	-2.8604E-03	-2.5383E-03
HE-0-7	5.3370E-03	5.6592E-03
HE-0-8	-2.8165E-04	4.0463E-05
HE-0-9	-2.3528E-03	-2.0307E-03
HE-0-10	8.3244E-04	1.1545E-03
HE-0-11	1.7422E-03	2.0643E-03
HE-0-12	3.3727E-03	3.6949E-03
*HE-0-13	-5.3815E-04	-2.1602E-04
HE-0-14	5.5341E-03	5.8563E-03
HE-0-15	-1.2328E-03	-9.1068E-04
HE-0-16	-2.2948E-03	-1.9727E-03
HE-0-17	3.3049E-04	6.5261E-04
HE-0-18	2.6247E-04	5.8460E-04
HE-0-19	-5.0796E-03	-4.7575E-03
HE-0-20	-4.7740E-03	-4.4519E-03
HE-0-21	-1.1112E-03	-7.8907E-04
HE-0-22	-7.9102E-03	-7.5881E-03

AVERAGE PRESSURE RESIDUAL -3.2212E-04

STANDARD ERROR OF THE AVERAGE PRESSURE RESIDUAL 9.3523E-04

STANDARD ERROR OF A SINGLE PRESSURE RESIDUAL 4.2857E-03

\* DATA FOR THIS RUN WERE OMITTED FROM THE CALCULATIONS.

TABLE 2. - PRESSURE RESIDUALS IN ATM, FOR A QUANTIC FIT IN P TO REPRESENT & TREATING ALL RUNS SIMULTANEOUSLY, WEIGHING FACTOR P SUB R TO THE -254

R=1

DEV. FROM AVG. PRESSURE RESIDUAL	(P, 082, -4, CAL.)	RUN NO.:
8.1518E-03	0.4388E-03	HE-0-1
5.2443E-03	5.2443E-03	HE-0-2
7.2008E-03	7.2008E-03	HE-0-3
-3.0855E-03	-4.0045E-03	HE-0-4
-7.2008E-03	-7.2008E-03	HE-0-5
-2.2387E-03	-5.0004E-03	HE-0-6
0.6825E-03	0.3370E-03	HE-0-7
4.0435E-03	-5.1185E-03	HE-0-8
-5.0307E-03	-7.2238E-03	HE-0-9
1.1055E-03	8.3504E-04	HE-0-10
2.7043E-03	1.7427E-03	HE-0-11
7.0949E-03	0.4375E-03	HE-0-12
-7.2008E-03	-2.2812E-03	HE-0-13
2.8839E-03	2.2812E-03	HE-0-14
-9.1085E-03	-1.2318E-03	HE-0-15
-1.9173E-03	-5.5008E-03	HE-0-16
4.2501E-03	3.2004E-03	HE-0-17
2.8002E-03	2.8002E-03	HE-0-18
-4.7373E-03	-2.0706E-03	HE-0-19
-4.4219E-03	-4.7702E-03	HE-0-20
-7.8007E-03	-1.1115E-03	HE-0-21
-7.2008E-03	-7.2008E-03	HE-0-22

AVERAGE PRESSURE RESIDUAL - 3.2515E-04  
 STANDARD ERROR OF THE AVERAGE PRESSURE RESIDUAL 0.2523E-04  
 STANDARD ERROR OF A SINGLE PRESSURE RESIDUAL 4.2822E-03  
 \* DATA FOR THIS RUN WERE OMITTED FROM THE CALCULATION.

TABLE 9. - PRESSURE RESIDUALS, IN ATM, FOR A QUARTIC FIT IN P  
TO REPRESENT Z, TREATING ALL RUNS SIMULTANEOUSLY,  
WEIGHTING FACTOR P SUB R TO THE  $-3/4$

R=2

RUN NO.	(P,OBS.-P,CAL.)	DEV. FROM AVG. PRESSURE RESIDUAL
HE-0-1	4.8717E-03	4.6943E-03
HE-0-2	3.8456E-03	3.6681E-03
HE-0-3	6.1297E-04	4.3548E-04
HE-0-4	-1.6425E-03	-1.8200E-03
HE-0-5	-2.6011E-03	-2.7786E-03
HE-0-6	-3.3315E-03	-3.5089E-03
HE-0-7	4.3843E-03	4.2068E-03
HE-0-8	4.6921E-03	4.5146E-03
HE-0-9	-3.3502E-03	-3.5277E-03
HE-0-10	2.2215E-03	2.0440E-03
HE-0-11	2.4180E-03	2.2405E-03
HE-0-12	3.1586E-03	2.9811E-03
*HE-0-13	-6.4667E-02	-6.4844E-02
HE-0-14	4.6756E-03	4.4981E-03
HE-0-15	-2.0612E-03	-2.2387E-03
HE-0-16	-3.5648E-04	-5.3397E-04
HE-0-17	1.2571E-05	-1.6491E-04
HE-0-18	4.9079E-04	3.1330E-04
HE-0-19	-4.5044E-03	-4.6819E-03
HE-0-20	-4.0421E-03	-4.2196E-03
HE-0-21	-2.4658E-03	-2.6433E-03
HE-0-22	-3.3012E-03	-3.4787E-03

AVERAGE PRESSURE RESIDUAL 1.7749E-04

STANDARD ERROR OF THE AVERAGE PRESSURE RESIDUAL 7.1064E-04

STANDARD ERROR OF A SINGLE PRESSURE RESIDUAL 3.2565E-03

\* DATA FOR THIS RUN WERE OMITTED FROM THE CALCULATIONS.

TABLE 2. - PRESSURE RESIDUALS, IN ATM, FOR A QUARTIC FIT IN P TO REPRESENT 1, TREATING ALL RUNS SIMULTANEOUSLY. WEIGHTING FACTOR P SUB R TO THE -3/4

R=5

DEV. FROM AVG. PRESSURE RESIDUAL	(P, OBS. - P, CAL.)	RUN NO.
4.871E-03	4.871E-03	HE-0-1
3.845E-03	3.845E-03	HE-0-2
6.159E-04	6.159E-04	HE-0-3
-1.645E-03	-1.645E-03	HE-0-4
-2.601E-03	-2.601E-03	HE-0-5
-3.331E-03	-3.331E-03	HE-0-6
4.384E-03	4.384E-03	HE-0-7
4.691E-03	4.691E-03	HE-0-8
-3.320E-03	-3.320E-03	HE-0-9
5.212E-03	5.212E-03	HE-0-10
2.418E-03	2.418E-03	HE-0-11
3.158E-03	3.158E-03	HE-0-12
-6.484E-03	-6.484E-03	HE-0-13
4.672E-03	4.672E-03	HE-0-14
-5.041E-03	-5.041E-03	HE-0-15
-3.748E-04	-3.748E-04	HE-0-16
1.271E-03	1.271E-03	HE-0-17
4.901E-04	4.901E-04	HE-0-18
-4.204E-03	-4.204E-03	HE-0-19
-4.041E-03	-4.041E-03	HE-0-20
-5.462E-03	-5.462E-03	HE-0-21
-3.301E-03	-3.301E-03	HE-0-22
-3.478E-03	-3.478E-03	HE-0-23
-5.643E-03	-5.643E-03	HE-0-24
-4.219E-03	-4.219E-03	HE-0-25
-4.081E-03	-4.081E-03	HE-0-26
3.133E-04	3.133E-04	HE-0-27
-1.244E-04	-1.244E-04	HE-0-28
-2.329E-04	-2.329E-04	HE-0-29
-2.328E-03	-2.328E-03	HE-0-30
4.438E-03	4.438E-03	HE-0-31
-6.484E-03	-6.484E-03	HE-0-32
2.981E-03	2.981E-03	HE-0-33
2.240E-03	2.240E-03	HE-0-34
2.044E-03	2.044E-03	HE-0-35
-3.257E-03	-3.257E-03	HE-0-36
4.214E-03	4.214E-03	HE-0-37
4.308E-03	4.308E-03	HE-0-38
-1.820E-03	-1.820E-03	HE-0-39
-2.786E-03	-2.786E-03	HE-0-40
-1.820E-03	-1.820E-03	HE-0-41
4.324E-03	4.324E-03	HE-0-42
3.681E-03	3.681E-03	HE-0-43
4.294E-03	4.294E-03	HE-0-44
4.894E-03	4.894E-03	HE-0-45
4.894E-03	4.894E-03	HE-0-46
4.894E-03	4.894E-03	HE-0-47
4.894E-03	4.894E-03	HE-0-48
4.894E-03	4.894E-03	HE-0-49
4.894E-03	4.894E-03	HE-0-50
4.894E-03	4.894E-03	HE-0-51
4.894E-03	4.894E-03	HE-0-52
4.894E-03	4.894E-03	HE-0-53

\* DATA FOR THIS RUN WERE OMITTED FROM THE CALCULATIONS.  
 STANDARD ERROR OF A SINGLE PRESSURE RESIDUAL 3.226E-03  
 STANDARD ERROR OF THE AVERAGE PRESSURE RESIDUAL 7.104E-04  
 AVERAGE PRESSURE RESIDUAL 1.774E-04

TABLE 9. - PRESSURE RESIDUALS, IN ATM, FOR A QUARTIC FIT IN P  
TO REPRESENT Z, TREATING ALL RUNS SIMULTANEOUSLY,  
WEIGHTING FACTOR P SUB R TO THE  $-3/4$

R=3

RUN NO.	(P,OBS.-P,CAL.)	DEV. FROM AVG. PRESSURE RESIDUAL
HE-0-1	3.1747E-03	2.7993E-03
HE-0-2	2.9828E-03	2.6074E-03
HE-0-3	2.6817E-05	-3.4864E-04
HE-0-4	-3.9924E-06	-3.7945E-04
HE-0-5	-1.4619E-03	-1.8373E-03
HE-0-6	2.3657E-05	-3.5180E-04
HE-0-7	2.9341E-03	2.5586E-03
HE-0-8	3.1807E-03	2.8053E-03
HE-0-9	3.1092E-04	-6.4544E-05
HE-0-10	8.2330E-04	4.4783E-04
HE-0-11	1.0911E-03	7.1570E-04
HE-0-12	2.0431E-03	1.6676E-03
*HE-0-13	2.6268E-03	2.2514E-03
HE-0-14	2.8325E-03	2.4571E-03
HE-0-15	-1.3536E-03	-1.7291E-03
HE-0-16	7.6693E-06	-3.6779E-04
HE-0-17	-3.5578E-04	-7.3125E-04
HE-0-18	5.2692E-04	1.5145E-04
HE-0-19	-3.8432E-03	-4.2186E-03
HE-0-20	-2.8591E-03	-3.2346E-03
HE-0-21	1.2377E-04	-2.5168E-04
HE-0-22	-2.3200E-03	-2.6954E-03

AVERAGE PRESSURE RESIDUAL 3.7546E-04

STANDARD ERROR OF THE AVERAGE PRESSURE RESIDUAL 4.4084E-04

STANDARD ERROR OF A SINGLE PRESSURE RESIDUAL 2.0202E-03

\* DATA FOR THIS RUN WERE OMITTED FROM THE CALCULATIONS.





TABLE 9. - PRESSURE RESIDUALS, IN ATM, FOR A QUARTIC FIT IN P  
TO REPRESENT Z, TREATING ALL RUNS SIMULTANEOUSLY,  
WEIGHTING FACTOR P SUB R TO THE  $-3/4$

R=4

RUN NO.	(P, OBS. - P, CAL.)	DEV. FROM AVG. PRESSURE RESIDUAL
HE-0-1	1.9169E-03	2.0373E-03
HE-0-2	1.4018E-03	1.5222E-03
HE-0-3	2.6712E-04	3.8751E-04
HE-0-4	4.3512E-04	5.5551E-04
HE-0-5	-1.0282E-03	-9.0783E-04
HE-0-6	-2.2081E-04	-1.0042E-04
HE-0-7	1.2416E-03	1.3620E-03
HE-0-8	1.7952E-03	1.9156E-03
HE-0-9	-2.0332E-04	-8.2930E-05
HE-0-10	9.1706E-04	1.0374E-03
HE-0-11	1.9715E-04	3.1754E-04
HE-0-12	1.1218E-03	1.2422E-03
*HE-0-13	1.2931E-03	1.4135E-03
HE-0-14	7.2289E-04	8.4328E-04
HE-0-15	-1.2864E-03	-1.1660E-03
HE-0-16	-6.7414E-04	-5.5375E-04
HE-0-17	-7.1516E-04	-5.9477E-04
HE-0-18	-6.0621E-04	-4.8582E-04
HE-0-19	-2.3467E-03	-2.2263E-03
HE-0-20	-2.3174E-03	-2.1970E-03
HE-0-21	-1.2094E-03	-1.0890E-03
HE-0-22	-1.9372E-03	-1.8168E-03

AVERAGE PRESSURE RESIDUAL  $-1.2039E-04$

STANDARD ERROR OF THE AVERAGE PRESSURE RESIDUAL  $2.8136E-04$

STANDARD ERROR OF A SINGLE PRESSURE RESIDUAL  $1.2893E-03$

\* DATA FOR THIS RUN WERE OMITTED FROM THE CALCULATIONS.



TABLE 9. - PRESSURE RESIDUALS, IN ATM, FOR A QUARTIC FIT IN P TO REPRESENT Z, TREATING ALL RUNS SIMULTANEOUSLY, WEIGHTING FACTOR P SUB R TO THE  $-3/4$

R=5

RUN NO.	(P,OBS.-P,CAL.)	DEV. FROM AVG. PRESSURE RESIDUAL
HE-0-1	9.8296E-04	1.5274E-03
HE-0-2	1.3768E-03	1.9212E-03
HE-0-3	8.7017E-04	1.4146E-03
HE-0-4	9.8514E-04	1.5296E-03
HE-0-5	-3.8596E-04	1.5850E-04
HE-0-6	3.7614E-05	5.8208E-04
HE-0-7	6.4391E-04	1.1883E-03
HE-0-8	1.3104E-03	1.8548E-03
HE-0-9	-3.4404E-03	-2.8960E-03
HE-0-10	-1.0876E-03	-5.4320E-04
HE-0-11	-3.7209E-04	1.7237E-04
HE-0-12	-7.2019E-04	-1.7571E-04
*HE-0-13	8.9225E-04	1.4367E-03
HE-0-14	2.5482E-04	7.9929E-04
HE-0-15	-1.4083E-03	-8.6390E-04
HE-0-16	-9.0554E-04	-3.6107E-04
HE-0-17	-1.1202E-03	-5.7579E-04
HE-0-18	-9.2913E-04	-3.8466E-04
HE-0-19	-2.1431E-03	-1.5986E-03
HE-0-20	-2.2177E-03	-1.6732E-03
HE-0-21	-1.3229E-03	-7.7845E-04
HE-0-22	-1.8422E-03	-1.2977E-03

AVERAGE PRESSURE RESIDUAL -5.4447E-04

STANDARD ERROR OF THE AVERAGE PRESSURE RESIDUAL 2.8437E-04

STANDARD ERROR OF A SINGLE PRESSURE RESIDUAL 1.3031E-03

\* DATA FOR THIS RUN WERE OMITTED FROM THE CALCULATIONS.



TABLE 9. - PRESSURE RESIDUALS, IN ATM, FOR A QUARTIC FIT IN P  
TO REPRESENT Z, TREATING ALL RUNS SIMULTANEOUSLY,  
WEIGHTING FACTOR P SUB R TO THE  $-3/4$

R=6

RUN NO.	(P,OBS.-P,CAL.)	DEV. FROM AVG. PRESSURE RESIDUAL
HE-0-1	1.2578E-03	1.3320E-03
HE-0-2	1.2157E-03	1.2899E-03
HE-0-3	1.2599E-03	1.3341E-03
HE-0-4	1.4043E-03	1.4785E-03
HE-0-5	3.0260E-04	3.7679E-04
HE-0-6	6.9078E-04	7.6498E-04
HE-0-7	2.0855E-04	2.8274E-04
HE-0-8	1.1057E-03	1.1799E-03
HE-0-9	-2.4364E-03	-2.3623E-03
HE-0-10	-2.3606E-04	-1.6187E-04
HE-0-11	4.6320E-04	5.3739E-04
HE-0-12	-2.4841E-04	-1.7421E-04
*HE-0-13	7.5738E-04	8.3157E-04
HE-0-14	2.1477E-04	2.8896E-04
HE-0-15	-5.3544E-04	-4.6124E-04
HE-0-16	-7.2157E-04	-6.4737E-04
HE-0-17	-8.0793E-04	-7.3373E-04
HE-0-18	-7.0474E-04	-6.3055E-04
HE-0-19	-1.4243E-03	-1.3501E-03
HE-0-20	-1.0012E-03	-9.2702E-04
HE-0-21	-5.7699E-04	-5.0280E-04
HE-0-22	-9.8847E-04	-9.1428E-04

AVERAGE PRESSURE RESIDUAL  $-7.4194E-05$

STANDARD ERROR OF THE AVERAGE PRESSURE RESIDUAL  $2.2335E-04$

STANDARD ERROR OF A SINGLE PRESSURE RESIDUAL  $1.0235E-03$

\* DATA FOR THIS RUN WERE OMITTED FROM THE CALCULATIONS.



TABLE 9. - PRESSURE RESIDUALS, IN ATM, FOR A QUARTIC FIT IN P TO REPRESENT Z, TREATING ALL RUNS SIMULTANEOUSLY, WEIGHTING FACTOR P SUB R TO THE  $-3/4$

R=7

RUN NO.	(P, OBS. - P, CAL.)	DEV. FROM AVG. PRESSURE RESIDUAL
HE-0-1	1.6471E-03	1.2247E-03
HE-0-2	1.7391E-03	1.3166E-03
HE-0-3	2.4100E-03	1.9876E-03
HE-0-4	9.3360E-04	5.1117E-04
HE-0-5	1.7530E-03	1.3305E-03
HE-0-6	1.7213E-03	1.2988E-03
HE-0-7	6.8881E-04	2.6638E-04
HE-0-8	1.2853E-03	8.6287E-04
HE-0-9	-7.1975E-05	-4.9440E-04
HE-0-10	-2.9266E-04	-7.1509E-04
HE-0-11	2.0025E-04	-2.2217E-04
HE-0-12	3.7806E-04	-4.4364E-05
*HE-0-13	2.1525E-03	1.7301E-03
HE-0-14	8.6457E-04	4.4214E-04
HE-0-15	3.8617E-04	-3.6258E-05
HE-0-16	-4.2284E-04	-8.4528E-04
HE-0-17	-7.5538E-04	-1.1778E-03
HE-0-18	-2.0436E-03	-2.4660E-03
HE-0-19	-2.2245E-04	-6.4488E-04
HE-0-20	-5.7982E-04	-1.0022E-03
HE-0-21	-1.0729E-04	-5.2972E-04
HE-0-22	-6.4035E-04	-1.0627E-03

AVERAGE PRESSURE RESIDUAL 4.2243E-04

STANDARD ERROR OF THE AVERAGE PRESSURE RESIDUAL 2.3772E-04

STANDARD ERROR OF A SINGLE PRESSURE RESIDUAL 1.0894E-03

\* DATA FOR THIS RUN WERE OMITTED FROM THE CALCULATIONS.





TABLE 10. - Mean pressure residual as a function of expansion number and pressure

Expansion No.	Average pressure	Mean pressure residual x 10 <sup>3</sup>	Standard error x 10 <sup>3</sup>	$\frac{\text{MPR}}{\text{SE}}$ <sup>1/</sup>
1	299.31	-0.322	$\pm 0.935$	0.34
2	139.56	.177	$\pm .711$	.25
3	67.54	.375	$\pm .441$	.85
4	33.28	-.120	$\pm .281$	.43
5	16.54	-.544	$\pm .284$	1.92
6	8.258	-.074	$\pm .223$	.33
7	4.132	.422	$\pm .238$	1.77

<sup>1/</sup> Mean pressure residual/standard error.



$$E = -(7.15 \pm 2.09) \cdot 10^{-15}, \text{ atm}^{-4}; \text{ and}$$

$$N = 1.994199 \pm 0.000030.$$

Observed experimental pressures, least-squares calculated pressures that satisfy the Burnett relationship, differences between experimental and calculated pressures, relative differences between experimental and calculated pressures, the sum of the weighted squares of the pressure residuals, and the parameters N, B, C, D, and E are contained in table 11. Calculated standard deviations of the parameters (designated SN, SB, SC, SD, and SE), the calculated variances of the parameters (designated S2N, S2B, S2C, S2D, and S2E), and the calculated covariances of the parameters (designated S2BC, S2BD, S2BE, S2BN, S2CD, S2CE, S2CN, S2DE, S2DN, and S2EN), are also recorded in table 11.

Variations and covariations of P, BP, CP, DP, and EP for integral pressure values are listed in table 12. These values are needed to calculate the standard deviation of a calculated compressibility factor.

Table 13 gives calculated values of the compressibility factor at integral values of the pressure, along with the calculated standard deviation SZ. The results of table 13 show that the calculated standard error in the compressibility factor at one atm is less than one part in  $10^6$ , while at the highest experimental pressure the calculated standard error is less than one part in  $10^4$ .

We believe the values given in table 13 are the best values obtainable from our data.



TABLE 11. - EXPERIMENTAL AND CALCULATED PRESSURES, IN ATM, PARAMETERS, STANDARD ERRORS, VARIANCES AND COVARIANCES, TREATING ALL RUNS SIMULTANEOUSLY, WEIGHTING FACTOR P SUB R TO THE -3/4

0 DEGREE C HELIUM ISOTHERM

R	P, OBS.	P, CAL.	P, OBS.-P, CAL.	REL. ERROR IN P
RUN NO. HE-0-1				
0	6.4728895E+02	6.4728895E+02	0.000000E-99	0.000000E-99
1	2.8125289E+02	2.8124746E+02	5.43552E-03	1.93261E-05
2	1.3168470E+02	1.3167982E+02	4.87179E-03	3.69959E-05
3	6.3853510E+01	6.3850335E+01	3.17479E-03	4.97200E-05
4	3.1491659E+01	3.1489742E+01	1.91697E-03	6.08724E-05
5	1.5661273E+01	1.5660290E+01	9.82963E-04	6.27639E-05
6	7.8217009E-00	7.8204430E-00	1.25787E-03	1.60818E-04
7	3.9151145E-00	3.9134673E-00	1.64718E-03	4.20725E-04
RUN NO. HE-0-2				
0	6.9039330E+02	6.9039330E+02	0.000000E-99	0.000000E-99
1	2.9760733E+02	2.9760470E+02	2.62208E-03	8.81056E-06
2	1.3883415E+02	1.3883030E+02	3.84563E-03	2.76994E-05
3	6.7203083E+01	6.7200100E+01	2.98289E-03	4.43862E-05
4	3.3114887E+01	3.3113485E+01	1.40187E-03	4.23337E-05
5	1.6462213E+01	1.6460837E+01	1.37680E-03	8.36339E-05
6	8.2197040E-00	8.2184882E-00	1.21576E-03	1.47908E-04
7	4.1139611E-00	4.1122220E-00	1.73912E-03	4.22738E-04
RUN NO. HE-0-3				
0	7.0128236E+02	7.0128236E+02	0.000000E-99	0.000000E-99
1	3.0170799E+02	3.0170075E+02	7.23852E-03	2.39918E-05
2	1.4061376E+02	1.4061315E+02	6.12973E-04	4.35926E-06
3	6.8033559E+01	6.8033533E+01	2.68172E-05	3.94176E-07
4	3.3517320E+01	3.3517053E+01	2.67126E-04	7.96980E-06
5	1.6660572E+01	1.6659701E+01	8.70172E-04	5.22294E-05
6	8.3186011E-00	8.3173412E-00	1.25993E-03	1.51459E-04
7	4.1639855E-00	4.1615754E-00	2.41007E-03	5.78790E-04
RUN NO. HE-0-4				
0	7.0574520E+02	7.0574520E+02	0.000000E-99	0.000000E-99
1	3.0337137E+02	3.0337537E+02	-4.00436E-03	-1.31995E-05
2	1.4133952E+02	1.4134116E+02	-1.64255E-03	-1.16213E-05
3	6.8373652E+01	6.8373656E+01	-3.99241E-06	-5.83910E-08
4	3.3682135E+01	3.3681700E+01	4.35127E-04	1.29186E-05
5	1.6741807E+01	1.6740822E+01	9.85147E-04	5.88435E-05
6	8.3590666E-00	8.3576622E-00	1.40434E-03	1.68002E-04
7	4.1826390E-00	4.1817054E-00	9.33609E-04	2.23210E-04
RUN NO. HE-0-5				
0	6.9787955E+02	6.9787955E+02	0.000000E-99	0.000000E-99
1	3.0041472E+02	3.0042229E+02	-7.57023E-03	-2.51992E-05
2	1.4005441E+02	1.4005701E+02	-2.60111E-03	-1.85721E-05
3	6.7772168E+01	6.7773630E+01	-1.46191E-03	-2.15709E-05
4	3.3390191E+01	3.3391220E+01	-1.02822E-03	-3.07941E-05
5	1.6597313E+01	1.6597699E+01	-3.85967E-04	-2.32548E-05
6	8.2868246E-00	8.2865220E-00	3.02603E-04	3.65161E-05
7	4.1479419E-00	4.1461888E-00	1.75300E-03	4.22620E-04



TABLE 11. - EXPERIMENTAL AND CALCULATED PRESSURES, IN ATM,  
PARAMETERS, STANDARD ERRORS, VARIANCES AND  
COVARIANCES, TREATING ALL RUNS SIMULTANEOUSLY,  
WEIGHTING FACTOR P SUB R TO THE -3/4

0 DEGREE C HELIUM ISOTHERM

R	P, OBS.	P, CAL.	P, OBS.-P, CAL.	REL. ERROR IN P
RUN NO. HE-0-6				
0	7.0298868E+02	7.0298868E+02	0.000000E-99	0.000000E-99
1	3.0233845E+02	3.0234131E+02	-2.86047E-03	-9.46117E-06
2	1.4088835E+02	1.4089168E+02	-3.33150E-03	-2.36463E-05
3	6.8163698E+01	6.8163674E+01	2.36573E-05	3.47066E-07
4	3.3579834E+01	3.3580055E+01	-2.20818E-04	-6.57592E-06
5	1.6690781E+01	1.6690743E+01	3.76142E-05	2.25359E-06
6	8.3334615E-00	8.3327707E-00	6.90785E-04	8.28929E-05
7	4.1709998E-00	4.1692785E-00	1.72130E-03	4.12683E-04
RUN NO. HE-0-7				
0	7.0208680E+02	7.0208680E+02	0.000000E-99	0.000000E-99
1	3.0200812E+02	3.0200278E+02	5.33708E-03	1.76719E-05
2	1.4074887E+02	1.4074449E+02	4.38437E-03	3.11503E-05
3	6.8097837E+01	6.8094903E+01	2.93412E-03	4.30868E-05
4	3.3548005E+01	3.3546763E+01	1.24161E-03	3.70100E-05
5	1.6674984E+01	1.6674340E+01	6.43915E-04	3.86156E-05
6	8.3248260E-00	8.3246174E-00	2.08550E-04	2.50516E-05
7	4.1658969E-00	4.1652080E-00	6.88819E-04	1.65347E-04
RUN NO. HE-0-8				
0	7.0061130E+02	7.0061130E+02	0.000000E-99	0.000000E-99
1	3.0144846E+02	3.0144874E+02	-2.81659E-04	-9.34355E-07
2	1.4050824E+02	1.4050355E+02	4.69212E-03	3.33939E-05
3	6.7985497E+01	6.7982316E+01	3.18078E-03	4.67862E-05
4	3.3494053E+01	3.3492257E+01	1.79522E-03	5.35984E-05
5	1.6648795E+01	1.6647484E+01	1.31040E-03	7.87086E-05
6	8.3123743E-00	8.3112685E-00	1.10579E-03	1.33029E-04
7	4.1598289E-00	4.1585436E-00	1.28530E-03	3.08979E-04
RUN NO. HE-0-9				
0	6.8457479E+02	6.8457479E+02	0.000000E-99	0.000000E-99
1	2.9540775E+02	2.9541010E+02	-2.35287E-03	-7.96483E-06
2	1.3787047E+02	1.3787382E+02	-3.35022E-03	-2.42997E-05
3	6.6752988E+01	6.6752677E+01	3.10920E-04	4.65777E-06
4	3.2896560E+01	3.2896763E+01	-2.03321E-04	-6.18062E-06
5	1.6350585E+01	1.6354026E+01	-3.44049E-03	-2.10420E-04
6	8.1629533E-00	8.1653898E-00	-2.43649E-03	-2.98482E-04
7	4.0856389E-00	4.0857109E-00	-7.19757E-05	-1.76167E-05
RUN NO. HE-0-10				
0	7.0727559E+02	7.0727559E+02	0.000000E-99	0.000000E-99
1	3.0394992E+02	3.0394908E+02	8.32446E-04	2.73876E-06
2	1.4159267E+02	1.4159045E+02	2.22150E-03	1.56893E-05
3	6.8490921E+01	6.8490097E+01	8.23304E-04	1.20206E-05
4	3.3738977E+01	3.3738060E+01	9.17063E-04	2.71811E-05
5	1.6767501E+01	1.6768589E+01	-1.08767E-03	-6.48679E-05
6	8.3712273E-00	8.3714634E-00	-2.36069E-04	-2.82001E-05
7	4.1883028E-00	4.1885954E-00	-2.92661E-04	-6.98759E-05





TABLE 11. - EXPERIMENTAL AND CALCULATED PRESSURES, IN ATM, PARAMETERS, STANDARD ERRORS, VARIANCES AND COVARIANCES, TREATING ALL RUNS SIMULTANEOUSLY, WEIGHTING FACTOR P SUB R TO THE  $-3/4$

0 DEGREE C HELIUM ISOTHERM				
R	P, OBS.	P, CAL.	P, OBS.-P, CAL.	REL. ERROR IN P
RUN NO. HE-0-11				
0	7.0340360E+02	7.0340360E+02	0.00000E-99	0.00000E-99
1	3.0249876E+02	3.0249702E+02	1.74220E-03	5.75936E-06
2	1.4096179E+02	1.4095937E+02	2.41802E-03	1.71537E-05
3	6.8196393E+01	6.8195302E+01	1.09117E-03	1.60004E-05
4	3.3595563E+01	3.3595366E+01	1.97155E-04	5.86849E-06
5	1.6697915E+01	1.6698287E+01	-3.72095E-04	-2.22839E-05
6	8.3369834E-00	8.3365202E-00	4.63204E-04	5.55602E-05
7	4.1713507E-00	4.1711504E-00	2.00252E-04	4.80065E-05
RUN NO. HE-0-12				
0	6.9905324E+02	6.9905324E+02	0.00000E-99	0.00000E-99
1	3.0086678E+02	3.0086341E+02	3.37279E-03	1.12102E-05
2	1.4025209E+02	1.4024894E+02	3.15862E-03	2.25210E-05
3	6.7865373E+01	6.7863330E+01	2.04313E-03	3.01056E-05
4	3.3435772E+01	3.3434651E+01	1.12184E-03	3.35521E-05
5	1.6618379E+01	1.6619100E+01	-7.20190E-04	-4.33369E-05
6	8.2969111E-00	8.2971595E-00	-2.48410E-04	-2.99400E-05
7	4.1518777E-00	4.1514997E-00	3.78067E-04	9.10593E-05
*RUN NO. HE-0-13				
RUN NO. HE-0-14				
0	6.9853895E+02	6.9853895E+02	0.00000E-99	0.00000E-99
1	3.0067567E+02	3.0067014E+02	5.53418E-03	1.84058E-05
2	1.4016953E+02	1.4016485E+02	4.67568E-03	3.33573E-05
3	6.7826865E+01	6.7824032E+01	2.83258E-03	4.17619E-05
4	3.3416347E+01	3.3415624E+01	7.22890E-04	2.16328E-05
5	1.6609979E+01	1.6609724E+01	2.54821E-04	1.53414E-05
6	8.2927140E-00	8.2924993E-00	2.14774E-04	2.58992E-05
7	4.1500376E-00	4.1491730E-00	8.64578E-04	2.08330E-04
RUN NO. HE-0-15				
0	7.0725396E+02	7.0725396E+02	0.00000E-99	0.00000E-99
1	3.0393974E+02	3.0394098E+02	-1.23280E-03	-4.05609E-06
2	1.4158487E+02	1.4158693E+02	-2.06125E-03	-1.45584E-05
3	6.8487098E+01	6.8488452E+01	-1.35368E-03	-1.97654E-05
4	3.3735978E+01	3.3737264E+01	-1.28645E-03	-3.81329E-05
5	1.6766788E+01	1.6768197E+01	-1.40837E-03	-8.39979E-05
6	8.3707330E-00	8.3712684E-00	-5.35440E-04	-6.39657E-05
7	4.1888843E-00	4.1884981E-00	3.86172E-04	9.21898E-05
RUN NO. HE-0-16				
0	7.0575241E+02	7.0575241E+02	0.00000E-99	0.00000E-99
1	3.0337578E+02	3.0337808E+02	-2.29483E-03	-7.56431E-06
2	1.4134198E+02	1.4134233E+02	-3.56484E-04	-2.52213E-06
3	6.8374213E+01	6.8374205E+01	7.66934E-06	1.12167E-07
4	3.3681291E+01	3.3681966E+01	-6.74146E-04	-2.00154E-05
5	1.6740047E+01	1.6740953E+01	-9.05548E-04	-5.40947E-05
6	8.3570058E-00	8.3577273E-00	-7.21573E-04	-8.63435E-05
7	4.1813150E-00	4.1817379E-00	-4.22849E-04	-1.01128E-04
*	DATA FOR THIS RUN WERE OMITTED FROM THE CALCULATIONS.			



TABLE 11. - EXPERIMENTAL AND CALCULATED PRESSURES, IN ATM, PARAMETERS, STANDARD ERRORS, VARIANCES AND COVARIANCES, TREATING ALL RUNS SIMULTANEOUSLY, WEIGHTING FACTOR P SUB R TO THE  $-3/4$

0 DEGREE C HELIUM ISOTHERM				
R	P, OBS.	P, CAL.	P, OBS.-P, CAL.	REL. ERROR IN P
RUN NO. HE-0-17				
0	6.9911233E+02	6.9911233E+02	0.00000E-99	0.00000E-99
1	3.0088594E+02	3.0088561E+02	3.30496E-04	1.09841E-06
2	1.4025861E+02	1.4025860E+02	1.25718E-05	8.96330E-08
3	6.7867489E+01	6.7867845E+01	-3.55787E-04	-5.24238E-06
4	3.3436121E+01	3.3436836E+01	-7.15165E-04	-2.13890E-05
5	1.6619056E+01	1.6620177E+01	-1.12026E-03	-6.74083E-05
6	8.2968869E-00	8.2976948E-00	-8.07930E-04	-9.73775E-05
7	4.1510115E-00	4.1517669E-00	-7.55380E-04	-1.81974E-04
RUN NO. HE-0-18				
0	7.0498797E+02	7.0498797E+02	0.00000E-99	0.00000E-99
1	3.0309166E+02	3.0309140E+02	2.62479E-04	8.66005E-07
2	1.4121823E+02	1.4121774E+02	4.90793E-04	3.47542E-06
3	6.8316532E+01	6.8316005E+01	5.26922E-04	7.71296E-06
4	3.3653188E+01	3.3653794E+01	-6.06215E-04	-1.80136E-05
5	1.6726144E+01	1.6727074E+01	-9.29137E-04	-5.55500E-05
6	8.3501239E-00	8.3508286E-00	-7.04749E-04	-8.43999E-05
7	4.1762502E-00	4.1782938E-00	-2.04364E-03	-4.89348E-04
RUN NO. HE-0-19				
0	6.9586241E+02	6.9586241E+02	0.00000E-99	0.00000E-99
1	2.9965869E+02	2.9966376E+02	-5.07965E-03	-1.69514E-05
2	1.3972241E+02	1.3972691E+02	-4.50444E-03	-3.22384E-05
3	6.7615486E+01	6.7619330E+01	-3.84323E-03	-5.68395E-05
4	3.3314160E+01	3.3316507E+01	-2.34672E-03	-7.04422E-05
5	1.6558741E+01	1.6560884E+01	-2.14313E-03	-1.29426E-04
6	8.2667975E-00	8.2682218E-00	-1.42434E-03	-1.72296E-04
7	4.1368299E-00	4.1370523E-00	-2.22456E-04	-5.37746E-05
RUN NO. HE-0-20				
0	6.8620552E+02	6.8620552E+02	0.00000E-99	0.00000E-99
1	2.9602082E+02	2.9602559E+02	-4.77402E-03	-1.61273E-05
2	1.3813812E+02	1.3814216E+02	-4.04212E-03	-2.92614E-05
3	6.6875363E+01	6.6878222E+01	-2.85917E-03	-4.27537E-05
4	3.2955262E+01	3.2957579E+01	-2.31742E-03	-7.03202E-05
5	1.6381782E+01	1.6384000E+01	-2.21771E-03	-1.35377E-04
6	8.1792899E-00	8.1802911E-00	-1.00122E-03	-1.22409E-04
7	4.0925711E-00	4.0931509E-00	-5.79828E-04	-1.41678E-04
RUN NO. HE-0-21				
0	7.7435393E+02	7.7435393E+02	0.00000E-99	0.00000E-99
1	3.2882507E+02	3.2882618E+02	-1.11120E-03	-3.37931E-06
2	1.5234062E+02	1.5234309E+02	-2.46583E-03	-1.61863E-05
3	7.3499612E+01	7.3499488E+01	1.23778E-04	1.68407E-06
4	3.6158408E+01	3.6159617E+01	-1.20940E-03	-3.34473E-05
5	1.7959522E+01	1.7960845E+01	-1.32292E-03	-7.36615E-05
6	8.9632908E-00	8.9638678E-00	-5.76999E-04	-6.43736E-05
7	4.4841902E-00	4.4842975E-00	-1.07298E-04	-2.39281E-05



TABLE 11. - EXPERIMENTAL AND CALCULATED PRESSURES, IN ATM, PARAMETERS, STANDARD ERRORS, VARIANCES AND COVARIANCES, TREATING ALL RUNS SIMULTANEOUSLY, WEIGHTING FACTOR P SUB R TO THE -3/4

0 DEGREE C HELIUM ISOTHERM				
R	P, OBS.	P, CAL.	P, OBS.-P, CAL.	REL. ERROR IN P
RUN NO. HE-0-22				
0	5.8218590E+02	5.8218590E+02	0.000000E-99	0.000000E-99
1	2.5608357E+02	2.5609148E+02	-7.91028E-03	-3.08894E-05
2	1.2058177E+02	1.2058508E+02	-3.30127E-03	-2.73779E-05
3	5.8627782E+01	5.8630102E+01	-2.32002E-03	-3.95720E-05
4	2.8951908E+01	2.8953845E+01	-1.93721E-03	-6.69115E-05
5	1.4406838E+01	1.4408680E+01	-1.84220E-03	-1.27869E-04
6	7.1967975E-00	7.1977859E-00	-9.88478E-04	-1.37349E-04
7	3.6018337E-00	3.6024741E-00	-6.40355E-04	-1.77785E-04

SUM OF THE WEIGHTED SQUARES OF THE RESIDUALS 3.54143E-05

PARAMETERS	VARIANCES	STANDARD ERRORS
N 1.994198697E-00	S2N 9.01723E-10	SN 3.00287E-05
B 5.352783000E-04	S2B 4.52016E-13	SB 6.72321E-07
C -6.909896798E-08	S2C 5.36547E-18	SC 2.31634E-09
D 2.447895123E-11	S2D 1.37560E-23	SD 3.70891E-12
E -7.145536278E-15	S2E 4.35240E-30	SE 2.08624E-15

COVARIANCES		
S2BC -1.53139E-15	S2BD 2.38348E-18	S2BE -1.29119E-21
S2BN -1.89920E-11	S2CD -8.52185E-21	S2CE 4.68937E-24
S2CN 6.07935E-14	S2DE -7.68235E-27	S2DN -9.21004E-17
S2EN 4.90323E-20		



TABLE 12. - VARIANCES AND COVARIANCES FOR INTEGRAL PRESSURES,  
TREATING ALL RUNS SIMULTANEOUSLY, WEIGHTING FACTOR  
P SUB R TO THE -3/4

0 DEGREE C HELIUM ISOTHERM

PRESSURE, ATM	S2P	S2BP	S2CP
1.000E-00	3.20062E-09	3.23666E-11	-1.00403E-13
2.000E-00	7.23117E-09	4.65290E-11	-1.42698E-13
5.000E-00	1.62005E-08	5.98508E-11	-1.77173E-13
1.000E+01	2.26992E-08	4.56537E-11	-1.21116E-13
2.500E+01	4.52488E-08	-5.30751E-11	2.07175E-13
5.000E+01	1.30110E-07	-1.61917E-10	5.28157E-13
7.500E+01	1.89756E-07	-1.47700E-10	4.22244E-13
1.000E+02	2.53640E-07	-4.33067E-11	1.93500E-14
1.250E+02	3.96468E-07	1.04154E-10	-5.11500E-13
1.500E+02	6.26075E-07	2.52180E-10	-1.02181E-12
2.000E+02	1.05897E-06	4.26982E-10	-1.56242E-12
2.500E+02	1.12715E-06	3.34745E-10	-1.12505E-12
3.000E+02	1.41314E-06	-2.90551E-11	2.63409E-13
3.500E+02	3.14773E-06	-5.64493E-10	2.21257E-12
4.000E+02	6.79395E-06	-1.11148E-09	4.13131E-12
4.500E+02	1.12756E-05	-1.49619E-09	5.39722E-12
5.000E+02	1.46683E-05	-1.57800E-09	5.52740E-12
6.000E+02	1.36301E-05	-7.16867E-10	2.16525E-12
7.000E+02	4.19139E-06	1.68368E-10	-6.20294E-13
8.000E+02	1.97774E-04	-3.68252E-09	1.53547E-11
9.000E+02	3.12412E-03	-2.18574E-08	8.60910E-11
1.000E+03	2.35944E-02	-7.00412E-08	2.69997E-10

PRESSURE, ATM	S2DP	S2EP
1.000E-00	1.50047E-16	-7.92294E-20
2.000E-00	2.12183E-16	-1.11699E-19
5.000E-00	2.59306E-16	-1.35206E-19
1.000E+01	1.68106E-16	-8.47941E-20
2.500E+01	-3.33802E-16	1.83120E-19
5.000E+01	-7.94516E-16	4.18826E-19
7.500E+01	-5.88824E-16	2.94408E-19
1.000E+02	6.72050E-17	-6.82188E-20
1.250E+02	9.04164E-16	-5.21194E-19
1.500E+02	1.68897E-15	-9.38136E-19
2.000E+02	2.45798E-15	-1.32063E-18
2.500E+02	1.66480E-15	-8.50659E-19
3.000E+02	-5.96025E-16	3.94462E-19
3.500E+02	-3.66120E-15	2.03019E-18
4.000E+02	-6.56706E-15	3.51752E-18
4.500E+02	-8.32776E-15	4.32074E-18
5.000E+02	-8.21527E-15	4.06615E-18
6.000E+02	-2.41547E-15	6.42822E-19
7.000E+02	1.01116E-15	-5.65463E-19
8.000E+02	-2.92537E-14	1.90494E-17
9.000E+02	-1.54144E-13	9.51045E-17
1.000E+03	-4.71702E-13	2.84455E-16





TABLE 13. - COMPRESSIBILITY FACTORS AND STANDARD ERRORS FOR INTEGRAL PRESSURES, TREATING ALL RUNS SIMULTANEOUSLY, WEIGHTING FACTOR P SUB R TO THE -3/4

0 DEGREE C HELIUM ISOTHERM

PRESSURE, ATM	Z	SZ
1.000E-00	1.0005352092E+00	6.95998E-07
2.000E-00	1.0010702803E-00	1.37286E-06
5.000E-00	1.0026746670E-00	3.35316E-06
1.000E+01	1.0053458975E-00	6.53600E-06
2.500E+01	1.0133391503E-00	1.53999E-05
5.000E+01	1.0265941827E-00	2.82401E-05
7.500E+01	1.0397672917E-00	3.89753E-05
1.000E+02	1.0528606047E-00	4.78728E-05
1.250E+02	1.0658761820E-00	5.51702E-05
1.500E+02	1.0788160172E-00	6.10892E-05
2.000E+02	1.1044761000E-00	6.96171E-05
2.500E+02	1.1298554608E-00	7.49808E-05
3.000E+02	1.1549676357E-00	7.84889E-05
3.500E+02	1.1798250887E-00	8.12136E-05
4.000E+02	1.2044392122E-00	8.39787E-05
4.500E+02	1.2288203267E-00	8.73501E-05
5.000E+02	1.2529776809E-00	9.16174E-05
6.000E+02	1.3006527435E-00	1.02413E-04
7.000E+02	1.3475169527E-00	1.12068E-04
8.000E+02	1.3936057118E-00	1.12825E-04
9.000E+02	1.4389372750E-00	1.11374E-04
1.000E+03	1.4835127470E-00	1.84123E-04

$$Z = 1 + BP + CP^2 + DP^3 + EP^4$$

$$B = (5.35278 \pm 0.00672) \cdot 10^{-4}, \text{ atm}^{-1}$$

$$C = -(6.9099 \pm 0.2316) \cdot 10^{-8}, \text{ atm}^{-2}$$

$$D = (2.4479 \pm 0.3709) \cdot 10^{-11}, \text{ atm}^{-3}$$

$$E = -(7.15 \pm 2.09) \cdot 10^{-15}, \text{ atm}^{-4}$$

$$N = 1.994199 \pm 0.000030$$



The results recorded in tables 11 through 13 are given in E format. The number to the left of E is to be multiplied by an exponent of ten given to the right of E.

Table 14 contains a comparison of the results obtained when the data were fitted simultaneously to a fourth degree polynomial in the pressure with the results obtained when the data were treated as separate runs. A weighting factor of  $P_r^{-3/4}$  was used in the calculations.

#### COMPARISON OF OUR RESULTS WITH THE WORK OF PREVIOUS INVESTIGATORS

Values of the second virial coefficient of helium at 0° C, obtained by various investigators, are listed in table 15 along with the value obtained in this research.

Compressibility factors obtained from our work were compared as a function of pressure with results obtained by other workers. Relative percentage deviations from our values are listed in table 16.

Our compressibility factors are higher than those of Holborn and Schultze (28) over the pressure range 0 to 150 atmospheres, but lower at 200 atm. The differences are plus 0.04 percent at 75 atm and minus 0.04 percent at 200 atm.

The results of this work are consistently higher, 0.3 percent at 200 atm, than those of Michels and Wouters (35); and are higher, 0.18 percent at 350 atm and 0.06 percent at 1,000 atm, than those of Wiebe, Gaddy, and Heins (51). Also, our results are consistently higher than the results published by Miller, Brandt, and Stroud (37), with a maximum deviation of 0.048 percent at 200 atm.

and 500 of the total of 1,000.

The first 500 of the total of 1,000 are to be used for the purpose of the first 500 of the total of 1,000. The second 500 of the total of 1,000 are to be used for the purpose of the second 500 of the total of 1,000.

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The fourth 500 of the total of 1,000 are to be used for the purpose of the fourth 500 of the total of 1,000. The fifth 500 of the total of 1,000 are to be used for the purpose of the fifth 500 of the total of 1,000.

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The tenth 500 of the total of 1,000 are to be used for the purpose of the tenth 500 of the total of 1,000. The eleventh 500 of the total of 1,000 are to be used for the purpose of the eleventh 500 of the total of 1,000.

The twelfth 500 of the total of 1,000 are to be used for the purpose of the twelfth 500 of the total of 1,000.

The thirteenth 500 of the total of 1,000 are to be used for the purpose of the thirteenth 500 of the total of 1,000. The fourteenth 500 of the total of 1,000 are to be used for the purpose of the fourteenth 500 of the total of 1,000.

The fifteenth 500 of the total of 1,000 are to be used for the purpose of the fifteenth 500 of the total of 1,000. The sixteenth 500 of the total of 1,000 are to be used for the purpose of the sixteenth 500 of the total of 1,000.

TABLE 14. - Comparison of results obtained from the separate and simultaneous methods

	Z(1 atm)	Z(700 atm)	N	
Data treated as separate runs	1.000541274 $\pm$ 0.000001513	1.348033 $\pm$ 0.000211	1.994059 $\pm$ 0.000053	
Data treated simultaneously	1.000535209 $\pm$ .000000696	1.347517 $\pm$ .000112	1.994199 $\pm$ .000030	
Bias	.000006065	.000516	.000140	
	$B \cdot 10^4, \text{atm}^{-1}$	$C \cdot 10^7, \text{atm}^{-2}$	$D \cdot 10^{10}, \text{atm}^{-3}$	$E \cdot 10^{13}, \text{atm}^{-4}$
Data treated as separate runs	5.41382 $\pm$ 0.01521	-1.0835 $\pm$ 0.0862	1.299 $\pm$ 0.223	-0.933 $\pm$ 0.180
Data treated simultaneously	5.35278 $\pm$ .00672	-.69099 $\pm$ .02316	.24479 $\pm$ .03709	-.0715 $\pm$ .0209
Bias	.06104	.3925	1.054	-.862



TABLE 15. - Comparison of the second virial coefficient of helium at 0° C obtained in this work with the value obtained by various other investigators

Investigator	B, cm <sup>3</sup> mole <sup>-1</sup>
Jacqueroed and Scheuer (31-32), 1905-1908	13.45
Onnes (41), 1908	11.49
Burt (13), 1910	0.00
Holborn, Otto, and Schultze (26-28) as given by Otto (43), 1915	11.77
Henning and Heuse (23), 1921	7.58
Baxter and Starkweather (4), 1926	0.00
Heuse (24), 1926	8.18
Boks and Onnes (7-8) as given by Nijhoff (39), 1928	11.73
Ellestad and Baxter (20), 1928	11.22
Ellestad and Baxter (21), 1929	9.42
Heuse and Otto (25), 1929	11.77
Wiebe, Gaddy, and Heins (51), 1931	11.69
Keesom and Santen (33), 1933, and Santen (44), 1934	11.27
Burnett (12), 1936	11.75
Michels and Wouters (35), 1941	11.87
Oishi (40), 1942	10.23
Schneider (45), 1949	11.82
Schneider and Duffie (46), 1949	11.77
White, Rubin, Camky, and Johnston (50), 1960	12.08
Miller, Brandt, and Stroud (37), 1961	11.86
Canfield, Leland, and Kobayashi (14-16), 1962-1965	12.09
Hoover, Canfield, Kobayashi, and Leland (30), 1964 [Retreatment of Canfield's (14) original data]	11.96
Blancett (6), 1966	11.91
This work, 1969	11.997 ±0.015





TABLE 16. - Comparison of values of the compressibility factor of helium at 0° C obtained in this study with values obtained by various other investigators (expressed in terms of a percentage relative difference)

Investigator	1 atm	2 atm	5 atm
Jacquerod and Scheuer ( <u>31-32</u> ), 1905-1908	-0.0065	—	—
Onnes ( <u>41</u> ), 1908	.0023	0.0046	0.0116
Burt ( <u>13</u> ), 1910	.0535	—	—
Holborn, Otto, and Schultze ( <u>26-28</u> ) as given by Otto ( <u>43</u> ), 1915	.0011	.0021	.0051
Henning and Heuse ( <u>23</u> ), 1921	.0197	—	—
Baxter and Starkweather ( <u>4</u> ), 1926	.0535	—	—
Heuse ( <u>24</u> ), 1926	.0170	—	—
Boks and Onnes ( <u>7-8</u> ) as given by Nijhoff ( <u>39</u> ), 1928	.0012	.0024	.0064
Ellestad and Baxter ( <u>20</u> ), 1928	.0035	—	—
Ellestad and Baxter ( <u>21</u> ), 1929	.0115	—	—
Heuse and Otto ( <u>25</u> ), 1929	.0011	—	—
Wiebe, Gaddy, and Heins ( <u>51</u> ), 1931	.0014	.0028	.0069
Keesom and Santen ( <u>33</u> ), 1933, and Santen ( <u>44</u> ), 1934	.0032	.0065	.0165
Burnett ( <u>12</u> ), 1936	.0011	.0022	.0053
Michels and Wouters ( <u>35</u> ), 1941	.0006	.0011	.0029
Oishi ( <u>40</u> ), 1942	.0079	—	—
Schneider ( <u>45</u> ), 1949	.0008	.0016	.0038
Schneider and Duffie ( <u>46</u> ), 1949	.0010	.0020	.0048
White, Rubin, Camky, and Johnston ( <u>50</u> ), 1960	-.0004	-.0007	-.0019
Miller, Brandt, and Stroud ( <u>37</u> ), 1961	.0006	.0012	.0029
Canfield ( <u>14</u> ), 1962	-.0005	-.0010	-.0025
Blancett ( <u>6</u> ), 1966	.0004	.0008	.0019



TABLE 16. - Comparison of values of the compressibility factor of helium at 0° C obtained in this study with values obtained by various other investigators (expressed in terms of a percentage relative difference)--Continued

Investigator	10 atm	25 atm	50 atm
Jacqueroed and Scheuer ( <u>31-32</u> ), 1905-1908	—	—	—
Onnes ( <u>41</u> ), 1908	0.0236	0.0611	0.1290
Burt ( <u>13</u> ), 1910	—	—	—
Holborn, Otto, and Schultze ( <u>26-28</u> ) as given by Otto ( <u>43</u> ), 1915	.0099	.0219	.0351
Henning and Heuse ( <u>23</u> ), 1921	—	—	—
Baxter and Starkweather ( <u>4</u> ), 1926	—	—	—
Heuse ( <u>24</u> ), 1926	—	—	—
Boks and Onnes ( <u>7-8</u> ) as given by Nijhoff ( <u>39</u> ), 1928	.0137	.0412	.1041
Ellestad and Baxter ( <u>20</u> ), 1928	—	—	—
Ellestad and Baxter ( <u>21</u> ), 1929	—	—	—
Heuse and Otto ( <u>25</u> ), 1929	—	—	—
Wiebe, Gaddy, and Heins ( <u>51</u> ), 1931	.0135	.0324	.0605
Keesom and Santen ( <u>33</u> ), 1933, and Santen ( <u>44</u> ), 1934	.0339	.0906	—
Burnett ( <u>12</u> ), 1936	.0102	.0229	.0369
Michels and Wouters ( <u>35</u> ), 1941	.0061	.0170	.0390
Oishi ( <u>40</u> ), 1942	—	—	—
Schneider ( <u>45</u> ), 1949	.0073	.0155	.0224
Schneider and Duffie ( <u>46</u> ), 1949	.0093	.0205	.0322
White, Rubin, Camky, and Johnston ( <u>50</u> ), 1960	-.0041	-.0128	—
Miller, Brandt, and Stroud ( <u>37</u> ), 1961	.0057	.0134	.0242
Canfield ( <u>14</u> ), 1962	-.0054	-.0119	-.0230
Blancett ( <u>6</u> ), 1966	.0037	.0087	.0156



TABLE 16. - Comparison of values of the compressibility factor of helium at 0° C obtained in this study with values obtained by various other investigators (expressed in terms of a percentage relative difference)--Continued

Investigator	75 atm	100 atm	125 atm
Jacqueroed and Scheuer ( <u>31-32</u> ), 1905-1908	—	—	—
Onnes ( <u>41</u> ), 1908	—	—	—
Burt ( <u>13</u> ), 1910	—	—	—
Holborn, Otto, and Schultze ( <u>26-28</u> ) as given by Otto ( <u>43</u> ), 1915	0.0401	0.0374	0.0274
Henning and Heuse ( <u>23</u> ), 1921	—	—	—
Baxter and Starkweather ( <u>4</u> ), 1926	—	—	—
Heuse ( <u>24</u> ), 1926	—	—	—
Boks and Onnes ( <u>7-8</u> ) as given by Nijhoff ( <u>39</u> ), 1928	.1859	—	—
Ellestad and Baxter ( <u>20</u> ), 1928	—	—	—
Ellestad and Baxter ( <u>21</u> ), 1929	—	—	—
Heuse and Otto ( <u>25</u> ), 1929	—	—	—
Wiebe, Gaddy, and Heins ( <u>51</u> ), 1931	.0847	.1053	.1227
Keesom and Santen ( <u>33</u> ), 1933, and Santen ( <u>44</u> ), 1934	—	—	—
Burnett ( <u>12</u> ), 1936	.0428	.0409	.0318
Michels and Wouters ( <u>35</u> ), 1941	.0640	.0905	.1174
Oishi ( <u>40</u> ), 1942	—	—	—
Schneider ( <u>45</u> ), 1949	.0213	.0126	—
Schneider and Duffie ( <u>46</u> ), 1949	.0357	.0316	—
White, Rubin, Camky, and Johnston ( <u>50</u> ), 1960	—	—	—
Miller, Brandt, and Stroud ( <u>37</u> ), 1961	.0325	.0387	.0431
Canfield ( <u>14</u> ), 1962	-.0330	-.0427	-.0520
Blancett ( <u>6</u> ), 1966	.0210	.0251	.0280



TABLE 16. - Comparison of values of the compressibility factor of helium at 0° C obtained in this study with values obtained by various other investigators (expressed in terms of a percentage relative difference)--Continued

Investigator	150 atm	200 atm	250 atm
Jacquerod and Scheuer ( <u>31-32</u> ), 1905-1908	---	---	---
Onnes ( <u>41</u> ), 1908	---	---	---
Burt ( <u>13</u> ), 1910	---	---	---
Holborn, Otto, and Schultze ( <u>26-28</u> ) as given by Otto ( <u>43</u> ), 1915	0.0107	-0.0415	---
Henning and Heuse ( <u>23</u> ), 1921	---	---	---
Baxter and Starkweather ( <u>4</u> ), 1926	---	---	---
Heuse ( <u>24</u> ), 1926	---	---	---
Boks and Onnes ( <u>7-8</u> ) as given by Nijhoff ( <u>39</u> ), 1928	---	---	---
Ellestad and Baxter ( <u>20</u> ), 1928	---	---	---
Ellestad and Baxter ( <u>21</u> ), 1929	---	---	---
Heuse and Otto ( <u>25</u> ), 1929	---	---	---
Wiebe, Gaddy, and Heins ( <u>51</u> ), 1931	.1371	.1582	.1707
Keesom and Santen ( <u>33</u> ), 1933, and Santen ( <u>44</u> ), 1934	---	---	---
Burnett ( <u>12</u> ), 1936	---	---	---
Michels and Wouters ( <u>35</u> ), 1941	.1436	.2990	---
Oishi ( <u>40</u> ), 1942	---	---	---
Schneider ( <u>45</u> ), 1949	---	---	---
Schneider and Duffie ( <u>46</u> ), 1949	---	---	---
White, Rubin, Camky, and Johnston ( <u>50</u> ), 1960	---	---	---
Miller, Brandt, and Stroud ( <u>37</u> ), 1961	.0459	.0478	.0459
Canfield ( <u>14</u> ), 1962	-.0597	-.0746	-.0871
Blancett ( <u>6</u> ), 1966	.0299	.0313	.0304





TABLE 16. - Comparison of values of the compressibility factor of helium at 0° C obtained in this study with values obtained by various other investigators (expressed in terms of a percentage relative difference)--Continued

Investigator	300 atm	350 atm	400 atm
Jacquerod and Scheuer ( <u>31-32</u> ), 1905-1908	—	—	—
Onnes ( <u>41</u> ), 1908	—	—	—
Burt ( <u>13</u> ), 1910	—	—	—
Holborn, Otto, and Schultze ( <u>26-28</u> ) as given by Otto ( <u>43</u> ), 1915	—	—	—
Henning and Heuse ( <u>23</u> ), 1921	—	—	—
Baxter and Starkweather ( <u>4</u> ), 1926	—	—	—
Heuse ( <u>24</u> ), 1926	—	—	—
Boks and Onnes ( <u>7-8</u> ) as given by Nijhoff ( <u>39</u> ), 1928	—	—	—
Ellestad and Baxter ( <u>20</u> ), 1928	—	—	—
Ellestad and Baxter ( <u>21</u> ), 1929	—	—	—
Heuse and Otto ( <u>25</u> ), 1929	—	—	—
Wiebe, Gaddy, and Heins ( <u>51</u> ), 1931	0.1763	0.1766	0.1727
Keesom and Santen ( <u>33</u> ), 1933, and Santen ( <u>44</u> ), 1934	—	—	—
Burnett ( <u>12</u> ), 1936	—	—	—
Michels and Wouters ( <u>35</u> ), 1941	—	—	—
Oishi ( <u>40</u> ), 1942	—	—	—
Schneider ( <u>45</u> ), 1949	—	—	—
Schneider and Duffie ( <u>46</u> ), 1949	—	—	—
White, Rubin, Camky, and Johnston ( <u>50</u> ), 1960	—	—	—
Miller, Brandt, and Stroud ( <u>37</u> ), 1961	.0417	—	—
Canfield ( <u>14</u> ), 1962	-.0989	-.1089	-.1171
Blancett ( <u>6</u> ), 1966	.0281	.0250	.0218



TABLE 16. - Comparison of values of the compressibility factor of helium at 0° C obtained in this study with values obtained by various other investigators (expressed in terms of a percentage relative difference)--Continued

Investigator	450 atm	500 atm	600 atm
Jacquerod and Scheuer ( <u>31-32</u> ), 1905-1908	---	---	---
Onnes ( <u>41</u> ), 1908	---	---	---
Burt ( <u>13</u> ), 1910	---	---	---
Holborn, Otto, and Schultze ( <u>26-28</u> ) as given by Otto ( <u>43</u> ), 1915	---	---	---
Henning and Heuse ( <u>23</u> ), 1921	---	---	---
Baxter and Starkweather ( <u>4</u> ), 1926	---	---	---
Heuse ( <u>24</u> ), 1926	---	---	---
Boks and Onnes ( <u>7-8</u> ) as given by Nijhoff ( <u>39</u> ), 1928	---	---	---
Ellestad and Baxter ( <u>20</u> ), 1928	---	---	---
Ellestad and Baxter ( <u>21</u> ), 1929	---	---	---
Heuse and Otto ( <u>25</u> ), 1929	---	---	---
Wiebe, Gaddy, and Heins ( <u>51</u> ), 1931	0.1659	0.1569	0.1355
Keesom and Santen ( <u>33</u> ), 1933, and Santen ( <u>44</u> ), 1934	---	---	---
Burnett ( <u>12</u> ), 1936	---	---	---
Michels and Wouters ( <u>35</u> ), 1941	---	---	---
Oishi ( <u>40</u> ), 1942	---	---	---
Schneider ( <u>45</u> ), 1949	---	---	---
Schneider and Duffie ( <u>46</u> ), 1949	---	---	---
White, Rubin, Camky, and Johnston ( <u>50</u> ), 1960	---	---	---
Miller, Brandt, and Stroud ( <u>37</u> ), 1961	---	---	---
Canfield ( <u>14</u> ), 1962	-.1245	-.1303	---
Blancett ( <u>6</u> ), 1966	.0188	.0163	.0134

Year	1920	1921	1922
1920 (1)	1000	1000	1000
1921 (2)	1000	1000	1000
1922 (3)	1000	1000	1000
1923 (4)	1000	1000	1000
1924 (5)	1000	1000	1000
1925 (6)	1000	1000	1000
1926 (7)	1000	1000	1000
1927 (8)	1000	1000	1000
1928 (9)	1000	1000	1000
1929 (10)	1000	1000	1000
1930 (11)	1000	1000	1000
1931 (12)	1000	1000	1000
1932 (13)	1000	1000	1000
1933 (14)	1000	1000	1000
1934 (15)	1000	1000	1000
1935 (16)	1000	1000	1000
1936 (17)	1000	1000	1000
1937 (18)	1000	1000	1000
1938 (19)	1000	1000	1000
1939 (20)	1000	1000	1000
1940 (21)	1000	1000	1000
1941 (22)	1000	1000	1000
1942 (23)	1000	1000	1000
1943 (24)	1000	1000	1000
1944 (25)	1000	1000	1000
1945 (26)	1000	1000	1000
1946 (27)	1000	1000	1000
1947 (28)	1000	1000	1000
1948 (29)	1000	1000	1000
1949 (30)	1000	1000	1000
1950 (31)	1000	1000	1000
1951 (32)	1000	1000	1000
1952 (33)	1000	1000	1000
1953 (34)	1000	1000	1000
1954 (35)	1000	1000	1000
1955 (36)	1000	1000	1000
1956 (37)	1000	1000	1000
1957 (38)	1000	1000	1000
1958 (39)	1000	1000	1000
1959 (40)	1000	1000	1000
1960 (41)	1000	1000	1000
1961 (42)	1000	1000	1000
1962 (43)	1000	1000	1000
1963 (44)	1000	1000	1000
1964 (45)	1000	1000	1000
1965 (46)	1000	1000	1000
1966 (47)	1000	1000	1000
1967 (48)	1000	1000	1000
1968 (49)	1000	1000	1000
1969 (50)	1000	1000	1000
1970 (51)	1000	1000	1000
1971 (52)	1000	1000	1000
1972 (53)	1000	1000	1000
1973 (54)	1000	1000	1000
1974 (55)	1000	1000	1000
1975 (56)	1000	1000	1000
1976 (57)	1000	1000	1000
1977 (58)	1000	1000	1000
1978 (59)	1000	1000	1000
1979 (60)	1000	1000	1000
1980 (61)	1000	1000	1000
1981 (62)	1000	1000	1000
1982 (63)	1000	1000	1000
1983 (64)	1000	1000	1000
1984 (65)	1000	1000	1000
1985 (66)	1000	1000	1000
1986 (67)	1000	1000	1000
1987 (68)	1000	1000	1000
1988 (69)	1000	1000	1000
1989 (70)	1000	1000	1000
1990 (71)	1000	1000	1000
1991 (72)	1000	1000	1000
1992 (73)	1000	1000	1000
1993 (74)	1000	1000	1000
1994 (75)	1000	1000	1000
1995 (76)	1000	1000	1000
1996 (77)	1000	1000	1000
1997 (78)	1000	1000	1000
1998 (79)	1000	1000	1000
1999 (80)	1000	1000	1000
2000 (81)	1000	1000	1000
2001 (82)	1000	1000	1000
2002 (83)	1000	1000	1000
2003 (84)	1000	1000	1000
2004 (85)	1000	1000	1000
2005 (86)	1000	1000	1000
2006 (87)	1000	1000	1000
2007 (88)	1000	1000	1000
2008 (89)	1000	1000	1000
2009 (90)	1000	1000	1000
2010 (91)	1000	1000	1000
2011 (92)	1000	1000	1000
2012 (93)	1000	1000	1000
2013 (94)	1000	1000	1000
2014 (95)	1000	1000	1000
2015 (96)	1000	1000	1000
2016 (97)	1000	1000	1000
2017 (98)	1000	1000	1000
2018 (99)	1000	1000	1000
2019 (100)	1000	1000	1000

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TABLE 16. - Comparison of values of the compressibility factor of helium at 0° C obtained in this study with values obtained by various other investigators (expressed in terms of a percentage relative difference)--Continued

Investigator	700 atm	800 atm	900 atm	1000 atm
Jacquerod and Scheuer (31-32), 1905-1908	---	---	---	---
Onnes (41), 1908	---	---	---	---
Burt (13), 1910	---	---	---	---
Holborn, Otto, and Schultze (26-28) as given by Otto (43), 1915	---	---	---	---
Henning and Heuse (23), 1921	---	---	---	---
Baxter and Starkweather (4), 1926	---	---	---	---
Heuse (24), 1926	---	---	---	---
Boks and Onnes (7-8) as given by Nijhoff (39), 1928	---	---	---	---
Ellestad and Baxter (20), 1928	---	---	---	---
Ellestad and Baxter (21), 1929	---	---	---	---
Heuse and Otto (25), 1929	---	---	---	---
Wiebe, Gaddy, and Heins (51), 1931	0.1131	0.0921	0.0737	0.0578
Keesom and Santen (33), 1933, and Santen (44), 1934	---	---	---	---
Burnett (12), 1936	---	---	---	---
Michels and Wouters (35), 1941	---	---	---	---
Oishi (40), 1942	---	---	---	---
Schneider (45), 1949	---	---	---	---
Schneider and Duffie (46), 1949	---	---	---	---
White, Rubin, Camky, and Johnston (50), 1960	---	---	---	---
Miller, Brandt, and Stroud (37), 1961	---	---	---	---
Canfield (14), 1962	---	---	---	---
Blancett (6), 1966	.0135	---	---	---



Our data are consistently lower than Canfield's (14), amounting to 0.13 percent at 500 atm, but are only slightly higher than the results obtained by Blancett (6). The maximum deviation from Blancett's data is 0.031 percent at 200 atm, and the deviation decreases to 0.014 percent at 700 atm.

#### DISCUSSION OF RESULTS

In all of the various data treatments, we assumed that the pressure distortion coefficients of the pressure vessels were exactly known, that the expansion numbers were free of error, that random errors occurred only in the observed pressures, and that these errors were normally distributed. We also assumed that all data were taken at exactly 0° C.

Temperature corrections to the observed pressures, based on the observed temperatures reported in table 4 and on the PVT properties of helium obtained by Wiebe, Gaddy, and Heins (51), did not change any of the calculated quantities by more than seven percent of their calculated standard errors. No temperature corrections are applied to the data in this report.

Values for the pressure distortion coefficients reported by Briggs and Barieau (10) were used for all data treatments. Completely neglecting the correction for distortion of the pressure containers would introduce an error of about 0.1 percent into the compressibility





factor for helium at 700 atm. The distortion coefficients are known with a precision of better than 1 percent; therefore, any error in the compressibility factor due to error in the distortion coefficients is assumed to be negligible.

The expansion number is an exact cardinal number only if the volume  $V_2$  is completely evacuated before expansion from  $V_1$ . In practice there was always a residual pressure of about  $1.3 \times 10^{-5}$  atm or less after evacuation. The error due to the residual pressure would be about 4 parts in  $10^6$  at the lowest experimental pressure. The sensitivity of the piston gage was about 50 parts in  $10^6$  at the lowest pressure; therefore, the errors due to a residual pressure are negligible at both high and low pressures.

National Bureau of Standards calibration of our barometer indicated that barometric pressures should be accurate to better than 0.0002 atmosphere or better than 0.01 percent of the lowest experimental pressure.

The piston gage area is accurate to better than 0.01 percent according to the manufacturer. Suppose there is a small systematic error in the piston gage area which would lead to a constant percentage systematic error in the pressures. The evaluation of a compressibility factor is essentially the determination of a PV product divided by the PV product of the same mass of gas extrapolated to zero pressure; therefore, any constant error of the area of the piston gage cancels in the calculation of the compressibility factor. It does lead to an



error in the pressure with which we identify the compressibility factor.

An error of 0.01 percent in the pressure would be equivalent to errors in the compressibility factor that are between 10 and 25 percent of the standard errors listed in table 13. We conclude that any systematic error in the pressure due to an error in the piston gage area is small compared to the random errors in the pressure.

The maximum change of the piston gage temperature from the calibration temperature was  $5^{\circ}$  C; therefore, completely neglecting the correction for change of piston gage temperature would introduce errors of less than 0.01 percent into the pressure measurements. The magnitude of the probable error in the piston gage area temperature coefficient is not known; however, the error introduced into the pressure measurements due to a systematic error in the temperature coefficient should be less than the error introduced by neglecting the correction entirely and should be negligibly small.

National Bureau of Standards calibration of a similar piston gage indicated that the piston gage area pressure coefficient could be in error by as much as 30 percent. A 30 percent error in this coefficient would introduce a systematic error of about 0.01 percent into the compressibility factors at the highest pressures.

We wanted to determine if our treatment of the experimental data had the characteristics of the treatment of data which are known to be random. To answer this question, a set of data containing known



random errors was constructed. We constructed the random error data set by accepting the values of the parameters and of the calculated pressures contained in table 11 as the true values. We then applied random deviations to these true values by the use of random deviates (49). Weighting factors of  $P_r^{-3/4}$  were assumed. The product of the weighting factor and the variance was taken as  $2.32 \cdot 10^{-7}$ , which was obtained from table 8. We thus generated a set of observed pressures that were known to contain random errors of a size consistent with our experimental data.

These generated data were then treated both as separate runs and simultaneously.

In the simultaneous treatment, the calculated value of B differed from the assumed true value by 0.92 times the calculated standard error of B. The calculated value of C differed from the true value by 1.11 times the calculated standard error of C. The corresponding factor for D was 1.23 and for E, 1.33. The calculated value of N differed from the true value by 0.52 times the calculated standard error of N. The calculated compressibility factors all differed from the true values by about 0.90 times the calculated standard errors. The product of the weighting factor and the variance was  $2.27 \cdot 10^{-7}$ , which is within 3 percent of the true value.

The treatment of the generated data as separate runs did not yield results that were consistent with the input data for the weighting factor.



Our experimental data treatment has all of the characteristics of the simultaneous treatment of data with known random errors, except in two respects. First, there is a significant bias between the results obtained when the experimental data were treated as separate runs and when the data were treated simultaneously. Second, two out of seven of the mean pressure residuals differed from zero by more than a standard deviation.

The stated standard deviations are our best estimates of the random errors associated with the quantities recorded in this report. The deviations are standard deviations calculated by the usual first approximation of the law for the propagation of errors (2, 5, 34).

We suggest that the standard errors of the compressibility factors of table 13 should be multiplied by a factor of two to estimate the total random and systematic errors.

2. *ibid.*, 1926, pp. 20-22.
5. Birge, Raymond T. The Calculation of Errors by the Method of Least Squares. *Phys. Rev.*, v. 10, April 15, 1917, pp. 207-227.
6. Biancetti, Allen Leroy. Volumetric Behavior of Helium-Neon Mixtures at High Pressures and Moderate Temperatures. Ph.D. Thesis, Univ. Oklahoma, 1966, 228 pp., Univ. Microfilms, Inc., Ann Arbor, Mich., Order No. 66-13,196.

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Titles enclosed in parentheses are translations from the language in which the item was originally published.





REFERENCES<sup>7/</sup>

1. Barieau, Robert E. The Density of Moist Air From 0° C to Near 25° C and Near Atmospheric Pressure. Helium Research Center Internal Report 36, August 1963, 20 pp. On file at the Bureau of Mines Helium Research Center, Amarillo, Tex.
2. Barieau, Robert E., and B. J. Dalton. A Method for Treating PVT Data From a Burnett Compressibility Apparatus. BuMines Rept. of Inv. 7020, September 1967, 34 pp.
3. \_\_\_\_\_. Nonlinear Regression and the Principle of Least Squares. A Method of Evaluating the Constants and a New Method for Calculating Variances and Covariances. BuMines Rept. of Inv. 6900, 1967, 21 pp.
4. Baxter, Gregory Paul, and Howard Warner Starkweather. The Density and Atomic Weight of Helium. II. Proc. Nat. Acad. Sci. U.S., v. 12, 1926, pp. 20-22.
5. Birge, Raymond T. The Calculation of Errors by the Method of Least Squares. Phys. Rev., v. 40, April 15, 1932, pp. 207-227.
6. Blancett, Allen Leroy. Volumetric Behavior of Helium-Argon Mixtures at High Pressure and Moderate Temperature. Ph.D. Thesis, Univ. Oklahoma, 1966, 228 pp., Univ. Microfilms, Inc., Ann Arbor, Mich., Order No. 66-14,196.

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<sup>7/</sup> Titles enclosed in parentheses are translations from the language in which the item was originally published.



7. Boks, Johan Diederik Anne. Isothermen van Helium bij Temperaturen van  $+20^{\circ}$  C. tot  $-270^{\circ}$  C. en Verandering van de Dichtheid van Vloeibaar Helium Tussen  $4.2^{\circ}$  K. en  $1.2^{\circ}$  K. (Isotherms of Helium at Temperatures from  $+20^{\circ}$  C to  $-270^{\circ}$  C and Change in Density of Liquid Helium Between  $4.2^{\circ}$  K and  $1.2^{\circ}$  K). Ph.D. Thesis, Univ. Leiden, 1924, Eduard Ijdo, Leiden, 1924, 25 pp. (in Dutch).
8. Boks, J. D. A., and H. Kamerlingh Onnes. Communication on the Isotherms of Helium from  $20^{\circ}$  to  $-259^{\circ}$  C. Proc. Fourth Intern. Congress of Refrigeration, v. 1, 1924, pp. 81a-87a (in English). Isotherms of Monatomic Substances and Their Binary Mixtures. XXIII. Isotherms of Helium from  $20^{\circ}$  to  $-259^{\circ}$  C. Leiden Comm. No. 170a (in English).
9. Briggs, Ted C. Temperature Measurement with Leeds & Northrup Platinum Resistance Thermometer No. 1586182. Helium Research Center Internal Report 53, June 1964, 17 pp. On file at the Bureau of Mines Helium Research Center, Amarillo, Tex.
10. Briggs, Ted C., and Robert E. Barieau. Elastic Pressure Distortion of the Volumes of a Burnett Compressibility Apparatus Over the Temperature Range  $0^{\circ}$  to  $80^{\circ}$  C. BuMines Rept. of Inv. 7136, June 1968, 32 pp.
11. Brombacher, W. G., D. P. Johnson, and J. L. Cross. Mercury Barometers and Manometers. National Bureau of Standards Mono. 8, May 20, 1960, 59 pp.
12. Burnett, E. S. Compressibility Determinations Without Volume Measurements. J. Appl. Mech., v. 3, No. 4, December 1936, pp. A136-A140.



13. Burt, F. P. The Compressibilities of Helium and Neon. Trans. Faraday Soc., v. 6, 1910, pp. 19-26.
14. Canfield, Frank B., Jr. The Compressibility Factors and Second Virial Coefficients for Helium-Nitrogen Mixtures at Low Temperature and High Pressure. Ph.D. Thesis, Rice Univ., May 1962, 321 pp.
15. Canfield, F. B., T. W. Leland, and R. Kobayashi. Volumetric Behavior of Gas Mixtures at Low Temperatures by the Burnett Method: The Helium-Nitrogen System, 0° to -140° C. Advances in Cryogenic Engineering, v. 8, K. D. Timmerhaus, editor, Plenum Press, New York, 1963, pp. 146-157.
16. Canfield, Frank B., T. W. Leland, and Riki Kobayashi. Compressibility Factors for Helium-Nitrogen Mixtures. J. Chem. and Eng. Data, v. 10, No. 2, April 1965, pp. 92-96.
17. Cross, J. L. Reduction of Data for Piston Gage Pressure Measurements. National Bureau of Standards Mono. 65, June 17, 1963, 9 pp.
18. Dalton, B. J. Local Value of Acceleration of Gravity at the Helium Research Center (Potsdam System). Helium Research Center Memorandum Report 43, April 1964, 13 pp. On file at the Bureau of Mines Helium Research Center, Amarillo, Tex.
19. Douglas, Edward L., and R. Leroy Moffitt. Nonlinear Least-Squares Curve Fitting Program for Treating PVT Data Obtained From a Burnett Compressibility Apparatus. Helium Activity Internal Report (in process).



20. Ellestad, R. B., and Gregory Paul Baxter. The Compressibility of Helium Below One Atmosphere. *J. Am. Chem. Soc.*, v. 50, No. 3, March 1928, p. 617, footnote 28. Footnote appears in an article by Gregory Paul Baxter, Thirty-Fourth Annual Report of the Committee on Atomic Weights. Determinations Published During 1927. *J. Am. Chem. Soc.*, v. 50, No. 3, March 1928, pp. 603-617.
21. \_\_\_\_\_. The Compressibility of Helium Below One Atmosphere. *Phys. Rev. Supplement*, v. 1, 1929, p. 21, footnote 12A. Footnote appears in an article by Raymond T. Birge, Probable Values of the General Physical Constants. *Phys. Rev. Supplement*, v. 1, 1929, pp. 1-73.
22. Grout, Jarrell C. A General Computer Program for Solving Nonlinear Regression Problems. Helium Activity Internal Report, 1967, 37 pp. On file at the Bureau of Mines Helium Research Center Library.
23. Henning, F., and W. Heuse. Über die Spannungs- und Ausdehnungskoeffizienten von Helium, Wasserstoff und Stickstoff. (Pressure Volume Expansion Coefficients of Helium, Hydrogen and Nitrogen). *Ztschr. Physik*, v. 5, Nos. 5 and 6, 1921, pp. 285-314, (in German). Redstone Scientific Information Center, RSIC-49, August 28, 1963, 35 pp., (in English).
24. Heuse, W. Gasthermometrische Untersuchungen mit Helium, Neon, Stickstoff und Sauerstoff. (Gas-Thermometric Investigations with Helium, Neon, Nitrogen and Oxygen). *Ztschr. Physik*, v. 37, 1926, pp. 157-164, (in German).





25. Heuse, W., and J. Otto. Über eine Neubestimmung des Grenzwertes der Ausdehnungs- und Spannungskoeffizienten von Helium, Wasserstoff und Stickstoff. (A New Determination of the Limiting Value for the Expansion and Pressure Coefficients of Helium, Hydrogen, and Nitrogen). *Ann. Physik, Ser. 5*, v. 2, 1929, pp. 1012-1030, (in German).
26. Holborn, L., and J. Otto. Über die Isothermen von Stickstoff, Sauerstoff und Helium. (Isotherms of Nitrogen, Oxygen, and Helium). *Ztschr. Physik*, v. 10, 1922, pp. 367-376, (in German). Translated by T. C. O'Callaghan Associates, National Press Building, Washington, D.C., for U.S. Department of the Interior, Bureau of Mines, Washington, D.C., 7 pp., (in English). Translated by Dr. Frank E. E. Germann, National Bureau of Standards, Boulder, Colo., June 1964, 3 pp., (in English).
27. \_\_\_\_\_. Über die Isothermen einiger Gase Zwischen  $+400^{\circ}$  und  $-183^{\circ}$ . (The Isotherms of Various Gases Between  $+400^{\circ}$  and  $-183^{\circ}$ ). *Ztschr. Physik*, v. 33, 1925, pp. 1-11, (in German). Translated by T. C. O'Callaghan Associates, 1329 E. Street, N.W., Washington, D.C., for U.S. Department of the Interior, Bureau of Mines, Washington, D.C., 7 pp., (in English). Translated by Dr. Frank E. E. Germann, National Bureau of Standards, Boulder, Colo., June 1964, 3 pp., (in English).
28. Holborn, L., and H. Schultze. Über die Druckwage und die Isothermen von Luft, Argon und Helium zwischen 0 und  $200^{\circ}$ . (Isotherms of



- Air, Argon and Helium Between 0 and 200°). *Ann Physik*, (4e), v. 47, 1915, pp. 1089-1111, (in German). Translation on file at the Bureau of Mines Helium Research Center Library, 17 pp., (in English).
29. Hoover, Alan Ellsworth. Virial Coefficients of Methane and Ethane. Ph.D. Thesis, Rice Univ., November 1965, 174 pp., Univ. Microfilms, Inc., Ann Arbor, Mich., Order No. 66-10,349.
30. Hoover, Alan E., Frank B. Canfield, Riki Kobayashi, and Thomas W. Leland, Jr. Determination of Virial Coefficients by the Burnett Method. *J. Chem. and Eng. Data*, v. 9, No. 4, October 1964, pp. 568-573.
31. Jacquerod, Adrien, and Otto Scheuer. Sur la Compressibilité de Différents Gaz Au-Dessous de  $1^{\text{atm}}$  et la Détermination de Leurs Poids Moléculaires. (On the Compressibilities of Different Gases at a Pressure of 1 atm and the Determination of Their Molecular Weights). *Compt. Rend.*, v. 140, 1905, pp. 1384-1386.
32. \_\_\_\_\_. Sur la Compressibilité de Quelques Gaz a 0° Au-Dessous de 1 Atmosphère. (On the Compressibility of Some Gases at 0° and at Less than 1 Atmosphere). *Mém. Soc. Phys. et Hist. Nat. de Genève*, v. 35, 1908, pp. 659-680.
33. Keesom, W. H., and J. J. M. Van Santen. Isothermals of Helium at Temperatures of 0, 20 and 100° C., and Pressures from 5.5 to 16.5 Atmospheres. *Proc. Roy. Acad. Sci. Amsterdam*, v. 36, 1933, pp. 813-821, (in English). Leiden Comm. No. 227b, (in English).



34. Merriman, Mansfield. A Textbook on the Method of Least Squares. John Wiley and Sons, Inc., New York, 8th ed., 1911, pp. 75-79.
35. Michels, A., and H. Wouters. Isotherms of Helium Between 0° and 150° C up to 200 Amagat. *Physica*, v. 8, No. 8, September 1941, pp. 923-932.
36. Miller, John E. Description of a High Pressure High Accuracy Burnett Compressibility Apparatus. BuMines Inf. Circ. 8350, October 1967, 10 pp.
37. Miller, J. E., L. W. Brandt, and L. Stroud. Compressibility Factors for Helium and Helium-Nitrogen Mixtures. BuMines Rept. of Inv. 5845, 1961, 11 pp.
38. Mueller, William H. Volumetric Properties of Gases at Low Temperatures by the Burnett Method. Ph.D. Thesis, Rice Univ., December 1959, 138 pp.
39. Nijhoff, Guillaume Paul. Metingen van den Tweeden Virial-Coëfficient van Zuurstof, Waterstof en Helium bij Lage Temperaturen. (Measurements of the Second Virial Coefficient of Oxygen, Hydrogen and Helium at Low Temperatures). Ph.D. Thesis, Univ. Leiden, 1928. Martinus Nijhoff, 1928, Boek-En Steendrukkeij Eduard Ijdo, Leiden, 80 pp., (in Dutch).
40. Oishi, Jiro. 0°- and 100°-Isotherms of Helium, Hydrogen, Neon, Argon, Air and Carbon Dioxide at Pressures Below 2 Atmospheres and the Absolute Temperature of 0° C. *J. Sci. Res. Inst. (Tokyo)*, v. 43, No. 1203, 1949, pp. 22-33 (220-231), (in English). *Bull. Inst. Phys. Chem. Res.*, v. 21, 1942, pp. 1119-1133, (in Japanese).



41. Onnes, H. Kamerlingh. Isothermen van één-Atomige Gassen en hun Binaire Mengsels. I. Isothermen van Helium Tusschen  $+100^{\circ}$  C. en  $-217^{\circ}$  C. (Isotherms of Monatomic Gases and Their Binary Mixtures. I. Isotherms of Helium Between  $+100^{\circ}$  C and  $-217^{\circ}$  C). Verslag Akad. Wetenschappen Amsterdam, v. 16, June 1908, pp. 495-501, (in Dutch). Leiden Comm. No. 102a, (in English). Proc. Roy. Acad. Sci. Amsterdam, v. 10, July 1908, pp. 445-450, (in English).
42. Osborne, Nathan S., Harold F. Stimson, and Defoe C. Ginnings. Thermal Properties of Saturated Water and Steam. J. Res. Nat. Bureau of Standards, v. 23, Research Paper RP 1229, August 1939, pp. 261-270.
43. Otto, Jos. Thermische Zustandsgrößen der Gase bei Mittleren und Kleinen Drucken. Handbuch der Experimentalphysik. W. Wien and F. Harms, editors, Akademische Verlagsgesellschaft M. B. H. Leipzig, v. 8, Part 2, 1929, pp. 79-240, (in German).
44. Santen, Jacobus Johannes Marie Van. Metingen van de Tweede Viriaalcoëfficient van Helium bij  $0^{\circ}$  C.,  $20^{\circ}$  C. en  $100^{\circ}$  C. (Measurements of the Second Virial Coefficient of Helium at  $0^{\circ}$  C,  $20^{\circ}$  C and  $100^{\circ}$  C). Ph.D. Thesis, Univ. Leiden, 1934, N. V. Boek-En Steendrukkeij Eduard Ijdo, Leiden, 88 pp., (in Dutch).
45. Schneider, W. G. Compressibility of Gases at High Temperatures. I. Methods of Measurement and Apparatus. Canadian J. Res., v. 27, Sec. B, April 1949, pp. 339-352.
46. Schneider, W. G., and J. A. H. Duffie. Compressibility of Gases at High Temperatures. II. The Second Virial Coefficient of Helium in the Temperature Range  $0^{\circ}$  C to  $600^{\circ}$  C. J. Chem. Phys.,





- v. 17, No. 9, September 1949, pp. 751-754.
47. Suh, Kyung Won. P-V-T Properties of Methyl Chloride at High Temperatures and Pressures. Ph.D. Thesis, Univ. of Missouri, June 1965, 166 pp., Univ. Microfilms, Inc., Ann Arbor, Mich., Order No. 65-14,505.
48. Suttle, Elmer T., David E. Emerson, and Diana W. Burfield. High Pressure Mass Spectrometry for Analysis of Trace Impurities in Helium. *Anal. Chem.*, v. 38, No. 1, January 1966, pp. 51-53.
49. The Rand Corporation. A Million Random Digits with 100,000 Normal Deviates. The Free Press, New York, Third Printing, 1966, 600 pp.
50. White, David, Thor Rubin, Paul Camky, and H. L. Johnston. The Virial Coefficients of Helium from 20 to 300° K. *J. Phys. Chem.*, v. 64, No. 11, November 1960, pp. 1607-1612.
51. Wiebe, R., V. L. Gaddy, and Conrad Heins, Jr. The Compressibility Isotherms of Helium at Temperatures from -70 to 200° and at Pressures to 1000 Atmospheres. *J. Am. Chem. Soc.*, v. 53, No. 5, May 1931, pp. 1721-1725.



## APPENDIX A

The compressibility apparatus used in this investigation was similar to Burnett's original apparatus. For completeness, the component parts of the apparatus are described.

The high-pressure jacketed containers used in this investigation were designed by Miller (36)<sup>1/</sup>. The containers were fabricated to

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<sup>1/</sup> See list of references at the end of the main report.

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Miller's specifications by Amarillo Helium Plant machine shop personnel. All other major equipment items incorporated into the present apparatus were obtained commercially.

The high-pressure containers were almost identical in size and were surrounded by integral oil-filled pressure jackets. The two containers had a volume ratio,  $(V_1 + V_2)/V_1$ , of about 1.99 when connected with the various valves and fittings which are component parts of  $V_1$  and  $V_2$ . Subsequent to Burnett's original publication, most investigators (including Burnett) have selected a volume ratio of about 1.5. The pressure jackets of the containers of this investigation were used to determine elastic pressure distortion coefficients as described by Briggs and Barieau (10), but the jackets were not used in the present study. All of the components constituting volumes  $V_1$  and  $V_2$  were assembled in a constant temperature bath; therefore, all



of the gas sample confined in volume  $V_1$  or  $(V_1 + V_2)$  was at the bath temperature.

The constant temperature bath used in this investigation was a Chandler Engineering Company<sup>2/</sup> model 22-1 bath assembly. It was

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<sup>2/</sup> Manufacturers are identified to allow the reader to obtain detailed descriptive literature of commercially available items. This identification should not be construed as Bureau of Mines endorsement or recommendation of any particular product or manufacturer.

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supplied with a 1,000-watt immersion heater, a 500-watt immersion heater controlled by a variable transformer, and a 100-watt immersion heater. Heat exchange coils of 1/4-inch outside diameter copper tubing were built into the bath. Various fluids could be circulated through the coils. The bath was supplied with an internal circulating pump for the bath fluid, and a 1/30 horsepower Aminco electric motor-driven propeller type stirrer was added to obtain sufficient agitation for good temperature control. Refrigeration was supplied to the compressibility bath by pumping fluid through the heat exchange coils from an external tank. The external tank contained a 750-watt immersion heater, a 500-watt immersion heater controlled by a variable transformer, a 100-watt immersion heater, and the refrigeration coils of a Tecumseh model C2513HTK refrigeration unit. The



refrigeration unit was controlled by a relay system actuated by a mercury thermoregulator. Temperature of the fluid in the external tank was controlled within about  $\pm 0.03^{\circ}$  C of the set temperature by the on-off action of the refrigeration unit. Fluid was pumped through the heat exchange coils of the compressibility bath by a Viking model F656G positive displacement pump with a built-in relief valve. There was a pressure drop of almost 50 psi through the heat exchange coils. The pump discharged about 1 1/2 gallons per minute of fluid and was driven by and mounted on a 1/3-horsepower explosion proof electrical motor. The pump operated at 1750 revolutions per minute.

Fine temperature control of the compressibility bath was obtained by supplying a small amount of extra refrigeration to the bath and controlling the temperature with the 100-watt immersion heater. Power to the 100-watt immersion heater was supplied through a Hallikainen model 1053A Thermotrol temperature controller with a model 1080A temperature-sensing element. The temperature controller was actuated by a  $\pm 0.001^{\circ}$  C change in the bath temperature. The Thermotrol temperature controller can be operated in any one of three modes designated by the manufacturer as on-off, proportional, or proportional with reset. For on-off operation, the controller is an alternating current Wheatstone bridge with the resistance thermometer sensing element the variable arm of the bridge. An adjustable arm of the bridge is used to select the temperature setting for bridge balance. A change of





resistance of the sensing element produces an alternating current voltage which is amplified by a resistance-coupled amplifier. This voltage is applied as a bias voltage to a thyratron tube which controls an enclosed mercury relay, thus turning the heater on and off. A negative feedback signal is applied during proportional operation to produce a heater-on period which is a function of the bridge unbalance voltage. A positive feedback circuit with an appropriate time constant is added to the negative feedback circuit in order to restore the alternating current bridge unbalance to zero during proportional with reset operation. The temperature controller proportions the heat output by time cycle modulations. The controller was operated in the proportional-with-reset mode for all of the experimental runs of this investigation. The setting of the temperature controller was sensitive to changes in the ambient temperature. It was necessary to adjust the setting of the controller occasionally in order to maintain a particular bath temperature if there were significant changes in the ambient temperature.

The compressibility bath was filled with a 10 percent by volume methyl alcohol in water antifreeze mixture for the 0° C compressibility runs. A 50 percent by volume ethylene glycol in water antifreeze mixture was circulated from the external tank through the compressibility bath heat-exchange coils.



Compressibility bath temperatures were measured with a Leeds & Northrup Company model 8163, serial No. 1586182 platinum resistance thermometer. The thermometer was calibrated by the company in February 1962 by measurements at the ice point, steam point, boiling point of sulphur, and boiling point of oxygen. Constants were supplied by the company for use in the Callendar and modified Callendar temperature interpolation formulas. Temperatures measured with the platinum resistance thermometer were in terms of the International Practical Temperature Scale (IPTS). The calibrated thermometer should reproduce temperatures on the IPTS within  $\pm 0.01^\circ \text{C}$ , provided the thermometer is used with a calibrated resistance bridge and a reliable value is used for the resistance of the thermometer at the ice point.

A value of  $25.54626 \pm 0.00004$  absolute ohms for the ice point resistance of platinum resistance thermometer serial No. 1586182 was derived from measurements made by Briggs (9) at the triple point of water. The measurements were made in this laboratory in June 1964 by using a Leeds & Northrup Company model 8069 G-2 Mueller bridge, serial No. 1603629. All subsequent resistance measurements for thermometer No. 1586182 were made with bridge No. 1603629. A constant current of 2 milliamperes was supplied through the thermometer for all resistance measurements. The bridge was calibrated by the manufacturer in August 1962. Corrections were provided with sufficient precision to determine a resistance greater than 1 ohm to about 2 parts in  $10^5$  at the time of



the calibration. The bridge can be used to measure resistances over the range 0 to 111.111 ohms. The smallest decade step is 0.0001 ohm. A temperature change of  $0.001^{\circ}$  C changed the resistance of the platinum resistance thermometer by about 0.0001 ohm at  $0^{\circ}$  C. The bridge was supplied with a mercury-contact commutator for reversing the connections to the four-lead platinum resistance thermometer for the purpose of minimizing the effect of thermometer lead resistance.

Critical resistance coils of the bridge were mounted by the manufacturer in a thermally insulated chamber, the temperature of which was kept constant by means of an electrical heater controlled by a thermoregulator. The manufacturer's literature states that the constant temperature chamber holds critical measuring resistors constant within  $\pm 0.01^{\circ}$  C. The bridge was calibrated with the built in thermometer reading  $34.5^{\circ}$  C. All platinum resistance thermometer measurements were made with the bridge thermometer indicating a constant temperature of  $34.5^{\circ}$  C. This arrangement eliminated the need to make temperature corrections to the bridge resistance readings.

A Keithley Instruments, Inc., model 149 electronic milli-microvoltmeter was used as a bridge null detector. The milli-microvoltmeter had a range of measurements from 0.1 microvolt full scale to 100 millivolts. All thermometer resistance measurements were made when the bridge thermoregulator was off. The null detector was rather sensitive to line voltage disturbances; however, the electronic null detector eliminated many of the problems associated with the use of a



moving-coil galvanometer.

Gas samples in the pressure containers were separated from oil of the pressure-measuring system by a Ruska Instrument Corporation model 2416, serial No. 9032 differential pressure cell. The differential pressure cell used in this investigation was modified by the manufacturer so that it could be immersed in the compressibility bath fluid. Oil of the pressure-measuring system was separated from gas of the sample system by a thin stainless steel diaphragm located within the differential pressure cell. The differential pressure cell was designed to safely withstand an overpressure of 15,000 psi on either side of the diaphragm. The pressure differential across the diaphragm was kept as small as possible during operation to insure maximum diaphragm life. The position of the diaphragm was established by the movement of a stem soldered to the diaphragm. As the diaphragm moved, the stem moved a core within the coils of a very sensitive differential transformer. Output of the differential transformer was indicated by an electronic meter. Maximum sensitivity of the differential pressure cell meter was about 0.0001 psi. The meter was zeroed before each run with atmospheric pressure applied to both sides of the diaphragm.

The zero of the differential pressure cell changed with changing operating pressure. Ruska Instrument Corporation provided calibration data to correct for a change of the cell zero due to a change of the cell operating pressure. Large overpressures were avoided on either





side of the diaphragm in order to prevent a change of the cell zero during a compressibility run. It was not possible to apply a numerical correction for zero shift due to overpressures; therefore, any small overpressures that were necessary during a run were applied consistently to the oil side of the diaphragm. The upper chamber of the diaphragm cell was oil-filled, and the lower chamber was connected to the gas sample volumes. Volumes of the upper and lower chambers of the cell were about  $29.5 \text{ cm}^3$  and  $0.6 \text{ cm}^3$ , respectively. Gas pressures on the sample side of the diaphragm were balanced on the oil side of the diaphragm by an oil-lubricated piston gage.

The piston gage used in this investigation was a Ruska Instrument Corporation model 2400 gage, serial No. 9274, with the high-range piston-cylinder assembly. It was calibrated in February 1962 by the manufacturer by comparison against Ruska Instrument Corporation master gage serial No. 7544. The effective area of the Ruska Instrument Corporation master gage was determined at the National Bureau of Standards and was reported by the manufacturer to be correct to one part in  $10^4$  at  $25^\circ \text{ C}$ . Since the comparison of gage No. 9274 against master gage No. 7544 was carried out with a precision of a few parts per million, then the calibration accuracy of gage No. 9274 should be of similar accuracy as the master gage.

Ruska Instrument Corporation supplied calibration data for the individual piston gage weights, a value for the effective piston gage



area at 25° C and atmospheric pressure, a coefficient to correct for a change of effective piston gage area as a function of pressure, and a coefficient to correct for change of gage temperature from the calibration temperature. The range of the piston gage used in this investigation was from 30 to 12,140 psig. A special weight set was purchased with the gage so that the entire pressure range could be covered in increments of 0.001 psig. The minimum resolution of the piston gage was stated by the manufacturer to be 5 parts per million at full load, decreasing to 50 parts per million at tare load. The cylinder of this piston gage is of the re-entrant type in which the effective portion of the cylinder is subjected to the measured pressure at the external cylinder wall; therefore, the gage can be used at high pressures without an excessive fall rate of the piston and weight load.

The height of the piston gage was adjusted, by placing accurately machined brass blocks under the piston gage legs, so that the reference plane of the piston gage was at the level of the diaphragm of the differential pressure cell. The zero of a Ruska Instrument Corporation model 2409 oil manometer was set at the level of the reference plane of the piston gage and the diaphragm of the differential pressure cell. No oil pressure head corrections were required for the apparatus used in this investigation.

The pressure containers were placed horizontally in the compressibility bath. The center of the jacketed container portion of  $V_1$  was



about 7.0 cm below the diaphragm of the differential pressure cell, and the center of the jacketed container portion of  $V_2$  was about 10.2 cm below the level of the diaphragm. A correction would obviously have to be made for a gas head if one were interested in the pressure at some level in the pressure containers below the level of the diaphragm. The gas head correction is small for helium (less than 1.5 parts per million at the center of  $V_2$  at 800 atmospheres) but would be more significant for a gas such as nitrogen. No gas head corrections were applied to the data of this report.

Barometric pressures were measured with a Henry J. Green Instruments, Inc., model 16, serial No. 13346 Fortin type mercurial barometer. Barometer serial No. 13346 was calibrated at the National Bureau of Standards in May 1964<sup>3/</sup>. All barometer readings for the data of this

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<sup>3/</sup> National Bureau of Standards Report of Calibration Identification No. P7068. On file in the Bureau of Mines Helium Research Center library.

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report were made to the nearest 0.05 millimeter of mercury. The barometer was supplied with an integral mercury-in-glass thermometer graduated in 0.05° C increments.

Relative humidity in the PVT laboratory was measured with a sensitive hygrometer manufacturer by Bacharach Industrial Instrument



Company. The hygrometer was read to the nearest 1 percent. The manufacturer stated an accuracy of  $\pm 1.5$  percent relative humidity for the hygrometer.

The PVT apparatus was evacuated with a Welch Scientific Company model 1400B high-vacuum pump. The manufacturer claimed an ultimate vacuum capability of 0.1 micron for the vacuum pump.

Vacuum was measured with a Consolidated Vacuum Corporation model GPH-100A vacuum gage with a GPH-001 cold cathode ionization tube. The vacuum gage was designed to measure pressures over the range  $1 \times 10^{-7}$  to  $25 \times 10^{-3}$  millimeters of mercury. The actual vacuum attained in the compressibility apparatus, as indicated by the vacuum gage, ranged between 5 and 10 microns.

The compressibility containers were filled with gas by use of a Corblin model B2C1000 diaphragm-type compressor. The compressor was designed for use to 15,000 psi with a compression ratio of 20 to one. Less than 5 minutes were required to fill the pressure containers to the maximum operating pressure with the Corblin compressor.





## APPENDIX B

The following description outlines the procedure used to obtain the data.

Temperature of the compressibility bath was lowered to  $0^{\circ}\text{C}$  by pumping refrigerated fluid through the heat exchange coils. The bath temperature controller and the refrigerator mercury thermoregulator were adjusted until the compressibility bath temperature was maintained at the desired level. Temperature of the external tank was controlled at about  $-3.5^{\circ}\text{C}$  in order to maintain the bath at  $0^{\circ}\text{C}$ .

The gas side of the differential pressure cell was opened to atmospheric pressure. The valve to the oil manometer was opened, and the level of the oil in the manometer was adjusted to correspond to the level of the diaphragm of the differential pressure cell. The readout meter of the differential pressure cell was set at maximum sensitivity, and the meter was zeroed.

The gas system was evacuated, then purged and filled to supply cylinder pressure with test gas. Volume  $V_1$ , which had been previously evacuated, was filled with test gas by slowly expanding the gas from  $V_2$  into  $V_1$  while simultaneously maintaining a slight overpressure on the oil side of the differential pressure cell diaphragm. The valve between  $V_1$  and  $V_2$  was closed, then  $V_2$  was filled with test gas to a high pressure by use of the compressor. Volume  $V_1$  was filled with test gas at high pressure by expansion from  $V_2$  while simultaneously maintaining a small overpressure on the oil side of the



differential pressure cell diaphragm by use of oil displacement pump No. 1. The valve was closed between  $V_1$  and  $V_2$ , and gas in  $V_2$  was vented to the atmosphere. Volume  $V_2$  was then evacuated with the vacuum pump. The rather awkward and inefficient filling procedure described above was necessary because the compressor and compressor controls were located in one room and the remainder of the apparatus was located in another room. In addition, it was necessary to avoid large overpressure on either the oil or gas sides of the differential pressure cell diaphragm to prevent a change in the cell zero during a run.

Gas in  $V_1$  was allowed to reach temperature equilibrium. Gas pressure in  $V_1$  was balanced with oil pressure by adjusting the piston gage load until the differential pressure cell meter indicated the null position. Temperature equilibrium was assumed to be established when the piston gage indicated a stable pressure. The designations of weights on the piston gage, piston gage temperature, barometer scale reading, barometer temperature, relative humidity, and the resistance of the platinum resistance thermometer were recorded. The differential pressure cell was closed off from the oil pump and piston gage, and the piston gage was lowered to its rest position by slowly decreasing the pressure with the oil displacement pump. The piston gage was isolated from the system by closing the valve between the oil pump and the piston gage. Oil pressure was raised to equal the gas pressure



by use of the oil displacement pump, and the valve to the differential pressure cell was opened. Vacuum in  $V_2$  was measured with the vacuum gage, the valve to the vacuum pump was closed, and the high-pressure exhaust valve from  $V_2$  was closed. Gas in  $V_1$  was slowly expanded into the evacuated  $V_2$ . A small overpressure was maintained on the oil side of the differential pressure cell diaphragm during the expansion. It was important that any over-pressure be maintained consistently on the oil side of the diaphragm. If large overpressures had been applied alternately to the oil and gas sides of the diaphragm, there would have been a change in the zero position of the diaphragm. Zero shift of the diaphragm due to large overpressures, alternately on the oil and gas sides of the diaphragm, could have introduced errors of as much as 0.02 psi in the measured pressures, according to the manufacturer's calibration report.

Gas in  $V_1$  and  $V_2$  was allowed to reach thermal equilibrium, as determined by a stable pressure indication. Usually, temperature equilibrium was attained in 30 minutes or less. The piston gage was isolated from the system, and the differential pressure indicator was maintained in the zero position with the oil displacement pump as the expansion valve between  $V_1$  and  $V_2$  was slowly closed. Gas in  $V_2$  was vented to the atmosphere and  $V_2$  was evacuated after the expansion valve was closed. There was no detectable change of temperature of  $V_1$  or of the compressibility bath temperature during the venting and



evacuation of  $V_2$ . The valve to the piston gage was reopened. Weights on the piston gage were adjusted until a null position was indicated by the differential pressure cell meter. All of the necessary observations were recorded. Then another expansion was made from  $V_1$  into an evacuated  $V_2$ . The measuring and expansion sequence was continued until the lowest pressure that could be measured with the piston gage was reached.







