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GRADUATE COLLEGE

# VOLUMETRIC BEHAVIOR OF THE HELIUM-ARGON SYSTEM AT HIGH PRESSURE AND LOW TEMPERATURE WITH A PERTURBATION EQUATION OF STATE FOR METHANE

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

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in partial fulfillment of the requirements for the

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DOCTOR OF PHILOSOPHY

BY

JOSEPH ALLAN PROVINE, JR.

Norman, Oklahoma

# VOLUMETRIC FEHAVIOR OF THE HELIUM-ARGON SYSTEM AT HIGH PRESSURE AND LOW TEMPERATURE WITH A PERTURBATION EQUATION OF STATE FOR METHANE

APPROVED BY

DISSERTATION COMMITTEE

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#### ABSTRACT

This work is a continuation of a project at the University of Oklahoma to measure compressibility factors of gases very accurately at high pressure and low temperature. A Burnett apparatus was used to obtain the experimental data for the helium-argon system. The results are reported for the two pure components and four mixtures for three isotherms ranging from 143°K to 183°K.

The method of treating the data to obtain the optimum virial coefficients and compressibility factors uses an orthonormal polynomial, nonlinear curve fitting technique to obtain initial estimates of the apparatus constants and virial coefficients. Then a Newton-Raphson procedure is used to converge to the optimum set of parameters based on a defined best fit criterion. The compressibility factors are calculated at each experimental pressure from the optimum virial coefficients using the Leiden form of the virial expansion. Estimates of the standard errors in the parameters and in the data are also determined.

A perturbation equation of state for methane is proposed that is based on theoretical results until the functional form of the cutoff parameter is determined.

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The analysis then becomes empirical in that experimental methane data along with an orthonormal polynomial curve fitting scheme are used to determine the coefficients in an expansion for the cutoff parameter. The curve fit uses a set of weighting factors that are calculated from the square of the changes in density with respect to cutoff parameter. The proposed equation of state covers the temperature range 114° to 623°K with most of the low temperature data in the liquid region. The equation of state predicts calculated densities that are within one percent or better of the experimental densities over the entire temperature range. The accuracy of prediction suffers somewhat for the present because of discrepancies in the low temperature data that were not determined until the work was completed.

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### NOMENCLATURE

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A	Free energy
A <sub>i</sub>	Run constant for i <sup>th</sup> run
B <sub>i</sub>	Virial Coefficients in Leiden expansion
<sup>B</sup> ij	Second interaction virial coefficients
c <sub>i</sub>	Coefficients of $\beta$ in equation of state development
C <sub>ijk</sub>	Third interaction virial coefficients
d <sup>2</sup>	Kaplan's prediction factor
DPC	Differential pressure cell
G (3)	Laplace transform of rg <sub>o</sub> (r)
MW	Molecular weight
MZS	Measured zero shift (MZS is negative in sign if the movement of the diaphragm after a pressure balance is toward the lower volume in order to obtain an electronic null reading).
N.j	Cell constant for j <sup>th</sup> expansion
N <sub>co</sub>	Cell constant at zero pressure
Р	Pressure
Po	Initial pressure
P <sub>B</sub>	Barometric pressure
P <sub>G</sub>	Gage Pressure .
P <sub>j</sub>	Pressure on j <sup>th</sup> expansion
P <sub>L</sub>	Pressure in lower chamber of differential pressure cell
P <sub>rj</sub>	Experimental pressures

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P <sub>U</sub>	Pressure in upper chamber of differential pressure cell
R	Gas constant
S	Objective function to be minimized
s <sup>2</sup>	Variance
т	Temperature, °K
т <sub>с</sub>	Critical temperature
T <sup>*</sup>	Reduced temperature
U <sub>1</sub> (s)	Inverse Laplace of ru(r)
U <sub>2</sub> (s)	Inverse Laplace of ru <sup>2</sup> (r)
U <sub>3</sub> (s)	Inverse Laplace of ru <sup>3</sup> (r)
v	Potential energy
v <sub>a</sub>	Volume of upper Burnett cell
v <sub>b</sub>	Volume of lower Burnett cell
v <sub>c</sub>	Critical volume
v <sub>o</sub>	Potential energy of unperturbed system
v <sub>1</sub>	Perturbation potential energy
W <sub>i</sub>	Statistical weighting factors
W <sub>rj</sub>	A priori weighting functions
Z	Compressibility factor
a (p)	Hard-sphere equation of state
a <sub>i</sub> (v)	Zwanzig's equation of state coefficients
a mn	Coefficients in expansion for cutoff parameter
a <sub>ts</sub>	Elements of coefficient matrix
Ъ	Hard-sphere second virial coefficient
b <b>(p)</b>	Coefficient of $\beta$ term
pq d	Elements of inverted coefficient matrix

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С	Cutoff parameter
c (p)	Coefficient of $\beta^2$ term
đ	Hard-sphere diameter
đ (p)	Coefficient of $\beta^3$ term
f <sup>*</sup> i	Kozak and Rice's fluctuation terms
f(s, <b>ŋ</b> )	$\frac{\partial}{\partial \rho} [\rho G(s)]$
g <sub>o</sub> (r)	Hard-sphere radial distribution function
k	Boltzmann's constant
k <sub>i</sub>	Pressure distortion correction constants
m	Mass
m i	Pressure distortion correction constants
n	Number of moles
r	Distance
S	Variable in Laplace domain for $G(s)$ and in inverse Laplace domain for $U_1(s)$
u(r)	Pair potential function
v	Molal volume
ν(d,σ, α,γ;R)	Barker and Henderson's modified pair potential function
×i	Mole fraction
Greek	
α	Inverse-steepness parameter
ß	Reciprocal of kT
γ	Depth parameter
∆ <sub>rj</sub>	Difference between experimental and calculated pressures
∆p <sub>H</sub>	Combined gaseous and hydraulic head correction

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<b>∆</b> P <sub>ZSC</sub>	Cryogenic DPI zero shift correction (sign same as MZS)
∆p <sub>zsr</sub>	Room temperature DPI zero shift correction (sign same as MZS)
E	Characteristic energy
η	Dimensionless product
θ <sub>i</sub>	General parameter in data analysis
Ę	Cube of cutoff parameter
ρ	Density
σ	Molecular diameter
<b>Φ(v)</b>	Zwanzig's rigid sphere equation of state

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# VOLUMETRIC BEHAVIOR OF THE HELIUM-ARGON SYSTEM AT HIGH PRESSURE AND LOW TEMPERATURE WITH A PERTURBATION EQUATION OF STATE FOR METHANE

#### CHAPTER I

#### INTRODUCTION

This thesis is a report of the experimental determination of the volumetric behavior of gaseous mixtures at moderately low temperatures and high pressure. An apparatus based on the experimental method of Burnett (7) was used to determine the compressibility factors of the helium-argon system. The results of the investigation are reported for helium, argon, and four mixtures having compositions of 21.99, 41.05, 59.35, and 80.00 mole percent helium in argon.

The experimental temperatures were chosen so that the resulting compressibility factors would be evenly spaced rather than the temperatures. The compressibility factors do not vary as rapidly at higher temperatures as they do at lower temperatures. Therefore the temperatures are more closely spaced at the lower values. The isotherms chosen were those at -90°C, -115°C, and -130°C. The selection of these temperatures also allowed comparison

of the pure helium data as reported by Canfield (8). At the first two temperatures all runs were made with an initial pressure of 10,000 psi. Since -130°C is below the critical temperature of argon, the initial pressure for all runs containing argon was determined from the heliumargon phase diagram presented by Streett (35).

The Burnett apparatus consists essentially of two thermostated cells of undetermined volume connected by a valve with the necessary pressure and temperature measuring instruments. When the cryostat is at the desired temperature and with the valves between the two cells closed, the upper cell is pressured up to the predetermined initial pressure. After the temperature has equilibrated, the pressure in the upper cell is measured. Then the gas is expanded into the lower cell by opening the valve. After the temperature has come to equilibrium again, the pressure is again determined. Then the valve is closed, and the lower cell is vented and evacuated. The gas is then expanded into the lower cell and the pressure measured after temperature equilibration is attained. This procedure of expanding, measuring pressure, venting, and evacuating is continued until the minimum pressure is reached. The series of pressures obtained constitutes a run. Other runs can be made with different starting pressures to better define the isotherm for a given gas composition.

As can be seen by the above description, neither the mass of the experimental gas nor the volumes of the cells is needed. This is one of the advantageous features of using the Burnett experimental method.

The following analysis conforms with the above procedure for using the Burnett apparatus. Initially the equation describing the gas in the cell is given by

$$P_{O}(V_{a})_{O} = n_{O}Z_{O}RT, \qquad (1)$$

where P is the pressure,  $V_a$  is the volume of the upper cell, n is the number of moles of gas, Z = PV/nRT is the compressibility factor, R is the gas constant, and T is the temperature.

After the first expansion the equation becomes

$$P_1(V_a + V_b)_1 = n_0 Z_1 RT,$$
 (2)

where  $V_{b}$  is the volume of the lower cell. When the value is closed and the gas in the lower cell is vented, the equation is

$$P_1(V_a)_1 = n_1 Z_1 RT$$
 (3)

If this is continued until the j<sup>th</sup> expansion, then before the j<sup>th</sup> expansion

$$P_{j-1}(v_a)_{j-1} = n_{j-1}Z_{j-1}^{RT}$$
 (4)

and after the j<sup>th</sup> expansion

$$P_{j}(V_{a} + V_{b})_{j} = n_{j-1}Z_{j}RT$$
 (4)

Dividing equation (5) by equation (4)

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$$\frac{P_{j}(V_{a} + V_{b})_{j}}{P_{j-1}(V_{a})_{j-1}} = \frac{n_{j-1}Z_{j}RT}{n_{j-1}Z_{j-1}RT}$$
(6)

If the cell constant  $N_j$  is defined to be

$$N_{j} = \frac{(v_{a} + v_{b})_{j}}{(v_{a})_{j-1}}$$
, (7)

then equation (6) can be written

$$\frac{z_{j}}{z_{j-1}} = \frac{P_{j}N_{j}}{P_{j-1}}$$
(8)

After the first expansion equation (8) with some rearrangement is

$$\frac{z_1}{P_1} = N_1 \frac{z_0}{P_0}$$
(9)

For the second expansion it becomes

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$$\frac{z_2}{P_2} = N_2 \frac{z_1}{P_1} = N_1 N_2 \frac{z_0}{P_0}$$
(10)

Similarly, for the j<sup>th</sup> expansion

$$\frac{z_j}{P_j} = N_1 N_2 \dots N_j \frac{z_o}{P_o}$$
(11)

The cell constant,  $N_{j},$  for each expansion can be related to the cell constant at zero pressure.  $N_{\infty},$  by

$$N_{j} = N_{\infty} \frac{k_{1} + k_{2}P_{j} + k_{3}P_{j}^{2} + \dots}{m_{1} + m_{2}P_{j-1} + m_{3}P_{j-1}^{2} + \dots}$$
(12)

where k<sub>i</sub> and m<sub>i</sub> are constants related to the distortion of the cells due to pressure (see Appendix A for the values of the constants). Blancett (5) discusses the determination of these constants. Therefore the compressibility factor for each expansion can be written

$$Z_{j} = P_{j} \frac{Z_{o}}{P_{o}} N_{\infty}^{j} \prod_{i=1}^{j} \left( \frac{k_{1} + k_{2}P_{i} + k_{3}P_{i}^{2} + \cdots}{m_{1} + m_{2}P_{i-1} + m_{3}P_{i-1}^{2} + \cdots} \right)$$
(13)

Thus the compressibility factor at each experimental pressure can be calculated if the cell constant at zero pressure,  $N_{\infty}$ , and the run constant,  $Z_0/P_0$ , can be determined.

These constants are classically determined by graphical extrapolation using the experimental data. In the limit as the pressure goes to zero and the compressibility factor to unity, equation (8) becomes

$$N_{\infty} = \lim_{P \to 0} \frac{\frac{P_{j-1}}{P_{j}}}{\frac{P_{j}}{P_{j}}}$$
(14)

The best value of this constant is determined using a gas for which the compressibility factor varies linearly with the pressure, such as helium. However, if the number of runs requires that the data be taken over a period of several months, it is best to determine  $N_{\infty}$  for each run as small changes could occur over an extended period of time. In a similar manner the run constant,  $Z_0/P_0$ , can be determined from equation (11) in the limit as pressure goes to zero.

$$\frac{z_o}{P_o} = \lim_{P \to 0} P_j N_1 N_2 \cdots N_j$$
(15)

Thus plots of  $P_{j-1}/P_j$  v.s.  $P_j$  and  $P_j(N_1N_2 \dots N_j)$  v.s.  $P_j$  extrapolated to zero pressure give the cell constant and run constant, respectively.

The compressibility factors reported for this investigation were calculated by making these extrapolations using an orthonormal polynomial curve fitting technique developed by Hall and Canfield (19) as an initial estimate. Then a Newton-Raphson procedure as presented by Hall and Canfield (20) was used to determine the virial coefficients that, with the optimum cell constants and run constants, gave the best values of the compressibility factors. Graham (17) has presented a similar procedure where the exponential virial equation was used. However, since this approach has convergence problems for data near the critical point, the procedure of Hall and Canfield was used to treat the data in this thesis. A summary of the complete data reduction analysis is given in Appendix B. The compressibility factors at each experimental pressure are presented in Chapter VI along with the virial coefficients for the pure components and mixtures.

The theoretical portion of this thesis is the development of an equation of state for pure methane. Methane was chosen as the material to be studied for two

reasons. First, methane PVT data were available that covered a wide range of temperature and density. Secondly, methane is representative of molecules that are of intermediate complexity and would provide a more severe test than argon. An equation of state for methane is the next step beyond an equation of state for the noble gases and provides a link between simple molecules, such as argon, and the more complex molecules of the heavier hydrocarbons. The details of the equation of state development are presented in Chapters IV and V.

#### CHAPTER II

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#### **REVIEW OF PAST WORK**

This review covers previous work of interest of two types--those concerning the P-V-T behavior of helium and argon and those concerning the P-V-T behavior of helium-argon mixtures. Blancett (5) has presented a sufficiently complete review on helium, argon, and helium-argon mixtures through 1965. To avoid needless repetition, this review will cover the work from 1965 to the present. All of the investigations cited individually below were performed on Burnett-type apparatus. Also, in each case, a reference having a rather extensive compilation of experimental compressibility data will be given.

#### P-V-T Behavior of Argon

The volumetric behavior of argon has been reported by numerous investigators. A book edited by Cook (12) gives a comprehensive review of the volumetric properties of argon through 1960.

Kalfoglou and Miller (22) made compressibility

factor measurements at 30°C and at 100°C intervals from 100°C to 500°C for argon at pressures between 3 and 80 atmospheres.

Blancett (5) has reported volumetric data for argon at -50°C, 0°C, and 50°C for pressures between 2 and 685 atmospheres.

Crain and Sonntag (13) give compressibility data for pure argon at four temperatures in the range -130°C to 0°C and at pressures to 690 atmospheres.

Rowlinson <u>et al</u>. (32) have recently reported second virial coefficients for pure argon at 17 temperatures between 80° and 190°K and at very low pressures since part of this work is below the critical temperature of argon.

#### P-V-T Behavior of Helium

Helium is one of the most widely studied gases in the literature. Cook (12) also gives a comprehensive review of the volumetric and thermodynamic properties of helium up to 1961.

Kalfoglou and Miller (22) have reported compressibility data for helium at 30°C and at 100° intervals from 100° to 500°C and at pressures up to 80 atmospheres.

Blancett (5) has given volumetric data for helium at -50°, 0°, and 50°C and at pressures up to 685 atmospheres.

Canfield (8) has reported compressibility data

and virial coefficients at six temperatures between -140° and 0°C and at pressures to 500 atmospheres.

Hall (18) presents volumetric data for pure helium at three temperatures between -190° and -160°C and at pressures to 685 atmospheres.

Sullivan and Sonntag (36) have covered the temperature range from 70° to 120°K for pressures up to 520 atmospheres.

#### P-V-T Behavior of Helium-Argon Mixtures

Despite theoretical interest in mixtures of simple molecules, such as helium and argon, this system has not been covered extensively. Kalfoglou and Miller (22) report compressibility data for seven mixtures of helium and argon at 30°C and at 100° intervals between 100° and 500°C and at pressures to 80 atmospheres.

Blancett (5) presents volumetric data for four helium-argon mixtures at 50°, 0°, and -50°C and at pressures up to 685 atmospheres, but below -50°C it appears that no data have been taken for this mixture.

Canfield (9) has recently compiled a summary of the mixture data currently available for the study of the volumetric behavior of simple gas mixtures. Also an NBS Report (30) is available that presents a bibliography giving references on the thermophysical properties of fifteen gases including helium and argon.

#### CHAPTER III

#### EXPERIMENTAL

In this chapter the experimental part of the work is described. The Burnett apparatus used in this study has been operated at various temperatures between +50°C and -190°C (5,18) with good success. This report covers the temperature range -90°C to -130°C for the helium-argon system. The first part of the chapter briefly describes the major pieces of equipment that comprise the Burnett apparatus. Because Blancett (5) has already described much of this apparatus in detail, the reader is referred to the above reference for more information. The last part of the chapter describes the operating procedure which is consistent with the analysis for Burnett data.

#### Cryostat

One of the unique features of this experimental apparatus is the gas-bath cryostat. A sketch of the cryostat showing the essential features is given by Hall (18). In the past cryostats usually used a liquid for the bath fluid with the inherent problems of toxicity and flammibility of the liquid and the probable use of two or more bath fluids to cover a wide range of temperature. In this cryostat gaseous nitrogen is the bath fluid for all temperatures from slightly below room temperature to -200°C. Above room temperature compressed air can be satisfactorily used as the bath fluid. The only disadvantage of using a gas as the bath fluid is the reduced heat transfer to objects in the bath. However once the bath was operating at steady state, this effect was only noticeable in the slightly longer equilibration time required after each expansion.

Liquid nitrogen was used as the coolant in the cryostat. It was received in a Linde LS-110 at a pressure of approximately 24 psi. Since the LS-110 did not have sufficient insulation to allow continuous transfer of nitrogen to the cryostat without excessive vaporization of the liquid, an intermediate 50 liter transfer dewar was used. The transfer dewar had a teflon head that allowed it to be refilled without interrupting the continuous flow to the cryostat. A positive pressure of 3-4 psi was required in the transfer dewar to transfer the liquid nitrogen in surging two-phase flow upward through a vacuum-jacketed transfer line and over to a permanently evacuated phase separator that was on top of the cryostat. Both the transfer line and the phase separator were made of 300 series stainless steel with the walls as thin as

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possible to reduce heat leakage.

In the phase separator the liquid nitrogen was kept at a constant level by a float valve assembly that allowed liquid nitrogen to enter at the same rate as it was leaving the bottom of the phase separator through a metering valve. The metering valve fed the liquid nitrogen at a constant rate through a 1/2" thin-wall, stainless steel tube into the vaporizer bundle where the nitrogen gave up its sensible and latent heat to cool the bath. The metering valve was adjusted to allow a slight excess of liquid nitrogen which was offset by the control heater. The vaporizer bundle was a finned surface that contained 10 square feet of surface area in a bundle 5 1/2 inches in diameter by 2 inches thick. Hall (18) gives the details on the construction of the vaporizer bundle.

After leaving the vaporizer bundle the nitrogen vapor passed through the control heater and a squirrelcage blower. The blower circulated the vapor downward past the equipment contained in the cryostat and then upward outside the radiation shield and vapor baffle where the nitrogen lost more sensible heat to further cool the contents of the cryostat. The vapor was then vented to atmosphere. The blower was used in place of a vaneaxial fan blade used by Hall to get increased circulation of the bath gas so that better heat transfer would result. The squirrel-cage blower did reduce the equilibration time

after an expansion somewhat, but the poor heat transfer rate is still a nuisance. It is now thought that the limiting factor in the heat transfer problem is the dead gas space in the pressure-jacketed Burnett cell. This will be discussed later in the chapter.

The blower is operated by a 1750 rpm motor mounted above the cryostat. The shaft enters the cryostat through a Materials Research Corp. V4-100 rotating vacuum seal and is supported at low temperature by a Barden Bar-Temp bearing.

The control heater was made of 25 gage coiled Nichrome wire strung within a 5 inch diameter phenolic frame. It is wired in series with a variable external resistor to give a control heater output of 10 to 100 watts. The heater is activated by a Hallikainen Model 1053A Thermotrol with proportional plus reset control. The sensing element is a Rosemont Model 104N48AAC.

Around the vaporizer bundle, blower, and heater is a styrofoam plug. Its purpose is twofold. It supports the radiation shield-vapor baffle and controls the amount of backmixing through the squirrel-cage blower. It is essential for good temperature control and small gradients in the cryostat. The construction of the plug is a trial and error procedure in which the plug is shaped and tried until it gives the minimum gradient.

With the Burnett apparatus in the cryostat at steady

state, the liquid nitrogen usage was approximately 3 liters/hour at temperatures between -90°C and -130°C. The temperature could be changed within these limits by changing the Thermotrol setting to correspond to the desired temperature without changing the liquid nitrogen metering valve. Thus the nitrogen consumption was essentially constant throughout the experimental runs. This consumption is the total amount used including transfer and phase separator boil-off losses. The average indicated steady-state gradient across the length of the Burnett cell was about 0.007°C for all runs. For some runs the gradient reached a minimum of 0.001°C and for other runs it sometimes was as high as 0.015°C.

#### Burnett Cells and Magnetic Pump

The Burnett cell used in this experiment was a double-walled pressure vessel. Its design and construction is given in detail by Blancett (5). The cell and jacket are shown in Figure 1. The cell was divided into two volumes connected by two expansion valves and the necessary tubing. A hole was drilled in each end of the cell for the insertion of two platinum resistance thermometers. The annular space between the two walls served as a pressure jacket so that the annulus would be at the same pressure as that inside the cell. This reduced the distortion of the cell due to the internal pressure.

While the pressure jacket solved one problem, it



FIGURE 1. HIGH PRESSURE BURNETT CELL

also created another as mentioned previously. Once the annulus is pressured, it becomes essentially a dead gas volume with the resultant low heat transfer. This causes an excessive equilibration time after each expansion. Although it has no affect on the experiment or the analysis, it is time consuming. Before other data are taken, some thought should be given to alleviating this problem.

In the line between the two volumes of the Burnett cell is a magnetic pump. A paper by Canfield, Watson, and Blancett (10) gives the details of construction and operation. It is used to speed temperature equilibration after an expansion by forced mixing of the gas in the two volumes. At low temperatures it also insured that the denser gases would be homogeneous after an expansion by providing circulation between the two chambers. However for some runs, the pump was not left on long enough for complete mixing to occur. This caused the first run to be at a different composition than the second run. This difficulty is explained more fully in the discussion of the results in Chapter VI.

The time that the pump should be left on varied with the pressure and the mixture. This was determined by experience. The pump was left on about 20 to 25 minutes on the first expansion. The ON time was gradually decreased for the subsequent expansions. The pump was not used for the last two or three expansions. If the

pump was left on too long, it hindered equilibration instead of helping. The energy dissipation of the pump caused the temperature to stabilize at a higher value than desired.

#### Temperature and Pressure Measurement

The temperature was determined by two Leeds and Northrup Model 8164 capsule-type platinum resistance thermometers, one in each end of the Burnett cell, in conjunction with a Leeds and Northrup G-2 Mueller Bridge. The temperature for the run was the average of the temperature indicated by the two thermometers. The calibration of the Mueller Bridge was re-checked before this series of runs was started and was used instead of the calibration made in 1963.

The thermometers were calibrated by the National Bureau of Standards, one in 1963 and the other in 1966, at the oxygen boiling point, the water boiling point, and the sulfur boiling point. The thermometers were made consistent with the Mueller Bridge in this laboratory by calibration with the water triple point. When calibrated properly, the thermometers were guaranteed to be in agreement with the International Temperature Scale within  $\pm$  0.01°C. However with the Mueller Bridge and a galvanometer, a change in temperature of 0.001°C could be detected. A computer printout of resistance vs. temperature calculated using the Callendar-Van Dusen equation,

was used to obtain the temperature from the bridge reading.

The system pressure is measured by one of two Ruska Instrument Corporation Model 2400 dead weight gages. One of the gages is used to measure pressures up to 165 atm., and the other is used for the remaining pressures up to 700 atm. The stainless steel weights were calibrated by the manufacturer against class S standards, and are therefore class P standard weights as certified by the National Bureau of Standards. The accuracy of the two gages is certified by the manufacturer to be 0.01 percent of the reading or better.

The pressure is transmitted from the Burnett cell to the external pressure gages by two Ruska differential pressure cells connected in series. In the Burnett analysis, as presented in Chapter 1, all of the experimental gas has to be at the experimental temperature. Since the lower chamber of one of the differential pressure cells is considered part of the Burnett cell upper volume, this resulted in having one of the differential pressure cells in the cryostat at the experimental temperature. This cell because of the extreme environment was especially designed and constructed by the Ruska Instrument Corporation. Because of the low temperatures inside the cryostat, the oil used in the piston gages could not be used as the pressure transmitting fluid between the two diaphragm pressure cells. The sample gas itself was used as the
intermediate pressure transmitting fluid. Thus the diaphragm of the cryogenic pressure cell separated the experimental gas, which was at constant temperature, from the intermediate gas, and the diaphragm of the room temperature pressure cell separated the intermediate gas from the oil used in the piston gages.

One of the problems inherent in using the diaphragm pressure cell is the zero shift effect. A differential transformer, located in the upper chamber of the pressure cell sends an electrical impulse to a differential pressure indicator whenever the diaphragm is deflected. This electrical output was indicated on the scale of the differential pressure indicator. When the pressure in both chambers was equal, the pressure cell was in the balanced condition, that is, the diaphragm was flat. However, the indicator was not in the null position. When the indicator is nulled, the diaphragm is deformed indicating a small difference in pressure between the two chambers of the pressure cell. This difference in pressure between the nulled position on the indicator and the balanced condition in the cell is called the zero shift. Before the correct pressure is known, a correction for this zero shift has to be made. Blancett (5) gives the technique used to determine this effect and a method to correct the measured values. The equation for the corrections are given later in this chapter.

The total pressure of the gas in the Burnett cell can be expressed as the corrected gage pressure plus the sum of four pressure correction terms:

$$P = P_{G} + P_{R} + \Delta P_{H} + \Delta P_{ZSR} + \Delta P_{ZSC} , \qquad (16)$$

where P is the total pressure exerted by the gas,  $P_{G}$  is the pressure exerted on the piston gage,  $P_{B}$  is the barometric pressure acting on the piston gage,  $\Delta P_{H}$  is the head correction,  $\Delta P_{ZSR}$  is the zero shift correction for the room temperature differential pressure indicator, and  $\Delta P_{ZSC}$  is the zero shift correction for the cryogenic differential pressure indicator. All pressures and corrections are given in atmospheres. The computation for these pressure corrections was done on the computer to speed up the calculations and to reduce human error.

The gage pressure had to be corrected for temperature and pressure. For the low-pressure gage the correction was

$$P_{G} = \frac{0.521989 \Sigma (M_{a})}{(1.0 + 1.7 \times 10^{-5} \Delta T) (1.0 - 4.8 \times 10^{-8} P)}$$
(17)

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and for the high-pressure gage

$$P_{\rm G} = \frac{2.610037 \ \Sigma \ (M_{\rm a})}{(1.0 + 1.7 \ \times \ 10^{-5} \Delta T) \ (1.0 - 3.6 \ \times \ 10^{-8} \rm P)} , \quad (18)$$

where  $\Sigma$  (M<sub>a</sub>) is the sum of the weights used in pounds

mass, AT is the difference between the gage temperature and 25°C, and P is the system pressure in psia.

A Welch Model 122A marine barometer was used to determine the atmospheric pressure acting on the piston gage. The corrected barometric pressure is given by

$$P_{\rm p} = 0.0333902 (R-r),$$
 (19)

where R is the barometric reading in inches of mercury and r is a temperature-dependent correction.

The head correction was calculated by one of the two following equations. For the high-pressure gage

$$P_{\rm H} = -0.00021 + (MW) [(-0.116)(\rho_{\rm g})_{\rm o} + (h)(\rho_{\rm g})_{\rm i}]$$
(20)

and for the low-pressure gage

$$P_{\rm H} = -0.00057 + (MW) [(-0.116)(\rho_{\rm g})_{\rm o} + (h)(\rho_{\rm g})_{\rm i}], \qquad (21)$$

where MW is the molecular weight of the experimental gas,  $(\rho_g)_0$  is the density of the experimental gas outside the cryostat,  $(\rho_g)_i$  is the density of the experimental gas inside the cryostat, and h is a multiplier that equals 0.0714 for the first pressure in each run and 0.0747 for all other pressures in the run.

The manufacturer of the differential pressure cells and indicators gave information on the zero shift effect. However, their values were used only for the room-temperature differential pressure indicator. Their equation was

$$\Delta P_{\rm ZSR} = 1.3 \times 10^{-7} P, \qquad (22)$$

where P is the system pressure.

Since the cryogenic differential pressure indicator is a function of both pressure and temperature, the measured zero shift had to be determined in the laboratory at the experimental temperatures. The equation used to obtain the zero shift from the measured zero shift is

$$\Delta P_{ZSC} = \frac{MZS}{1.0 - 0.0277 \ (\partial P/\partial \ln v)_{m}}$$
 (23)

where MZS is the measured zero shift in atmospheres, P is the system pressure, and v is the molar volume in cc/mole. The factor  $(\partial P/\partial \ln v)_T$  was determined in the following manner. The molar volume was calculated using v = ZRT/P, where the values of the compressibility factors for helium were interpolated from data presented by Canfield (8). A plot of P vs. ln v was made, and the slopes,  $(\partial P/\partial \ln v)_T$ , were calculated at the pressures for which the zero shifts were being determined. Figure 2 is a plot of  $\Delta P_{ZSC}$  vs. P for the experimental temperatures.

# Compressor and Valves

A Corblin # B2C1000 single-stage diaphragm compressor was used to compress the gas from cylinder pressure to the initially desired system pressure. The compressor was somewhat oversized so that some care had to be taken when pressuring the system so as to not overpressure the cryogenic differential pressure indicator. The diaphragm kept the sample gas pure while it was being compressed.



FIGURE 2. ZERO SHIFT VS. PRESSURE FOR CRYOGENIC DIFFERENTIAL PRESSURE INDICATOR

All the values were High Pressure Inc. 30,000 psi midget line with two-piece nonrotating stems. Four of the values were in the cryostat to insure that all of the experimental sample gas was at constant temperature. The values came with o-ring seals. These worked fine at room temperature, but the values in the cryostat leaked badly at the low temperatures. The solution to the problem involved using a material with a very low coefficient of contraction as thrust washers for teflon packing and the proper dimensions to assure that the packing would not shrink away from the stem or body of the value. Hall (18) gives the equations to determine the proper dimensions.

Another problem with the values was the tendency for the value stem threads to gall after extended use at the extreme environment. Whenever this occurred, it necessitated a lengthy delay while the cryostat was warmed, the value replaced, and the cryostat again cooled to the experimental temperature. This was solved by treating the value stem threads in the following manner. First, the lubricant, that came in the value stems, was removed from a very inaccessible constriction by gently heating the value stem with a flame. Then the value stem threads were coated with Molykote X-106, a trademark of The Alpha-Molykote Corporation, in solution form and baked in an oven for about three hours. When this was done, galling of the value stem threads was no longer a problem in any of the

experimental runs.

#### Procedure

The experimental procedure is designed to be consistent with the Burnett analysis as given in Chapter I. There are three assumptions that are involved in the development of the Burnett equations. The equilibrium temperature before and after the expansion should be equal. The amount of gas in the upper volume of the Burnett cell before an expansion is equal to the amount of gas in the upper and lower volumes after an expansion. The amount of gas in the upper volume should be the same before and after closing the expansion valve during a measurement.

# Cool Down

The first step in the procedure was to get the cryostat from room temperature to the experimental temperature. Liquid nitrogen was allowed to flow from the transfer dewar through the transfer line to the phase spearator. The fan and control heater were turned on and the thermotrol was set at the predetermined position to control the bath at the experimental temperature. When the liquid level in the phase separator had built up, the metering valve was opened several turns and cool-down was started. It usually took about four hours for the cryostat to cool down to the desired temperature. As the temperature was reached, the metering value was gradually closed until it was open about 1 1/4 turns. The control heater wattage was adjusted to about 40-50 watts with 1/4 ON time. Small adjustments usually had to be made on the thermotrol setting to get the temperature in the cryostat controlling at the experimental temperature within  $\pm 0.002$ °C. An additional eight to twelve hours were required to get temperature control after the cryostat had attained temperature.

To change from one experimental temperature to another, the only significant change that had to be made was the thermotrol setting. If the temperature change was as much as 20° or 30°C, small changes sometimes had to be made in the heater wattage and the metering valve controlling the liquid nitrogen flow into the cryostat.

# Differential Pressure Indicator Adjustments

When the cryostat was at the control temperature, the cryogenic electronic differential pressure indicator had to be adjusted. This adjustment had to be made whenever the temperature was changed because the operation of the electronic indicator was a definite function of temperature. The adjustment was made on a trim pot in the back of the indicator with a corresponding change of the zero adjustment control. These two adjustments were made until the minimum variation about the null position was attained. This deflection was specified by the manufacturer to be ± 1 division while the sensitivity knob was turned full range. When the trim pot was changed a very small amount, the electronic circuitry was upset and a wait of about an hour was required for it to settle down again. Eventually the setting was found that seemed to give the minimum deflection about the null point. At this time the indicator was allowed to sit for about six hours. If it still possessed the required characteristics after the wait, it was ready for use. If not, the above procedure was followed until it did operate properly.

A similar procedure was followed to adjust the room-temperature differential pressure indicator. This was done with atmospheric pressure on both sides of the diaphragm. However, since it remained at one temperature throughout all of the experimental runs, this adjustment had to be made only once.

## Sequence of Runs

In determining the sequence of runs there was an option of two procedures to follow: the completion of all runs for a given composition while changing temperature or the completion of all runs at a given constant temperature while changing compositions. The latter procedure requires the use of more gas because the system has to be purged each time the composition is changed. However, due to the uncertainty in adjusting the cryogenic differential pressure indicator as explained above.

the latter procedure was followed so that the indicator would have to be adjusted as few times as possible. Thus the sequence consisted of making two runs for each composition at the same temperature with a purging of the system each time the composition was changed.

# Final Leak Check

Before the experimental runs were started, the entire system was checked for leaks by pressuring to 12,000 psi, which was a greater pressure than any of the experimental pressures. This was necessary because in tightening the flared fittings, some other fitting might unknowingly be loosened. The pressure was monitored for several hours with the piston gage to determine if the system pressure was changing. This was the most sensitive test for leaks.

# Purging and Charging the Burnett Cell

When the equipment was ready to make the initial experimental run, the system was purged three times with the first gas composition in the following manner. First the cold trap filled with ethyl alcohol in the line between the sample gas cylinder and the compressor was frozen by passing liquid nitrogen through the cooling coils of the trap. Next, the system was evacuated to 10 microns and the sample gas was carefully bled into the system until a pressure of 10 atmospheres was attained.

In all manipulations when gas was either being added to the system or bled from the system, the valves were to be opened very slowly to prevent a sudden overpressure on the diaphragm of the differential pressure cell. Because of the design of the pressure cells, a large overpressure from the bottom was to be avoided. Such an overpressure would crimp the diaphragm causing a change in the null position of the differential pressure indicator. The gas was then vented at several points, and the system was again evacuated to 10 microns. This was repeated until the system had been purged a minimum of three times. This purging procedure had to be followed each time the composition of the gas was changed.

The next step was to charge the Burnett cell to the predetermined initial pressure. This was accomplished in the following manner. The cold trap was refrozen if necessary. The cryogenic differential pressure indicator was rechecked to insure that it was still operating properly. The two expansion valves between the upper and lower chambers of the Burnett cell were closed. The piston gage was loaded with weights equivalent to the initial pressure. A slight overpressure from the top was applied to the room temperature differential pressure indicator. Sample gas was carefully bled into the system, while watching the cryogenic differential pressure indicator scale to prevent sudden overpressure, until cylinder

pressure was attained. The compressor was then turned on and the charging was continued until the desired system pressure was reached. As the pressure in the system increased, the oil pressure in the room-temperature differential pressure cell was increased by turning the hand pump so that the diaphragm was always overpressured from the top.

The charging of the Burnett cell caused the cryostat temperature to increase. The sample gas was allowed to soak until the cryostat temperature was again stablized. The time required for this depended on the initial pressure and the composition of the gas. The time varied from about three hours at the lower initial pressures to approximately eight hours when the Burnett cell was pressured to 10,000 psi.

# Pressure Measurement and Subsequent Expansion

When the temperature had equilibrated, the charging valves were closed to isolate the experimental gas from the intermediate gas. The pressure was then measured by nulling both differential pressure indicators simultaneously. While the indicators were both nulled, the weights on the piston gage were recorded and double checked, and the temperatures of the two platinum resistance thermometers were recorded. Other data that were recorded at this time were the barometer reading, room temperature, and the temperature at the piston gage.

After the data had been recorded, the vent valve was closed and the gas was expanded into the previously evacuated lower volume by very carefully opening one of the expansion valves. The expansion was made as slowly as practical to minimize the temperature upset caused by the expansion. During the expansion the lower cell was heated and the upper cell was cooled. After the expansion was completed, both expansion valves were opened several turns and the magnetic pump was turned on. The time that it was left on depended on the magnitude of the temperature upset. This was determined by experience. The ON times ranged from approximately 20 to 25 minutes for the first expansion to not being used for the last two or three expansions. If it were left on too long, the cryostat would equilibrate at a higher temperature than desired because of the energy dissipation of the pump. The intermediate gas was bled to the atmosphere until the differential pressure indicator showed that the overpressure from the top had been relieved.

The sample gas was again allowed to soak until the temperature equilibrated. The time for equilibration depended on the experimental pressure. On the first expansion from 10,000 psi, the temperature upset was quite large and it required about six hours for the cryostat to re-equilibrate. On the subsequent expansions, the upset was somewhat smaller each time until on the last few

expansions only about an hour was required for temperature equilibration.

When the cryostat temperature had equilibrated, one of the expansion values was closed and the other was left 1/8th turn open. This was done so that the sample gas would be apportioned correctly between the two volumes of the Burnett cell. The system pressure was then measured with the piston gage and the necessary data recorded as explained above. With the differential pressure indicators nulled, the expansion value was closed. The gas in the lower volume was vented to the atmosphere and the lower chamber was evacuated to less than 5 microns. This required approximately 25-30 minutes and was a good check on the expansion values to see if they were leaking.

When the lower volume was evacuated, the vent value was closed and the second expansion was started by slowly opening one of the expansion values. From this point on, the procedure is the same as for the first expansion outlined above. This procedure of expanding the gas into the lower volume, measuring the system pressure after temperature equilibration, venting to the atmosphere, and evacuating the lower volume was continued until the system pressure was less than 2 atmospheres. At the end of each run both differential pressure indicators were checked to see if there had been a permanent zero shift during the run. If the null position hadn't changed, then the run was good. If there had been a change and it was known when it had occurred, then a correction could be calculated and applied to all of the experimental pressures taken after the shift had occurred. If it was not known when the shift had happened, then the indicator had to be rezeroed and the run repeated. If the first run was good, then a second run at the same temperature and composition was made starting at an initial pressure midway between the first two pressures of the first run. After the second run, the system was purged three times with the sample gas of the next composition, and two runs with the new mixture were made.

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#### CHAPTER IV

# EQUATION OF STATE: THEORETICAL DEVELOPMENT

Renewed interest in an equation of state based on a perturbational approach began when Zwanzig (45) proposed an equation of increasing powers of reciprocal temperature with the coefficients derived from perturbation theory. The perturbational theory treats the attractive forces in a fluid as perturbations on a hardcore potential. Since Zwanzig introduced his perturbation theory, a number of investigators have tried various approaches in formulating their equations of state, but the basic theoretical ideas are the same. Several of these approaches are mentioned in the following discussion of previous work in this area.

### Previous Perturbation Procedures

Zwanzig (45) first proposed the perturbation theory in which the potential energy, V, was divided into two parts, the potential energy of the unperturbed system,  $V_0$ , and the perturbation,  $V_1$ .

$$\mathbf{v} = \mathbf{v}_0 + \mathbf{v}_1 \tag{24}$$

He chose the following as the general form of the equation:

$$\frac{Pv}{RT} = \Phi_{0}(v) + \frac{a_{1}(v)}{RT} + \frac{a_{2}(v)}{(RT)^{2}} + \dots, \qquad (25)$$

where  $\Phi_{O}(v)$  was the rigid sphere equation of state with an appropriate hard-sphere diameter, which was kept as an adjustable parameter. Equation (25) was truncated after the second term so that the compressibility was linear in reciprocal temperature. The repulsive potential was taken to be the hard-sphere potential and the attractive potential was the Lennard-Jones 12:6 potential. The Lennard-Jones parameters were adjusted according to the value of c, which was set as zero for the literature values of  $\epsilon$  and  $\sigma$ .

Equation (25) could be compared to experimental data by plotting Pv/RT as a function of 1/T for various densities and taking the intercepts as  $\Phi_0$  and the slopes as  $a_1(v)$ . He determined that the best fit at low densities was obtained by setting c = 1/1.08, and that at high densities, c = 1/1.1 gave a better fit. This indicated that the resulting equation is quite sensitive to the value of c chosen. The overall accuracy of the predicted values of Pv/RT when compared to experimental data was given as five to ten percent, with the poorer accuracy at the higher densities. He concluded that the results were in fair agreement with experiment for the noble gases at high temperature.

Smith and Alder (34) also proposed using Zwanzig's

approach to develop an equation of state. They used the hard-sphere potential as a basis for their equation of state and Lennard-Jones potential as the perturbation. They used three parameters with two being characteristic of the normal Lennard-Jones potential and the third, a cutoff parameter. The Lennard-Jones parameters were adjusted in the same way that Zwanzig adjusted his param-They also used the same truncated form of the eters. equation of state that Zwanzig used but determined the coefficients in a different way. The virial expansion was used to determine the coefficients in a power series of inverse temperature at different values of c, the cutoff parameter. Results were presented at c = 1/1.1 but they stated that c = 1/1.095 gave better results. This indicated that the results were sensitive to the value of c used. They concluded that the first two terms of the perturbation equation of state approximated the equation of state, Pv/RT, for a reduced temperature greater than two to within 0.03 unit up to almost solid densities. Their cutoff parameter was not made a function of temperature because of the small temperature range used in their study.

 $M^{C}$ Quarrie and Katz (27) also used an approach similar to Zwanzig in that they used a perturbation on the hardsphere equation. They used a system with a pairwiseadditive intermolecular potential u(r) = (r<sup>-n</sup> - r<sup>-6</sup>).

However, instead of treating the entire 12:6 potential as the perturbation, they chose to treat the attractive  $r^{-6}$  term as the perturbation. In doing this they obtained an equation of state of the form:

$$\frac{P}{\rho kT} = A + B/T + C \log T .$$
 (26)

Thus they were one of the first to extend Zwanzig's approach beyond the linear equation of state by approximating the higher order reciprocal temperature terms by C log T.

When their predicted results were compared to experimental results for helium, argon, and neon, they found that n = 15 gave better results than other values for n. They concluded that they have an equation of state with no adjustable parameters that reliably reproduced PVT data up to densities of 40 mole/liter and reduced temperatures greater than three.

Frisch, <u>et al</u>. (16) used the same form of the equation truncated after the second term and the same repulsive and attractive potentials as Zwanzig, i.e.,

$$P/\rho kT = a(\rho) + b(\rho)/kT + c(\rho)/(kT)^{2} + ...$$
 (27)

where  $a(\rho)$  was the hard-sphere equation of state using the radial distribution function of the approximate Percus-Yevick theory. The  $b(\rho)$  was expressed directly as a quadrature of the Laplace transform of the approximate radial distribution function which is explicitly known. The

solution required no inversion of the transform. They compared their results term by term with experimental argon data in the temperature range 0° to 150°C. They found that the comparison of the calculated  $b(\rho)$  with the experimental b(p) was poor even though they modified the Lennard-Jones parameters as Zwanzig did by the use of cutoff parameter c. By varying the values of c,  $\epsilon$ , and  $\sigma$  by about five percent, they correctly reproduced the behavior of the slope but the agreement was only fair with a mean deviation of about nine percent. They used two values of the cutoff parameter c, 0.889 and 0.903, and concluded from their results that there was a deviation of the compressibility of argon from a linear relation in reciprocal temperature for densities larger than 400 amagats. They also stated that they have shown their theory to be consistent with the high temperature data for argon, but that the great sensitivity of the results on the location of the hard-sphere cutoff parameter, c, limited the usefulness of the theory.

Kozak and Rice (24) used the same repulsive and attractive potential as Zwanzig and a similar form of the equation of state except that they called the third and succeeding terms, fluctuation terms:

$$\frac{P}{\rho kT} = (P/\rho kT)_{0} + a/T + \sum_{m=2}^{\infty} f_{m}^{*} \rho^{*m-1} . \qquad (28)$$

They expanded both sides of this equation to determine

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the  $f_i^*$  in terms of the Lennard-Jones virial coefficients,  $B_m$ , by equating equal powers of  $\rho^n$  and obtained expressions for each of the terms in their equation of state truncating after  $f_5^*$ . They eliminated c from the equation of state by requiring at equilibrium  $\partial A/\partial \xi = 0$  where  $\xi = c^3$ . They found that the particular  $\boldsymbol{\xi}$  which minimized A was dependent only on density and not on temperature for the range of temperature considered in their study. They used reduced temperatures ranging from  $T^{\ddagger} = 1.28$  to  $T^{\ddagger} = 2.74$  in comparing with argon data and Monte Carlo results. They also found that two  $\xi$ 's satisfy the condition  $\partial A/\partial \xi = 0$ , resulting in two branches when  $\boldsymbol{\xi}$  was plotted versus reduced density. The lower branch led to the greatest lowering of the free energy at elevated temperatures, whereas in the neighborhood of the critical point, the upper branch was selected. In their plot of compressibility versus reduced density, their agreement with argon data was good at low densities and began to deviate from experiment at reduced densities greater than 0.2. They concluded that their theory gave good results at temperatures as low as the critical temperature of argon,  $T^{\ddagger} = 1.26$ , but that below this, the predicted equation of state deteriorated in quality.

Barker and Henderson (1,2,3) defined a modified potential involving three parameters; a hard-sphere diameter, an inverse-steepness parameter for the repulsive region, and a depth parameter for the attractive region. Their modified potential has the form:

$$\mathbf{v}(\mathbf{d},\sigma,\alpha,\gamma;\mathbf{R}) = \begin{cases} \mathbf{u} \ [\mathbf{d}+(\mathbf{R}-\mathbf{d})/\alpha], & \mathbf{d}+(\mathbf{R}-\mathbf{d})/\alpha < \sigma \\\\ 0, & \sigma < \mathbf{d}+(\mathbf{r}-\mathbf{d})/\alpha < \mathbf{d}+(\sigma-\mathbf{d})/\alpha & (29) \\\\ \gamma \mathbf{U}(\mathbf{R}) \ , & \sigma < \mathbf{R} \end{cases}$$

They derived their equation of state by expanding the configuration integral in a double Taylor series in  $\alpha$  and  $\gamma$  about the point  $\gamma = \alpha = 0$ , which corresponds to the hard-sphere potential:

$$A = A_{0} + \alpha \left(\frac{\partial A}{\partial \alpha}\right)_{\alpha=0} + \gamma \left(\frac{\partial A}{\partial \gamma}\right)_{\gamma=0} + \dots \quad (30)$$

They set  $\alpha = \gamma = 1$  so that the original potential u(r) was regained. In one paper (2) they gave results for the square-well potential, and in another (3), they gave results for the Lennard-Jones 12:6 potential. They eliminated the term of order  $\alpha$  by setting

$$d = \int_{0}^{\sigma} \{1 - \exp[-\beta u(z)]\} dz$$
 (31)

This made d a function of temperature only and not density. For the hard-sphere radial distribution function they used the solution of the Percus-Yevick equation given in analytic form by Wertheim (43) for the range d < R < 2d and interpolated from the tables of Throop and Bearman (39) for 2d < R < 3.95d. For R > 3.95d the hard-sphere radial distribution function was approximated by one. Thus their equation was not completely analytic.

In deriving the equation of state in the way that they did, the first order term in y was evaluated exactly and the second order term  $\gamma^2$  was evaluated approximately. The other second-order terms and all higher order terms were neglected. The improvement of their results as compared to others was due to the fact that they have a good approximation for the second order This extended downward the range of temperatures term. for which their equation gave good results. They concluded that their form of perturbation theory gave excellent results at temperatures that are not too low and good results even at the lowest temperatures that are physically relevant for compressed gases and liquids. But they also stated that quantitatively there were small discrepancies with experiment and simulation studies at low temperatures.

### Present Perturbation Procedure

In the present perturbation procedure the equation of state was developed as far as possible with theoretical significance. At this point experimental data were used to empirically determine constants that could not be

determined explicitly with theory. The rest of this chapter develops the final form of the theoretical equation of state that was used to obtain the empirical constants and final results. All detailed derivations needed in this development are presented in Appendix C. The results are then presented in Chapter V.

The following development is a combination of the better features of the previous perturbation procedures. In the present method the perturbation equation of state takes the general form

$$A/NkT = A_0/NkT + C_1\beta + C_2\beta^2 + C_3\beta^3 + ...,$$
 (32)

where  $\beta = 1/kT$ . Equation (32) is the free energy equation of state. The perturbation equation of state can also be expressed in general form in terms of the pressure:

$$P/\rho kT = a(\rho) + b(\rho)\beta + c(\rho)\beta^{2} + d(\rho)\beta^{3} + ..., \quad (33)$$

where  $a(\rho)$  is the hard-sphere equation of state,  $P_{o}/\rho kT$ . Equation (33) can be derived from equation (32) by differentiating each term in equation (32) with respect to density and multiplying by density, i.e.,

 $\frac{P}{\rho} = \rho \left(\frac{\partial A}{\partial \rho}\right)_{T}$ (34)

and

$$b(\rho) = \rho \left(\frac{\partial C_1}{\partial \rho}\right)_{T} \qquad (35)$$

The  $C_i$  in equation (32) are the coefficients for the

macroscopic compressibility case. The expressions for these coefficients were obtained from Mansoori (26) and are given by the following:

$$C_{1} = 2\pi \int_{c\sigma}^{\infty} \rho u(r) g_{0}(r) r^{2} dr$$
(36)

$$C_{2} = -\pi kT \left(\frac{\partial \rho}{\partial P}\right)_{O} \int_{CO}^{\infty} \rho u^{2}(r) g_{O}(r) r^{2} dr \qquad (37)$$

$$c_{3} = \frac{2}{3!} \pi \frac{(1-\eta)^{7} (6\eta^{2}+7\eta-1)}{(1+2\eta)^{5}} \int_{c\sigma}^{\infty} \rho u^{3}(r) g_{0}(r) r^{2} dr, \quad (38)$$

where  $\rho$  is the density,  $\sigma$  is the molecular diameter, c is a cutoff parameter,  $c\sigma$  is the hard-sphere diameter,  $\eta = \frac{\pi (c\sigma)^3 \rho}{6}$ , u(r) is any potential function,  $(\frac{\partial \rho}{\partial P})_0$  is the hard-sphere compressibility, and  $g_0(r)$  is the hardsphere radial distribution function. By making the appropriate change of variables, taking the Laplace transform of  $rg_0(r)$ , as suggested by Frisch, et al. (16) and differentiating with respect to density, the coefficients, as a function of density, appearing in equation (33) can be obtained (see Appendix C for the detailed development).

$$b(\rho) = 12\eta \int_{0}^{\infty} f(s,\eta) U_{1}(s) ds \qquad (39)$$

$$c(\rho) = R(\eta) \int_{0}^{\infty} f(s,\eta) U_{2}(s) ds + V(\eta) \int_{0}^{\infty} G(s) U_{2}(s) ds \qquad (40)$$

$$d(\rho) = W(\eta) \int_{0}^{\infty} f(s,\eta) U_{3}(s) ds + Y(\eta) \int_{0}^{\infty} G(s) U_{3}(s) ds \qquad (41)$$

where G(s) is the explicit Laplace transform of the

hard-sphere radial distribution function obtained by Wertheim (43) and by Thiele (38),  $f(s,\eta)$  is the  $\frac{\partial}{\partial\rho}[\rho G(s)]$ and is given by equation (C-3) in Appendix C,  $U_1(s)$  is the inverse Laplace transform of the potential function,  $U_2(s)$  is the inverse Laplace transform of the square of the potential function,  $U_3(s)$  is the inverse Laplace transform of the cube of the potential function, and R, V, W, and Y are coefficients that are a function of  $\eta$ only and are given by equations (C-32), (C-33), (C-37), and (C-38), respectively, in Appendix C.

One of several different methods could be used to calculate the hard-sphere equation of state,  $P_0/\rho kT$ . The analytic solution of the Percus-Yevick equation obtained by Wertheim (43) or Thiele (38) for the compressibility equation yielded the result:

$$P_{0}/\rho kT = \frac{1+\eta+\eta^{2}}{(1-\eta)^{3}}$$
(42)

The Pade' approximate of Ree and Hoover (31) given by

$$P_{o}/\rho kT = \frac{b\rho (1 + 0.063507b\rho + 0.017329b^{2}\rho^{2})}{(1 - 0.561493b\rho + 0.081313b^{2}\rho^{2})} + 1$$
(43)

where  $b = 2\pi (c\sigma)^3/3$ , could be used to obtain a value for the hard-sphere equation of state. Also Mansoori (26) has found that an average of the compressibility and pressure equation of state given by

$$P_{0}/\rho kT = \frac{1 + \eta + \eta^{2} - 1.5\eta^{2}}{(1-\eta)^{3}}$$
(44)

yields good results. Carnahan and Starling (11) have

derived an expression for the hard-sphere equation of state based on an analysis of the reduced virial series. Their equation is given by

$$P_{0}'\rho kT = \frac{1 + \eta + \eta^{2} - \eta^{3}}{(1-\eta)^{3}}$$
(45)

Whichever of the four is chosen, the hard-sphere compressibility,  $\left(\frac{\partial \rho}{\partial P}\right)_{O}$ , should be determined so that it is consistent with the hard-sphere equation of state that is used.

The potential function, u(r), chosen for use in the calculations in this thesis was one which describes the molecules interacting according to the 12:6 potential:

$$u(r) = 4 \in [(\sigma/r)^{12} - (\sigma/r)^{6}]$$
 (46)

The inverse Laplace transform of this potential with the same change of variable as used in going from equation (36) to equation (39) becomes

$$U_1(s) = 4 \in \left[ \frac{1}{c^{12}} \frac{s^{10}}{10!} - \frac{1}{c^6} \frac{s^4}{4!} \right]$$
 (47)

The expressions for  $U_2(s)$  and  $U_3(s)$  are obtained after squaring and cubing, respectively, the potential function and taking the inverse Laplace transform. These expressions and the details of the development are presented in Appendix C.

To make the integrals appearing in equations (39), (40), and (41) more tractable for use on a computer, another change of variable was made so that the range of integration was from zero to one. The resulting expressions for  $b(\rho)$ ,  $c(\rho)$ , and  $d(\rho)$  after the change of variable, s = (1-x)/x, are given in Appendix C. In all of this work, the integrations were performed numerically. To insure that the integrals were being evaluated correctly, the interval size was continually halved and the integrals evaluated until two successive values of the integrals were identically the same to seven or eight significant digits.

Equation (33) was solved for the pressure, which was a function of temperature, density, cutoff parameter c,  $\epsilon$ , and  $\sigma$ . The parameters  $\epsilon$  and  $\sigma$  could be made adjustable along with c, but in this work, the values of  $\in$  and  $\sigma$  were the literature values given by Hirschfelder, Curtiss, and Bird (21). Thus for a given temperature and density, the value of c could be determined that made the calculated pressure as close to the experimental pressure as desired. This was done using a combination of a half-interval search to get close to the solution, and then a Newton-Raphson search to converge to the solution. The test for convergence was that the calculated pressure less the experimental pressure divided by the experimental pressure was arbitrarily small, i.e.,  $(P_{CALC} - P_{EXP})/P_{EXP} < 10^{-5}.$ 

Equation (33) was programmed so that the pressure

could be calculated using the  $\beta$  term only, the  $\beta$  and  $\beta^2$  terms, or the  $\beta$ ,  $\beta^2$ , and  $\beta^3$  terms to see how many terms were necessary to get the best results. The results from using only the  $\beta$  term indicated that the data were nonlinear in  $\beta$  and other terms were required. The results from using the  $\beta$  and  $\beta^2$  terms were a distinct improvement over the use of only one term. When the cutoff parameter c was plotted versus density at constant temperature and versus temperature at constant density, the resulting curves had a slight curvature and indicated that c was definitely a function of both temperature and density. This plot for c versus density at various temperatures is presented in Figure 3. The results from using all three terms were not quite as good as with two. The graph showed slightly more curvature than in the previous plot. This plot is given in Figure 4. Since the addition of the third term about doubled the computer run time and the results were not as good, the equation of state truncated after the  $\beta^2$  term was used for the remainder of the calculations. The final form of the equation of state, using equation (42) for the hard-sphere, was

$$\frac{P_{\text{CALC}}}{\rho kT} = \frac{1+\eta+\eta^2}{(1-\eta)^3} + \frac{12\eta}{kT} \left(\frac{4\epsilon}{c^6}\right) (1) + \frac{1}{(kT)^2} \left(\frac{16\epsilon^2}{c^{12}}\right) \times \times \left[R(\eta) (J) - V(\eta) (K)\right]$$
(48)



FIGURE 3. CUTOFF PARAMETER VS. DENSITY THROUGH  $\beta^2$  TERM



CUTOFF PARAMETER VS. DENSITY THROUGH  $\beta^3$  TERM FIGURE 4.

where I, J, and K are integrals given by equations (C-41), (C-42), and (C-43), respectively, in Appendix C.

With the integrals in the pressure form of the perturbation equation of state defined as they are in equations (C-17), (C-29), and (C-35), the potential function goes abruptly to infinity at the cutoff parameter c. To avoid this abruptness with which the potential function went to infinity, an attempt was made to use an approach similar to that of Barker and Henderson (3). This required that the integrals be evaluated between  $\sigma$  and infinity instead of between  $c\sigma$ , the hardsphere diameter, and infinity, as in equation (48). To accomplish this, the contribution of the integrals between  $c\sigma$  and  $\sigma$  could be subtracted from the result in equation (48). Barker and Henderson (3) chose their hard-sphere diameter so that it was a function of temperature only by use of equation (31), thus making the  $\alpha$ term in equation (30) zero. However, the results discussed above indicated that the hard-sphere diameter, co, was definitely a function of both temperature and density. Therefore, instead of eliminating the  $\alpha$  term, it was evaluated as the contribution between zero and  $\sigma$ .

In outline form the above changes resulted in the following equation of state:

$$\frac{P_{CALC}}{\rho kT} = \delta_{p} - 2\pi\rho\alpha - 2\pi\rho\beta\gamma + \pi\rho\beta^{2}\gamma^{2} , \qquad (49)$$

where  $\delta_{p}$  is the right-hand side of equation (48) and  $\alpha$ ,  $\gamma$ , and  $\gamma^2$  are given in Appendix C by equations (C-51), (C-53) and (C-55), respectively. When the results using equation (49) were compared to Barker and Henderson's results, the agreement was guite good except at high temperature and high density. The two approaches are similar except that equation (49) used the macroscopic compressibility coefficient, whereas Barker and Henderson used the local compressibility coefficient. Wertheim's analytic solution (43) for d<r<2d, where d is the hardsphere diameter, was used for the hard-sphere radial distribution function,  $g_{0}(r)$ . This was possible because Wertheim's solution in this range was valid for the integration from  $c\sigma$  to  $\sigma$  as long as c is greater than The advantage of equation (49) is that it is com-0.5. pletely analytic whereas Barker and Henderson's approach required interpolation of tabular values for  $g_0(r)$  for 2d < r < 3.95d and an approximation of one for  $g_0(r)$  for r > 3.95d.

When equation (49) was used to determine the value of the cutoff parameter, c, that makes the calculated pressure equal the experimental pressure, the results indicated that multiple values of c satisfy equation (49). These results are presented in Figure 5 as a plot of  $P_{CALC} - P_{EXP}$  versus c. These are examples which cover the temperature and density range used. If there



FIGURE 5. CALCULATED PRESSURE DEVIATION VS. CUTOFF PARAMETER

were only one solution, there would be only one place where P<sub>CALC</sub> - P<sub>EXP</sub> was zero. However, from the plot it can be seen that there are several values of c where  $P_{CALC} - P_{RXP}$  is zero. This is somewhat analogous to the double branches that appeared in Kozak and Rice's results (24). However, further study of this unexpected result showed no consistent method of choosing values of the cutoff parameter that were meaningful. Values of c between 0.9 and 1.0 at various temperatures and densities were calculated using equation (49). This range was chosen because Barker and Henderson's results indicated that for any of the temperatures used here, c would be greater than 0.9 but less than 1.0. The results of these calculations are presented in Table 1. In some cases the iterative procedure would not converge for a value of c in this range.

To see what effect the choice of the hard-sphere equation of state had on the results, values of the cutoff parameter c were calculated using equation (48) with the hard-sphere equation of state given by the Percus-Yevick solution, equation (43), and by the Carnahan-Starling expression, equation (45), for several data points that covered the temperature and density ranges of all of the data. These results are presented in Table 2. A comparison of the two values of c indicated that c was not greatly changed by using a different hard-

sphere equation of state, i.e., the range of the values of c was not decreased although the values did change slightly. Also the sensitivity of c indicated by  $\Delta P/\Delta c$  did not change appreciably. Therefore, equation (48), with the Percus-Yevick hard-sphere equation of state, was used as the basis for equation of state calculations. The results of using this as a perturbation equation of state are presented and discussed in the next chapter.
# CUTOFF PARAMETER RESULTS FOR EQUATION (49) USING AVERAGE HARD-SPHERE EQUATION

Temperature °K	Pressure atm.	Density gm/cc	Cutoff Parameter	
623.294	51.7135	0.01604	DC*	
623.294	377.366 0.10428 0.9		0.964852	
473.213	38.7272	0.01604	DC	
473.213	392.389	0.14438	0.966591	
323.151	25.6660	0.01604	1.074710	
323.151	162.061	0.11230	DC	
323.151	322.698	0.20053	0.971119	
233.522	40.4539	0.04095	0.957960	
234.417	80.3681	0.10357	DC	
236.577	184.358	0.23967	0.975902	
234.397	676.072	0.35838	1.001588	
114.530	8.8265	0.41933	1.013021	
114.530	308.888	0.44293	1.016288	

\* Didn't converge

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## COMPARISON OF CUTOFF PARAMETER C OBTAINED FROM TWO HARD-SPHERE EQUATIONS

°K T	P Atm.	p gm/cc	cPY	cCS	PY Δp Δc	CS <u>Ap</u> Ac
623.294	51.7135	0.01604	0.885059	0.885124	7.22	6.76
623.294	377.366	0.10428	0.816059	0.816331	2.11(10 <sup>3</sup> )	2.08(10 <sup>3</sup> )
473.213	38.7272	0.01604	0.901740	0.901687	4.52	4.51
473.213	392.389	0.14438	0.804645	0.805155	6.91(10 <sup>3</sup> )	6.79(10 <sup>3</sup> )
323.151	25.6660	0.01604	0.918250	0.918276	3.37	3.37
323.151	162.061	0.11230	0.838988	0.839378	1.99(10 <sup>3</sup> )	1.96(10 <sup>3</sup> )
323.151	322.698	0.20053	0.790861	0.791892	2.48 (10 <sup>4</sup> )	2.40(10 <sup>4</sup> )
233.522	40.4539	0.04095	0.902815	0.902909	43.8	43.6
234.417	80.3681	0.10357	0.857768	0.858154	1.20(10 <sup>3</sup> )	1.18(10 <sup>3</sup> )
236.577	184.358	0.23967	0.783103	0.784677	5.19(10 <sup>4</sup> )	4.96(10 <sup>4</sup> )
234.397	676.072	0.35838	0.731836	0.736259	4.18(10 <sup>5</sup> )	3.81(10 <sup>5</sup> )
114.530	8.8265	0.41933	0.722529	0.727388	1.19(10 <sup>6</sup> )	1.02(10 <sup>6</sup> )
114.530	308.888	0.44293	0.712844	0.718016	1.76(10 <sup>6</sup> )	1.47 (10 <sup>6</sup> )

PY Percus-Yevick Equation (42)

CS Carnahan-Starling Equation (45)

#### CHAPTER V

#### **EQUATION OF STATE: RESULTS**

Until the work of Barker and Henderson (3), the proposed perturbation equations of state were designated as high temperature equations of state for the noble gases. However, Barker and Henderson's good approximation for the second order term in reciprocal temperature made the perturbation theory feasible at temperatures lower than the critical point and for the liquid state. In this work methane data were chosen to use in conjunction with equation (48) because the methane molecule is more complicated than the noble gases. Methane would therefore be a more severe test of an equation of state than the noble gases. The resulting equation to predict the properties for methane, with appropriate changes in the constants, would also be an acceptable equation of state for predicting the properties of the noble gases.

#### Selection of Data

Methane was selected because of the availability of data over a wide range of temperature with an approximately even distribution of the data, i.e., there were

no large gaps for which data were not available. Douslin et al. (15) present pure component data in the temperature range 273° to 623°K, for pressures between 16 and 400 atmospheres, and at densities between 0.012 and 0.201 grams/cc. Vennix (41) gives pure methane data in the region 150° to 275°K, 15 to 676 atmospheres, and 0.041 to 0.360 grams/cc. Van Itterbeek et al. (40) have liquid methane data in the region 114° to 190°K, 8 to 312 atmospheres, and 0.262 to 0.443 grams/cc. These three data sources had approximately seven hundred data points. But because of computer size limitations and the excessive run times that would be required for using all of the data, only about two hundred of the data points were used in determining the equation of state constants. However, the two hundred points used were selected so that they were representative of the complete temperature and density ranges of the seven hundred data points.

#### Data Treatment Procedure

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Equation (48) was solved for the pressure explicitly, and then the experimental pressure was subtracted from both sides to give an equation of the form

$$f(T, P, \rho; c) = 0$$
 (50)

This equation was solved at each experimental data point for the value of c that made equation (50) an identity.

The method of solution was to use a half-interval search to get close to the answer, and then switch to a Newton-Raphson search to converge more guickly to the solution. The values of c were plotted versus temperature and density and found to have a slight curvature. However, when c was plotted versus various functions of temperature and density, no simple functionality was found that gave good results in the liquid and dense gas region at low temperature. From the plots it was apparent that c was definitely a function of both temperature and density. The cutoff parameter was then curve fitted with a general least squares procedure using orthonormal functions. This procedure, developed by Hall and Canfield (19), is called ORNOR for convenience in making reference to it. The form of the equation selected for which the best constants were to be chosen in a least squares sense is given by

$$\mathbf{c} = \sum_{m=0}^{3} \sum_{n=0}^{3} \mathbf{a}_{mn} \boldsymbol{\rho}^{m} \mathbf{T}^{n} \qquad (51)$$

The ORNOR procedure is very flexible in that it allows one to select whatever functionality is to be tested and picks the best fit based on the best fit criteria as discussed by Hall and Canfield (19). It also has a weighting factor in it so that the data can be weighted if necessary. When ORNOR was first used in trying to fit c versus temperature and density, the weighting factors were taken to be one. A comparison

was then made between the calculated pressure, based on the value of c calculated using equation (51) with the coefficients selected by ORNOR, with the experimental pressure. This gave excellent results at high temperature and low density but poor results at low temperature and high density. Thus, it was necessary to select a series of weighting factors that would not appreciably affect the results at high temperature and low density, but that would improve the results at low temperature and high density by giving more emphasis or weight to these data points in the curve-fitting procedure.

After studying the results obtained using a weighting factor of one, it was determined that a comparison of the difference between equation (50) at convergence and equation (50) one trial before convergence with the difference between the value of c at convergence and the value of c one trial before convergence gave a good indication of when good results in the comparison of the calculated pressure with the experimental pressure This ratio,  $\Delta P/\Delta c$ , was small in the would be obtained. region where good results were obtained and gradually increased until it became guite large in the region of poorest agreement between the calculated and the experimental pressures. This ratio was normalized by dividing it for each point by the highest value of  $\Delta P/\Delta c$ . The weighting factors were then taken as the square of the normalized ratios.

The results obtained using this set of weighting factors gave errors as large as six percent for two of the data points. Both of these points were in the category of high density and low pressure from Van Itterbeek et al.'s data at temperatures well below the critical temperature of methane. It was determined that the percent errors could be reduced significantly just by changing the densities within experimental error. This indicated that the calculated pressures in this region were quite sensitive to how accurately the experimental densities are determined. For points in the critical region, it was determined that the calculated pressures agreed reasonably well with the experimental pressures, but that the calculated densities exhibited significant error. The results based on the pressure-dependent weighting factors are summarized in Tables 3 and 4.

This set of weighting factors based on pressure improved the results, but the range of the weighting factors was quite large. Since there was greater experimental error in the determination of density than in pressure, another set of weighting factors based on density,  $(\Delta \rho / \Delta c)^2$ , was tried. These weighting factors were obtained by incrementing the density by 0.0001 $\rho$  to get  $\Delta \rho$  and using the combination of half-interval and Newton-Raphson searches to calculate a new cutoff parame-

ter c at the new density to get a  $\Delta c$ . The square of the ratio,  $\Delta \rho / \Delta c$ , at each data point was used as the set of weighting factors. The range of these weighting factors was several orders of magnitude less than the  $(\Delta P / \Delta c)^2$  weighting factors.

With  $(\Delta \rho / \Delta c)^2$  as weighting factors, the coefficients in equation (51) were determined using ORNOR. These coefficients are presented in Table 5. The calculated density was determined based on the best set of coefficients. Since equation (48) cannot be solved explicitly for density, a Newton-Raphson procedure was used to get a calculated density with the experimental density as the first guess. This allowed a comparison of the calculated and experimental densities for each data point. The results of this comparison are presented in Table 6 as percent error deviation from the experimental density. The number of data points in various density percent error ranges is given by the distribution presented in Table 7.

#### Equation of State Comparison

Vennix and Kobayashi (42) have presented an equation of state for methane over the temperature range 130°K to 625°K of the form

$$P = A + BT + Ce^{ET} + De^{F/T}$$
(52)

where the parameters A through F were functions of density. When these density dependencies are determined,

a mn	Coefficient
a.00	0.9545166049
a <sub>01</sub>	-1.183946501(10 <sup>-4</sup> )
<b>a</b> 10	-0.4202296521
a <sub>11</sub>	-2.2201321019(10 <sup>-3</sup>
a <sub>20</sub>	-0.3568076293
a <sub>21</sub>	5.587394360 (10 <sup>-3</sup> )
a <sub>02</sub>	5.230952723 (10 <sup>-8</sup> )
a <sub>12</sub>	2.838548311(10 <sup>-6</sup> )
a <sub>22</sub>	1.382944748 (10 <sup>-6</sup> )
a <sub>20</sub>	0.3789722080
30 a <sub>31</sub>	-2.555974520 (10 <sup>-3</sup> )
a <sub>22</sub>	-1.101158536 (10 <sup>-5</sup> )
a <sub>02</sub>	-2.563357752(10 <sup>-11</sup> )
03 ā <sub>12</sub>	-0.606002106(10-10,
12	-9.000893100(10)
<sup>a</sup> 23	-7.337450048(10)
a 33	1.001863633(10 <sup>-8</sup> )

## COEFFICIENTS IN EXPANSION FOR c FOR PRESSURE -DEPENDENT WEIGHTING FUNCTION

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Error Range %	Number of Points in Error Range
0.00 - 0.05	25
0.05 - 0.10	18
0.10 - 0.15	28
0.15 - 0.20	31
0.20 - 0.30	17
0.30 - 0.40	17
0.40 - 0.50	13
0.50 - 0.75	17
0.75 - 1.00	10
1.00 - 1.50	7
1.50 - 2.00	9
2.00 - 3.00	3
3.00 - 5.00	4
5.00 - 7.00	2

## DISTRIBUTION OF PERCENT ERROR IN CALCULATED PRESSURE BASED ON PRESSURE -DEPENDENT WEIGHTING FUNCTION

a mn	Coefficient
a <sub>00</sub>	0.9431335622
<b>a</b> <sub>01</sub>	6.787113475(10 <sup>-6</sup> )
<b>a</b> 10	-0.2546629657
a <sub>11</sub>	-3.489001609(10 <sup>-3</sup> )
a <sub>20</sub>	-0.7267769659
a <sub>21</sub>	6.528846879(10 <sup>-3</sup> )
a <sub>02</sub>	-1.771537368 (10 <sup>-7</sup> )
a <sub>12</sub>	3.778138717 (10 <sup>-6</sup> )
a <sub>22</sub>	1.122410498(10 <sup>-5</sup> )
a <sub>30</sub>	0.6044837121
a <sub>31</sub>	-1.905725456 (10 <sup>-3</sup> )
a <sub>32</sub>	-1.801666731(10 <sup>-5</sup> )
a <sub>03</sub>	1.139291111(10 <sup>-10</sup> )
a <sub>13</sub>	-1.186370 <b>78</b> 2 (10 <sup>-9</sup> )
a <sup>23</sup>	-1.083679821(10 <sup>-8</sup> )
a <sub>22</sub>	-2.393723741 (10 <sup>-8</sup> )
53	- •

# COEFFICIENTS IN EXPANSION FOR C FOR DENSITY-DEPENDENT WEIGHTING FUNCTION

Temperature °K	Pressure atm	Density gm/cc	Density Error*	
623.294	51.7135	0.01604	0.02758	
623.294	104.859	0.03209	0.02894	
623.294	132.137	0.04011	0.01018	
623.294	188.443	0.05615	-0.00646	
623.294	217.607	0.06417	0.00189	
623.294	247.584	0.07219	0.00660	
623.294	310.315	0.08823	0.01285	
623.294	377.366	0.10428	-0.04519	
598.285	49.5510	0.01604	0.01020	
598.285	100.309	0.03209	0.02838	
598.285	152.779	0.04813	0.00592	
598.285	207.506	0.06417	0.01097	
598.285	265.158	0.08021	0.01970	
598.285	326.437	0.09626	0.02908	
598.285	391.861	0.11230	-0.00391	
573.274	47.3886	0.01604	0.00858	
573.274	95.7579	0.03209	0.02428	
573.274	145.577	0.04813	0.01398	
573.274	197.433	0.06417	0.00362	
573.274	251.930	0.08021	0.00070	
573.274	309.736	0.09626	0.01212	
573.274	371.469	0.11230	-0.00063	
548.260	45.2272	0.01604	0.00109	
548.260	114.629	0.04011	-0.00446	
548.260	162.627	0.05615	-0.00870	
548.260	212.701	0.07219	-0.02194	
548.260	265.369	0.08823	-0.00220	
548.260	321.402	0.10428	0.01534	
548.260	381.550	0.12032	-0.03052	

# DENSITY ERRORS FOR EXPERIMENTAL METHANE DATA

\*Calculated by: % Error =  $100 (\rho_{EXP} - \rho_{CALC}) / \rho_{EXP}$ 

Temperature °K	Pressure atm	Density gm/cc	Density Error	
523.245	45.0621	0.01604	-0.00231	
523.245	86.6533	0.03209	-0.00161	
523.245	131.203	0.04813	-0.01225	
523.245	177.253	0.06417	-0.01822	
523.245	225.361	0.08021	-0.02117	
523.245	276.096	0.09626	0.00714	
523.245	330.194	0.11230	0.02064	
523.245	388.486	0.12834	-0.02947	
498.229	40.8956	0.01604	0.01178	
489.229	82.0866	0.03209	-0.01099	
498.229	123.999	0.04813	-0.03385	
498.229	145.375	0.05615	-0.02732	
498.229	212.021	0.08021	-0.02171	
498.229	259.190	0.09626	0.01407	
498.229	309.437	0.11230	0.02120	
498.229	335.895	0.12032	0.03247	
498.229	392.131	0.13636	-0.01044	
473.213	38.7272	0.01604	-0.01186	
473.213	77.5132	0.03209	-0.02215	
473.213	116.775	0.04813	-0.04566	
473.213	156.955	0.06417	-0.02327	
473.213	198.575	0.08021	0.00532	
473.213	242.212	0.09626	0.03457	
473.213	288.562	0.11230	0.03516	
473.213	338.389	0.12834	0.02534	
473.213	392.389	0.14438	-0.00586	
448.197	36.5563	0.01604	-0.01607	
448.197	72.9238	0.03209	-0.02381	
448.197	146.794	0.06417	-0.04515	
448.197	205.003	0.08823	-0.00313	
448.197	246.246	0.10428	-0.00795	
448.197	313.265	0.12834	0.00250	
448.197	389.120	0.15241	-0.04958	

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TABLE 6 (CONTINUED)

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Temperature °K	Pressure atm	Density gm/cc	Density Error
423.183	34, 3851	0.01604	-0,02591
423,183	68.3413	0.03209	-0.04839
423,183	102.263	0.04813	-0.07591
423,183	136,573	0.06417	-0.05105
423,183	171.732	0.08021	-0.00827
423,183	208.271	0.09626	0.02113
423,183	246.763	0.11230	0.01722
423.183	287.947	0.12834	-0.00438
423,183	332.497	0.14438	0.01293
423.183	381.333	0.16043	0.03368
398.170	32.2098	0.01604	-0.01299
389.170	63.7372	0.03209	-0.05780
398.170	79.3594	0.04011	-0.07414
398.170	94.9708	0.04813	-0.09023
398.170	110.607	0.05615	-0.08679
398.170	158.249	0.08021	-0.02527
398.170	191.168	0.09626	0.03162
398.170	225.715	0.11230	0.02772
398.170	282.021	0.13636	-0.02506
398.170	345.911	0.16043	0.02009
398.170	394.299	0.17647	0.03704
373.160	30.0335	0.01604	-0.04336
373.160	59.1366	0.03209	-0.09305
373.160	87.6730	0.04813	-0.12927
373.160	116.039	0.06417	-0.09061
373.160	144.666	0.08021	-0.02018
373.160	174.002	0.09626	0.04849
373.160	204.636	0.11230	0.02294
373.160	236.939	0.12834	0.02271
373.160	271.832	0.14438	-0.01064
373.160	310.141	0.16043	-0.00972
373.160	352.625	0.17647	0.06335
373.160	400.624	0.19251	0.07090

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TABLE 6 (CONTINUED)

Temperature °K	Pressure atm	Density gm/cc	Density Error	
348 153	27,8521	0 01604	-0 04859	
348,153	67.4960	0.04011	-0.13367	
348,153	118.352	0.07219	-0.08372	
348,153	156.818	0.09626	0.01834	
348.153	197.194	0.12032	0.03606	
348.153	257.611	0.15241	-0.11932	
348.153	310.911	0.17647	-0.04285	
348.153	375.024	0.20053	0.12281	
323.151	25.6660	0.01604	-0.04831	
323.151	49.8695	0.03209	-0.12423	
323.151	72.9595	0.04813	-0.18930	
323.151	95.3217	0.06417	-0.16998	
323.151	117.357	0.08021	-0.08832	
323.151	139.414	0.09626	0.05840	
323.151	162.061	0.11230	0.08323	
323.151	185.682	0.12834	0.04601	
323.151	210.964	0.14438	-0.09330	
323.151	238.376	0.16043	-0.16349	
323.151	268.975	0.17647	-0.19090	
323.151	303.533	0.19251	-0.06695	
323.151	322.698	0.20053	0.02558	
303.152	23.9153	0.01604	-0.05187	
303.152	46.1416	0.03209	-0.12972	
303.152	67.0516	0.04813	-0.24821	
303.152	96.7208	0.07219	-0.21420	
303.152	115.913	0.08823	-0.06881	
303.152	135.131	0.10428	0.07443	
303.152	154.733	0.12032	0.17698	
303.152	175.412	0.13636	0.07751	
303.152	197.499	0.15241	-0.03946	
303.152	221.865	0.16845	-0.20059	
303.152	249.205	0.18449	-0.23757	
303.152	280.535	0.20053	-0.11705	

TABLE 6 (CONTINUED)

TABLE 6	(CONTINUED)
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Temperature °K	Pressure atm	Density gm/cc	Density Error	
273.160	21.2760	0.01604	-0.01877	
273.160	31.1261	0.02406	-0.06343	
273.380	50.3899	0.04088	-0.21215	
273.160	66.3433	0.05615	-0.28362	
273.160	82.0686	0.07219	-0.26355	
273.160	104.298	0.09626	0.03653	
273.171	121.889	0.11561	0.22279	
273.160	133.639	0.12834	0.28445	
273.160	149.119	0.14438	0.21013	
273.160	174.687	0.16845	-0.06247	
272.698	198.417	0.18803	-0.37911	
273.153	250.234	0.21977	-0.21161	
275.155	297.529	0.23921	0.23871	
272.981	360.223	0.26397	0.66043	
272.927	485.083	0.29535	-0.26734	
252.821	45.2967	0.04092	-0.15587	
251.363	93.7745	0.10348	0.04883	
252.875	138.551	0.16341	0.26231	
253.272	161.843	0.18821	-0.25896	
252.960	180.949	0.20581	-0.48874	
253.099	200.350	0.21999	-0.45871	
253.056	232.881	0.23947	-0.15818	
254.520	294.129	0.26422	0.48140	
253.114	395.112	0.29564	0.72610	
253.816	517.995	0.31954	-0.97303	
233.522	40.4539	0.04095	-0.03032	
234.417	80.3681	0.10357	-0.00397	
236.376	110.305	0.15752	0.69385	
233.137	117.563	0.17865	0.44593	
233.379	124.326	0.18839	0.16409	
233.248	150.885	0.22020	-0.52946	
236.577	184.358	0.23967	-0.43262	
232.788	215.494	0.26450	0.03303	
233.055	256.563	0.28109	0.38677	
233.371	303.659	0.29594	0.69305	
235.756	534.466	0.33293	-0.82565	

TABLE 6	(CONTINUED)	)
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Temperature	Pressure	Density	Density
۰K	atm	gm/cc	Error
208.541	59.4822	0.10369	-0.16463
208.191	62.0863	0.11597	-0.32630
209.262	84.9837	0.20625	0.81580
207.164	86.2956	0.22048	0.39180
207.594	99.2583	0.24001	-0.25010
207.737	124.523	0.26483	-0.34911
208.789	155.366	0.28144	-0.22174
208.181	185.059	0.29632	0.07791
188.190	52.5620	0.26187	0.71910
188.190	71.7925	0.28353	-0.18303
188.190	87.2775	0.29456	-0.30152
188.190	117.948	0.30987	-0.31172
188.190	159.341	0.32489	-0.01824
188.190	214.493	0.33930	0.22512
188.190	287.925	0.35382	0.56381
172 790	26 5665	0 30327	0 21117
172.790	42.5451	0.31353	-0.22178
172.790	64.6694	0.32387	-0.43221
172.790	92.7263	0.33390	-0.45077
172.790	127.268	0.34355	-0.37557
172.790	167.238	0.35305	-0.10199
172.790	216.219	0.36257	0.19480
172.790	275.498	0.37225	0.54670
150 750	30 6120	0 36383	_0 11530
150.750	74 1346	0.37166	-0.24066
150 750	126 397	0 38021	-0 22126
150.750	187,514	0.38864	-0.05963
150.750	262.917	0.39744	0.20526
		•••••	
131.000	14.8269	0.39454	0.12085
131.000	78.3059	0.40317	-0.02126
131.000	155.673	0.41042	-0.31203
131.000	246.038	0.41853	-0.20602
114.530	8.8265	0.41933	1.17066
114.530	74.4346	0.42531	0.38330
114.530	131.507	0.43003	0.01344
114.530	229.401	0.43740	-0.25004
114.530	308.888	0.44293	-0.25278

# DISTRIBUTION OF PERCENT BRROR IN CALCULATED DENSITY BASED ON DENSITY-DEPENDENT WEIGHTING FUNCTION

Brror Range %	Number of Points in Error Range
0.00 - 0.05	101
0.05 - 0.10	24
0.10 - 0.15	10
0.15 - 0.20	11
0.20 - 0.30	26
0.30 - 0.40	10
0.40 - 0.50	7
0.50 - 0.75	8
0.75 - 1.00	3
1.00 - 1.25	1

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the final equation has twenty-five constants, which are determined empirically from experimental data. They used the data of Vennix (41) and Douslin <u>et al.</u> (15), but do not use the data of Van Itterbeek <u>et al</u>. (40). They state that there are serious discrepancies in the low temperature data of Van Itterbeek <u>et al</u>., and that this data set has been remeasured but has not yet appeared in the literature. Their equation of state predicted pressures that varied from the experimental pressure by an average absolute error of 0.04% with no deviation greater than 0.6%.

The present equation of state has sixteen constants in the expression for c. This equation predicts densities that vary from the experimental density by an average absolute error of 0.2% with a maximum error of 1.17%. These errors are not as small as those using the Vennix-Kobayashi equation with twenty-five constants. However, the present equation constants were derived using the Van Itterbeek <u>et al</u>. data as it now appears in the literature. When the revised data are presented, the cutoff parameter constants can be redetermined with an expected increase in the accuracy of predicting results. Also, a different form of the expression for c might improve the results appreciably.

#### Conclusions

The equation of state presented in this thesis

is a preliminary look at the feasibility of using a perturbation approach with empirically determined constants to represent PVT data over a wide temperature range that includes both the gas and liquid states. A survey of the results in Table 4 indicates that this approach shows promise. As the equation stands now, it is adequate for prediction in cases where extreme accuracy is not required. This reduced accuracy is to a great extent due to the discrepancies of the Van Itterbeek <u>et al</u>. low temperature data. When these data as presented in the literature were plotted, discrepancies much greater than can be attributed to reasonably expected experimental error were observed.

There are several possibilities for improving the results. The expression for the cutoff parameter could be reformulated using an approach that systematically handles the treatment of an expression that is a function of two variables. An approach such as this might reduce the number of constants required to adequately express c over the entire temperature range. Also, the two parameters  $\epsilon$  and  $\sigma$  could be allowed to vary in the curve-fitting procedure, instead of fixing their values as was done here. A combination of these changes might in the final analysis give the greatest accuracy using this perturbation approach in predicting PVT behavior.

#### CHAPTER VI

# DATA AND APPLICATIONS

The results of the treatment of the data are presented in this chapter. A discussion of the three gas analysis methods used to determine the composition of the gases is given so that a comparison can be made and the one that gives the most accurate results can be chosen. The reliability of the data is given in terms of the discrepancies between the experimental points from the fitted curves. The optimum values of the parameters that resulted in the best fit of the data are given in terms of the apparatus constants and the virial coefficients. Also, a comparison of results with other investigators is given for data where other values are available in the literature.

## Gases Used

The helium used in this work was Grade-A helium supplied by the U. S. Bureau of Mines and was selected for its high purity. The lower portion of Table 8 gives the Bureau of Mines composition analysis for helium with the total impurities present amounting to 1.7 parts per million. The argon was Matheson's prepurified grade having a quoted purity of 99.998 mole percent. The helium-

argon mixtures were prepared by the Matheson Company in size 1-A cylinders. Both the pure argon and the mixtures were the same ones used by Blancett (5) in his earlier work in this laboratory.

In addition to the composition analysis supplied by Matheson, an analysis of samples of both pure components and all mixtures was made by the U.S. Bureau of Mines Helium Research Center in Amarillo, Texas. These two sets of values were checked by a molecular weight determination in this laboratory. The method was similar to that described by Canfield (8). The molecular weights of the mixtures were determined by using a constant temperature bath that was set up adjacent to the Burnett apparatus described in Chapter III. The bath fluid was air and the temperature was controlled at 50°C by using a small heating element that was activated by a Hallikainen Thermotrol with proportional plus reset control. The temperature was determined using a Leeds and Northrup platinum resistance thermometer in conjunction with the G-2 Mueller Bridge described in Chapter III. A short run of 1/8 inch copper tubing connected the sample bomb inside the temperature bath with the Burnett apparatus so that the dead weight gages could be used to accurately measure the pressure.

After the temperature in the bath had been constant for several hours, the sample bomb was purged with the

mixture that was being studied by pressuring the bomb, venting, and evacuating it three or more times. The sample bomb was then pressured with the sample gas to approximately 250 psi and a valve in the neck of the bomb was closed from outside the temperature bath using a specially designed rod that extended into the bath. When the temperature had restabilized, the pressure was measured using the piston gages. The bomb was then carefully weighed several times over a period of several hours using a 300 gram capacity Right-A-Weigh analytical balance made by William Ainsworth and Sons, Inc. At each weighing the temperature and barometric pressure were recorded in addition to the weight, so that buoyancy corrections The mass of the gas in the bomb was then could be made. determined by subtracting the weight of the bomb empty from the weight of the bomb full.

The volume of the bomb was determined by assuming that the argon was pure. Equation (53) was then solved for the volume, and this volume was used in determining the molecular weights of the mixtures. Shana'a (33), who had the bomb constructed, gives the change in volume due to an increase in the internal pressure. The compressibility factor was determined at 50°C using data presented by Blancett (5) for these same mixtures. A Newton-Raphson procedure was used to determine the compressibility factor for the measured pressure by comparing

guesses of compressibility factors with those compressibility factors calculated using the virial coefficients presented by Blancett (5) until the values differed by less than 0.00001. This usually required only one or two iterations to converge depending on the initial guess. Thus, the temperature, pressure, volume, mass, and compressibility factor were known. The molecular weight of the mixtures could be calculated by

$$\mathbf{MW}_{Mix} = \frac{\mathbf{Z}\mathbf{m}\mathbf{R}\mathbf{T}}{\mathbf{PV}} \cdot$$
(53)

The mole fraction argon was then determined by

$$x_{Ar} = \frac{MW_{Mix} - MW_{He}}{MW_{Ar} - MW_{He}}$$
 (54)

The gas compositions determined by these three procedures are summarized in Table 8. The data in this thesis are based on the U.S. Bureau of Mines analysis.

#### TABLE 8

HELIUM-ARGON MIXTURE COMPOSITIONS

Mixture	Molecular Weight	U.S. Bureau of Mines	Matheson
A	79.86	80.00	79.70
В	59.31	59.35	59.40
С	40.96	41.05	40.20
D	21.85	21.99	22.00

\*All entries are mole percent helium.

Component	Amount, parts per million
н <sub>2</sub> 0	1.0
Ne	0.4
N <sub>2</sub>	0.2
°2	0.1
	Total 1.7 ppm

Analysis of Impurities in Helium:

#### Experimental Data

The compressibility factors determined in this work are presented in Tables 9 through 31, where they are listed with the corresponding experimental and calculated pressures and the pressure deviations. Bach table gives the optimal results for one isocomp-isotherm. The compressibility factor is presented as calculated from the Burnett analysis, equation (13), and from the virial expansion, equation (55), along with the deviation between the two. The deviations printed are sometimes not the exact difference between pressures or between compressibility factors because of truncation error in the computer calculations. The estimated standard errors for each pressure and for each compressibility factor are also tabulated. These estimates were calculated using equations (D-7) and (D-8) of the procedure described in Appendix D.

The cell constants and run constants for the two runs are presented in the second part of the tables. The

# EXPERIMENTAL AND CALCULATED RESULTS FOR 100.00% HELIUM AT -90°C

P(EXP) ATM.	P(CALC) Atm.	DEV. In P	STANDARD Error In P	Z(BURNETT)	Z(VIRIAL)	DEV. In Z	STANDARD Error in Z
675.3889	675.3842	0.0047	0.0278	1.51136	1.51135	0.00001	0.00024
368.3178	368.3276	-0.0097	0.0128	1.28798	1.28801	-0.00003	0.00020
214.1958	214.1846	0.0113	0.0052	1.17039	1.17033	0.00006	0.00014
129.2930	129.2894	0.0036	0.0028	1.10385	1.10382	0.00003	0.00012
79 . 798 1	79.7974	0.0007	0.0015	1.06448	1.06447	0.00001	0.00010
49.9187	49.9220	-0.0033	0.0009	1.04041	1.04048	-0.00007	0.00009
31.4930	31.4948	-0.0018	0.0006	1.02554	1.02560	-0.00006	0.00008
19.9741	19.9743	-0.0001	0.0004	1.01626	1.01626	-0.00001	0.00007
12.7103	12.7100	0.0003	0.0003	1.01038	1.01036	0.00002	0.00005
8.1045	8.1047	-0.0002	0.0002	1.00658	1.00661	-0.00003	0.00005
5.1751	5.1751	0.0000	0.0002	1.00423	1.00422	0.00001	0.00006
3.3076	3.3072	0.0004	0.0001	1.00283	1.00270	0.00013	0.00008
517.5289	517.5330	-0.0041	0.0176	1.39830	1.39831	-0.00001	0.00022
291.2623	291.2567	0.0055	0.0073	1.22968	1.22966	0.00002	0.00016
172.4757	172.4837	-0.0080	0.0042	1.13776	1.13782	-0.00005	0.00012
105.2434	105.2465	-0.0030	0.0023	1.08473	1.08476	-0.00003	0.00011
65.3857	65.3845	0.0013	0.0012	1.05294	1.05292	0.00002	0.00010
41.0726	41.0711	0.0015	0.0008	1.03338	1.03335	0.00004	0.00009
25.9776	25.9769	0.0007	0.0005	1.02116	1.02113	0.00003	0.00008
16.5018	16.5013	0.0005	0.0004	1.01347	1.01344	0.00003	0.00006
10.5111	10.5109	0.0002	0.0002	1.00859	1.00857	0.00002	0.00005
6.707.2	6.7069	0.0003	0.0002	1.00552	1.00547	0.00005	0.00005
4.2840	4.2843	-0.0003	0.0001	1.00342	1.00350	-0.00008	0.00007
2 .7 38 4	2.7388	-0.0004	0.0001	1.00209	1.00224	-0.00015	0.0009

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 PARAMETER	VALUE	STANDARD ERROR	
A(1)	446.8739676	0.0712413	
A(2)	370.1130478	0.0545304	
N(1)	1.5623974	0.0000265	
N(2)	1.5623632	0.0000251	
B(2)	0.12271634D 02	0.27934578D-01	
B(3)	0.12369844D 03	0.16045562D 01	
B(4)	0.14105876D 04	0.36202677D 02	
 BFC =0.57907	D-02	$\Sigma (P_E - P_C) = 0.377050-04$	

TABLE 9 (CONTINUED)

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# EXPERIMENTAL AND CALCULATED RESULTS FOR 80.00% HELIUM AT -90°C

P( EXP) A TM.	P(CALC) Atm.	DEV. In p	STANDARD Error in P	Z(BURNETT)	Z(VIRIAL)	DEV. In Z	<b>STANDA</b> RD Error in Z
676.2770	676.2771	-0.0001	0.0202	1.57663	1.57663	-0.00000	0.00026
353.6133	353.6197	-0.0064	0.0091	1.28825	1.28827	-0.00002	0.00019
203.3839	203.3851	-0.0012	0.0037	1.15774	1.15775	-0.00001	0.00015
122.7151	122.7113	0.0038	0.0020	1.09144	1.09140	0.00003	0.00012
75.9150	75:-9133	0.0017	0.0012	1.05493	1.05491	0.00002	0.00010
47.6138	476132	0.0007	0.0007	1.03376	1.03375	0.00001	0.00009
30.0997	30.1003	-0.0006	0.0004	1.02103	1.02105	-0.00002	0.00008
19.1184	19.1186	-0.0002	0.0003	1.01324	1.01325	-0.00001	0.00007
12.1779	12.1782	-0.0003	0.0002	1.00837	1.00839	-0.00002	0.00005
7.7709	7.7711	-0.002	0.0001	1.00531	1.00533	-0.00002	0.00005
4.9643	4.9643	-0.0001	0.0001	1.00338	1.00340	-0.00002	0.00005
3.1738	3.1736	0.0003	0.0001	1.00225	1.00217	0.00008	0.00006
511.0311	511.0300	0.0011	0.0142	1.42890	1.42890	0.00000	0.00022
280.0519	280-0424	0.0095	0.0062	1.22360	1.22356	0.00004	0.00019
164.8747	164.8821	-0.0074	0.0031	1.12557	1.12562	-0.00005	0.00014
100.6917	100.6902	0.0015	0.0016	1.07403	1.07401	0.00002	0.00011
62 .697 4	62.7004	-0.0030	0.0009	1.04488	1.04493	-0.00005	0.00010
39.4733	39.4730	0.0003	0.0006	1.02781	1.02780	0.00001	0.00009
25.0091	25.0091	-0.0000	0.0004	1.01741	1.01742	-0.00000	0.00008
15.9067	15.9060	0.0007	0.0003	1.01104	1.01099	0.00004	0.00006
10.1402	10.1402	0.0000	0.0002	1.00698	1.00697	0.00000	0.00005
6.4742	6.4739	0.0003	0.0001	1.00449	1.00444	0.00005	0.00004
4.1369	4.1370	-0.0000	0.0001	1.00283	1.00283	-0.00000	0.00005
2.6449	2.6452	-0.0002	0.0001	1.00172	1.00181	-0.00009	0.00007

 PARAMETER	VALUE	STANDARD Error	
A(1)	428.9372836	0.0685960	
A(2)	357.6387542	0.0562270	
N(1)	1.5623644	0.0000247	
N(2)	1.5623731	0.000254	
8(2)	0.10246538D 02	0.39867953D-01	
B(3)	0.24083183D 03	0.43904148D 01	
8(4)	0.274406130 04	0.23217797D 03	
B(5)	0.36462861D 05	0.39508133D 04	
BFC =0.33260	D-02	$\Sigma (P_E - P_C) =42620D - 05$	

TABLE 10 (CONTINUED)

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P(CALC) ATM.	DEV.	STANDARD Error in P	Z(BURNETT)	Z(VIRIAL)	DEV. In Z	STANDARD Error in Z
671.2617	0-0002	0.0406	1.57971	1.57971	0.00000	0.00074
330.8239	0.0026	0-0178	1.21616	1.21615	0.00001	0.00051
189.9044	-0.0007	0.0079	1.09040	1.09040	-0.00000	0.00043
116-1140	0.0061	0.0044	1.04136	1.04131	0.00005	0.00035
72.8578	-0.0017	0.0024	1.02046	1.02048	-0.00002	0.00028
46.2118	0.0004	0.0014	1.01091	1.01091	0.00001	0.00024
29.4494	-0.0005	0.0009	1.00613	1.00615	-0.00002	0.00021
18.8086	-0.0023	0.0006	1.00349	1.00361	-0.00012	0.00018
12-0258	-0-0008	0.0004	1.00212	1.00218	-0-00007	0.00015
7-6936	0.0011	0.0003	1.00149	1.00135	0.00014	0.00011
4.9237	0.0004	0.0002	1.00091	1.00084	0.00007	0.00010
3-1516	0.0000	0.0002	1.00053	1.00053	0.00000	0.00013
495.5130	-0.0009	0.0296	1.38761	1.38761	-0.00000	0.00062
263.3676	-0.0024	0.0140	1.15211	1.15212	-0.00001	0.00045
155.9887	-0.0006	0.0062	1.06591	1.06592	-0.00000	0.00039
96.6043	-0.0032	0.0031	1.03108	1.03112	-0.00003	0.00031
60.9340	-0.0015	0.0021	1.01586	1.01589	-0.00003	0.00026
38.7339	0.0023	0.0012	1.00873	1.00866	0.00006	0.00023
24.7076	0.0016	0.0008	1.00503	1.00497	0.00006	0.00020
15.7868	0.0008	0.0006	1.00301	1.00296	0.00005	0.00017
10.0955	0.0002	0.0004	1.00183	1.00180	0.00002	0.00014
6.4591	-0.0011	0.0003	1.00095	1.00112	-0.00017	0.00011
4.1336	0.0002	0.0002	1.00075	1.00070	0.00004	0.00010
2.6457	-0.0002	0.0002	1.00038	1.00044	-0.0006	0.00014
	P(CALC) ATH. 330.8239 189.9044 116.1140 72.8578 46.2118 29.4494 18.8086 12.0258 7.6936 4.9237 3.1516 155.9887 96.6043 60.9340 38.7339 24.7076 15.7868 10.0955 6.4591 4.1336	P(CALC) DEV.   ATM. IN P   1N P 10.0002   330.8239 0.0002   116.1140 0.0001   12.8578 -0.0001   146.2118 0.0004   29.4494 -0.0005   189.9044 -0.0001   146.2118 0.0004   29.4494 -0.0002   12.0258 -0.0004   7.6936 -0.0002   12.0258 -0.0004   12.0258 -0.0004   12.0258 -0.0002   263.3676 -0.0001   155.9887 -0.0002   263.3676 -0.0002   96.6043 -0.0002   96.6043 -0.0002   96.6043 -0.0002   15.7868 0.0002   10.0023 -0.0002   2.6457 -0.0002   2.6457 -0.0002	PICALCJ DEV. STANDARD   4714. IN P ERROR IN P   330.8239 0.0002 0.0017   189.9239 0.0004 0.0007   116.1140 0.0004 0.0004   12.8578 -0.00017 0.0004   13.0.8239 0.0004 0.0004   116.1140 0.0004 0.0004   12.8578 -0.00017 0.00024   13.1516 -0.00023 0.0004   12.0258 -0.00011 0.0004   12.0258 -0.00011 0.0004   14.9237 0.0004 0.0004   15.5.9887 -0.0002 0.0002   15.5.9887 -0.0002 0.00296   24.7076 0.0014 0.0002   0.0015 0.0012 0.0012   15.7868 0.0002 0.0021   16.4591 -0.0002 0.0002   16.4591 -0.0002 0.0002   2.6457 -0.0002 0.0004   15.7868 0.0002 0.0002   0.0002 0.0002 0.0002   0.0002	PICALCJ   DEV.   STANDARD   ZIBURNETTJ     ATM.   IN P   ERROR IN P   ERROR IN P     330.8239   0.0002   0.0002   0.0017     116.1140   0.0004   1.051971   0.0024     12.8578   -0.00017   0.0004   1.04136     12.8578   -0.0003   0.0004   1.04136     12.0258   -0.0003   0.0004   1.00109     12.0258   -0.0003   0.0004   1.00109     12.0258   -0.0003   0.0004   1.00212     12.0258   -0.0003   1.00109   1.00214     12.0258   -0.0004   1.00212   1.00053     14.9237   0.0004   1.00212   1.00053     15.5.9887   -0.0002   1.00212   1.00212     155.9887   -0.0002   1.00214   1.00212     155.9887   -0.0022   1.00253   1.00149     155.7868   0.0002   1.00253   1.00253     15.7868   0.0002   1.00503   1.00503     15.	PICALC)   DEV.   STANDARD   ZIGURNETT   ZIVIRIAL)     671.2617   0.0002   0.0406   1.57971   1.57971     330.8239   0.0026   0.0178   1.21616   1.21616     189.9044   -0.0007   0.0004   1.09040   1.09040     116.1140   0.0004   0.0004   1.02046   1.021616     12.0578   -0.0017   0.0004   1.02046   1.02046     12.02348   -0.0005   0.0004   1.001091   1.01091     12.0235   -0.0008   0.0004   1.00212   1.00218     7.6936   -0.0003   1.001491   1.00191   1.00218     7.6936   -0.0004   1.00212   1.00218   1.00218     7.6936   -0.0002   1.00053   1.00211   1.00218     15.9887   -0.0002   1.00053   1.00218   1.00135     15.9887   -0.0024   0.0021   1.00553   1.00253     15.9887   -0.0015   0.0021   1.05211   1.15212     1.0.0183 <td>PICALCI ATH.   DEV. IN P   STANDARD ERROR   ZIBURNETTI ZIBURNET ZIBURNETTI ZIBURNETTI ZIBURNETTI ZIBURNETTI ZIBURNETTI ZIBURNETTI</td>	PICALCI ATH.   DEV. IN P   STANDARD ERROR   ZIBURNETTI ZIBURNET ZIBURNETTI ZIBURNETTI ZIBURNETTI ZIBURNETTI ZIBURNETTI ZIBURNETTI

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TABLE 11

# EXPERIMENTAL AND CALCULATED RESULTS FOR 59.35% HELIUM AT -90°C

PARAMETER	VALUE	STANDARD Error	
 A(1)	424.9274677	0.1969315	
A(2)	357-0970392	0.1559100	
N(1)	1.5617856	0.0000690	
N(2)	1.5619351	0.000664	
B(2)	0.24650806D 01	0.140813270 00	
8(3)	0.328789340 03	0.24469097D 02	
B(4)	0.13795749D 05	0.215101680 04	
8(5)	-0.28605727D 06	0.83002474D 05	
8(6)	0.65374880D 07	0.11792527D 07	
BFC =0.1488	90-01	$\Sigma (P_E - P_C) =103940 - 05$	

TABLE 11 (CONTINUED)

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# EXPERIMENTAL AND CALCULATED RESULTS FOR 41.05% HELIUM AT -90°C

P( EXP) A TM.	P(CALC) Atm.	DEV. In p	STANDARD Error in P	Z(BURNETT)	Z(VIRIAL)	DEV. In Z	STANDARD Error in Z
674.3078	674.3079	-0.0001	0.0418	1.55937	1.55937	-0.00000	0.00071
301.9050	301.9078	-0.0027	0.0170	1.09101	1.09102	-0.00001	0.00044
173.6286	173-6237	0.0049	0.0074	0.98038	0.98035	0.00003	0.00038
108.8380	108.8415	-0.0035	0.0042	0.96018	0.96021	-0.00003	0.00031
69 • 962 9	69.9662	-0.0033	0.0024	0.96434	0.96439	-0.00005	0.00026
45 .1953	45.1963	-0.0010	0.0014	0.97329	0.97331	-0.00002	0.00023
29.1701	29.1683	0.0018	0.0009	0.98146	0.98140	0.00006	0.00020
18.7867	18.7852	0.0014	0.0006	0.98757	0.98749	0.00008	0.00018
12.0761	12.0755	0.0006	0.0004	0.99180	0.99175	0.00005	0.00014
7.7513	7.7514	-0.0001	0.0003	0.99461	0.99462	-0.00002	0.00011
4.9702	4.9708	-0.0006	0.0002	0.99639	0.99652	-0.00013	0.00010
3.1855	3.1856	-0.0001	0.0002	0.99773	0.99776	-0.00003	0.00013
488 .4096	488.4091	0.0005	0.0300	1.31733	1.31733	0.00000	0.00058
245.3280	245.3250	0.0030	0.0135	1.03403	1.03402	0.00001	0.00039
146.9995	147.0081	-0.0086	0.0060	0.96815	0.96821	-0.00006	0.00034
93 .332 0	93.3220	0.0100	0.0031	0.96048	0.96038	0.00010	0.00028
60.1627	60.1604	0.0023	0.0021	0.96741	0.96737	0.00004	0.00024
38 .8 53 8	38.8583	-0.0046	0.0012	0.97619	0.97631	-0.00011	0.00022
25.0590	25.0586	0.0004	0.0008	0.98375	0.98373	0-00002	0.00020
16.1255	16.1259	-0.0004	0.0006	0.98912	0.98915	-0.00003	0.00017
10.3593	10.3596	-0-0003	0-0004	0.99285	0.99288	-0.00003	0.00014
6.6468	6.6469	-0-0000	0.0003	0.99537	0.99537	-0.00001	0.00011
4 260 9	4.2611	-0.0001	0.0002	0.99699	0.99701	-0.00002	0.00010
2.7305	2.7300	0.0005	0.0002	0.99826	0.99807	0.00019	0.00014

PARAMETER	VALUE	STANDARD Error	
A(1)	432.4233538	0.1951460	
A(2)	370.7567042	0.1577948	
N(1)	1.5623533	0.000678	
N(2)	1.5624772	0.0000650	
B(2)	-0.10695041D 02	0.12855899D 00	
B(3)	0.62492613D 03	0.22989253D 02	
B(4)	0.14281530D 05	0.19866612D 04	
B(5)	-0.34073028D 06	0.750778410 05	
B(6)	0.12323874D 08	0.10618170D 07	
8FC =0.1579	1D-01	$\Sigma (P_E - P_C) = 0.312260 - 04$	

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TABLE 12 (CONTINUED)

# EXPERIMENTAL AND CALCULATED RESULTS FOR 21.99% HELIUM AT -90°C

P(EXP) ATM.	P(CALC) ATM.	DEV. In P	STANDARD Error in P	Z(BURNETT)	Z(VIRIAL)	DEV. In Z	STANDARD Error in Z
673.7275	673.7290	-0.0015	0.0497	1.53885	1.53885	-0.00000	0.00115
251.6036	251.6162	-0.0126	0.0177	0.89801	0.89806	-0.00005	0.00062
146.7417	146.7481	-0.0063	0.0094	0.81829	0.81832	-0.00004	0.00049
96 .695 0	96.6843	0.0107	0.0047	0.84242	0.84233	0.00009	0.00047
64.9073	64.8988	0.0085	0.0026	0.88346	0.88335	0.00012	0.00041
43.2329	43.2328	0.0001	0.0019	0.91934	0.91933	0.00000	0.00036
28.4761	28.4774	-0.0013	0.0011	0.94603	0.94607	-0.00004	0.00032
18.5848	18.5849	-0.0001	0.0008	0.96459	0.96459	-0.00000	0.00029
12.0481	12.0488	-0.0007	0.0006	0.97693	0.97699	-0.00006	0.00024
7.7767	7.7766	0.0001	0.0004	0.98514	0.98513	0.00001	0.00018
5.0041	5.0045	-0.0004	0.0003	0.99036	0.99043	-0.00007	0.00014
3.2146	3.2144	0.0002	0.0003	0.99391	0.99385	0.00006	0.00016
480.2563	480.2531	0.0032	0.0354	1.23657	1.23657	0.00001	0.00091
212.5397	212.5240	0.0157	0.0143	0.85494	0.85488	0.00006	0.00057
130.5473	130-5498	-0.0025	0.0063	0.82030	0.82031	-0.00002	0.00050
86 •905 2	86.9136	-0.0084	0.0044	0.85299	0.85308	-0.00008	0.00047
58.2890	58.2960	-0.0071	0.0024	0.89367	0.89378	-0.00011	0.00040
38.7233	38.7228	0.0006	0.0016	0.92738	0.92736	0.00001	0.00035
25.4411	25.4412	-0.0001	0.0010	0.95171	0.95172	-0.00000	0.00032
16.5746	16.5729	0.0018	0.0007	0.96850	0.96840	0.00010	0.00028
10.7318	10.7315	0.0003	0.0005	0.97953	0.97950	0.00003	0.00022
6.9212	6.9213	-0.0001	0.0003	0.98675	0.98677	-0.00002	0.00016
4.4521	4.4522	-0.0001	0.0003	0.99146	0.99148	-0.00002	0.00013
2.8591	2.8591	0.0001	0.0003	0.99456	0.99453	0.00002	0.00017

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PARAMETER	VALUE	STANDARD Error	
A(1)	437.8128960	0.3244913	
A(2)	388.3765324	0.2857555	
N(1)	1.5622774	0.0001058	
N(2)	1.5620088	0.0001081	
B(2)	-0.28752386D 02	0.25881107D 00	
B(3)	0.83131611D 03	0.67980755D 02	
B(4)	0.45253027D 05	0.85132376D 04	
B(5)	-0.25678667D 07	0.52597950D 06	
B(6)	0.812122450 08	0.15774997D 08	
B(7)	-0.49470306D 09	0.17943458D 09	
BFC =0.24710	5D-01	$\Sigma (P_E - P_C) =101040 - 04$	

TABLE 13 (CONTINUED)

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## EXPERIMENTAL AND CALCULATED RESULTS FOR 100.00% ARGON AT -90°C

P(EXP) ATN.	P(CALC) Atm.	DEV. In p	STANDARD Error in P	Z(BURNETT)	Z(VIRIAL)	DEV. In Z	STANDARD Error in Z
657.3672	657.3670	0.0002	0.0399	1.50767	1.50767	0.00000	0.00085
159.8933	159.8915	0.0018	0.0095	0.57298	0.57297	0.00001	0.00030
101.8641	101.8615	0.0026	0.0054	0.57023	0.57021	0.00001	0.00026
76.1874	76.1932	-0.0058	0.0030	0.66623	0.66628	-0.00005	0.00028
55.8203	55.8180	0.0023	0.0018	0.76251	0.76248	0.00003	0.00026
39.2912	39.2966	-0.0055	0.0014	0.83841	0.83853	-0.00012	0.00024
26.7921	26.7903	0.0018	0.0009	0.89306	0.89300	0.00006	0.00023
17.8632	17.8628	0.0005	0.0006	0.93012	0.93010	0.00002	0.00021
11.7382	11.7377	0.0005	0.0005	0.95474	0.95470	0.00004	0.00018
7.6412	7.6407	0.0005	0.0003	0.97085	0.97079	0.00006	0.00014
4.9436	4.9439	-0.0002	0.0002	0.98116	0.98121	-0.00005	0.00011
3.1864	3.1866	-0.0003	0.0002	0.98786	0.98794	-0.00008	0.00013
394.3160	394.3164	-0.0004	0.0240	1.01460	1.01460	-0.00000	0.00057
136.1060	136.1087	-0.0027	0.0079	0.54721	0.54722	-0.00001	0.00028
94.2986	94.2983	0.0003	0.0037	0.59232	0.59232	0.00000	0.00028
70.5673	70.5656	0.0016	0.0030	0.69252	0.69250	0.00002	0.00029
51.1609	51.1567	0.0041	0.0017	0.78440	0.78434	0.00006	0.00027
35.6771	35.6769	0.0002	0.0012	0.85460	0.85459	0.00000	0.00025
24.1577	24.1585	-0.0008	0.0008	0.90406	0.90409	-0.00003	0.00023
16.0343	16.0350	-0.0006	0.0006	0.93747	0.93751	-0.00004	0.00020
10.5051	10.5052	-0.0000	0.0004	0.95957	0.95957	-0.00000	0.00017
6.8249	6.8249	-0.0000	0.0003	0.97395	0.97395	-0.00000	0.00012
4.4098	4.4102	-0.0004	0.0002	0.98318	0.98326	-0.00008	0.00010
2 .840 6	2.8401	0.0004	0.0002	0.98941	0.98926	0.00015	0.00014

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PARA	AETER V/	ALUE	STANDARD ERROR	
A(	(1) 436.(	01652 <b>76</b>	0.244330	1
A	388.0	5417357	0.218917	B
N	(1) 1.9	5620835	0.00080	8
N	(2) 1.9	5623030	0.000083	8
8(	(2) -0.56479	549D 02 0.	18432967D 0	0
B	(3) 0.128694	467D 04 0.	53310580D 0	2
B	(4) 0.90391	637D 05 0.	67263649D 0	<b>4</b>
В	(5) -0.70502	503D 07 0.	42028103D 0	6
8	(6) 0.21739	1120 09 0.	12780101D 0	8
B	(7) -0.10360	2390 10 0.	145293820 0	9
BFC =(	0.15959D-01	Σ(P <sub>e</sub>	- P <sub>C</sub> )=0.179	28D-04

TABLE 14 (CONTINUED)

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## EXPERIMENTAL AND CALCULATED RESULTS FOR 100.00% HELIUM AT -115°C

P( EX P) A TM.	P(CALC) Atm.	DEV. In P	STANDARD Error in P	Z(BURNETT)	Z(VIRIAL)	DEV. In Z	STANDARD Error in Z
701.7420	701.7736	-0.0316	0.0823	1.61937	1.61944	-0.00007	0.00076
371.6829	371.7175	-0.0346	0.0370	1.34050	1.34063	-0.00012	0.00062
212.7295	212.7532	-0.0237	0.0148	1.19896	1.19910	-0.00013	0.00043
127 <b>.2</b> 69 1	127.2482	0.0209	0.0079	1.12089	1.12071	0.00018	0.00034
78.1040	78.0947	0.0094	0.0042	1.07490	1.07478	0.00013	0.00030
48.6876	48.6815	0.0060	0.0026	1.04704	1.04691	0.00013	0.00027
30 • 6 4 3 3	30.6408	0.0025	0.0018	1.02974	1.02965	0.00009	0.00023
19.4043	19.4029	0.0014	0.0012	1.01891	1.01883	0.00007	0.00019
12.3324	12.3338	-0.0014	0.0008	1.01188	1.01199	-0.00012	0.00016
7.8587	7.8594	-0.0007	0.0006	1.00756	1.00765	-0.00009	0.00015
5.0154	5.0160	-0.0006	0.0005	1.00477	1.00489	-0.00012	0.00018
3 • 2 0 3 9	3.2044	-0.0005	0.0004	1.00295	1.00312	-0.00017	0.00024
532.7730	532.7091	0.0639	0.0521	1.47920	1.47902	0.00018	0.00069
292.9683	292.9637	0.0046	0.0209	1.27117	1.27115	0.00002	0.00049
171.2861	171.2746	0.0115	0.0117	1.16137	1.16129	0.00008	0.00036
103.6959	103.7098	-0.0140	0.0066	1.09865	1.09880	-0-00015	0.00031
64.1145	64.1220	-0.0074	0.0035	1.06145	1.06158	-0.00012	0-00028
40.1491	40.1545	-0.0054	0.0022	1.03863	1.03877	-0.00014	0-00026
25.3409	25.3463	-0.0054	0.0015	1.02434	1.02456	-0-00022	0.00022
16.0812	16.0794	0.0018	0.0010	1.01573	1.01562	0-00011	0.00018
10.2350	10.2331	0.0019	0.0007	1.01014	1.00996	0.00019	0-00016
6.5260	6.5256	0.0005	0.0005	1.00643	1.00636	0.00007	0.00016
4.1672	4.1667	0.0005	0.0004	1.00417	1.00406	0.00011	0-00019
2.6630	2.6627	0.0003	0.0004	1.00269	1.00260	0.00010	0.00026

PARAMET	TER VALUE	STANDARD Error	
A(1)	433.3433792	0.2017476	
A(2)	360.1758989	0.1553819	
N(1)	1.5625762	0.0000773	
N(2)	1.5625505	0.0000733	
B(2)	0.126626440 02	0.738156870-01	
B(3)	0.112983100 03	0.372378080 01	
B(4)	0.18964162D 04	0.771355090 02	
BFC =0.5	50937D-01	$\Sigma (P_E - P_C) =242350 - 03$	

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TABLE 15 (CONTINUED)

#### EXPERIMENTAL ANC CALCULATED RESULTS FOR 80.00% HELIUM AT -115°C

P{ EXP} ATM.	P(CALC) Atn.	DEV. In P	STANDARD Error in P	Z(BURNETT)	Z(VIRIAL)	DEV. In Z	STANDARD Error in Z
667.9564	667.9530	0.0034	0.0537	1.65813	1.65812	0.00001	0.00107
338.4657	338.4426	0.0232	0.0241	1.31274	1.31265	0.00009	0.00075
192.2765	192.2943	-0.0178	0.0106	1.16504	1.16515	-0.00011	0.00063
115.5430	115.5502	-0.0072	0.0058	1.09369	1.09375	-0.00007	0.00051
71.4028	71.4059	-0.0030	0.0032	1.05582	1.05586	-0.00004	0.00041
447778	44.7765	0.0013	0.0019	1.03432	1.03429	0.00003	0.00034
28.3081	28.3070	0.0011	0.0011	1.02146	1.02142	0.00004	0.00030
17.9819	17.9806	0.0013	0.0008	1.01359	1.01351	0.00007	0.00026
11.4560	11.4543	0.0017	0.0006	1.00873	1.00858	0.00015	0.00020
7.3098	7.3099	-0.0000	0.0004	1.00545	1.00546	-0.00001	0.00015
4.6695	4.6703	-0.0008	0.0003	1.00332	1.00348	-0.00016	0.00013
2.9856	2.9860	-0.0004	0.0003	1.00210	1.00223	-0.00013	0.00017
503.6550	503.6665	-0.0115	0.0399	1.48563	1.48566	-0.00003	0.00092
269.4156	269.4287	-0.0130	0.0189	1.24172	1.24178	-0.00006	0.00067
157.1779	157.1586	0.0193	0.0083	1.13184	1.13171	0.00014	0.00057
95.6791	95.6717	0.0075	0.0041	1.07645	1.07637	0.00008	0.00045
59.5138	59.5149	-0.0010	0.0027	1.04609	1.04611	-0.00002	0.00037
37 .452 3	37.4535	-0.0011	0.0015	1.02850	1.02853	-0.00003	0.00032
23.7227	23.7253	-0.0026	0.0010	1.01779	1.01790	-0.00011	0.00029
15.0873	15.0879	-0.0006	0.0007	1.01128	1.01132	-0.00004	0.00024
9.6175	9.6180	-0.0005	0.0005	1.00714	1.00719	-0.00006	0.00019
6.1405	6.1403	0.0001	0.0003	1.00460	1.00458	0.00002	0.00015
3.9242	3.9238	0.0004	0.0003	1.00303	1.00293	0.00010	0.00014
2.5093	2.5089	0.0003	0.0003	1.00201	1.00187	0.00014	0.00019

PA	RAMETER	VALUE	STANDAR Error	D
	A(1)	402.8379741	0.25768	37
	A(2)	339.0187437	0.20481	24
	N(1)	1.5621135	0.0009	50
	N(2)	1.5623027	0.0009	17
	B(2)	0.96572578D 01	0.18112552D	00
	8(3)	0.15222850D 03	0.277402350	02
	B(4)	0.110291730 05	0.222453960	04
	B(5)	-0.23362159D 06	0.78454798D	05
	8(6)	0.342305650 07	0.101278770	07
BFC	=0.25973	D-01	$\Sigma (P_{E} - P_{C}) = 0.29$	084D-04

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TABLE 16 (CONTINUED)

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## EXPERIMENTAL AND CALCULATED RESULTS FOR 59.35% HELIUM AT -115°C (FLUID-FLUID PHASE SEPARATION SUSPECTED)

P(EXP) Atm.	P(CALC) ATM.	DEV. In P	STANDARD Error in P	Z(BURNETT)	Z(VIRIAL)	DEV. In Z	STANDARD Error in Z
674.5533	674.5191	0.0342	0.3398	1.55047	1.55039	0.00008	0.00367
309.3210	309.4213	-0.1003	0.1472	1.11179	1.11215	-0.00036	0.00255
174.7575	174.6073	0.1502	0.0607	0.98212	0.98127	0.00084	0.00169
108.3656	108.4611	-0.0955	0.0371	0.95217	0.95301	-0.00084	0.00141
69.5962	69.6000	-0.0038	0.0194	0.95609	0.95615	-0.00005	0.00134
45.0127	44.9960	0.0167	0.0125	0.96680	0.96644	0.00036	0.00126
29.0801	29.0741	0.0060	0.0086	0.97652	0.97632	0.00020	0.00111
18.7409	18.7417	-0.0007	0.0054	0.98392	0.98395	-0.00004	0.00090
12.0518	12.0535	-0.0016	0.0034	0.98924	0.98937	-0.00013	0.00071
7.7368	7.7383	-0.0014	0.0025	0.99287	0.99305	-0.00018	0.00066
4.9612	4.9617	-0.0005	0.0022	0.99540	0.99550	-0-00009	0.00086
3.1796	3.1787	0.0009	0.0020	0.99738	0.99709	0.00029	0.00121
	PARAMETER VALUE			ST. E			
	A(1)	43	35.0643913	1.	0223176		
	N(1)		1.5634322	0.	0003960		
	8(2)	-0.120	006470D 02	0.30756	313D 00		
	B(3)	0.72	634649D 03	0.17427	4030 02		
	B(4)	0.36	233647D 04	0.42845	016D 03		
	8FC =0.579	957D 00	·	$\Sigma (P_E - P_C)$	=0.414110-	02	

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#### EXPERIMENTAL AND CALCULATED RESULTS FOR 59.35% HELIUM AT -115°C

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P(EXP) Atm.	P(CALC) ATM.	DEV. In P	STANDARD Error in P	Z(BURNETT)	Z(VIRIAL)	DEV. In Z	STANDARD Error in Z
495.1707	495.1704	0.0002	0.0213	1.40319	1.40318	0.00000	0.00053
251.0876	251.0888	-0.0012	0.0108	1.11217	1.11217	-0.00001	0.00037
147.5220	147.5195	0.0025	0.0059	1.02130	1.02128	0.00002	0.00032
92.0363	92.0374	-0.0011	0.0027	0.99586	0.99587	-0.00001	0.00025
58.5947	58-5970	-0.0023	0.0018	0,99090	0.99094	-0.00004	0.00021
37.5268	37.5255	0.0013	0.0010	0.99185	0.99181	0,00003	0.00019
24-0608	24.0596	0.0012	0.0006	0.99390	0.99385	0.00005	0.00017
15-4230	15,4231	-0.0001	0.0004	0.99570	0.99571	-0.00001	0.00014
9.8820	9,8823	-0.0003	0.0003	0.99708	0.99711	-0.00001	0.00011
6.3289	6.3294	-0.0005	0.0002	0.99700	0.99809	-0.00003	0.00001
4.0525	4.0525		0.0002	0.99876	0.99876		0.00008
2.5944	2.5941	0.0003	0.0002	0.99931	0.99920	0.00011	0.00012
	PARAMETE	R	VALUE	ST. E	ANDARD RROR		
	A(1)	3!	52.8903834	0.	1311920		
	N(1)		1.5628770	0.	0000577		
	B(2)	-0.41	004249D 01	0.93877	331D-01		
	B(3)	0.40	585040D 03	0.12266	814D 02		
	B(4)	0.13	037747D 05	0.70322	403D 03		
	B(5)	-0.87	042034D 05	0.12430	659D 05		
	BFC =0.27	1370-02		$\Sigma (P_E - P_C)$	=0.35 <b>787</b> D-	04	

#### EXPERIMENTAL AND CALCULATED RESULTS FOR 41.05% HELIUM AT -115°C (FLUID-FLUID PHASE SEPARATION SUSPECTED)

P(EXP) Atm.	P{CALC} ATM.	DEV. In p	STANDARD Error in P	Z(BURNETT)	Z(VIRIAL)	DEV. In Z	STANDARD Error in Z
671.0606	671.0962	-0.0355	0.6431	1.42826	1.42833	-0.00008	0.00523
267.4633	267.4174	0.0458	0.2445	0.89139	0.89124	0.00015	0.00322
147.6388	147.6250	0.0137	0.1028	0.77037	0.77030	0.00007	0.00196
96.1876	96.3116	-0.1240	0.0629	0.78577	0.78679	-0.00101	0.00177
65.4764	65.3967	0.0797	0.0347	0.83741	0.83639	0.00102	0.00185
44.2038	44.1612	0.0426	0.0238	0.88508	0.88423	0.00085	0.00183
29.3934	29.3949	-0.0015	0.0163	0.92139	0.92144	-0.00005	0.00166
19.2996	19.3159	-0.0162	0.0101	0.94713	0.94793	-0.00080	0.00138
12.5594	12.5729	-0.0135	0.0065	0.96493	0.96597	-0.00104	0.00116
8.1243	8.1306	-0.0062	0.0050	0.97720	0.97795	-0.00075	0.00121
5.2419	5.2351	0.0068	0.0044	0.98706	0.98578	0.00128	0.00161
3.3649	3.3612	0.0038	0.0038	0 <b>•99198</b>	0.99087	0.00111	0.00220
	PARAMETE	ARAMETER VALUE		ST.	ANDARD RROR		
	A(1)	40	9.8456262	1.	6959197		
	N(1)		1.5655429	0.	0006314		
	B(2)	-0.352	295112D 02	0.33714	611D 00		
	B(3)	0.136	509393D 04	0.20302	861D 02		
	B(4)	-0.163	385742D 04	0.53393	451D 03		
	BFC =0.20	771D 01		$\Sigma (P_E - P_C)$	<b>45</b> 866D-	02	

#### EXPERIMENTAL AND CALCULATED RESULTS FOR 41.05% HELIUM AT -115°C

P(EXP) ATM.	P(CALC) ATM.	DEV. In P	STANDARD Error in P	Z(BURNETT)	Z(VIRIAL)	DEV. In Z	STANDARD Error in Z
471.1520	471.1470	0.0050	0.2608	1.18162	1.18161	0.00001	0.00488
217.9367	217.9601	-0.0235	0.1211	0.85484	0.85493	-0.00009	0.00314
129.0395	128.9767	0.0629	0.0679	0.79155	0.79116	0.00039	0.00276
85.4114	85.4948	-0.0834	0.0336	0.81933	0.82013	-0.00080	0.00222
57.8188	57.7903	0.0284	0.0225	0.86736	0.86693	0.00043	0.00200
38.7185	38.6995	0.0190	0.0125	0.90831	0.90786	0.00044	0.00192
25.5770	25.5769	0.0002	0.0087	0.93831	0.93830	0.00001	0.00178
16.7195	16.7241	-0.0045	0.0061	0.95918	0.95944	-0.00026	0.00151
10.8486	10.8526	-0.0040	0.0038	0.97326	0.97362	-0.00036	0.00117
7.0049	7.0065	-0.0016	0.0026	0.98273	0.98295	-0.00022	0.00089
4.5087	4.5081	0.0006	0.0024	0.98916	0.98903	0.00014	0.00097
2.8961	2.8943	0.0018	0.0023	0.99358	0.99295	0.00062	0.00146
	PARAMETE	R	VALUE	ST			
1.441 - 11. ∰r 1				E	RROR		
• •							
·· ·	A(1)	3	98.7343331	1.	6299486		
۰.	N(1)		1.5637869	0.	0006460		
• •	B(2)	-0.31	609867D 02	0.80577	331D 00		
• • •	B(3)	0.10	297669D 04	0.10812	021D 03		
	B(4)	0.17	661667D 05	0.57970	561D 04		
. •	8(5)	-0.37	211159D 06	0.92207	799D 05		
•	BFC =0.40	81 <b>90</b> 00	:	$\Sigma (P_E - P_C)$	=0.86549D-	03	

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## EXPERIMENTAL AND CALCULATED RESULTS FOR 21.99% HELIUM AT -115°C (RUN 1)

P(EXP) Atm.	P(CALC) Atm.	DEV. In P	STANDARD Error in P	Z(BURNETT)	Z(VIRIAL)	DEV. In Z	STANDARD Error in Z
677.1749	677.1747	0.0001	0.0800	1.44262	1.44262	0.00000	0.00198
202.5354	202.5357	-0.0004	0.0242	0.67412	0.67412	-0.00000	0.00084
113.4282	113.4267	0.0014	0.0136	0.58974	0.58973	0.00001	0.00065
79.6751	79.6788	-0.0036	0.0091	0.64707	0.64710	-0.00003	0.00067
58.2855	58.2827	0.0028	0.0050	0.73940	0.73936	0.00004	0.00061
41.4389	41.4348	0.0041	0.0036	0.82113	0.82105	0.00008	0.00057
28.4710	28.4759	-0.0049	0.0021	0.88124	0.88139	-0.00015	0.00055
19.0833	19.0850	-0.0017	0.0015	0.92263	0.92271	-0.00008	0.00049
12.5821	12.5803	0.0018	0.0011	0.95019	0.95006	0.00013	0.00040
8.2059	8.2049	0.0010	0.0007	0.96798	0.96787	0.00011	0.00029
5.3152	5.3152	-0.0000	0.0006	0.97936	0.97937	-0.00001	0.00022
3.4280	3.4285	-0.0005	0.0006	0.98663	0.98677	-0.00014	0.00030
	PARAMETE	PARAMETER VALUE		ST. El	ANDARD RR OR		
	A(1)	4	69.4072867	0.	6435764		
	N(1)		1.5620016	0.	0002022		
	B(2)	-0.49	550057D 02	0.31528	314D 00		
	B(3)	0.46	2813210 03	0.661004	476D 02		
	B(4)	0.13	589306D 06	0.55644	899D 04		
	B(5)	-0.57	760478D 07	0.19490	812D 06		
	B(6)	0.82	134809D 08	0.24703	492D 07		
	8FC =0.44	7750-01	;	$\Sigma (P_E - P_C)$	=0.17270D-	04	

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### EXPERIMENTAL AND CALCULATED RESULTS FOR 21.99% HELIUM AT -115°C (RUN 2)

P(EXP) ATM.	P(CALC) ATM.	DEV. In p	STANDARD Error In P	Z(BURNETT)	Z(VIRIAL)	DEV. In Z	STANDARD Error in Z
450.6008	450.6006	0.0002	0.1203	1.07901	1.07901	0.00000	0.00353
169.8654	169.8664	-0.0010	0.0458	0.63520	0.63521	-0.00000	0.00189
.103.5528	103.5478	0.0050	0.0282	0.60464	0.60461	0.00003	0.00160
74.0452	74.0609	-0.0158	0.0191	0.67508	0.67522	-0.00014	0.00165
53.8250	53.8028	0.0222	0.0105	0.76623	0.76591	0.00032	0.00150
37.8586	37.8654	-0.0067	0.0074	0.84150	0.84165	-0.00015	0.00140
25.8111	25.8178	-0.0066	0.0043	0.89580	0.89603	-0.00023	0.00132
17.2107	17.2110	-0.0003	0.0032	0.93265	0.93266	-0.00002	0.00118
11.3092	11.3064	0.0029	0.0022	0.95690	0.95665	0.00024	0.00096
7.3598	7.3587	0.0011	0.0014	0.97232	0.97217	0.00015	0.00068
4.7613	4.7613	0.0000	0.0012	0.98216	0.98216	0.00000	0.00051
3.0684	3.0693	-0.0009	0.0012	0.98827	0.98857	-0.00029	0.00070
	PARAMETE	R	VALUE	ST/ El	ANDARD RROR		
	A(1)	4	17.6050116	1.	3627479		
	N(1)		1.5613886	0.	0004805		
	B(2)	-0.47	315380D 02	0.85760	815D 00		
	B(3)	0.85	797935D 02	0.19580	923D 03		
	B(4)	0.17	390236D 06	0.18053	1400 05		
	B(5)	-0.77	728266D 07	0.69832	157D 06		
	B(6)	0.11	308533D 09	0.96684	552D 07		
	BFC =0.10	132D 00		$\Sigma (P_E - P_C)^{\dagger}$	=0.34463D-	04	

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#### EXPERIMENTAL AND CALCULATED RESULTS FOR 100.00% ARGON AT -115°C

P(EXP) ATM.	P(CALC) ATM.	DEV. In p	STANDARD Error in P	Z(BURNETT)	Z(VIRIAL)	DEV. In Z	STANDARD Error in Z
647.7303	647.7284	0.0019	0.0703	1.59251	1.59250	0.00000	0.00247
83 - 580 5	83.5771	0.0035	0.0098	0.32117	0.32115	0.00001	0.00045
61.6081	61.5981	0.0101	0.0065	0.36991	0.36985	0.00006	0.00047
54.5344	54.5400	-0.0056	0.0043	0.51163	0.51169	-0.00005	0.00059
44 .4484	44.4483	0.0001	0.0038	0.65159	0.65159	0.00000	0.00066
33 .292 8	33.2989	-0.0062	0.0024	0.76260	0.76275	-0.00014	0.00064
23 • 534 2	23.5381	-0.0038	0.0015	0.84232	0.84246	-0.00014	0.00059
16.0381	16.0368	0.0012	0.0011	0.89693	0.89686	0.00007	0.00054
10.6772	10.6774	-0.0002	0.0008	0.93302	0.93304	-0.00002	0.00045
7.0072	7.0071	0.0001	0.0006	0.95677	0.95676	0.00001	0.00034
4.5572	4.5567	0.0005	0.0005	0.97228	0.97216	0.00011	0.00023
2.9466	2.9461	0.0005	0.0005	0.98228	0.98212	0.00016	0.00026
343.9010	343.9031	-0.0021	0.0373	0.93718	0.93719	-0.00001	0.00132
72.3768	72.3818	-0.0050	0.0086	0.30818	0.30820	-0.00002	0.00040
60.1068	60.1145	-0.0077	0.0057	0.39984	0.39989	-0.00005	0.00045
52.4855	52.4829	0.0025	0.0043	0.54547	0.54544	0.00003	0.00057
41.8848	41.8768	0.0080	0.0027	0.68006	0.67993	0.00013	0.00060
30 .893 1	30.8907	0.0023	0.0024	0.78363	0.78357	0.00006	0.00058
21.6219	21.6215	0.0004	0.0016	0.85685	0.85684	0.00002	0.00055
14.6420	14.6414	0.0005	0.0010	0.90651	0.90647	0.00003	0.00051
9.7123	9.7118	0.0005	0.0008	0.93941	0.93936	0.00005	0.00044
6.3586	6.3588	-0.0001	0.0006	0.96084	0.96086	-0.00002	0.00035
4.1286	4.1293	-0.0006	0.0004	0.97466	0.97482	-0.00015	0.00027
2.6671	2.6676	-0.0005	0.0004	0.98365	0.98383	-0.00018	0.00029

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## TABLE 23 (CONTINUED)

PARAMETER	VALUE	S TANDARD ERROR	
 A(1)	406.7364660	0.6286140	
A(2)	366.9511196	0.5158406	
N(1)	1.5625218	0.0002204	
N(2)	1.5622752	0.0001990	
B(2)	-0.77870274D 02	0.52444806D 00	
B(3)	0.222990700 04	0.194201200 03	
B(4)	-0.44084186D 05	0.31719833D 05	
B(5)	0.12310159D 08	0.27734736D 07	
B(6)	-0.11107092D 10	0.132514140 09	
B(7)	0.38552947D 11	0.32308967D 10	
B(8)	-0.42516799D 12	0.31639000D 11	

#### EXPERIMENTAL AND CALCULATED RESULTS FOR 100.00% HELIUM AT -130°C

P( EXP) A TM.	P(CALC) ATN.	DEV. In p	STANDARD Error in P	Z(BURNETT)	Z(VIRIAL)	DEV. In Z	STANDARD Error in Z
690,7059	690.7081	-0.0022	0.0150	1.67237	1.67237	-0.00001	0.00021
360.1319	360.1282	0.0036	0.0067	1.36267	1.36266	0.00001	0.00015
204 • 4 5 4 2	204.4557	-0.0016	0.0027	1.20886	1.20887	-0.00001	0.00012
121.7921	121.7887	0.0034	0.0014	1.12521	1.12518	0.00003	0.00009
74.5963	74.5979	-0.0016	0.0009	1.07685	1.07687	-0.00002	0.00007
46 . 4 58 4	46.4597	-0.0013	0.0005	1.04790	1.04793	-0.00003	0.00007
29.2318	29.2306	0.0011	0.0003	1.03021	1.03017	0.00004	0.00006
18.5064	18.5070	-0.0006	0.0002	1.01907	1.01910	-0.00003	0.00005
11.7636	11.7638	-0.0002	0.0001	1.01213	1.01214	-0.00002	0.00004
7.4963	7.4962	0.0001	0.0001	1.00775	1.00774	0.00001	0.00003
4.7844	4.7844	0.0001	0.0001	1.00496	1.00494	0.00002	0.00003
3.0567	3.0566	0.0001	0.0001	1.00317	1.00316	0.00002	0.00004
529 •402 1	529.3983	0.0038	0.0106	1.52400	1.52399	0.00001	0.00018
286.9808	286.9889	-0.0081	0.0046	1.29102	1.29105	-0.00004	0.00015
166 .532 9	166.5297	0.0032	0.0023	1.17066	1.17063	0.00002	0.00011
100 .452 2	100.4517	0.0005	0.0012	1.10338	1.10338	0.00001	0.00009
61 .9877	61.9883	-0.0006	0.0007	1.06390	1.06391	-0.00001	0.00007
38.7807	38.7810	-0.0003	0.0004	1.04001	1.04001	-0.00001	0.00007
24 .467 7	24.4675	0.0002	0.0003	1.02526	1.02525	0.00001	0.00006
15.5183	15.5181	0.0001	0.0002	1.01603	1.01602	0.00001	0.00005
9.8748	9.8747	0.0002	0.0001	1.01021	1.01019	0.00002	0.00004
6.2969	6.2967	0.0002	0.0001	1.00653	1.00650	0.00003	0.00003
4.0203	4.0205	-0.0002	0.0001	1.00410	1.00415	-0.00005	0.00004
2 .569 2	2.5693	-0.0001	0.0001	1.00262	1.00265	-0.00004	0.00005

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PARAMETER	VALUE	STANDARD Errdr	
A(1) .	413.0112077	0.0495342	
A(2)	347.3765046	0.0410054	
N(1)	1.5624628	0.000185	
N(2)	1.5624923	0.0000190	
B(2)	0.12127116D 02	0.24710349D-01	
B(3)	0.14678233D 03	0.21545631D 01	
B(4)	0.11431125D 04	0.93127002D 02	
8(5)	0.96932153D 04	0.12985991D 04	
BFC =0.18280	D-02	$\Sigma (P_E - P_C) =217480 - 04$	

## TABLE 24 (CONTINUED)

## EXPERIMENTAL AND CALCULATED RESULTS FOR 80.00% HELIUM AT -130°C (Run 1)

P(EXP) ATM.	P(CALC) ATM.	DEV. In P	STANDARD Error in P	Z(BURNETT)	Z(VIRIAL)	DEV. In Z	STANDARD Error in Z
518.4114	518.4112	0.0002	0.0336	1.53103	1.53103	0.00000	0.00092
269.9484	269.9495	-0.0011	0.0175	1.24576	1.24577	-0.00000	0.00066
156.0200	156.0172	0.0028	0.0094	1.12499	1.12497	0.00002	0.00056
94.8497	94.8533	-0.0037	0.0042	1.06857	1.06861	-0.00004	0.00043
59.0749	59.0724	0.0025	0.0027	1.03983	1.03979	0.00004	0.00036
37.2311	37.2321	-0.0010	0.0015	1.02389	1.02392	-0.00003	0.00031
23.6159	23.6162	-0.0003	0.0009	1.01470	1.01472	-0.00001	0.00028
15.0340	15.0332	0.0007	0.0007	1.00924	1.00919	0.00005	0.00023
9.5899	9.5897	0.0003	0.0004	1.00582	1.00579	0.00003	0.00017
6.1247	6,1250	-0.0003	0.0003	1.00362	1.00367	-0.00005	0.00012
3-9144	3-9151	-0.0007	0.0003	1.00216	1.00233	-0.00017	0.00012
2.5043	2.5038	0.0005	0.0003	1.00169	1.00149	0.00020	0.00018
	PARAMETE	R	VALUE	ST ( Ei	ANDARD RROR		
	A(1)	33	38.6025878	0.	2010742		
	N(1)		1.5623641	0.	0000915		
	B(2)	0.69	345047D 01	0.14747	176D 00		
	B(3)	0.23	597229D 03	0.17146	919D 02		
	B(4)	0.65	832654D 04	0.92406	262D 03		
	8(5)	-0.32	785289D 05	0.15624	332D 05		
	BFC =0.67	<b>66 9D-02</b>		$\Sigma (P_E - P_C)$	=0.28553D-	04	

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## EXPERIMENTAL AND CALCULATED RESULTS FOR 80.00% HELIUM AT -130°C (Run 2)

P(EXP) ATM.	P(CALC) ATM.	DEV. In p	STANDARD Error in P	Z(BURNETT)	Z(VIRIAL)	DEV. In Z	STANDARD Error in Z
398.3139	398.3138	0.0001	0.0048	1.39624	1.39624	0.00000	0.00010
217.8214	217.8219	-0.0005	0.0025	1.19306	1.19306	-0.00000	0.00008
128.8386	128.8377	0.0009	0.0011	1.10259	1.10258	0.00001	0.00006
79.1306	79.1311	-0.0005	0.0007	1.05805	1.05806	-0.00001	0.00005
49.5103	49.5107	-0.0005	0.0003	1.03430	1.03431	-0.00001	0.00004
31.2777	31.2774	0.0004	0.0002	1.02087	1.02086	0.00001	0.00004
19.8639	19.8635	0.0004	0.0001	1.01294	1.01292	0.00002	0.00003
12.6531	12.6532	-0.0002	0.0001	1.00808	1.00810	-0.00001	0.00003
8.0746	8.0748	-0.0002	0.0001	1.00509	1.00511	-0.00002	0.00002
5.1588	5.1587	0.0000	0.0000	1.00325	1.00324	0.00000	0.00002
3.2981	3.2980	0.0000	0.0000	1.00208	1.00206	0.00002	0.00002
2.1093	2.1093	0.0000	0.0000	1.00132	1.00132	0.00000	0.00003
	PARAMETER	R	VALUE	ST.	ANDARD RROR		
	A(1)	2	85.2756024	0.	0199053		
	N(1)		1.5623561	0.	0000117		
	B(2)	0.72	977738D 01	0.14069	216D-01		
	B(3)	0.25	554634D 03	0.98693	525D 00		
	B(4)	0.47	663382D 04	0.26668	638D 02		
	BFC =0.117	759D-03		$\Sigma (P_E - P_C)$	=0.59879D-	05	

#### EXPERIMENTAL AND CALCULATED RESULTS FOR 59.35% HELIUM AT -130°C (GAS-LIQUID PHASE SEPARATION SUSPECTED)

P(EXP) ATM.	P(CALC) Atm.	DEV. In P	STANDARD Error in P	Z(BURNETT)	Z(VIRIAL)	DEV. In Z	STANDARD Error in Z
168.8216	168.8217	-0.0000	0.0071	1.02048	1.02048	-0.00000	0.00073
103.6586	103.6583	0.0002	0.0044	0.97889	0.97889	0.00000	0.00062
66.0263	66.0272	-0.0009	0.0027	0.97408	0.97409	-0.00001	0.00056
42.4905	42•4888	0.0017	0.0014	0.97929	0.97926	0.00004	0.00046
27.3655	27.3668	-0.0012	0.0009	0 <b>• 98529</b>	0.98534	-0.00004	0.00039
17.6034	17.6035	-0.0001	0.0005	0.99014	0.99015	-0.00000	0.00034
11.3074	11.3068	0.0006	0.0004	0.99358	0.99353	0.00005	0.00028
7.2542	7.2543	-0.0001	0.0002	0.99579	0.99580	-0.00001	0.00020
4.6503	4.6506	-0.0003	0.0002	0.99723	0.99729	-0.00006	0.00013
2.9800	2.9798	0.0001	0.0002	0•99830	0.99826	0.00004	0.00011
	PARAMETE	R	VALUE	SŤ	ANDARD RROR		
	A(1)	14	5. 4227914	0	1177622		
	N(1)		1.5621083		0001203		
	8(2)	-0.69	878050 01	0.29214	7870 00		
	8(3)	0.20	54860D 03	0.65657	7500 02		
	B(4)	0.430	342125D 05	0.65391	51 2D 04		
	8(5)	-0.11	571023D 07	0.21718	711D 06		
	8FC =0.30	023D-03	2	$E (P_E - P_C)$	=0.24691D-	05	

## EXPERIMENTAL AND CALCULATED RESULTS FOR 59.35% HELIUM AT -130°C

P(EXP) ATM.	P(CALC) ATM.	DEV. In p	STANDARD ERROR IN P	Z(BURNETT)	Z(VIRIAL)	DEV. In Z	STANDARD Error in Z
138.1775	138.1776	-0.0001	0.0043	1.00583	1.00583	-0.00000	0.00028
86.4019	86.4013	0.0006	0.0026	0.98260	0.98259	0.00001	0.00025
55.2362	55.2368	-0.0006	0.0013	0.98138	0.98139	-0.00001	0.00020
35.4989	35.4991	-0.0002	0.0008	0.98534	0.98534	-0.00001	0.00017
22.8205	22.8204	0.0001	0.0004	0.98958	0.98957	0.00001	0.00015
14.6573	14.6567	0.0006	0.0003	0.99296	0.99292	0.00004	0.00013
9.4041	9.4043	-0.0001	0.0002	0.99529	0.99531	-0.00001	0.00010
6.0291	6.0295	-0.0004	0.0001	0.99686	0.99693	-0.00007	0.00007
3.8637	3.8637	0.0000	0.0001	0.99802	0.99801	0.00001	0.00006
2.4750	2.4749	0.0002	0.0001	0.99878	0.99872	0.00006	0.00009
	PARAMETE	R	VALUE	ST.	ANDARD RROR		
	A(1)	1	37.3771210	0.	0385339		
	N(1)		1.5622529	0.	0000521		
	B(2)	-0.61	746247D 01	0.95413	351D-01		
	B(3)	0.41	383618D 03	0.13736	371D 02		
	B(4)	0.13	400376D 05	0.67434	503D 03		
	BFC =0.913	372D-04	Σ	C (P <sub>E</sub> - P <sub>C</sub> )	=0.12352D-	04	

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# EXPERIMENTAL AND CALCULATED RESULTS FOR 41.05% HELIUM AT -130°C

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P(EXP) ATM.	P(CALC) ATM.	DEV. In p	STANDARD Error in P	Z(BURNETT)	Z(VIRIAL)	DEV. In Z	STANDARD Error in Z
73.6126	73.6175	-0.0049	0.0214	0.86253	0.86259	-0.00006	0.00036
49.1401	49.1741	-0.0341	0.0091	0.89967	0,90029	-0.00062	0.00024
32.5543	32.5578	-0.0035	0.0059	0.93126	0.93137	-0.00010	0.00027
21.3507	21.3458	0.0050	0.0033	0.95432	0.95410	0.00022	0.00031
13.8902	13.8864	0.0037	0.0021	0.97008	0.96981	0.00026	0.00035
8.9870	8.9840	0.0030	0.0015	0.98068	0.98035	0.00033	0.00038
5.7918	5.7905	0.0013	0.0011	0.98752	0.98729	0-00023	0-00041
3.7228	3.7229	-0.0001	0.0007	0.99178	0.99181	-0.00003	0.00042
2.3907	2.3897	0.0010	0.0005	0.99514	0.99473	0.00041	0.00042
61.5804	61.5526	0.0278	0.0123	0.88021	0.87981	0.00040	0.00029
40.9799	40.9769	0.0030	0.0075	0.91524	0.91517	0.00007	0.00026
27.0113	27.0076	0.0038	0.0042	0.94260	0.94247	0.00013	0.00020
17.6427	17.6405	0.0022	0.0025	0.96197	0.96185	0.00012	0.00033
11.4436	11.4448	-0.0012	0.0018	0.97494	0.97504	-0.00011	0.00037
7.3886	7.3906	-0.0020	0.0013	0.98354	0.98380	-0.00027	0.00040
4.7556	4.7576	-0.0020	0.0009	0.98913	0.98954	-0.00041	0.00043
3.0540	3.0564	-0.0024	0.0006	0.99249	0.99327	-0.00078	0.00045
1.9600	1.9609	-0.0008	0.0004	0.99525	0.99568	-0.00043	0.00046

PA1	RAMETER	VALUE	STANDAI Error	RD .
	A(1)	85.3445671	0.0196	270
	A(2)	69.9611200	0.0167	028
	N(1)	1.5624775	****	**
	N(2)	1.5624775	****	**
	B(2)	-0.25942313D 02	0.14382175D	00
	B(3)	0.967590190 03	0.200091960	02
BFC	=0.340650	-02	$\Sigma (P_{E} - P_{C}) =3$	14610-03

TABLE 29 (CONTINUED)

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#### EXPERIMENTAL AND CALCULATED RESULTS FOR 21.99% HELIUM AT -130°C

P(EXP) Atm.	P(CALC) ATN.	DEV. In p	STANDARD Error in P	Z(BURNETT)	Z(VIRIAL)	DEV. In Z	STANDARD Error in Z
				- 705/3			
42.0382	42.0342	0.0039	0.0051	0.78541	0.78534	0.00007	0.00014
29.7113	29.7132	-0.0019	0.0024	0.85514	0.85519	-0.00005	0.00010
20.1111	20.1082	0.0029	0.0015	0•90442	0.90428	0.00013	0.00012
13.3442	13.3420	0.0022	0.0009	0.93765	0.93750	0.00016	0.00014
8.7381	8.7393	-0.0012	0.0006	0.95935	0.95949	-0.00013	0.00016
5.6760	5.6770	-0.0010	0.0005	0.97370	0.97386	-0.00017	0.00018
3.6671	3.6681	-0.0010	0.0003	0.98292	0.98319	-0.00026	0.00019
2.3620	2.3620	0.0000	0.0002	0.98922	0.98920	0.00001	0.00020
36.2558	36.2613	-0.0055	0.0030	0.82022	0.82034	-0.00013	0.00012
24.8977	24.8979	-0.0001	0.0019	0.88010	0.88010	-0.00000	0.00011
16.6802	16.6798	0.0005	0.0011	0.92127	0.92125	0.00003	0.00013
10.9944	10.9941	0.0003	0.0007	0.94880	0.94877	0.00003	0.00016
7.1708	7.1706	0.0002	0.0005	0.96691	0.96688	0.00003	0.00018
4.6446	4.6452	-0.0005	0.0004	0.97855	0.97866	-0.00011	0.00019
2.9965	2.0041	0.0004	0.0003	0 09663	0 09620	0 00013	0.00021
1 0 2 0 0	207701		0.0003	0.001/5	0.70027	0.00013	0.00021
1.7200	1.92(1	0.0009	0.0002	0.33102	0.99120	0.00045	0.00021

PA	RAMETER	VALUE	STANDARD Error	
	A(1)	54.2878401	0.0059880	
	A(2)	44.2025458	0.0050572	
	N(1)	1.5624775	*****	
	N(2)	1.5624775	*****	
	B(2)	-0.534153050 02	0.96897306D-01	
	B(3)	0.15077540D 04	0.21018117D 02	
BFC	=0.189550	0-03	$\Sigma (P_E - P_C) = 0.15802D - 03$	

TABLE 30 (CONTINUED)

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#### EXPERIMENTAL AND CALCULATED RESULTS FOR 100.00% ARGON AT -130°C

P(EXP) ATM.	P(CALC) ATM.	DEV. In P	STANDARD Error in P	Z(BURNETT)	Z(VIRIAL)	DEV. In Z	STANDARD Error in Z
30.3901	30.4090	-0.0189	0.0187	0.67295	0.67337	-0.00042	0.00066
22.6192	22.6278	-0.0086	0.0093	0.78261	0.78291	-0.00030	0.00052
15.8673	15.8666	0.0007	0.0061	0.85780	0.85776	0.00004	0.00065
10.7467	10.7449	0.0018	0.0039	0.90777	0.90762	0.00015	0.00079
7.1265	7.1246	0.0018	0.0028	0.94056	0.94032	0.00024	0.00092
4.6645	4.6629	0.0016	0.0021	0.96191	0.96158	0.00033	0.00102
3.0288	3.0269	0.0019	0.0015	0.97592	0.97532	0.00061	0.00109
26.6933	26.6530	0.0402	0.0108	0.73188	0.73078	0.00110	0.00054
19.1872	19.1979	-0.0107	0.0076	0.82199	0.82245	-0.00046	0.00058
13.2030	13.2095	-0.0065	0.0045	0.88378	0.88421	-0.00044	0.00072
8.8420	8.8443	-0.0023	0.0032	0.92477	0.92502	-0.00024	0.00086
5.8225	5.8234	-0.0009	0.0024	0.95150	0.95165	-0.00015	0.00098
3.7946	3.7946	-0.0000	0.0018	0.96890	0.96891	-0.00001	0.00108
2.4567	2.4565	0.0002	0.0013	0.98011	0.98004	0.00007	0.00114

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PA1	RAMETER	VALUE	STANDARD Error	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
	A(1)	45.1593994	0.0279321	
	A(2)	36.4721930	0.0231011	
	N(1)	1.5624775	*****	
	N(2)	1.5624775	*****	
	B(2)	-0.94044109D 02	0.56505588D 00	
	B(3)	0.23631502D 04	0.14938246D 03	
BFC	=0.2429	LD-02	$\Sigma (P_E - P_C) = 0.20179D - 03$	

TABLE 31 (CONTINUED)

run constant,  $P_0/Z_0$ , is given by A(I) and the cell constant, N<sub>m</sub>, is given by N(I). The subscript indicates whether the apparatus constant is for the first or second run. These are the optimal values and are consistent with the compressibility factors in the first part of the table and the virial coefficients, which are presented following the apparatus constants. The procedure used in obtaining the optimum number and values of the virial coefficients was the method developed by Hall and Canfield (20). Their procedure gives the optimum coefficients for the expansion

$$Z = PV/RT = 1 + B_2 \rho + B_3 \rho^2 + ...$$
 (55)

The estimated standard errors for the apparatus constants and the optimum virial coefficients were determined using equation (D-2).

Although the data analysis discussed above was used for treating the data, certain variations were made because each of the isotherms presented a somewhat different situation. The -90°C isotherm was approximately 30° above the critical temperature of the least volatile component, argon. There were no problems in treating the four mixtures or the two pure components by the procedure described in Appendix B.

However, the -115°C isotherm was only about 6° above the critical temperature of argon. When the maximum starting pressures were chosen before the start of the

experimental runs, it was thought that there would be no problems using an initial pressure of 10,000 psi. But a preliminary analysis of the data indicated otherwise. To check the consistency of the two runs, a plot of  $P_{j-1}/P_j$  versus  $P_j$  is made at the end of each run. If the two runs are consistent, the points will be on one continuous smooth curve. For two mixtures (59.4% He and 40.2% He) at -115°C, this plot resulted in two distinct curves indicating a change in composition had occurred sometime during one of the runs. The separation of the 'curves is shown in Figure 6. This change in composition is thought to be due to the phenomenon of fluid-fluid phase separation coupled with incomplete mixing after the first expansion.

The phenomenon of fluid-fluid phase equilibrium is an equilibrium that exists between two separate, distinct gas phases that occur at high pressures in a region that for most systems would be a region of homogeneous fluid mixtures. These phase separations can occur at temperatures between the critical temperatures of the two pure components or above the critical temperature of the least volatile component. Streett (35) has presented the experimental observance of fluid-fluid phase separation between the critical temperatures of the two components. At the present time the occurence of fluid-fluid phase separation above the critical temperature of argon has

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FIGURE 6. RESULTS OF COMPOSITION CHANGE IN BURNETT RUNS AT -115°C

not been experimentally observed. Streett proposes to study the helium-argon system further at pressures to 60,000 psi and temperatures around the critical temperature of argon to better define the critical curve. However, Kaplan (23) has a qualitative method of predicting whether a phase separation will occur in a given system above the critical temperatures of the pure components based on the  $D^2$  factor ( $D^2 = 3RT_c/2V_c$ ). He presents an extensive list of systems known or predicted to exhibit this behavior. The helium-argon system is predicted to show this phenomenon.

Therefore in the present work, it is thought that the first run which was started at approximately 10,000 psi somehow underwent a fluid-fluid phase separation which permanently changed the composition of the mixture after the first expansion. If complete mixing with the magnetic pump were attained, the equilibrium composition would be regained after the first expansion. Apparently the magnetic pump was not left on long enough to achieve complete mixing. This then resulted in a permanent change in composition. The first run is therefore made for an unknown composition, and the second run, starting at a lower pressure, is made using a gas sample of the known composition. This explains the separation in the curves appearing in Figure 6. The two runs for each of the two mixtures that exhibit this behavior were treated individually instead of combining the two runs as suggested in Appendix B. The two runs for the mixture containing 21.99% helium were also treated individually because of inconsistencies in the two runs when treated together. Tables 17 through 22 have a different format than the other tables for these reasons. The other mixture and pure component data for the -115°C isotherm were treated in the same way as the -90°C isotherm was, that is, by using the procedure in Appendix B.

The -130°C isotherm was below the critical temperature of argon. Therefore, the helium-argon phase diagram presented by Streett (35) was used to determine the maximum starting pressures so that the sample would always be in the gas phase. However, the mixture containing 59.4% helium was apparently started at a pressure that crossed the phase boundary, so that the two runs again were for mixtures of slightly different composition. These two runs had to be treated separately, so Tables 27 and 28 also follow a different format. The mixture containing 80.00% helium was treated for the two runs together and individually. When treated individually, the parameters and compressibility factors agreed quite well. However when treated together, the results were not as good as the individual runs indicated. Since there was no basis for choosing between the two data treatment procedures, the results for this mixture are presented in Tables 25 and

26 for the two runs treated individually.

Since only the 100% helium data could be started at 10,000 psi, the other mixtures and 100% argon results have fewer data points per run due to the lower initial pressures. Preliminary attempts at fitting these runs indicated that there were too many adjustable parameters for the number of data points. Therefore, for these runs the values of the cell constants,  $N_{\infty}$ , obtained from the 100% helium runs were used and held constant in the Newton-Raphson determination of the optimum virial coefficients. Aside from this change, the data treatment for the multiple runs was the same as discussed above.

At the end of each table, two quantities are presented which give some insight into the confidence of the data. They are the optimal estimated value of the best fit criterion, BFC, defined by equation (B-6), and the sum of the deviations between the experimental pressures and the calculated pressures. The latter number is an indicator to see whether or not a least squares fit was obtained. This number should be less than or the same order of magnitude as the smallest deviation. The details of the determination of all the values presented in Tables 9 through 31 are given in the discussions of the data reduction analysis in Appendix B and the estimation of standard errors of the parameters and data in Appendix D.

#### Factors Influencing Best Virial Coefficients

Sengers (32a) has used the principles of statistical analysis to study the effect of various factors on the determination of the optimum values of the lower virial coefficients. She found that the standard error in the coefficients increases as the number of coefficients used is increased and that the standard error decreases as the number of data points used is increased. She concluded that in deriving the second virial coefficient from PVT data over a wide density range, that it was better to use a second or third degree polynomial while holding a predetermined value of the first coefficient fixed. This resulted in the minimum standard error in the second virial coefficient.

This type of analysis was tried for the -90°C isotherm for the pure helium run and also for the pure argon run to see if the second virial coefficient having the minimum standard error could be obtained. This was done by first making the data analysis for all of the data. Then succeeding runs were made with one data point removed from the analysis each time. The results of this analysis are shown in Table 32. Although the results indicate that the standard error improves with increasing number of data points for the same degree of fit and with decreasing degree of fit, the analysis is inconclusive at this time. It is difficult to determine which value of

#### RESULTS OF THE ANALYSIS FOR THE DETERMINATION OF THE OPTIMUM VALUES OF VIRIAL COEFFICIENTS

	Number of Points	<sup>B</sup> 2	Standard Error	B <sub>3</sub>	Standard Error	Best Fit
100% Helium						
	24	12.2716	0.02793	123.6984	1.6046	3
	23	12.2589	0.03509	124.7825	2.3885	3
	22	12,2214	0.04947	128.6345	4.3181	3
	21	12.2286	0.06461	127.7427	6,6495	3
	20	12.2557	0.09789	123,6370	12.8323	3
	19	12.1247	0.04190	147.5579	7.6220	2
100% Argon						
-	24	-56.4795	0.1843	1286.947	53.310	6
•	23	-56.4431	0.2484	1273.465	80.592	6
	22	-56.6103	0.1797	1346.623	50.642	5
•	21	-56.8128	0.2835	1422.345	96.246	5
	20	-57,9232	0.0955	1840.407	16.952	3
	19	-57 8038	0 0284	1816 008	2 365	2

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the virial coefficients are best just by looking at the results in Table 32. This is due in part to the fact that this analysis includes random error only and does not consider systematic error.

#### Interaction Virial Coefficients

The second interaction virial coefficient, B<sub>12</sub>, was determined from the mixture values. It is defined by the Lennard-Jones and Cook equation:

$$B_{M} = X_{1}^{2}B_{11} + 2X_{1}X_{2}B_{12} + X_{2}^{2}B_{22}$$
(56)

where  $B_{11}$  and  $B_{22}$  are the two pure component second virial coefficients and  $X_1 + X_2 = 1$ . For the experimental data in this work there are six values of  $B_M$ , two pure components and four mixtures. The three coefficients,  $B_{11}$ ,  $B_{12}$ , and  $B_{22}$ , in equation (56) were determined using ORNOR in a least-squares fit of  $B_M$  versus  $X_1$  in the following manner:

$$B_{M} = X_{1}^{2}B_{11} + 2X_{1}(1 - X_{1})B_{12} + (1 - X_{1})^{2}B_{22}.$$
 (57)

This fit was made using a weighting function that was proportional to the square of the reciprocal of the standard error in the second virial coefficients. The interaction coefficients for the three experimental temperatures are presented in Table 33.

Temperature	B <sub>He-Ar</sub> (cc/mole)	Standard Brror	
-90°C	14.62	0.24	
-115°C	11.60	0.48	
-130°C	10.38	0.095	

#### SECOND INTERACTION VIRIAL COEFFICIENT FOR HELIUM-ARGON MIXTURES

The third interaction virial coefficient was also - determined using the mixture values. It is defined by

$$c_{M} = x_{1}^{3}c_{111} + 3x_{1}^{2}x_{2}c_{112} + 3x_{1}x_{2}^{2}c_{122} + x_{2}^{3}c_{222}$$
(58)

where  $C_{111}$  and  $C_{222}$  are the pure component third virial coefficients. The interaction coefficients,  $C_{112}$  and  $C_{122}$ , were determined by a least-squares fit using ORNOR in a manner similar to that for the  $B_{12}$  above. The third interaction coefficients for two experimental temperatures are presented in Table 34.

#### TABLE 34

## THIRD INTERACTION VIRIAL COEFFICIENTS, C<sub>He-He-Ar</sub> and C<sub>He-Ar-Ar</sub>

C <sub>He-He-Ar</sub>	C <sub>He-Ar-Ar</sub>	
299	528	
275	551	
	C <sub>He-He-Ar</sub> 299 275	

All values in (cc/mole)

#### Comparison with Other Investigators

The compressibility factors used in the comparison were calculated from the virial coefficients given in Tables 9 through 31. The literature values were calculated in a similar manner. The comparison for helium could be made at all three experimental temperatures. However, comparisons for argon were available at only one of the temperatures. The results of the comparison are presented in Table 35. A comparison of the optimum second virial coefficients obtained from the data analysis with other available literature values is given in Table 36.

Since an adequate comparison for the pure argon data and mixtures was not possible due to lack of data at the experimental temperatures, a graphical presentation is used to show that the data are consistent with other data taken at other temperatures. Figure 7 shows the values of the argon second virial coefficient at the three experimental temperatures along with values obtained by other investigators at different temperatures. Figure 8 gives the second interaction virial coefficients at the experimental temperatures and at other temperatures found in the literature.
## TABLE 35

## COMPARISON OF COMPRESSIBILITY FACTORS WITH OTHER INVESTIGATORS

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<u>Helium</u>				
P(atm.)	Reference	-90°C	-115°C	-130°C
25	This Work	1.02034	1.02423	1.02580
	Canfield(8)	1.02043	1.02365	1.02601
50	This Work	1.04055	1.04817	1.05157
	Canfield(8)	1.04074	1.04721	1.05192
100	This Work	1.08059	1.09534	1.10291
	Canfield(8)	1.08099	1.09401	1.10342
200	This Work	1.15930	1.18751	1.20439
	Canfield(8)	1.16009	1.18621	1.20491
500	This Work	1.38553	1.45129	1.49640
	Canfield(8)	1.38721	1.45098	1.49750
Argon				
P(atm.)	Reference	-130°C		
20	This Work Crain(13) Levelt(25) Michels(28)	0.8135 0.8115 0.8131 0.8126		

=

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## TABLE 36

#### COMPARISON OF SECOND VIRIAL COEFFICIENTS WITH OTHER INVESTIGATORS

Helium			
Reference	-90°C	-115°C	-130°C
This Work Canfield(8)	12.27 12.30	12.66 12.25	12.13 12.20
<u>Argon</u>	Reference	-130°C	
	This Work Crain (13) Michels (28)	-94.04 -94.69 -94.43	

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FIGURE 7. SECOND VIRIAL COEFFICIENTS FOR ARGON VS. TEMPERATURE



COEFFICIENTS FOR HELIUM-ARGON SYSTEM VS. TEMPERATURE

#### CHAPTER VII

#### **CONCLUSIONS**

A Burnett apparatus that had been used successfully at temperatures ranging from -190°C to +50°C was available for the experimental work. The equipment was modified slightly in attempts to reduce nitrogen usage due to boiloff, to increase the heat transfer rate to the cell in the cryostat, and to eliminate the galling of the valve stems inside the cryostat. A definite improvement was made in each of these changes, but the heat transfer rate is still a problem that should be studied further.

Also, in the future it would be advisable to consider a slight change in the operational procedure concerning the zero shift correction. The zero shift should be determined in the same way as discussed by Blancett(5). Then after the differential pressure indicator is nulled for a pressure measurement during a run, the amount of weight corresponding to the predetermined zero shift correction should be added to or subtracted from the dead weight gage (depending on direction of correction). Then the expansion valve, that was left 1/8

turn open, should be closed. This would make the pressure on both sides of the diaphragm equal. Following such a procedure would delete the pressure correction due to cryogenic differential pressure indicator zero shift in the calculation of the corrected pressure. Also, the volume distortion correction would be simplified by not having to consider the volume change due to diaphragm movement caused by a zero shift.

In this experimental work helium, argon, and four mixtures of the two were studied at three temperatures between -90°C and -130°C using the Burnett apparatus. Two runs were made for each sample gas at the three experimental temperatures. From the Burnett data, the compressibility factors and optimum virial coefficients were determined. Also the standard errors for the parameters and data were determined for each set of two runs.

The compressibility factors and virial coefficients were determined using a procedure in which the Burnett apparatus constants and the virial coefficients were determined by ORNOR for initial estimates. Then a Newton-Raphson procedure was used to converge to the best set of parameters that satisfied a minimum best fit criterion. The compressibility factors for each experimental pressure could then be calculated with the virial expansion.

A preliminary attempt to see if a perturbational equation of state for methane were feasible has been presented. The proposed equation of state covered the

temperature range 114° to 623°K with most of the low temperature data in the liquid region. The accuracies of the proposed equation of state are not as good as they could be due to discrepancies in the data used at the lower temperatures. When the remeasured data become available, the constants can be redetermined. This is expected to improve the calculated pressures and densities predicted by the perturbation equation of state. Nevertheless, the present results indicate that the approach shows promise and that it would be worthwhile to pursue the idea further. Improvement might be made in the formulation of the cutoff parameter dependence on temperature and density and in the choice of weighting factors used.

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#### APPENDIX A

#### SPECIFIC INFORMATION ABOUT EQUIPMENT

This appendix gives more specific information concerning calibrations and certifications of the components of the apparatus that were described in Chapter III. It should prove useful to others using this apparatus or similar apparatus. It is divided into two parts - temperature measurement and pressure measurement.

#### Temperature Measurement

For the temperatures at which the data in this thesis were taken, the Callendar-Van Dusen Equation is used to define the temperature:

$$R_{T} = R_{0} + \alpha R_{0} \left[ \frac{(1+\delta)}{10^{2}} T - \frac{\delta}{10^{4}} T_{+}^{2} \frac{\beta}{10^{6}} T^{3} - \frac{\beta}{10^{8}} T^{4} \right]$$
(A-1)

Where  $R_T$  is the resistance at T°C,  $R_O$  is the resistance at 0°C, and  $\alpha,\beta$ , and  $\delta$  are calibration constants. The values of these constants are

> Thermometer # 1617523 Date of Calibration: May 17, 1963 Range: 444.6°C to -182.97°C  $\alpha = 0.0039266_{19}$

 $\beta = 0.110_{35} \text{ (below 0°C)}$   $\delta = 1.491_{36}$   $R_{o} \text{ (May 30, 1966)} = 25.5512\Omega(\text{ice point})$ Thermometer # 1665930
Date of Calibration: March 9, 1966
Range: 444.6°C to -261.15°C  $\alpha = 0.003926145$   $\beta = 0.11054 \text{ (below 0°C)}$   $\delta = 1.49154$   $R_{o} \text{ (May 30, 1966)} = 25.5331\Omega(\text{ice point})$ 

The G - 2 Mueller Bridge used in this work was tested in February, 1963, by the Leeds and Northrup Company. A calibration certificate was issued which gave the correction to be applied to the bridge reading. The bridge was recalibrated in this laboratory just prior to the start of this experimental work. The corrections determined then were slightly different than those given by the manufacturer and were used as suggested by the manufacture to attain higher accuracy.

#### Pressure Measurement

The equipment used in the pressure measurement were the dead-weight gages, the weights, and the differential pressure indicators. This section gives some specific details about each of these items.

The Ruska Instrument Corporation supplied the following instrument constants for the piston gages used in this laboratory.

	High Pressure Gage	Low Pressure Gage
Bffective Area at 25°C and Atmospheric Pressure, square inches	0.0260430	0.130220
Coefficient of Superficial Thermal Expansion, (°C) <sup>-1</sup>	$1.7 \times 10^{-5}$	$1.7 \times 10^{-5}$
Fraction Change of Area per Unit Change of Pres- sure, (psi) <sup>-1</sup>	-3.6 x 10 <sup>-8</sup>	$-4.8 \times 10^{-8}$
Resolution	<5 PPM	<5 PPM
Plane of Reference	0.04 inch below line on sleeve weight	0.10 inch below line of sleeve weight

The precision machined stainless steel weights provided by the manufacturer were calibrated against Class S standards. Results of the calibration are presented in Table A-1. A set of Class C standard weights up to 500 mg was used for fine balancing.

The specifications for accuracy and sensitivity of the differential pressures indicators were

Accuracy:  $\pm 1 1/2$  scale divisions at null

Sensitivity: 0.0001 psi/scale division, maximum Blancett (5) measured the sensitivity of the indicators in the laboratory and found that the room temperature indicator exhibited 0.00005 psi/division and the cryogenic

## TABLE A-1

Weight Letter Designation	Apparent Mass vs Brass Pounds
A	26.03576
B	26.03564
c	26.03567
D	26.03569
B	26.03575
F	26.03500
G	26.03511
H	26.03504
I	26.03513
J	26.03543
К	26.03552
L	13.01812
M	5.20716
N	5.20718
ο	2.60351
P	1.30167
Q	0.52073
R	0.52075
S	0.26034
T	0.13018
U	0.05207
V	0.05206
W	0.02603
x	0.01302
<u>A</u>	0.00521
B	0.00260
<u>c</u>	0.00130
Tare High	0.78104
Tare Low	0.78107

## CALIBRATION DATA FOR PISTON GAGE WEIGHTS

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indicator exhibited 0.0004 psi/division at -183.C. These results were taken as indicative of the behavior under the conditions experienced in this work.

The cell constant,  $N_j$ , can be related to  $N_{\omega}$ , the cell constant at zero pressure, by multiplying by a correction factor due to the pressure distortion of the experimental volume. The pressure distortion correction is given by

$$N_{j} = N_{m} \frac{\left[1 + \frac{\Delta(v_{a} + v_{b})_{j}}{(v_{a} + v_{b})_{P = 0}}\right]}{\left[1 + \frac{\Delta(v_{a})_{j-1}}{(v_{a})_{P = 0}}\right]}$$
(A-2)

where  $\Delta(v_a)_{j=1}$  is the change in the volume before an expansion and  $\Delta(v_a + v_b)$  is the change in the volume after an expansion. The  $k_i$  and  $m_i$  given in Equations 12 and 13 are constants for the pressure distortion correction given in Equation A-2. These constants were determined taking into account the pressure deformation of the Burnett cells, the magnetic pump, the cryogenic valves, the connecting tubing, and the cryogenic differential pressure cell. Also, there is a change in volume due to the zero shift of the cryogenic differential pressure cell. This was included in deriving the constants  $k_i$  and  $m_i$ , which are given in Table A-2. This change in pressure is defined by

$$\Delta P_{ZSC} = P_{L} - P_{U} \qquad (A-3)$$

T°C	ĸı	к2	K <sub>3</sub>	ĸ <sub>4</sub>
- 90.00	1.0	-3.22(10 <sup>-7</sup> )	2.22(10 <sup>-11</sup> )	8.01(10 <sup>-16</sup> )
-115.00	1.0	-2.92 (10 <sup>-7</sup> )	8.18(10 <sup>-12</sup> )	-3.08 (10 <sup>-14</sup> )
-130.00	1.0	-3.13(10 <sup>-7</sup> )	2.40(10 <sup>-11</sup> )	-1.03(10 <sup>-14</sup> )
<b>T</b> °C	Ml	M <sub>2</sub>	M <sub>3</sub>	M4
- 90.00	1.0	-4.66 (10 <sup>-7</sup> )	3.49(10 <sup>-11</sup> )	1.26(10 <sup>-15</sup> )
-115.00	1.0	-4.22(10 <sup>-7</sup> )	1.28(10 <sup>-11</sup> )	-4.85 (10 <sup>-14</sup> )
-130.00	1.0	-4.51(10 <sup>-7</sup> )	3.77 (10 <sup>-11</sup> )	-1.62(10 <sup>-14</sup> )

#### TABLE A-2

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#### PRESSURE DISTORTION CORRECTION CONSTANTS

where  $P_L$  is the pressure in the lower chamber of the differential pressure cell and  $P_U$  is the pressure in the upper chamber of the differential pressure cell. This definition is consistent with the one used by Blancett (5) and applies to both the cryogenic and room temperature differential pressure cells. See Blancett for a detailed analysis of this development.

#### APPENDIX B

#### DATA REDUCTION ANALYSIS

This appendix is a summary of the procedure used to get compressibility factors and virial coefficients from the experimental data, which consisted of a series of pressures at constant temperature. The procedure given here is one that has been developed by Hall and Canfield (20).

#### Selection of Objective Function

The objective function must be chosen so that it is consistent with the Burnett analysis given in Chapter I. It should describe the difference between an observed and calculated variable and contain all the parameters which are to be determined. It is also desirable to use data from more than one run at the same experimental conditions to obtain values for the apparatus constants and virial coefficients simultaneously. The function selected that met these conditions was the sum of the weighted squares of the difference between the experimental and calculated pressures.

$$S = \sum_{r=1}^{NR} \sum_{j=1}^{J} w_{rj} \Delta_{rj}^{2} = \text{minimum} (B-1)$$

where  $\Delta_{rj} = P_{rj} - P_{CALC}$ ,  $P_{rj}$  is the experimental pressure, NR is the total number of runs,  $J_r$  is the number of data points in the r<sup>th</sup> run, and  $W_{rj}$  is an appropriate weighting function. The calculated pressure is given by the following:

$$P_{CALC} = RT \sum_{k=1}^{m} B_k \rho_{rj}^k$$
(B-2)

where  $B_k$  are the virial coefficients and m is the number of coefficients required. The density,  $\rho_{rj}$ , appearing in equation (B-2) is given by

$$\rho_{rj} = \frac{\left(\frac{P_o/Z_o\right)_r}{RT \xi_j N_{\omega r}^j}, \qquad (B-3)$$

where  $\xi_j$  is the product of the summations given in equation (13).

#### **Bvaluation of Initial Estimates**

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The same general least squares procedure, ORNOR, that was used in Chapter V, was used to obtain the initial estimates of the apparatus constants and the virial coefficients. The initial approximations of the cell constant and the run constant were determined using the classical limiting procedure given by equations (14) and (15), respectively. ORNOR was used to fit the low pressure data points where these expressions are more nearly linear, and then the results were extrapolated to zero pressure. With these estimated values, the densities could be calculated using equation (B-3) and the compressibility factors by use of equation (13). ORNOR was again used to fit the virial equation to obtain initial estimates of the virial coefficients and the optimum number of coefficients. The initial estimate of best fit was checked after the final values of the parameters were determined.

#### Calculation of Parameters

Equation (B-1) can be solved by a Newton-Raphson iteration procedure because of the accuracy with which the initial approximations of the cell constants and run constants can be determined. First, the normal equations are formed as

$$\frac{\partial S}{\partial x_{i}} = 2 \sum_{r=1}^{NR} \sum_{j=1}^{J} w_{rj} \Delta_{rj} \frac{\partial \Delta_{rj}}{\partial x_{i}} = 0 \qquad (B-4)$$

where X<sub>i</sub> represent the apparatus constants for either run and the virial coefficients. Each of these normal equations is then approximated by a first-order Taylor's series around the initial estimates of the parameters:

$$\frac{\partial s}{\partial x_{i}} = \left(\frac{\partial s}{\partial x_{i}}\right)_{o} + \sum_{\ell=1}^{m} \left(\frac{\partial^{2} s}{\partial x_{\ell} \partial x_{i}}\right)_{o} \Delta x_{\ell}$$
(B-5)

where the subscript o indicates that the quantity is evaluated at the initial values of the parameters. The partial derivatives in equation (B-5) were determined analytically. Initial estimates of the cell constants, run constants, and virial coefficients were then used to evaluate the partials, and the resulting equations were solved for  $\Delta X_{j}$ . The parameters were then adjusted by adding these corrections to get new estimates of the parameters. The iterations were continued until the changes in the parameters were arbitrarily small and the first partials of S were near zero.

Because the converged values of the parameters might change the optimum number of virial coefficients, the Newton-Raphson iteration was used for different values of m. The iterations were started for an m of two less than the estimate of best fit and continued until the best fit criterion was a minimum. Hall and Canfield (19) have established a best fit criterion to determine the truncated polynomial series which best approximates the infinite series. This criterion is given by

 $(2m - N)\sigma^2 + \langle (\Delta_m, \Delta_m) \rangle = minimum,$  (B-6)

where m is the number of parameters and N is the number of data points. Since the expected values of variables and  $\sigma^2$  are not known, approximations for these values muxt be introduced. The variance in the data,  $\sigma^2$ , was approximated by the minimum objective function for the polynomial, which is found to be the best fit, divided by the degrees of freedom, N-m.

#### Calculation of Compressibility Factors

When the optimal values of the cell constants and run constants had been determined, equation (13) was used to calculate the Burnett compressibility factors and equation (B-3) was used to calculate the densities. The virial compressibility factors were calculated using the virial equation with the optimum virial coefficients and these densities. The two sets of compressibility factors could then be compared. These comparisons are given in the tabulated results in Chapter VI.

#### Selection of Weighting Factors

The weighting functions,  $W_{rj}$ , in equation (B-1) could be taken as one if all pressures were of equal reliability. However in the Burnett procedure the higher pressures can be determined more accurately than the lower pressures can. Therefore, weighting factors are needed to weight the pressures in each run. The error that was independent of the pressure being measured was approximated as  $3(10^{-4})$ . The pressure dependent error was determined to be  $10^{-4}$ P. Thus the weighting factors used in the final treatment of the experimental data were given by

$$W_{rj} = 1/[3(10^{-4}) + 10^{-4}P_{rj}]^2$$
 (B-7)

Various values for the constants in equation (B-7) were tried to see if the results were affected by the choice of the weighting factor. As long as the values were

within a reasonable range for the equipment used, the results were the same for different choices of the weighting factor. The weighting factors in equation (B-7) were normalized by dividing each one by  $W_{11}$ .

#### APPENDIX C

## PERTURBATION BQUATION OF STATE DERIVATIONS

This appendix presents the derivations needed in the perturbation equation of state theory that were too lengthy to present in Chapter IV.

## Laplace Transform of $rg_0(r)$ .

Wertheim (43) and Thiele (38) give the explicit Laplace transform, G(s), of the approximate hard-sphere radial distribution,  $rg_0(r)$ , satisfying the Percus-Yevick integral equation as

$$G(s) = \frac{sL(s)e^{-s}}{12\eta L(s)e^{-s} + S(s)}$$
(C-1)

where  $S(s) = (1-\eta)^2 s^3 + 6\eta (1-\eta) s^2 + 18\eta^2 s - 12\eta (1+2\eta)$ and  $(s) = (1+2\eta)s + (1+2\eta)$ . A new function  $f(s,\eta)$  can be defined as follows:

$$f(s,\eta) = \frac{\partial}{\partial \rho} \left[ \rho G(s) \right]. \qquad (C-2)$$

When the lengthy differentiation with respect to density in equation (C-2) is performed, the result is

$$f(s,\eta) = \frac{s^4 e^{-s} \left[S(1 + \eta - 2\eta^2) + (2\eta + 1)^2\right]}{\left\{12\eta L(s)e^{-s} + S(s)\right\}^2} . \quad (C-3)$$

The perturbing potential function used in this thesis is given by

$$u(\mathbf{r}) = \begin{cases} 0 & \mathbf{r} < c\sigma \\ (C-4) \\ 4 \in [(\sigma/\mathbf{r})^{12} - (\sigma/\mathbf{r})^{6}], \mathbf{r} > c\sigma \end{cases}$$

With the change of variable  $z = r/c\sigma$ , equation (C-4) becomes

$$u(z) = 4 \in [\frac{1}{(cz)^{12}} - \frac{1}{(cz)^6}],$$
 (C-5)

or 
$$z \quad u(z) = 4 \in \left[\frac{1}{c^{12}} \frac{1}{z^{11}} - \frac{1}{c^6} \frac{1}{z^5}\right].$$
 (C-6)

The inverse Laplace transform of  $z^{-n}$  is given by

$$L^{-1}\left(\frac{1}{z^{n}}\right) = \frac{z^{n-1}}{(n-1)!}.$$
 (C-7)

Applying this to equation (C-6), the inverse Laplace transform of the potential function,  $U_1$  (s), is obtained.

$$U_1(s) = 4 \in \left[\frac{1}{c^{12}} \frac{s^{10}}{10!} - \frac{1}{c^6} \frac{s^4}{4!}\right]$$
 (C-8)

The inverse Laplace transforms of the square and cube of the potential function are also required. Equations (C-9) and (C-10) present the square and cube of the potential function, respectively, after the change of variable has been made.

#### APPENDIX C

#### PERTURBATION EQUATION OF STATE DERIVATIONS

This appendix presents the derivations needed in the perturbation equation of state theory that were too lengthy to present in Chapter IV.

# Laplace Transform of $rg_0(r)$ .

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Wertheim (43) and Thiele (38) give the explicit Laplace transform, G(s), of the approximate hard-sphere radial distribution,  $rq_0(r)$ , satisfying the Percus-Yevick integral equation as

$$G(s) = \frac{sL(s)e^{-S}}{12\eta L(s)e^{-S} + S(s)}$$
(C-1)

where  $S(s) = (1-\eta)^2 s^3 + 6\eta (1-\eta) s^2 + 18\eta^2 s - 12\eta (1+2\eta)$ and  $L(s) = (1+3\eta)s + (1+2\eta)$ . A new function  $f(s,\eta)$  can be defined as follows:

$$f(s,\eta) = \frac{\partial}{\partial \rho} \left[ \rho G(s) \right]. \qquad (C-2)$$

When the lengthy differentiation with respect to density in equation (C-2) is performed, the result is

$$f(s,\eta) = \frac{s^4 e^{-s} \left[ S(1 + \eta - 2\eta^2) + (2\eta + 1)^2 \right]}{\left\{ 12\eta L(s) e^{-s} + S(s) \right\}^2} . \quad (C-3)$$

#### Inverse Laplace Transform of Potential Function

The perturbing potential function used in this thesis is given by

$$u(r) = \begin{cases} 0 & r < c\sigma \\ (C-4) \\ 4 \in [(\sigma/r)^{12} - (\sigma/r)^{6}]. & r > c\sigma \end{cases}$$

With the change of variable  $z = r/c\sigma$ , equation (C-4) becomes

$$u(z) = 4 \in [\frac{1}{(cz)^{12}} - \frac{1}{(cz)^6}],$$
 (C-5)

or 
$$z \quad u(z) = 4 \in \left[\frac{1}{c^{12}} \frac{1}{z^{11}} - \frac{1}{c^6} \frac{1}{z^5}\right].$$
 (C-6)

The inverse Laplace transform of  $z^{-n}$  is given by

$$L^{-1}\left(\frac{1}{z^{n}}\right) = \frac{s^{n-1}}{(n-1)!}.$$
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Applying this to equation (C-6), the inverse Laplace transform of the potential function,  $U_1(s)$ , is obtained.

$$U_1(s) = 4 \in \left[\frac{1}{c^{12}} \frac{s^{10}}{10!} - \frac{1}{c^6} \frac{s^4}{4!}\right]$$
 (C-8)

The inverse Laplace transforms of the square and cube of the potential function are also required. Equations (C-9) and (C-10) present the square and cube of the potential function, respectively, after the change of variable has been made.

$$u^{2}(z) = 16\epsilon^{2}\left[\frac{1}{(cz)^{24}} - \frac{2}{(cz)^{18}} + \frac{1}{(cz)^{12}}\right]$$
 (C-9)

$$u^{3}(z) = 64\epsilon^{3} \left[ \frac{1}{(cz)^{36}} - \frac{3}{(cz)^{30}} + \frac{3}{(cz)^{24}} - \frac{1}{(cz)^{18}} \right] (C-10)$$

When the result of equation (C-7) is applied to equations (C-9) and (C-10),  $U_2(s)$  and  $U_3(s)$  are obtained.

$$U_{2}(s) = 16\epsilon^{2} \left[ \frac{1}{c^{24}} \frac{s^{22}}{22!} - \frac{2}{c^{18}} \frac{s^{16}}{16!} + \frac{1}{c^{12}} \frac{s^{10}}{10!} \right] (c-11)$$

$$U_{3}(s) = 64\epsilon^{3} \left[ \frac{1}{c^{36}} \frac{s^{34}}{34!} - \frac{3}{c^{30}} \frac{s^{28}}{28!} + \frac{3}{c^{24}} \frac{s^{22}}{22!} - \frac{1}{c^{18}} \frac{s^{16}}{16!} \right] - \frac{1}{c^{18}} \frac{s^{16}}{16!} \right]$$

$$(c-12)$$

#### Derivation of Pressure Coefficients

Equation (32), which gives the perturbation equation of state in terms of the free energy, must be differentiated with respect to volume to get the pressure form of the equation. From the differential equation for the free energy in thermodynamics,

$$dA_{m} = -S dT - P dV \qquad (C-13)$$

or

$$P = -\left(\frac{dA}{dV}\right)_{T} . \qquad (C-14)$$

In terms of density instead of volume, equation (C-14) can be written

$$\frac{P}{\rho} = \rho \left(\frac{\partial A}{\partial \rho}\right)_{\rm T} \tag{C-15}$$

Therefore, to get the first coefficient in the pressure form of the equation, the first coefficient in the free energy form must be differentiated with respect to density and multiplied by density

$$b(\rho) = \rho \left(\frac{\partial C_1}{\partial \rho}\right)_{T}$$
 (C-16)

or

$$b(\rho) = 2\pi\rho \frac{\partial}{\partial\rho} \int_{co}^{\infty} \rho u(r) g_{0}(r) r^{2} dr . \qquad (C-17)$$

With the change of variable  $z = r/c\sigma$ , equation (C-17) becomes

$$b(\rho) = 2\pi\rho(c\sigma)^{3} \frac{\partial}{\partial\rho} \int_{1}^{\infty} \rho u(z)g_{0}(z)z^{2}dz \quad (C-18)$$

Wertheim (43) and Thiele (38) have obtained the explicit Laplace transform, G(s), of the approximate hard-sphere radial distribution function,  $rg_{o}(r)$ :

$$G(s) = \int_{c\sigma}^{\infty} e^{-ST} g_{o}(r) r dr . \qquad (C-19)$$

If it is assumed that ru(r) possesses a continuous inverse transform, then

$$ru(r) = \int_{0}^{\infty} e^{-sr} U_{1}(s) ds \qquad (C-20)$$

or making the same change of variable as before, equations (C-19) and (C-20), respectively, become

$$G(s) = (c\sigma)^2 \int_{1}^{\infty} e^{-sc\sigma z} g_0(z) z dz \qquad (C-21)$$

$$c\sigma z_{1}(z) = \int_{0}^{\infty} e^{-s c\sigma z} U_{1}(s) ds$$
 (C-22)

After substituting the right-hand side of equation (C-22) for its equivalent in equation (C-18), the result is

$$b(\rho) = 2\pi\rho(c\sigma)^{3} \frac{\partial}{\partial\rho} \int_{1}^{\infty} \int_{0}^{\infty} \rho e^{-sc\sigma z} U_{1}(s) dsg_{0}(z) z dz. (C-23)$$

When the order of integration in equation (C-23) is changed and the left-hand side of equation (C-21) is substituted for its equivalent, equation (C-23) becomes

$$b(\rho) = 2\pi\rho(c\sigma)^{3} \frac{\partial}{\partial\rho} \int_{0}^{\infty} \rho G(s) U_{1}(s) ds \qquad (C-24)$$

Remembering equation (C-2), equation (C-24) becomes

$$b(\rho) = 2\pi\rho(c\sigma)^3 \int_0^\infty f(s,\eta)U_1(s)ds \qquad (C-25)$$

If the dimensionless parameter  $\eta$  is defined as

$$\eta = \frac{\pi (c\sigma)^3 \rho}{6} , \qquad (C-26)$$

then equation (C-25) becomes

$$b(\rho) = 12\eta \int_{0}^{\infty} f(s,\eta) U_{1}(s) ds \qquad (C-27)$$

where  $f(s,\eta)$  and  $U_1(s)$  are defined by equations (C-3) and (C-8), respectively.

In a similar manner the coefficient of the  $\beta^2$  term can be derived.

$$c(\rho) = \rho \left(\frac{\partial c_2}{\partial \rho}\right)_{T} \qquad (C-28)$$

or

$$C(\rho) = -\pi \rho \frac{\partial}{\partial \rho} \left[ kT \left( \frac{\partial \rho}{\partial P} \right)_{O} \int_{CO}^{\infty} \rho u^{2}(r) g_{O}(r) r^{2} dr \right], \qquad (C-29)$$

- - ----

where

$$kT\left(\frac{\partial\rho}{\partial P}\right)_{O} = \frac{(1-\eta)^{4}}{1+4\eta+4\eta^{2}} \qquad (C-30)$$

This is the hard-sphere compressibility based on the Percus-Yevick hard-sphere equation of state given by equation (42). The same change of variables and substitutions are made as before in the case of  $b(\rho)$ . The only difference is that this time, the differentiation with respect to density requires the differentiation of a quotient because  $\eta$  is a function of density. When these operations are performed, the final result is

$$c(\rho) = R(\eta) \int_{0}^{\infty} f(\eta, s) U_{2}(s) ds$$
  
-  $V(\eta) \int_{0}^{\infty} G(s) U_{2}(s) ds,$  (C-31)

where

$$R(\eta) = \frac{-6\eta (1-\eta)^4}{1 + 4\eta + 4\eta^2}$$
(C-32)

and

$$\mathbf{V}(\eta) = -6\eta \left[ \frac{4\eta (1-\eta)^{3}}{1+4\eta+4\eta^{2}} + \frac{4\eta (1+2\eta) (1-\eta)^{4}}{(1+4\eta+4\eta^{2})^{2}} \right] \quad (C-33)$$

Likewise, the coefficient of the  $\beta^3$  term can be derived following the same procedure as for the other two.

$$d(\rho) = \rho \left(\frac{\partial C_3}{\partial \rho}\right)_{T}$$
 (C-34)

$$d(\rho) = \frac{2}{3!} \pi \rho \frac{\partial}{\partial \rho} \left[ \frac{(1-\eta)^{7} (6\eta^{2} - 7\eta - 1)}{(1+2\eta)^{5}} \times \int_{c\sigma}^{\sigma} \rho u^{3}(r) g_{0}(r) r^{2} dr \right]. \qquad (C-35)$$

The differentiation with respect to density is similar to the case of  $c(\rho)$  except that it is more lengthy to perform. The final result for the  $\beta^3$  term coefficient is

$$d(\rho) = W(\eta) \int_{0}^{\infty} f(\eta, s) U_{3}(s) ds + V(\eta) \int_{0}^{\infty} G(s) U_{3}(s) ds, \quad (C-36)$$

where

$$W(\eta) = \frac{2\eta(1-\eta)^{7}(12\eta-7)}{(1+2\eta)^{5}}$$
(C-37)

and

$$Y(\eta) = 2\eta \left[ \frac{\eta (1-\eta)^{7} (12\eta-7)}{(1+2\eta)^{5}} - \frac{7\eta (1-\eta)^{6} (6\eta^{2}-7\eta-1)}{(1+2\eta)^{5}} - \frac{10\eta (1-\eta)^{7} (6\eta^{2}-7\eta-1)}{(1+2\eta)^{6}} \right]$$
(C-38)

## Hard-Sphere Compressibility

The hard-sphere compressibility,  $(\partial \rho / \partial P)_{0}$ , can be determined by differentiating equation (42) with respect to density and taking the reciprocal. This section shows how equation (C-30) is derived from equation (42) by this procedure.

$$P_{0} = \rho kT \left[ \frac{1 + \eta + \eta^{2}}{(1 - \eta)^{3}} \right]$$

$$\left( \frac{\partial P}{\partial \rho} \right)_{0} = kT \left[ \frac{1 + \eta + \eta^{2}}{(1 - \eta)^{3}} + \rho \frac{\partial}{\partial \rho} \left\{ \frac{1 + \eta + \eta^{2}}{(1 - \eta)^{3}} \right\} \right]$$

$$= kT \left[ \frac{(1 - \eta)(1 + \eta + \eta^{2}) + (1 - \eta)(\eta + 2\eta^{2}) + 3\eta(1 + \eta + \eta^{2})}{(1 - \eta)^{4}} \right]$$

$$= kT \left[ \frac{1 + 4\eta + 4\eta^{2}}{(1 - \eta)^{4}} \right] .$$
(42)

or

$$kT\left(\frac{\partial\rho}{\partial P}\right)_{O} = \frac{\left(1-\eta\right)^{4}}{1+4\eta+4\eta^{2}}$$
(C-30)

## Change of Variable for Numerical Integration

In order to make the numerical integration more easily manageable, it is necessary to make a change of variable in the following manner:

$$s = \frac{1-x}{x}$$
 (C-39)

with

$$ds = -dx/x^2$$
 . (C-40)

Thus the integral in equation (C-27) becomes

$$I = \int_{0}^{1} \frac{1}{x^{2}} f(\frac{1-x}{x}, \eta) U_{1}(\frac{1-x}{x}) dx \qquad (C-41)$$

-----
in which s is replaced by (1-x)/x in f(s, $\eta$ ) and U<sub>1</sub>(s). The integrals in equation (C-31) become

$$J = \int_{0}^{1} \frac{1}{x^{2}} f\left(\frac{1-x}{x}, \eta\right) U_{2}\left(\frac{1-x}{x}\right) dx \qquad (C-42)$$

and

$$K = \int_{0}^{1} \frac{1}{x^{2}} G \left(\frac{1-x}{x}\right) U_{2} \left(\frac{1-x}{x}\right) dx \qquad (C-43)$$

in which s is replaced by (1-x)/x in G(s), U<sub>2</sub>(s), and f(s,  $\eta$ ).

# Derivation of Other Terms

The expressions derived in this section are the additional terms in equation (49). Since these terms are evaluated in the range from zero to  $\sigma$ , the molecular diameter, the Laplace transform, G(s), of the hard-sphere radial distribution function,  $g_o(r)$ , as suggested by Frisch, <u>et al</u>. (16) cannot be used. However, Wertheim (43) and Thiele (38) have also presented an analytic expression for  $xg_o(x)$ , where x is a dimensionless distance,  $r/c\sigma$ , for a shell defined by the range 1 < x < 2.

This expression in the first shell is given by

$$xg(x) = (1 - \eta)^{-2} \sum_{l=0}^{2} A_{l} \exp t_{l} (x-1),$$
 (C-44)

where  $t_{\ell} = 2\eta (1-\eta)^{-1} [-1 + x_{+}j^{\ell} + x_{-}j^{-\ell}], j = \exp(\frac{2}{3}\pi i),$ 

$$x_{+} = [f + (f^{2} + \frac{1}{8})^{1/2}]^{1/3}, x_{-} = [f - (f^{2} + \frac{1}{8})^{1/2}]^{1/3},$$
  
and  $f = (3 + 3\eta - \eta^{2})/4\eta^{2}$ . The A<sub>4</sub> in equation (C-44)  
are given by

$$A_{l} = \frac{1}{3} \sum_{m=0}^{2} H_{m} j^{ml}, \qquad (C-45)$$

where

$$H_{0} = 1 + 1/2\eta,$$

$$H_{1} = -(4\eta)^{-1}(f^{2}+1/8)^{-1/2} [x_{2}^{2}(1-3\eta-4\eta^{2}) + x_{4}(1-\frac{5}{2}\eta^{2})],$$

$$H_{2} = (4\eta)^{-1}(f^{2}+1/8)^{-1/2} [x_{4}^{2}(1-3\eta-4\eta^{2}) + x_{4}(1-\frac{5}{2}\eta^{2})].$$

When these equations are substituted into equation (C-44), and it is expanded, the imaginary terms drop out, and a completely analytic expression for xg(x) is obtained:

$$g(x) = \frac{1}{3x(1-\eta)^2} [(H_0 + H_1 + H_2) \exp (AA) + (2C \cos B - 2D \sin B) \exp(A)], \quad (C-46)$$

where

$$AA = \frac{2\eta}{(1-\eta)} (x-1) [-1 + x_{+} + x_{-}],$$

$$A = -\frac{2\eta}{(1-\eta)} (x-1) [1 + 0.5(x_{+} + x_{-})],$$

$$B = \frac{2\eta}{(1-\eta)} (x-1) (.86603)(x_{+} - x_{-}),$$

$$C = H_0 - 0.5 (H_1 + H_2)$$
,

and

$$D = 0.86603 (H_1 - H_2)$$
.

The  $\alpha$  term in equation (49) is given by

$$\alpha = \frac{\partial}{\partial \rho} \left\{ (c\sigma)^2 \rho g_0(c\sigma) [c\sigma - \int_0^{\sigma} \{1 - \exp(-\beta u)\} dz] \right\}, \quad (C-47)$$

where the differentiation with respect to density is required to convert from free energy to pressure. In equation (C-47) only  $\rho$  and  $g_0(c\sigma)$  are a function of density. Therefore equation (C-47) can be rewritten as

$$\alpha = (c\sigma)^{2} [c\sigma - \int_{0}^{\sigma} \{1 - \exp(-\beta u)\} dz] \frac{\partial}{\partial \rho} [\rho g_{0}(c\sigma)] \quad (C-48)$$

Throop and Bearman (39) give an expression for the hardsphere radial distribution function evaluated at the hard-sphere diameter,  $g_o(c\sigma)$ .

$$g_{0}(c\sigma) = \frac{(1 + \frac{1}{2}\eta)}{(1 - \eta)^{2}},$$
 (C-49)

When equation (C-49) is substituted into equation (C-48) and the differentiation is performed, equation (C-48) becomes

$$\alpha = (c\sigma)^{2} [c\sigma - \int_{0}^{\sigma} \{1 - \exp(-\beta u)\} dz] [\frac{1+2\eta}{(1-\eta)^{3}}] . \quad (C-50)$$

The integration in equation (C-50) is done numerically after the change of variable,  $x = z/\sigma$ , is made.

$$\alpha = (c\sigma)^{2} [c\sigma - \sigma \int_{0}^{1} \{1 - \exp(-\beta u)\} dx] [\frac{1+2\eta}{(1-\eta)^{3}}] \quad (C-51)$$

The  $\gamma$  term in equation (49) is given by

$$\gamma = \frac{\partial}{\partial \rho} \int_{c\sigma}^{\sigma} \rho g_{0}(r) u(r) r^{2} dr, \qquad (C-52)$$

where the differentiation with respect to density is again required to change from free energy to pressure. When the differentiation is performed, two integrals are obtained. After the change of variable,  $x = r/c\sigma$ , is made and the 12:6 potential is substituted, equation (C-52) becomes

$$\gamma = 4 \in (c\sigma)^{3} \left[ \int_{1}^{1/c} g_{0}(x) \left[ \frac{1}{(cx)^{12}} - \frac{1}{(cx)^{6}} \right] x^{2} dx + \rho \int_{1}^{1/c} \frac{\partial g_{0}(x)}{\partial \rho} \left[ \frac{1}{(cx)^{12}} - \frac{1}{(cx)^{6}} \right] x^{2} dx . \quad (C-53)$$

The derivative,  $\frac{\partial g_{0}(x)}{\partial \rho}$ , is evaluated numerically by evaluating  $g_{0}(x)$  at the required density, incrementing the density by 0.00001 $\rho$ , and evaluating  $g_{0}(x)$  again. This resulted in approximating  $\frac{\partial g_{0}(x)}{\partial \rho}$  by  $\frac{\Delta g_{0}(x)}{\Delta \rho}$ . Several incrementing factors, varying by two orders of magnitude, were tried, but the results were not affected by the choice of an incrementing factor within this range. The  $\gamma^2$  term in equation (49) is given by

$$\gamma^{2} = \frac{\partial}{\partial \rho} \left[ kT \left( \frac{\partial \rho}{\partial P} \right)_{O} \int_{CO}^{O} \rho g_{O}(r) u^{2}(r) r^{2} dr \right] . \qquad (C-54)$$

After the differentiation of the quantity in the brackets with respect to density is performed, the change of variable,  $x = r/c\sigma$ , is made, and the 12:6 potential is substituted, equation (C-54) becomes

$$\gamma^{2} = 16\epsilon^{2}(c\sigma)^{3} \frac{(1-\eta^{4})^{2}}{(1+2\eta)^{2}} \left[ \left\{ 1 - \frac{4\eta}{(1-\eta)} - \frac{4\eta}{(1+2\eta)} \right\} \right]$$

$$\int_{1}^{1/c} \left[ \frac{1}{(cx)^{24}} - \frac{2}{(cx)^{18}} + \frac{1}{(cx)^{12}} \right] g_{0}(x) x^{2} dx \qquad (C-55)$$

$$+ \rho \int_{1}^{1/c} \left[ \frac{1}{(cx)^{24}} - \frac{2}{(cx)^{18}} + \frac{1}{(cx)^{18}} \right] \frac{\partial g_{0}(x)}{\partial \rho} x^{2} dx \qquad (C-55)$$

$$\frac{\partial g_{0}(x)}{\partial \rho} x^{2} dx = 0$$

where the derivative,  $\frac{\partial g_0(x)}{\partial \rho}$ , is evaluated numerically as for the  $\gamma$  term.

.

# APPENDIX D

# ESTIMATION OF STANDARD ERRORS OF PARAMETERS AND DATA

This appendix presents the development of expressions that estimate the standard error in the parameters that appear in equation (B-2) in a nonlinear manner. Using the standard error in the parameters, the standard errors in each data point were estimated with a procedure given by Deming (14). A set of statistical weighting factors was determined from the standard error of the dependent variable and the standard errors of the individual data points.

# Standard Brror of Parameters

The variances of the parameters were calculated using the elements of the inverse of the coefficient matrix, A. The elements in the coefficient matrix were determined by

$$a_{ts} = \sum_{i=1}^{N} W_i \left( \frac{\partial \Delta_i}{\partial \theta_t} \right) \left( \frac{\partial \Delta_i}{\partial \theta_s} \right)$$
(D-1)

where the  $\Delta_i$  are the deviations between the observed and calculated values of the dependent variable,  $\theta_i$  are

the m parameters,  $W_{i}$  are the weighting factors, and N is the number of data points. The matrix, whose elements are defined by equation (D-1), was inverted using the Guass-Jordan-Rutishauser double-pivoting method to obtain the inverse matrix B. The variances of the parameters were then calculated by multiplying the diagonal elements of the inverse matrix by the variance of the dependent

$$s_{\theta p}^2 = b_{pp} s^2 \qquad (D-2)$$

where  $S^2$  is given by

$$s^{2} = \frac{\sum_{i=1}^{N} w_{i} \Delta_{i}^{2}}{N-m}$$
 (D-3)

The standard error was calculated by taking the square root of the variance. The covariances of the parameters could be determined by multiplying the off-diagonal elements by  $S^2$ ,

$$s_{\theta p \theta q}^{2} = b_{pq} s^{2}$$
 (D-4)

Barieau and Dalton (4) have derived an expression for the estimation of the variance of nonlinear parameters by using a truncated Taylor series approximation for the law of propagation of errors. Box (6) was one of the first to suggest an approach similar to this. They found that the elements in the coefficient matrix A, discussed above, were given by

$$a_{ts} = \sum_{i=1}^{N} W_{i} \left[ \left( \frac{\partial \Delta_{i}}{\partial \theta_{t}} \right) \left( \frac{\partial \Delta_{i}}{\partial \theta_{s}} \right) + \Delta_{i} \left( \frac{\partial^{2} \Delta_{i}}{\partial \theta_{s} \partial \theta_{t}} \right) \right]. (D-5)$$

Their expression for the variance of the parameters was given by

$$s_{\theta p}^{2} = b_{pp}s^{2} - s^{2} \sum_{s=1}^{m} \sum_{t=1}^{m} b_{ps}b_{pt} \sum_{i=1}^{N} w_{i}\Delta_{i} \times \left(\frac{\partial^{2}\Delta_{i}}{\partial \theta_{s}\partial \theta_{t}}\right) \qquad (D-6)$$

This expression is the same as equation (D-2) with an additional term added to it. The additional term in equation (D-6) becomes significant if the parameters are highly nonlinear. In the data treatment in this thesis, the estimates of the standard errors of the parameters were determined using the square root of equation (D-2) because it is a good approximation for equation (D-6) for the parameters appearing in equation (B-2).

# **<u>Bstimated Variance in Data</u>**

The estimated variance in the individual data points was determined following the method given by Deming (14). His procedure was to estimate the variance by

$$S_{P_{i}}^{2} = \sum_{j=1}^{m} (P_{\theta j}^{i} S_{\theta j})^{2} + \sum_{\substack{j=1 \ j \neq k}}^{m} \sum_{\substack{j=1 \ j \neq k}}^{m} P_{\theta j}^{i} P_{\theta k}^{j} S_{\theta j} S_{\theta k}^{r} \theta_{j} \theta_{k} \qquad (D-7)$$
  
where  $P_{i}$  are the pressure data points,  $P_{\theta j}^{i}$  is the  $\frac{\partial P_{i}}{\partial \theta_{j}}$ ,

and  $r_{\theta j \theta k}$  is a correlation parameter that is zero if the parameters are independent and nonzero if the parameters are interdependent. The parameters in this work are interdependent and the product  $S_{\theta j}S_{\theta k}r_{\theta j \theta k}$  is the covariance given by equation (D-4). In applying equation (D-7), all of the quantities in the second term need not be determined because the inverted matrix is symmetrical about the diagonal. Therefore, only the off-diagonal elements above the diagonal were used, and the results were multiplied by two. The standard errors for the data were calculated by taking the square root of the variance determined in equation (D-7).

The variances in the compressibility factor were calculated using an expression similar to equation (D-7):

$$s_{z_{i}}^{2} = \sum_{j=1}^{m} (z_{\theta j}^{i} s_{\theta j})^{2} + \sum_{\substack{j=1 \ j \neq k}}^{m} \sum_{k=1}^{m} z_{\theta j}^{i} z_{\theta k}^{j} s_{\theta j}^{k} s_{\theta j}^{$$

where  $Z_{\theta j}^{i}$  is the  $\frac{\partial Z_{i}}{\partial \theta_{j}}$  and was determined using a combination of equations (13) and (55) with the  $\frac{\partial P_{i}}{\partial \theta_{j}}$ . The standard errors were determined by taking the square root of equation (D-8).

# Statistical Weighting Factors

Deming (14) defines a set of statistical weighting factors by

$$W_{P_{i}} = \frac{s^{2}}{s_{P_{i}}^{2}}$$
 (D-9)

where  $S^2$  is the variance of the dependent variable defined by equation (D-3) and  $S_{P_1}^2$  are the variances in the data that are calculated by equation (D-7). These statistical weighting factors were normalized by dividing each one by the weighting factor for the first data point, so that they would be consistent for comparison with the a priori weighting factors calculated using equation (B-7). This comparison showed that the normalized weighting factors used in the data analysis were consistent with the normalized statistical weighting factors.

#### APPENDIX E

### COMPUTER PROGRAMS

This appendix presents the computer programs used in this thesis. The first program was used to determine the virial coefficients and compressibility factors along with the standard errors in the data treatment. A list of the nomenclature used in the data treatment precedes the computer program listing. The next three programs were used to determine the value of the cutoff parameter c for each methane data point, the coefficients in the expression for c, and the difference between experimental and calculated densities in the equation of state calculations. Before these three program listings, there is a list of nomenclature used in the equation of state calculations.

# NOMENCLATURE FOR DATA TREATMENT

# COMPUTER PROGRAMS

- A Matrix of second partials of objective function with respect to parameters (calculated in IMPK as FZ and used in SOLVE as A)
- A General matrix inverted in place in GJR
- A General matrix used in MATMPY
- Al Run constant for first run
- A2 Run constant for second run
- AlK Parameter used to save run constant for first run
- A2K Parameter used to save run constant for second run
- B Dummy matrix used to save matrix A
- B Column matrix in GJR used to save, one at a time, the columns in the matrix to be inverted on the Jordan step
- B General matrix used in MATMPY
- BA Virial coefficients
- BFC Best fit criterion
- BSUM Sum of product of diagonal elements of variancecovariance matrix with first derivative of  $\Delta_{ij}$ (see thesis nomenclature)
- C Matrix of first partials of objective function with respect to parameters (calculated in IMPK as F and used in SOLVE as C)
- C Product of matrices A and B in MATMPY
- C Column matrix in GJR used to save, one at a

time, the rows in the matrix to be inverted on the Jordan step

- CK Relative change in parameter
- CO Pressure distortion correction factors for cell constants
- CORN Subroutine that calculates pressure distortion correction factors for cell constants
- D Dummy column matrix used to save matrix C
- **DEL** Difference between experimental pressure and calculated pressure
- DELK Absolute change in parameters
- DIAG Diagonal element of coefficient matrix used in SOLVE
- DZ Difference between Burnett compressibility factor and virial compressibility factor
- F First partials of objective function with respect to parameters
- FS Product of coefficient matrix with its inverse
- F2 Second partials of objective function with respect to parameters in IMPK (also coefficient matrix in MAIN)
- GJR Gauss-Jordan-Rutishauser matrix inversion subroutine
- IMPK Subroutine that calculates first and second partials of objective function with respect to parameters
- JCR Number of points to be deleted from ORNOR fit in determining initial values of parameters
- K1-K6 Pressure distortion correction constants for numerator of correction factor
- MATMPY Matrix multiplication subroutine
- MINK Optimum number of virial coefficients
- M1-M6 Pressure distortion correction constants for denominator of correction factor

- NORM Convergence check in SOLVE
- NTL Number of data points in first run
- NT2 Number of data points in second run
- Nl Cell constant for first run
- N2 Cell constant for second run
- NIK Parameter used to save cell constant for first run
- N2K Parameter used to save cell constant for second run
- OFFSUM Sum of product of off-diagonal elements of variance - covariance with first derivative of  $\Delta_{ij}$
- ORNOR Generalized orthonormal polynomial leastsquares subroutine (see next nomenclature listing for variables used in ORNOR)
- P Experimental pressure in atmospheres
- PC Calculated pressure in atmospheres
- **PIVOT** Pivot element in matrix inversion subroutine
- Q First partials of  $\Delta_{i,j}$  (see thesis nomenclature) with respect to parameters
- QZ First partials of compressibility factors with respect to parameters
- Q2 Second partials of objective function with respect to parameters
- RGC Gas constant
- S Objective function representation in IMPK
- SAVE Matrix used to save coefficient matrix before it is inverted in place
- SF Objective function representation in MAIN
- SOLVE Subroutine to solve linear set of equations
- SS Variance in dependent variable

- SSP Variance in pressure data
- SSZ Variance in compressibility factors
- ST Variable used to temporarily save parameters or changes in parameters
- T Numerator of pressure distortion correction factor
- **TEMP Temperature** in °K
- **TEMP** Variable in SOLVE used to temporarily save another variable
- W A priori weighting factors
- WNCAL Calculated statistical weighting factors
- X Density in MAIN
- X Absolute change in parameters (used in SOLVE and equivalent to DELK in MAIN)
- Y Difference between experimental pressure and calculated pressure
- Z Virial compressibility factors
- Z Variable in GJR used to temporarily save another variable
- ZETA Parameter that sets minimum size of elements as check in inversion subroutine
- ZX Burnett compressibility factors

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Ç	THIS PROGRAM USED IN TREATMENT OF EXPERIMENTAL
C	HELIUN-ARGON DATA
	DIMENSION X(30), PR(18)
	INTEGER NT1,NT2,NIN,M,NT,HINK,J1,L1,JCR,JJ
	DOUBLE PRECISION P(2,15),CO(2,15),DELK(15),DEL(2,15),
	18A(15),F(15,30),Y(39),A1,A2,N1,N2,RGC,TENP,CK(15),S,
	2\$\$,A1K,A2K,N1K,N2K,F1(15),SF(15),BFC(15),F2(15,15),PC,
	32,2X, DZ, W(2,15),Q(15,30), BSUM 30), SSP(30),QZ(15,30),
	4WNCAL(30), OFFSUN(30), SSZ(30), SAVE(15,15), FSAVE(15,15),
	SFSF(15,15),F2NEW(15,15),DIFF,FS(15,15),TRIAL(15,15),
	6CHECK(15,15)
	CONMON P.CO.F2.F1.DELK.TEMP.RGC.DEL.BA.W.AL A2.N1.N2.
	· 1F.Y.A(15.15).WN(30)
	NUH=2
	DD 67 IJK=1.NUM
	READ (5.89) (PR(().[+].]A)
	READ (5.101) NTL.NT2.JCR.TERP
	READ (5.102) CONV
	READ (5-102) (R(1-1)-4=1-HT1)
	RFAD (5.102) (P(2.3), 1=1, NT1)
	WR(TF (6.89) (PR(1), (=1.18))
	Hai
	595-1.5-04
	AECT=1.512
	DFG1=10542 CA14 [004 [NT] NT3]
	CALL CURA INILINIZI
	UU L J=LINTL UU L J=LINTL
•	WLL1JJ=LL0V/LJ0C=UTTL0C=UTTL1L1JJJJ]=+2 WL2 JL=/1 0//2 E_0/41 E_0/40/2 JLLL442
1	#\Z #J]=\LoV/\JoE=V#+LoE=V#+Y\Z#J#J##Z 7=1411_1
	VI Z J=19711
•	
6	₩ ( ∠ p J ) = ₩ ( ∠ p J ) / ∠ NT-NT- 1
	Y[J-J[K]#P[1,J]/P[1,J+]]
•	F(1, j-jCR) = 1.0
3	₩₩{J-JCK}=₩{L+J}/₩{L+J}
	00 4 K=Z, M
	DO 4 J=JJ;NT
4	F(K,J-JCR)=P(1,J+1)==(K-1)
	NT=NT-JCR
	GALL ORNOR (NT.M.MIN,EPS)
	NL=A(HEN, 1)
	NT=NT [
	00 5 Jejjent
	Y{J-JCR}=P{1,J}=N1=+{J-1}=CO(1,J)
_	WN(J-JCR)=1.0
5	F(1+J-JCR)=1.0
	00 4 K=2,H

DO 6 J=JJ, NT F(K,J-JCR)=P(1,J)\*\*(K-1) 6 NT=NT-JCR CALL ORNOR (NT.M.MIN.EPS) A1=A(MIN,1) NT=NT 2-1 DO 7 J=JJ.NT Y(J-JCR) = P(2,J)/P(2,J+1)F(1, J-JCR) = 1.07 WN(J-JCR) = W(2, J) / W(2, J+1)DO 8 K=2.M DO 8 J=JJ.NT 8 F(K,J-JCR) = P(2,J+1) \* \* (K-1)NT=NT-JCR CALL ORNOR (NT.M.NIN.EPS) N2=A(MIN,1)NT=NT2 DO 9 J=JJ.NT Y(J-JCR)=P(2,J)\*N2\*\*(J-1)\*CO(2,J) $MN{J-JCR}=1.0$ F(1.J-JCR)=1.0 9 DO 10 K=2,M DO 10 J=JJ,NT 10 F(K,J-JCR)=P(2,J)\*\*(K-1)NT=NT-JCR CALL ORNOR (NT, M.MIN, EPS) A2=A(MIN,1)NT=NT1+NT2 READ (5,92) H J=2\*NT1-1 DO 11 K=1,J,2 J1=(K+1)/2Y(K) = P(1, J1) - A1 / (N1 + + (J1 - 1) + CO(1, J1))Y(K+1)=P(2,J1)-A2/(N2\*\*(J1-1)\*CO(2,J1))WN(K)=W(1,J1) 11 WN(K+1) = W(2, J1)DO 12 K=1.J.2 J1=(1-K)/2X(K)=(A1\*N1\*\*J1)/(RGC\*TEMP\*CO(1.J1+K)) 12 X(K+1)=(A2\*N2\*\*J1)/(RGC\*TEMP\*CO(2,J1+K))DO 13 K=1.M DO 13 N=1,NT 13  $F(K_N) = RGC + TEMP + X(N) + + (K+1)$ CALL ORNOR (NT, M, MIN, EPS) MIN=M WRITE (6,76) MIN AlK=Al N1K=N1 A2K=A2 N2K=N2 MINK=MIN-4

14	IF (MINK-M) 15,15,58
15	WRITE (6,75) MINK
	A1=A1K
	A2=A2K
	NI=NIK
	N2=N2K
14	
10	N-MINKAI
	N-MINNY1 MOITE (/ 77)
	NKITE (Dy//)
	WKIIE (6,69) AL
	WRITE (6,70) A2
	WRITE (6,71) N1
	WRITE (6,72) N2
	WRITE (6,73) [J,BA(J),J=2,K)
	L1=0
17	Ll=L1+1
	IF (L1-20) 18.63.63
18	
	CALL IMPK (NTLANT2 MINKALLAL2 CONV.S)
	$1 = \{A\}\} = 10.44.10$
10	16 (AL) 17907917 WDITE /4 40\ 11 C
13	. WRITE (0:00/ L1:5)
	CK(2)=DELK(2)/NL
	CK(3) = DELK(3)/A2
	CK(4)=DELK(4)/N2
	A1=A1+DELK(1)
	N1=N1+DELK(2)
	A2=A2+DELK(3)
	NZ=N2+DELK(4)
	DO 20 K=1,MINK
	L=K+4
	CK(L)=DELK(L)/BA(K+1)
20	BA(K+1) = BA(K+1) + DELK(L)
	NINK4=MINK+4
	WRITE (6.85)
	WRITE $(6,84)$ (CK(1),1=) MINKA)
	MIN-MINEAR CORESPOSE FAIRER
	HOTTE ( L LON AN
	#REIE (0:07) AL
	WRITE (DyTU) AZ
	NKILE (O, /L) NL
	WRITE (6,72) NZ
	WRITE (6,73) (J,BA(J),J=2,MLM)
	IF (L2) 17,21,17
21	CONTINUE
	DO 22 K=1,HINK4
	IF (DABS(CK(K))-1.D-06) 22,22,17
22	CONTINUE
	WRITE (6,79)
	WRITE (6,82)
	Y(27) = 0.0

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• \_

	M 201-0
	Y(10)=0.0
	Y(11)=0.0
	Y(12)=0.0
	DO 24 J=1,NT1
	2=1.0
	MENKC=HINK+1
22	UU ZJ N-ZYNENNG 7-7-04/V34/414144/1-11///0664TEM0460/1-1111444/V-11
23	2=2+DA(K)+(A1+N1++(1-J)/(KGC+)CMP+GU(1+J))++(K-1)
	PC = A1 = N1 = (1 - J) = Z/CO(1 + J)
	ZX=P(1,J)*N1**(J-1)*CO(1,J)/A1
	DZ=ZX-Z
	Y(3) = P(1, J) - PC
	Y(25)=P(1,J)/(ZX*RGC*TEMP)
	$Y(26) \neq (7X-1,0)/Y(25)$
	V(27)=V(27)+V(3)
	V[20]+V[20]ADA0C/V[2]]
	V/201-1120/*VAD3(1(3// V/201-1120/*VAD3(1(3//
	T\3U}=W\1pJJ+T\3J++Z
	Y(LU)=Y(LU)+DZ++Z
	Y(11)=Y(11)+DABS(DZ)
	Y(12)=Y(12)+DZ
24	WRITE (6,87) P(1,J),PC,Y(3),Y(30),ZX,Z,DZ,Y(25),Y(26)
	DO 26 J=1,NT2
	Z=1.0
	DQ 25 K=2.MINKC
25	- 7=7+BA(K)+(A2+N2++(1-1)/(RGC+TEMP+CO(2.1)))++(K-1)
27	$DC = A2 \pm N2 \pm \pm 11 \pm 11 \pm 77 CO(2, 1)$
	TU-A2+N2+T(1-1)+2/UU(2)J) 7V-D/2, 1)+N2++/1-1++CC/2, 1)/A2
	Y(3)=P(2,J)-PC
	Y(25)=P(2+J)/(ZX*RGC*TEMP)
	Y(26)=(ZX-1.0)/Y(25)
	Y(27)=Y(27)+Y(3)
	Y(28)=Y(23)+DABS(Y(3))
	Y(30)=W(2,J)+Y(3)++2
	Y(10) = Y(10) + DZ = 2
	Y(11) = Y(11) + DABS(D7)
	Y(12) = Y(12) + D7
26	WRITE (6.87) 012.11.00.9(3).9(30).78.7.07.91251.91261
20	WALLE 104017 F(240/4FC4115741150/42A4240241125/41120)
	T 1 2 7 / - T 1 2 0 / / 1 1 1 1 1 1 2 / V/ 1 3 1 V/ 1 3 1 // 1 1 1 1 1 1 2 1
	T(13) = T(12) / (N(1+N)2)
	WKIIE (6,90) Y(2/)
	WRITE (6,91) Y(29)
	WRITE (6,93)
	WRITE (6,94) Y(10)
	WRITE (6,95) Y(11)
	WRITE (6,96) Y(13)
	SF(MINK)=0.0
	00 27 I=1.NT1
27	SE(MINK)=SE(MINK)+W(1,1)+DE(11,1)++2
<b>**</b> *	$\frac{1}{10} = \frac{1}{10} $
	VU LU I-191116

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SF(MINK)=SF(MINK)+W(2,I)+DEL(2,I)++2 WRITE (6.78) SF(MINK) WRITE (6,69) A1 WRITE (6,70) A2 WRITE (6.71) N1 WRITE (6,72) N2 WRITE (6,73) (J,BA(J),J=2,MIM) SS=S/(NT1+NT2-HINK-4) BFC(MINK)=SF(MINK)+(2\*MINK+8-NT1-NT2)\*SS WRITE (6.74) BFC(MINK) MINKC=MINK+1 DO 29 J=1.NT1 WN(J)=W(1,J) DO 30 J=1.NT2 JNT1=J+NT1 WN(JNT1) = W(2,J)00 -31\_J=1,NT1 Q(1,J) = -N1 + (1-J)/CO(1,J)Q(2,J) = -(1-J) \* (A1/(CO(1,J) \* N1 \* J))Q(3,J)=0.0Q(4, J) = 0.0DO 31 K=2,MINKC IX = K + (1 - J) - 1Q(1,J)=Q(1,J)-K\*8A(K)\*RGC\*TEMP\*A1\*\*(K-1)\*(N1\*\*(1-J)/( 1RGC\*TEMP\*CO(1,J)))\*\*K Q(2,J)=Q(2,J)+K\*BA(K)\*RGC\*TEMP\*(J-1)\*(A1/(RGC\*TEMP\* 1CO(1,J)))\*\*K\*N1\*\*IX L=K+3 Q(L,J)=-RGC\*TEMP\*(A1\*N1\*\*(1-J)/(RGC\*TEMP\*CO(1.J)))\*\*K DO 32 J=1.NT2 JNT1=J+NT1 Q(1, JNT1) = 0.0Q(2, JNT1) = 0.0Q(3,JNT1) = -N2 + (1 - J)/CO(2,J)

- Q(4, JNT1) = -(1-J) \* (A2/(CO(2, J) \* N2 \* + J))
- DO 32 K=2,MINKC IX=K\*(1-J)-1
- Q(3,JNT1)=Q(3,JNT1)-K\*BA(K)\*RGC\*TEMP\*A2\*\*(K-1)\*(N2\*\* 1(1-J)/(RGC\*TEMP\*CO(2,J)))\*\*K
- Q(4,JNT1)=Q(4,JNT1)+K\*BA(K)\*RGC\*TEMP\*(J-1)\*(A2/(RGC\* 1TEMP\*CO(2,J)))\*\*K\*N2\*\*IX
- L=K+3 32 Q(L,JNT1)=-RGC\*TEMP\*(A2\*N2\*\*(1-J)/(RGC\*TEMP\*CD(2,J))) 1\*\*K MINK4=MINK+4
  - NT=NT1+NT2 DO 33 IT=1.MINK4
  - DO 33 JT=1,MINK4
  - F2(IT,JT)=0.0
  - 00 33 J=1,NT
- 33

28

29

30

31

F2(IT,JT)=F2(IT,JT)+Q(IT,J)+Q(JT,J)+WN(J)

WRITE (6,106) DO 34 [T=1.MINK4 34 WRITE (6,103) (F2(IT,JT),JT=1,MINK4) DD 35 I=1,MINK4 DO 35 J=1,MINK4 35 SAVE(I,J)=F2(I,J)ZETA=1.D-30 CALL GJR (MINK4,ZETA) WRITE (6,97) DO 36 I=1.NINK4 WRITE (6,103) [F2(I,J),J=1,MINK4) 36 CALL MATMPY (F2, MINK4, MINK4, SAVE, MINK4, FS) WRITE (6,100) DO 37 I=1.MINK4 WRITE (6,103) (FS(1,J), J=1, MINK4) 37 DELK(1) = F2(1,1) + SSDELK(2)=F2(2,2)+SS DELK(3)=F2(3,3)+SS DELK(4)=F2(4,4)\*SS DO 38 [=5, N[NK4 DELK([)=F2(I.])\*SS 38 DO 39 [=1, MINK4 39 DELK(I)=DSQRT(DELK(I)) WRITE (6,105) WRITE (6,69) DELK(1) WRITE (6,70) DELK(3) WRITE (6,71) DELK(2) WRITE (6,72) DELK(4) WRITE (6,73) (J,DELK(J+3),J=2,MINKC) MINK3=MINK+3 DO 40 I=1,MINK4 DD 40 J=1,NINK4 40 F2(1,J)=SS\*F2(1,J) DO 43 J=1,NT1BSUM( J) =0.0 DO 41 L=5,MINK4 41 BSUM(J)=BSUM(J)+F2(L,L)+Q(L,J)++2 OFFSUM(J)=0.0 DO 42 I=1,MINK3 K1 = [+1]DO 42 K=K1, MINK4 42 OFFSUM(J)=OFFSUM(J)+F2([,K)+Q([,J)+Q(K,J) 43 SSP(J)=F2(1,1)+Q(1,J)++2+F2(2,2)+Q(2,J)++2+BSUM(J)+ 12.0\*0FF SUM(J) NT11=NT1+1 NT22=NT2+NT1 DO 46 J=NT11,NT22 BSUN(J)=0.0 DO 44 L=5,终NK4 44 BSUM(J)=BSUM(J)+F2(L,L)+Q(L,J)++2 DFFSUM(J)=0.0

DO 45 I=1, MINK3 K1 = I + 1DO 45 K=K1,MINK4 45 OFFSUM(J)=OFFSUM(J)+F2(I,K)+Q(I,J)+Q(K,J) 46 SSP(J)=F2(3,3)+Q(3,J)++2+F2(4,4)+Q(4,J)++2+BSUN(J)+ 12.0\*DFF SUM(J) NT=NT1+NT2 Z=SSP(1) DO 47 J=1.NT 47 WNCAL(J)=Z/SSP(J) DO 48 J=1,NT1QZ(1,J)=-N1\*\*(J-1)\*CO(1,J)\*P(1,J)/A1\*\*2+N1\*\*(J-1)\* 1CO(1,J)\*Q(1,J)/A1 QZ(2,J)=(J-1)\*N1\*\*(J-2)\*CD(1,J)\*P(1,J)/A1+N1\*\*(J-1) 1\*CO(1,J)\*Q(2,J)/A1 QZ(3, J) = 0.0QZ(4, J) = 0.0DO 48 L=5,MINK4 QZ(L,J)=N1\*\*(J-1)\*CO(1,J)\*Q(L,J)/A148 DO 49 J=1,NT2JNT1=J+NT1 QZ(1, JNT1) = 0.0QZ(2, JNT1) = 0.0QZ(3,JNT1)=-N2\*\*(J-1)\*CB(2,J)\*P(2,J)/A2\*\*2+N2\*\*(J-1)\* 1CD(2, J) \*Q(3, JNT1)/A2 QZ{4,JNT1}=(J-1)\*N2\*\*(J-2)\*CD(2,J)\*P(2,J)/A2+N2\*\*(J-1) 1+CO(2,J)+Q(4,JNT1)/A2 DO 49 L=5,MINK4 49 QZ(L,JNT1)=N2\*\*(J-1)\*CO(2,J)\*Q(L,JNT1)/A2 DO 52 J=1+NT1 BSUM(J)=0.0 DO 50 L=5,MINK4 50 BSUM(J)=BSUM(J)+F2(L,L)\*QZ(L,J)\*\*2 OFFSUM(J)=0.D DO 51 I=1,MINK3 K1=[+1 DO 51 K=K1,MINK4 51 OFFSUM(J)=OFFSUM(J)+F2(I,K)+QZ(I,J)+QZ(K,J) 52 SSZ(J)=F2(1,1)+QZ(1,J)++2+F2(2,2)+QZ(2,J)++2+BSUM(J)+ 12.0\*DFF SUM(J) NT11=NT1+1 NT22=NT1+NT2 DO 55 J=NT11,NT22 BSUM(J)=0.0 DD 53 L=5,MINK4 BSUN(J) = BSUM(J) + F2(L,L) + Q2(L,J) + 253 OFFSUM(J)=0.0 DO 54 I=1,MINK3 K1 = I + 1DO 54 K=K1,MINK4 54 OFFSUM(J)=OFFSUM(J)+F2(I,K)+QZ(I,J)+QZ(K,J)

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55 SSZ(J)=F2(3,3)\*QZ(3,J)\*\*2+F2(4,4)\*QZ(4,J)\*\*2+BSUM(J)\* 12.0+0FF SUM(J) NT = NT 1 + NT 2DO 56 [=1,NT SSP(I)=DSQRT(SSP(I)) 56 SSZ(1)=DSORT(SSZ(1)) WRITE (6,98) WRITE (6,99) DO 57 I=1.NT 57 WRITE (6,104) SSP(I), SSZ(I), WN(I), WNCAL(I) IF (BFC(MINK)-BFCT) 62,58,58 58 WRITE (6.86) SS=SF(MINK-1)/(NT1+NT2-MINK-3) J=MIN-5 BFC(J)=1.E12 59 J=J+1IF (J-M) 60,60,61 BFC(J)=SF(J)+(2\*J+8-NT1-NT2)\*SS 60 WRITE (6,83) J,8FC(J) MOPT=J-1 IF (BFC(J)-BFC(MOPT)) 59,61,61 61 WRITE (6.88) MOPT GD TO 66 BFCT=BFC(MINK) 62 GO TO 65 63 WRITE (6.80) WRITE (6,81) 64 65 MINK=MINK+1 GO TO 14 CONTINUE 66 67 CONTINUE STOP 68 FORMAT(//, OBJECTIVE FUNCT S BEFORE ITERATION +, 12,  $1^{\circ} = {}^{\circ}, D20, 10, // \}$ 69 FORMAT (//,10X, "A1=",D20.10) 70 FORMAT (10X, \* A2=\*, D20, 10) FORMAT (10X, \*N1=\*, D20.10)71 FORMAT (10X, \*N2=\*, D20.10) 72 73 FORMAT (10X, B(\*, 12, \*) = \*, D20, 10)74 FORMAT(///,15X,\*BEST FIT CRITERION =\*,D20.10,///) 75 FORMAT(///,5X,\*ITERATION FOR \*,12,\* COEFFICIENTS\*,///) 76 FORMAT(//, \* ESTIMATION OF BEST FIT =\*,12,//) FORMAT(/, \* INITIAL ESTIMATES OF PARAMETERS \*,/) 77 78 FORMAT(//, S = , D20.10)79 FORMAT(//, FINAL RESULTS OF ITERATION,//) FORMAT(//, \* DID NOT CONVERGE IN 20 ITERATIONS\*,//) 80 FORMAT(//, ITERATION TERMINATED FOR REASONS GIVEN 81 1ABOVE • , //) FORMAT(//,T7,'P',T20,'P CAL',T33,'DEV',T41,'W\*(DEV)\*\*2' 82

1,T54,'Z EXP',T65,'Z CAL',T77,'DEV',T88,'DENSITY', 2T101,'(Z-1)/RHD'//)

**\*\***,020.10) DATA',//) FACT USED' FORMAT (4E18.6) FORMAT(//, RELATIVE CHANGE IN PARAMETERS,//) FORMAT(//, REVISED BEST FIT CRITERION..//) FORMAT (014.6.D15.7.2011.3.2F11.7.D11.3.2D14.6) FORMAT(/, BEST FIT HAS '.12.' VIRIAL COEFFICIENTS',/) ~ . **='**, D20.10 SUBROUTINE CORN (NT1,NT2) DOUBLE PRECISION P(2,15),CO(2,15),T,B,K1,K2,K3,K4,K5 MATRIX AND ITS INVERSE .. //) ESTIMATION OF STANDARD ERROR OF BY LINEAR METHOD',//) ERROR MATRIX BEFORE INVERSION',//) (28-2V) SQUAREO =',D20.10) Absolute value of (28-2V) FORMAT(//, SUM OF ABSOLUTE VALUE OF (28-2V) FORMAT(//, AVERAGE (28-2V) =, D20.10) FORMAT(//, INVERTED MATRIX, //) FORMAT(//, ESTIMATION OF STANDARD ERROR IN FORMAT(//,T10,'SSP(1)',T28,'SSZ(1)',T43,"WT FORMAT(//, PRODUCT OF MATRIX AND ITS INVERS QUANTIES FOR 2..//) **8**S = ,020.10) = ,020.10) m m \*\* ( .... •.I2. T=Kl+K2\*P(l,))+K3\*P(L,J)\*\*2+K4\*P(l,J)\*\* B=Ml+M2\*P(l,1)+M3\*P(l,1)\*\*2+M4\*P(l,1)\*\* FOR FORMAT (1844) FORMAT(//, SUM OF DEVIATIONS FORMAT(//, AVERAGE DEVIATION FORMAT(//, AVERAGE DEVIATION CRITERION FORMAT(//, ESTIMATION OF COEFFICIENTS BY LINEAR ME STATISTICAL SUM OF (28-2 SUM OF ABSOL DEGREES (3110,F20.10) K6, M1, M2, M3, M4, M5, M6 FIT CO(1, J) =CO(1, [) +T/B (4024.12) 158 (F20.10) (4D18.6) INTEGER NT1,NT2 EST FORMAT(//. FORMAT(//. 4 K2=-2.920-07 N2=-4.22D-07 N4=-4.850-14 CO(1,1)=1.0 CO(2,1)=1.0 , NTL DO 1 J=2,NT1 ð FORMAT(//. COMMON P.CO K AND M FOR K3=8.19D-12 K4=-3.08D-1 M3=1.280-11 J=2 **ORMAT(** FORMAT FORMAT FORMAT K1=1.0 N1=1.0 FORMAT 1-7=1 N END 8 -----100 101 102 103 104 05 90 98 66

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S

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I=J-1 T=K1+K2\*P(2,J)+K3\*P{2,J}\*\*2+K4\*P{2,J}\*\*3 B=M1+M2\*P(2,1)+M3\*P(2,1)\*\*2+M4\*P(2,1)\*\*3 2 CO(2, J) = CO(2, I) + T/BRETURN END SUBROUTINE MATMPY(A,N,N,B,L,C) DOUBLE PRECISION A(15,15), B(15,15), C(15,15) DO 1 I=1,NDO 1 J=1.L C(1, J) = 0.0DO 1 K=1.M 1 C(I,J)=C(I,J)+A(I,K)+B(K,J)RETURN END SUBROUTINE ORNOR (NT, M, MIN, EPS) INTEGER NT, M, MIN, NOR, N, K, R, I, J, MINA, P, KM1, RPKM1, RMKP1 DIMENSION SSQ(15),SSD(15),RE(15),T(15,15),G3(15,15), 1G4(15,15),G5(15,15),BFF(15) DOUBLE PRECISION PR(2,15),CO(2,15),DELK(15),TEMP,RGC, 1DUH(2,15),BA(15),W2(2,15),A1,A2,N1,N2,F(15,30),Y(30), 2YP, S1, S2, S3, D(15), B(15), S4, S5, S6, SIGSQ, PSI(15, 30), 3FSUB(15,30),C(15,15),G(15,15),G1(15,15),PHE(15,30), 4G2(15,15), RTP(15), F3(15,15), F1(15) COMMON PR,CO,F3,F1,DELK,TEMP,RGC,DUM,BA,W2,A1,A2,N1, 1N2,F,Y,A(15,15),W(30) NOR=1 С NOR IS NUMBER REORTHONORMALIZATION YP=0. DO 1 N=1,NT YP=YP+(Y(N)\*Y(N)\*W(N))CONTINUE 1 2 CONTINUE DO 3 N=1.NT PSI(1,N) = F(1,N)3 CONTINUE IF (M-1) 4,9,4 4 DO 8 K=2,M DO 7 N=1,NT S1=0.0 KM1 = K - 1DO 6 R=1,KM1 S2=0.0 S3=0.0 DO 5 I=1.NT S2=S2+PS[(R,I)\*PSI(R,I)\*W(I) S3=S3+PSI(R,I)\*F(K,I)\*W(I)

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.

5	CONTINUE
	C(K,R)=-S3/S2
	S1=S1+C(K,R)*PSI(R,N)
6	CONTINUE
	PSI(K,N)=S1+F(K,N)
7	CONTINUE
8	CONTINUE
9	CONTINUE
	DO 14 K=1.M
	IF (K-1) 10,13,10
10	KM1=K-1
	DO 12 $R=1, KM1$
	\$1=0.0
	DO 11 J=R,KM1
• -	S1=S1+(G(J,R)+C(K,J))
11	CONTINUE
• •	G(K,R)=S1
12	CONTINUE
13	G(K,K)=1.0
14	CUNTINUE
	ILI=NUK
	DU 21 K=1.M
	52-C(X D)
	52-01NFKF CO TO (15-14-17 19 19), ICT
15	$G_{1}(K, p) = S_{2}$
16	62(K,R) = S2
	GO TO 20
17	G3(K,R) = S2
	GO TO 20
18	G4(K,R)=S2
	GO TO 20
19	G5(K,R)=S2
20	CONTINUE
21	CONTINUE
	DO 24 K=1,M
	DO 23 N=1,NT
	S1=0.0
22	51=51+P51(K,1)+P51(K,1)+W(1)
	KIMIKI=D2AKI(21)
22	CONTINUE
23	CONTINUE
27	DD 26 KalaM
	DO 25 N=1.NT
25	S1=S1+Y(N)*PHI(K.N)*W(N)
	B(K)=S1
	D(K) = SI/RTP(K)

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26	CONTINUE
	SSD(1)=YP-8(1)*8(1)
	SSQ(1)=SSD(1)/(NT-1)
	IF (H-1) 27,29,27
27	DO 28 K=2,M
	SSD{K}=SSD(K-L)-B{K}*B{K}
	SSQ(K)=SSD(K)/(NT-K)
28	CONTINUE
29	CONTINUE
	NMMM=H-1
	DO 32 K=1,MMMM
	IF (ABS(SSQ(K+1))-ABS(SSQ(K))) 30,31,31
30	MINA=K
31	CONTINUE
32	CONTINUE
	DO 33 K=1,M
	BFF(K)=(2+K-NT)+SSQ(HINA)+SSD(K)
33	CONTINUE
	DO 36 K=1,MHMM
	IF (ABS(BFF(K+1))-ABS(BFF(K))) 34,35,35
34	MIN=K+1
35	CONTINUE
36	CONTINUE
	00 39 K=1,M
	S1=0.0
	DO 38 J=1,M
	S2=0.0
	$DO_3/N=1$ , NT
<b></b>	$SZ=SZ+PHI(J_N) \neq PHI(K_N) \neq W(N)$
51	
20	21=21+B{J}+22
38	
20	KE1KJ=1.U-5[/8[K]
37	
	DU 48 K=L+M 15 (505 A05(05(4))) (0 (7 (7
4.0	IF (EPS-ABS(KE(K))) 40,47,47
40	1r (NUK~3/ 43)41/43
41 40	UU 42 I=197 Continue
42	CONTINUE
43	
43	CUNTENUC DO 44 I-1 M
	DO 46 N-1.NT
	00 40 N-19NI IE (NOD-1) 45 44 45
<b>6</b> 6	1F (NUN-17 43944943) ECHR/T.N1-E/T.N1
45	$F_{1}(1) = D_{1}(1) = D_{1}(1)$
7J 66	ει τη μεροποιού του
TU	
	WRITE (6.70)
47	CONTINUE

48	CONTINUE
49	DD 50 K=1,M
	T[1,K]=D(K)
50	CONTINUE
	DO 67 R=2,M
	MNRP1=N-R+1
	DD 67 K=1,MMRP1
	ICT1=NOR
	GO TO 151.52.54.59.61). [CT]
51	RPKM1=R+K-1
	SI=GI(RPKM1.K)
	60 TO 66
52	RPKM1=R+K-1
~	$S_{1=0}$
	DD 53 (1=K_PPKN)
	S1 = SI + G2 (DDKN1, 1) + G1 (1, K)
53	CONTINUE
23	
54	
24	
	KKVII=K VVKV
	DU 38 J≖K∉KPKA1
	5 <b>2</b> =0.0
	$\begin{array}{c} DU  DI  L \cong K_{F}J \\ DU  DI  DU = I I = I I I I I I I I$
	$S2=S2+G2(J_{1})+G1(I_{1}K)$
	S2=0.0
	$DU 56 I=K_{*}J$
	S3=0.0
	00 55 P=K,I
	\$3=\$3+G2(I,P)*G1(P,K)
55	CONTINUE
	\$2=\$2+G3{J,[}*\$3
56	CONTINUE
57	CONTINUE
	\$1=\$1+G3(RPKM1,J)*\$2
58	CONTINUE
	GO TO 66
59	S1=0.0
	RPKM1=R+K-1
	DO 60 J=K,RPKM1
	Sl=Sl+G4(RPKMl,J)+S2
60	CONTINUE
	GD TO 66
61	\$1=0.0
	RPKM1=R+K-1
	DO 65 J=K.RPKM1
	S2=0.0
	DO 64 [=K,J
	S3=0.0
	DO 63 P=K,I
	S4=0.0
	DD 62 N=K.P

----

	S4=S4+G2(P,N)+G1(N,K)
62	
	53=53+63(1+P)=54
63	
	SZ= 52+64{J+1}=53
04	
	51=51+65(KPKH1+J)=52
07	
00	KPKR1=K+K-1
47	1(K,K)=1(K-1,K)+1(1,KPKM1)=51 CONTINUE
01	
	DD (0 K=1 D
	UU 00 K#19K
	KMKF1=K=K=L A/D Klatonkol Kl
60	A4 N 9N / = ] ( K/INF L 9N / CONTINUE
60	
07	DETION
70	ECONATI //// DEODTHONODMALIZATIONS - THE DOUNDOES
10	IERRAR IS THE RECEIPTION ON THE RECHTER DOLYNONIALS
	21/1
	FND
	•
	SUBROUTINE SOLVE (N,E,K1,EPS,E1,E2)
	INTEGER N,K1,I,J,K,J1,K2,L,E1,E2,F(15),II,N
	DOUBLE PRECISION P(2,15),CO(2,15),X(15),Q,D(15),NORM,
	IUIAG, 1EMP, A(15, 15), B(15, 15), C(15), EN, E
	CUMMUN POLUDADCOX
	£1=U F2=0
	EZ=U
	DU I I=I N DO 1 1-1 N
1	DU L J-L9N Rff. 13+Aff. 13
4	D(1)=A(1)] No 15 (-) N
	1-1-1
	$\mathbf{D}$ $\mathbf{A}$ $\mathbf{I} \neq \mathbf{I}$ $\mathbf{N}$
	IF (1) 2.4.2
2	00.3  K=1.1
3	Q=R(J-K)+R(K-I)+Q
4	B(J,I)=B(J,I)-Q
	BIG=0.0
	K2=1
	DO 6 K=I,N
	IF {DABSIB(K,I)}-BIG} 6,6,5
5	BIG=DABS(B(K,I))
	K2=K
6	CONTINUE
	IF (BIG-EPS) 34,34,7
7	F[])=K2

	15 (K2-1) 8-10-8
0	1F (NE-1) 091090
0	TEND-A(K2 K)
	IERF-ALKZIKI Alko kumale ku
	ALN2;NJ=ALI;NJ A/5 // - TCMD
	A(1+K)=1EMP
	IEMP=B(K2,K)
	B(K2,K)=B(1,K)
9	B(I,K)=TEMP
10	DIAG=B(I,I)
	II=I+1
	IF (11-N) 11,11,15
11	DO 14 J=II,N
	Q=0.0
	[F (L) 12,14,12
12	DO 13 K=1,L
13	Q=B(I,K)*B{K,J}+Q
14	B(I,J)=[B(I,J)-Q)/DIAG
15	CONTINUE
	DO 16 I=1,N
	J=F([)
	TEMP=C(J)
	C(J)=C(I)
	C(I)=TEMP
16	D(I)=TEMP
	DO 19 $I=1,N$
	L=I-1
	<b>Q=0.</b> 0
	IF (L) 17,19,17
17 ·	DO 18 K=1,L
18	Q=B([,K)*D(K)+Q
19	D(I) = (D(I) - Q) / B(I, I)
	DO 22 J=1,N
	I=N+1-J
	Q=0.0
	M=I+1
	IF (M-N) 20,20,22 ·
20	DO 21 K=M,N
21	Q=B(1,K)*X(K)+Q
22	X(I)=D(I)-Q
	IF (E) 23,36,23
23	J1=0
24	IF (J1-K1) 25,35,35
25	NORM=0.0
	DO 29 $I=1,N$
	Q=0.0
	L=[-]
	DO 26 K=1.N
26	Q=Q+A[I,K]+X(K)
	D(I)=C(I)-Q
	NORM=NORM+DABS(D(1))
	Q=0.0

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```
IF (L) 27,29,27
27
      DO 28 K=1.L
28
       Q=Q+B([,K)+D(K)
29
      D(I) = (D(I) - Q)/B(I,I)
      DO 32 J=1,N
       I=N+1-J
      Q=0.0
      M=I+1
      IF (N-N) 30,30,32
      DO 31 K=M.N
30
31
      O=O+B(I \cdot K) = D(K)
32
      X(I) = X(I) + D(I) - 0
      J1=J1+1
      EN=E*N
      IF (NORM-EN) 33,33,24
33
      CONTINUE
      WRITE (6.39) J1
      GO TO 36
34
      E1 = 1
      WRITE (6,37)
      GO TO 36
35
      E2=1
      WRITE (6.38)
      CONTINUE
36
      RETURN
      FORMAT(//, * ELEMENT IN MATRIX IS LESS THAN EPS*,//)
37
38
      FORMAT(/, SOLVE DID NOT CONVERGE IN K1 ITERATIONS ./)
39
      FORMATI//, ITERATIONS REQUIRED IN SOLVE= ,12,//)
      END
      SUBROUTINE IMPK (NT1,NT2,MINK,L1,L2,CONV,S)
      INTEGER MINK, MINK2, MINK4, NT1, NT2, E1, E2, L1, L2
      DOUBLE PRECISION P(2.15).CO(2.15).DELK(15).TEMP.RGC.
     1DEL(2,15),BA(15),W(2,15),A1,A2,N1,N2,Q(15,18),F2(15,
     215),Q2(15,15,18),PC,F(15),F3(15,30),V(30),ST,S,Z
      COMMON P.CO.F2.F.DELK.TEMP.RGC.DEL.BA.W.A1.A2.N1.N2.
     1F3.Y.A(15.15).WN(30)
      MINKC=MINK+1
      S=0.0
      DO 2 J=1.NT1
      Z=1.0
      DO 1 K=2,MINKC
1
      Z=Z+BA(K)*(A1*N1**(1-J)/(RGC*TEMP*CO(1.J)))**(K-1)
      PC=A1*N1**(1-J)*Z/CO(1,J)
      DEL(1,J) = P(1,J) - PC
2
      S=S+W(1,J)*DEL(1,J)**2
      DO 4 J=1.NT2
      Z=1.0
      DO 3 K=2.MINKC
3
      Z=Z+BA(K)*(A2*N2**(1-J)/(RGC*TEMP*CO(2,J)))**(K-1)
```

## PC=A2+N2++(1-J)+Z/CO(2,J) DEL(2,J) = P(2,J) - PC4 S=S+W(2,J)\*DEL(2,J)\*\*2DO 5 J=1,NT1Q(1,J) = -N1 + (1-J)/CO(1,J)Q(2,J)=-(1-J)\*(A1/(CO(1,J)\*N1\*\*J)) Q(3, J) = 0.0Q(4, J) = 0.0DO 5 K=2, MINKC IX = K + (1 - J) - 1Q(1,J)=Q(1,J)-K\*BA(K)\*RGC\*TEMP\*A1\*\*{K-1)\*(N1\*\*(1-J)/ 1 {RGC\*TENP\*CO{1, J}} \*\*K Q(2,J)=Q(2,J)+K+BA(K)+RGC+TEMP+(J-1)+(A1/(RGC+TEMP+ 1CO(1.J)))\*\*K\*N1\*\*IX L=K+3 Q{L +J}=-RGC+TEMP\*(A1\*N1\*\*(1-J)/(RGC+TEMP\*CQ(1,J))\*\*K 5 MINK4=MINK+4 DO 6 I=1.MINK4 F(I) = 0.0DO 6 J=1.NT1F(1)=F(1)+2.\*W(1,J)\*DEL(1,J)\*Q(1,J)6 DO 8 J=1,NT1Q2(1, 1, J)=0.0Q2(2,2,J)=J\*(1-J)\*(A1/(CO(1,J)\*N1\*\*(J+1))) Q2(1,2,J)=(J-1)\*(1.0/(CO(1,J)\*N1\*+J))Q2(1,3,J)=0.0Q2(1,4,J)=0.0Q2(2, 1, J) = Q2(1, 2, J)Q2(2,3,J)=0.0Q2(2,4,J)=0.0DO 7 K=2,MINKC 7 Q2{1,1,J}=Q2{1,1,J}-K\*(K-1)\*BALK}\*RGC\*TEMP\*A1\*\*{K-2}\* 1(N1\*\*(1-J)/(RGC\*TEMP\*CO(1,J)))\*\*K DO 8 K=2,MINKC IX = K + (1 - J) - LL=K+3 Q2(1,2,J)=Q2(1,2,J)+K\*K\*(J-1)\*BA(K)\*RGC\*TEMP\*A1\*\*(K-1) 1\*(1./(RGC\*TEMP\*CO(1,J)))\*\*K\*N1\*\*IX Q2(1+L,J)=-K\*RGC\*TEMP\*A1\*\*(K-1)\*(N1\*\*(1-J)/(RGC\*TEMP\* 1CO(1, J)))\*\*K Q2(2,1,J)=Q2(1,2,J)Q2(2,2,J)=Q2(2,2,J)+K\*(J-1)\*IX\*BA(K)\*RGC\*TEMP\*(A1/ 1(RGC\*TEMP\*CO(1,J)))\*\*K\*N1\*\*(IX-1) Q2(2,L,J)=K\*(J-1)\*RGC\*TEMP\*(A1/(RGC\*TEMP\*CO(1,J)))\*\*K 1\*N1\*\*[X $Q2\{L, 1, J\}=Q2\{1, L, J\}$ 8 Q2(L,2,J)=Q2(2,L,J)D0 9 I = 1, 2DD 9 L=1.MINK4 F2(1,L)=0.0 D0 9 J=1,NT1

•

9	F2([,L)=F2(I,L)+2.*W(1,J)*(DEL(1,J)*Q2([,L,J)+Q(I,J)*
	1Q(L,J))
	DO 10 I=5, MINK4
	DO 10 $L=1,2$
	$F_{2}(I,L)=0.0$
• •	DO 10 J=1,NT1
10	F2(I,L)=F2(I,L)+2.*W(1,J)*(DEL(1,J)*Q2(I,L,J)+Q(I,J)
	1*Q(L,J))
	DO 11 [=5,N[NK4
	DO 11 L=5,MINK4
	F2(1,L)=0.0
• •	DO II J=1,NTI
11	FZ(1,L)=FZ(1,L)+Z.▼W(1,J)*Q(1,J)*Q(L,J)
	$Q(3_{0}J) = -N2 \mp \mp (1-J) / CU(2_{0}J)$
	Q[4;J]=-[1-J]=[AZ/[[U[2;J]=NZ==J]]
	DU 12 K=29 MINKL
	Q(3;J)=Q(3;J)=K+DA(K)+KUL+1EMP+A2++(K-1)+(N2++(L-J)/
	1 ( KUL+1 CMF+LU(2) J / J J ++K 0/4 / 1 - 0/4 / 1 + K+0 A/K \+DCC+TEMD+/ / 1 ++/+D//DCC+TEMD+
	V[4]J]=V[4]J]TR+DALR]+RUL+1EMP+[J=1]+[AZ/[RUL+1EMP+ 10012 11]]++PH2+17
	160121J///**N*NZ**IX 1-K42
12	L=NTJ (// . /)+_DCC+TEND+/A2+N2++/1_ /)//DCC+TEND+CO/2 /1))+++/
12	$\frac{12}{12} = \frac{12}{12} = 12$
	$\frac{1}{12} \frac{1}{1} 1$
13	F(1)=F(1)+7,=H(2, 1)=DF(12, 1)=O(1, 1)
	F(2)=0.0
	F(4)=0.0
	00 15 J=1.NT2
	02(3,3,1)=0.0
	$(2^{4}, 4, 4) = (1 + (1 - 4) + (1 $
	(2(3,1,J)=0.0
	(2(3,2,1)=0.0)
	$02(3 \cdot 4 \cdot J) = (J-1) * (1 \cdot 0 / (CO(2 \cdot J) * N2 * * J))$
	Q2(4.1.J)=0.0
	Q2(4,2,J)=0.0
	Q2(4,3,J)=Q2(3,4,J)
	DD 14 K=2, MINKC
14	Q2(3,3,J)=Q2(3,3,J)-K*(K-L)*BA(K)*RGC*TEMP*A2**(K-2)*
	1(N2**(1-J)/(RGC*TEMP*CD(2,J)))**K
	DO 15 K=2,MINKC
	IX=K*(1-J)-1
	L=K+3
	Q2(3,4,J)=Q2(3,4,J)+K*K*[J-1)*BA(K)*RGC*TEMP*A2**(K-1)
	1*(1./(RGC*TEMP*C0(2,J)))**K*N2**IX
	Q2(3,L,J)=-K*RGC*TEMP*A2**(K-1)*(N2**(1-J)/(RGC*TEMP*
	1CO(2,J)))**K
	Q2(4,3,J)=Q2(3,4,J)

	Q2(4,4,J)=Q2(4,4,J)+K*(J-1)*IX*BA1K)*RGC*TEMP*IA2/
	L(RGC# TEMP*CU(2, J)))**K*N2**(IX-L)
	V2(4+L+J)=K*(J-L)*KGC*TEMP*(A2/(RGC*TEMP*CO(2+J)))**K
	$Q_2(L_+3_+J) = Q_2(3_+L_+J)$
12	$QZ(L_14_1J)=QZ(4_1L_1J)$
	$00 \ 16 \ 1=3,4$
	DU 16 L=1,MINK4
• •	
10	$F2(1_{1}L)=F2(1_{1}L)+2_{0}\neq W(2_{1}J)\neq (UEL(2_{1}J)\neq Q2(1_{1}L_{1}J)\neq Q(1_{1}J)\neq Q(1_{1}J)=Q(1_{1}J)$
	LW(L)JJJ DD 17 L-E MINKA
	DU 1/ 1=0,71NK4
	00 17 L-394 52/1 11-0 0
	F2(1)L/~V+V 00 17 1-1 NF2
17	52/[.]]=52/[.]]A2.#4/2.]]#/05/(2.]]#02/[.].(\A0/[.])#
* •	10(1.11)
	NN 18 ISS.MINKA
	DO 18 1 = 5. MINK4
	$DO 18 J_2 J_N I2$
18	F2(1,))=F2(1,1)+2,+W(2,1)+Q(1,1)+Q(1,1)
	FPS=1_F-50
	$E = 1 \cdot D - 10$
	K1=10
	WRITE (6.38)
	WRITE (6.39) (F(J).J=1.MINK4)
	WRITE (6.40)
	DD 19 I=1, MINK4
19	WRITE (6,39) (F2(I,J),J=1,MINK4)
	DO 20 I=1,NINK4
	ST=F2(1,1)
	F2(1,1)=F2(4,1)
20	F2(4,1)=ST
	DO 21 I=1,HINK4
	ST=F2(1,1)
	F2(I,1)=F2(I,4)
21	F2(1,4)=ST
	ST=F(1)
	F(1)=F(4)
	F(4)=51
	ΠΙΝΚ2≈ΠΙΝΚ4~2 Ις.(1 1 2) 22 22 20
22	IF (L1-3) 22922920 DD 33 1-1 MINKS
<i>4.4</i>	00 23 1=1971NK2 5({}=5({}=5)
	FLIJFLIVZJ NG 22 I+1_NINK2
	67/1, 1)=67/147, 147)
22	CANTINUE
~. J	MINK3=KINK4=1
	F(MINK3)=1.0
	$F[MINK4]=1_0$
	· · · · · · · · · · · · · · · · · · ·

.

	DO 24 [=1,MINK4
	IF (DABS(F(I))-1.D-06) 24,24,25
24	CONTINUE
	GO TO 26
25	L2=1
26	CONTINUE
	CALL SOLVE (MINK2,E,K1,EPS,E1,E2)
	00 27 [=1,H[NK2
	L=#[NK4-[+]
27	DELK(L)=DELK(L-2)
	DELK(1)=0.0
	DELK(2) = 0.0
	GO TO 33
28	DQ 29 I=1.MINK4
29	F(I) = -F(I)
	00 30 I=1-NENK4
	IE (DARS(E(1))-1,D-06) = 30, 30, 31
30	CONTINUE
30	
21	
32	
32	CALL COLVE (MINKA E VI EDS EL ED)
23	LALL JULYE AMINKYJEINIJEFJJEIJEZJ
33	IF (EL=1) 34,30,34
34	IF (E2~1) 37,30,37
32	
	DELK(1)=DELK(4)
	DELK(4)=ST
	GO TO 37
36	AL=0.0
37	CONTINUE
_	RETURN
38	FORMAT(//, FIRST PARTIAL OF S',/)
39	FORMAT (4E18.6)
40	FORMAT(//, * SECOND PARTIAL OF S*,//)
	END
	SUBROUTINE GJR (K,ZETA)
<b>C</b> -	GAUSS-JORDAN-RUTISHAUSER MATRIX INVERSION WITH DOUBLE
C	PIVOTING
	DOUBLE PRECISION A(15,15),B(15),C(15),PIVOT,ZETA,
	1P1(2,15),CO(2,15),Z
	INTEGER P(15),Q(15)
	COMMON P1,CO,A
	DO 14 N=1.K
C	DETERMINATION OF PLVOT ELEMENT
-	PIVOT=0_0
	D0 2 I=N.K
	$IE (DARS(A(I_{A},I)) - DARS(P(V(I_{A})) - 2,2,1)$
1	
4	F1 VUI-A11 #37

•

	P(N)=I
	Q{N}=J
2	CONTINUE
	IF (DABS(PIVOT)-ZETA) 22,22,3
C	EXCHANGE THE PIVOTAL ROW WITH KTH ROW
3	IF (P(N)-N) 4,6,4
4	DO 5 J=1,K
	L=P(N)
	Z=A{L+J}
	A(L,J)=A(N,J)
5	A(N,J)=Z
C	EXCHANGE OF PIVOTAL COLUMN WITH THE NTH COLUMN
6	IF (Q(N)-N) 7,9,7
7	DO 8 (=1,K
	L=Q(N)
	L=AligL]
•	ALL9L/=ALL9N/ A/T_N\_7
0	
7	LUNILAUE LORAN STER
L.	DO 13 Ist.K
	IE (J-N) 11,10,11
10	
••	$C(J) = 1_0$
	GO TO 12
11	B(J) = -A(N,J)/PEVOT
	C(J)=A(J,N)
12	A(N,J)=0.0
13	A(J,N)=0.0
	DO 14 [=1,K
	DO 14 J=1,K
14	A(I,J)=A(I,J)+C(I)+B(J)
C	RECORDING OF MATRIX
	DO 20 M=1,K
	1F (P(N)-N) 15, 17, 15
12	DU 16 1=1,K
	L=P1N) 7-A/I
	L-ALLI ALI_1A-ALI_NA
16	A(1/L)-A(1/A) A(1,N)=7
17	$I \in \{0(N) - N\}$ 18,20,18
18	DO 19 J=1.K
•••	L=0{N}
	Z=A(L.J)
	$A(L_{y}J)=A(N_{y}J)$
19	$A(N_{y}J)=Z$
20	CONTINUE
21	CONTINUE
	RETURN
22	DD 23 N=1,K

.
23 WRITE (6,24) P(K),Q(K),PIVOT GO TO 21

24 FORMAT(16HOSINGULAR MATRIX3H I=I3,3H J=I3,7H PIVOT= 1E16.8/) END

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## NOMENCLATURE FOR EQUATION OF

## STATE COMPUTER PROGRAMS

- A Matrix of coefficients for the M desired polynomials used to print out results and in common with MAIN
- ABTA  $(1 + \eta)/2$
- AVNUM Avogadro's number
- B Coefficients for orthonormal functions in ORNOR
- BETA  $1 + 2\eta$
- BFF Best fit criterion in ORNOR
- BK Boltzmann's constant
- BMW Molecular weight of methane
- C Coefficients obtained from the Gram-Schmidt algorithm used to orthogonalize the original functions in ORNOR
- C&CD Cutoff parameter
- CBK Corrected Boltzmann's constant (to get units consistent)
- CDIFF Difference in c on two successive iterations
- CETA  $1 \eta$
- CHECK Convergence check in NRS and also in density error program
- COEFI  $(48\eta/c^6) (\epsilon/kT)$
- COEFJK  $(96\eta/c^{12})(\epsilon/kT)^2$
- CORR Correction factor to get Boltzmann's constant in correct units

Intermediate	values	of	c in	iterative	procedure
Product of c	& σ				

- Cl First initial guess for c
- C2 Second initial guess for c (need two to start HINT)
- C3 Reciprocal of c<sup>3</sup>

CSIG

CX

- C6 Reciprocal of c<sup>6</sup>
- Cl2 Reciprocal of c<sup>12</sup>
- D Coefficients for orthogonal functions in ORNOR
- DEL Ratio of difference in (P<sub>CALC</sub> P<sub>EXP</sub>) on two successive iterations to difference in c on two successive iterations
- DELIT Difference in DEL on two successive iterations
- DETA  $1 + \eta 2\eta^2$
- DIFF Difference between experimental density and calculated density
- DPC Difference in (P<sub>CALC</sub> P<sub>EXP</sub>) for two successive iterations
- DRHOGM Difference in density for two successive iterations
- **BP** Value of convergence criterion to determine when to switch from HINT to NRS
- **EPOVK**  $\epsilon/k$
- EPS Value of convergence criterion in NRS
- **ERROR** Percent error in density defined by  $100(\rho_{C}-\rho_{R})/\rho_{C}$
- ETA  $\pi(c\sigma)^{3}\rho/6.0$
- ETAJ  $(1 \eta)^4 / (1 + 4\eta + 4\eta^2)$
- ETAK1  $4\eta (1-\eta)^3 / (1+4\eta+4\eta^2)$
- ETAK2  $4\eta (1+2\eta) (1-\eta)^4 / (1+4\eta+4\eta^2)^2$
- EXDIV 1/exp (XDIV)

- F Defines functional form for T & p in ORNOR
- FA Value of (P<sub>CALC</sub> P<sub>EXP</sub>) for first initial guess of c
- FB Value of (P<sub>CALC</sub> P<sub>EXP</sub>) for second initial guess of c
- **FDENOM** Denominator of  $f(s,\eta)$
- FDIFF Difference in (P<sub>CALC</sub> P<sub>EXP</sub>) on two successive iterations
- **FNUMER** Numerator of  $f(s, \eta)$
- FSUB Matrix used to save original matrix F
- FX Intermediate values of (P<sub>CALC</sub> P<sub>EXP</sub>) in iterative procedure
- FXETA FNUMER/FDENOM
- G Coefficients, calculated from the C coefficients, that are in a more convenient form for use
- GDENOM Denominator of G(s)
- GETA  $1 + 4n + 4n^2$
- GNUMER Numerator of G(s)
- GXETA GNUMER/GDENOM
- Gl to G5 Coefficient matrices that are needed if it is necessary to reorthonormalize the functions to minimize round-off error (if G5 is included, five reorthonormalizations are possible)
- H Interval size in Simpson's rule
- HINT Half interval search subroutine
- Hl Interval size for first region of integration
- H2 Interval size for second region of integration
- H3 Interval size for third region of integration
- H4 Interval size for fourth region of integration
- M Number of parameters used in ORNOR

MIN	Optimum number of parameters in ORNOR
N	Number of methane data points
NOR	Number of reorthonormalizations
NRS	Newton-Raphson search subroutine
NT	Number of data points used in ORNOR fit
Nl	Number of steps in first region of integration
N2	Number of steps in second region of integration
N3	Number of steps in third region of integration
N4	Number of steps in fourth region of integration
ORNOR	Generalized orthonormal polynomial least-squares subroutine
P	Experimental pressure in atmospheres
PC	Value of $(P_{CALC} - P_{EXP})$ in density error program
PCALC	Subroutine to calculate pressure
PC2	Calculated pressure in atmospheres
PHI	Orthonormal functions in ORNOR
PHS	Hard-sphere pressure
PI	Calculated pressure contribution for term involving integral J
РК	Calculated pressure contribution for term involving integral K
PSI	Orthogonal functions in ORNOR
RE	Relative round-off error in ORNOR
RHO	Number density
RHOGM	Density in grams/cc
RHOGMX	Experimental density used as first guess in finding calculated density in density error program
RHOKT	ρkT

- RTP Square root of the weighted inner product of PSI
- SDB Standard deviation of the coefficients
- SIGMA Molecular diameter
- SIGSQ Estimated variance in data
- SLON Parameter that controls the amount of output in ORNOR
- SSD Sum of the square of the discrepancies between Y observed and Y calculated
- SSQ Gauss parameter squared

SUM Value of one region of integral

- S1 to S6 Parameters used to calculate various weighted inner products in ORNOR
- T Temperature in °K
- T Matrix in ORNOR that gives optimum coefficients for all fits through M
- V Calculated factorial
- VALUE Value of total integral

W Weighting factor in ORNOR

- WTFAC Weighting factor
- X Integral increment
- $XDIV \quad (1 X)/X$
- XFI X4V (C<sup>6</sup>\*X6VOV (1)-1)
- XFJK X10V (1+X6VOV (2) \* ( $c^{12}$ \*X6VOV (3))-2 $c^{6}$ )

**XINV2** Reciprocal of  $x^2$ 

 $x_2 x_{DIV}^2$ 

- x3 xdiv<sup>3</sup>
- x4 xDIV<sup>4</sup>

\_\_\_\_

x6 xdiv<sup>6</sup>

	10
<b>X10</b>	XDIV

X4V X4 divided by 4 factorial

X10V X10 divided by 10 factorial

X6VOV X6 multiplied by ratio of factorials

Y Integrand in Simpson's rule

Y Column matrix in ORNOR for dependent variable

YEVEN Even-numbered integrands

YN Last value of integrand

- YODD Odd-numbered integrands
- YP Weighted square of dependent variable
- Y0 Initial value of integrand

C C	THIS PROGRAM USED TO DETERMINE VALUE OF CUTDEF Parameter C for each methane data point Double precision t.p.rhogm.avnum.bmw.rhd.eps.cl.c2.
	1FA,FB,CX(50),FX(50) N=200
	DO 1 JJ=1+N
C	READ IN TEMPERATURE, PRESSURE, AND DENSITY READ (5,2) T,P,RHOGM
	WRITE (6,3)
	WRITE (6,2) T,P,RHOGM
	AVNUM=0.602295D+24
	BMW=16.043
	RHD=(RHUGM#AVNUM)/BMW
	LALL PLALL (FA, LL, I, P, RH))
	WRITE (0)/)
	WKIIC (0+8) UI+FA C2-1 A
	CALL PCALC (EP CO T P DUD)
	GALL FGALG (FD9GZ919F9KH(J) HDITE // 0)
	WRITE 16.03 77.59
	CALL HINT (C).C2.FA.FR.P.T.PHO.IT.CY.FY)
	WRITE (6.4) IT
	WRITE (6.5) CX(IT)
	WRITE $(6.6)$ EX(1T)
1	CONTINUE
-	STOP
2	FORMAT (3D20.10)
3	FORMAT(//,T11, *TEMP*,T29, *PRESSURE*,T48,*RHD(GM/CC)*
	1,//)
4	FORMAT(//,T3,"CONVERGED ON ITERATION ",12,//)
5	FORMAT(//,T3, BEST VALUE OF PARAMETER C=+,F16.10,//)
6	FORMAT(//,T3, CONVERGENCE VALUE OF FX=*,D20.10,//)
7	FORMAT {//,T9,*C1*,T29,*FA*,//)
9	FORMAT (2020.10)
9	FORMAT (//,T9,°C2',T29,°FB',//) END
	SUBROUTINE PCALC (PC2+C+T+P+RHO)
	DUUBLE PRECISION Y(1000), V(6), YODD(4), YEVEN(4), SU4(4),
	IVALUE(5),X6V0V(5),T,P,RH0,BK,CORR,CBK,RH0KT,ETA,C,PC2,
	ZLI, LZ, L3, FA, FB, FNUMER, GNUMER, FDENDM, GDENOM, FXETA, GXETA
	JOLUEPIOUEPJKO ETAJOETAKIOETAKZOPHSOPIOPJOPKOVOOVNO
	4AEIA, DEIA, LEIA, DEIA, GETA, HETA, H, HI, HZ, H3, H4, SIGMA, CR,
	$\frac{1}{2} \sum_{i=1}^{2} \sum_{j=1}^{2} \sum_{i=1}^{2} \sum_{i=1}^{2} \sum_{i=1}^{2} \sum_{j=1}^$
r	CALCULATION OF FACTORIALS
<b>`</b>	UALOULATION OF FACTURIALS
	T \ I J ~ C 7 K = 4

K=4 DO 1 I=2,6

	V(I)=V(I-1)
	DO 1 J=1.6
	K=K+1
1	
•	SIGMA=0.29170=07
	510HA-0655110-07 500W-149 2
	EFUVN=1900/7/D 15
	BK=U.138U474U-15
	LUKK=0.00000224809/(0.15499969*14.696)
	CBK=BK*CORR
	RHOKT=RHO <b>*C</b> BK <b>*</b> T
<del>~</del>	CSIG=C*SIGMA
	CR=1.0/C
	C3=CR**3
	C6=C3**2
	C12=C6**2
	ETA=(3.14159265*(CSIG**3)*RHD)/6.0
	AFTA=1.0+FTA/2.0
	RFTA=1.0+2.0+FTA
	CETA=1.0-ETA
	DETA-1 04ETA-2 0+ETA++2
	0514-1007514-2007514++2 CETA-1 016 04671446 046714++2
r	UCIA=I+UTT++UTCIAT4+UTCIA++2 INTCODAL EVALUATIONS AND DOINTOUTS
6	INTEGRAL EVALUATIONS AND PRINTUALS
-	$1 + (K-1) 2_{1} + 5_{2}$
2	IF (K-2) 3,20,3
3	IF (K-3) 4,20,4
4	CONTINUE
5	M1=20
	M2=300
	M3=600
	M4=1000
	INC1=10
	INC2=2
	INC3=5
	INC4=25
	i=1
	146-1461 1-0
0	UU 13 L=N+M+INL
	AL=L
	X=AL/1000.0
	I=[+]
	XDIV=(1.0-X)/X
	X2=XDIV**2
-	X3=X2*XDIV
	X4=X2*X2
	X6=X4*X2
	X10=X6*X4
	X4V=X4/V(1)

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-----

X10V = X10/V(2)DO 7 MV = 1.37  $X6VOV(MV) = X6 \neq V(MV) / V(MV+1)$ XFI=X4V+{C6+X6V0V(1)-1.0) XFJK=X10V+(1.0+X6V0V(2)+(C12+X6V0V(3)-2.0+C6)) XINV2=1.0/X\*\*2 EXDIV=1.0/DEXP(XDIV) GNUMER=XDIV\*EXDIV\*(XDIV\*AETA+BETA) GDENOM=12.0\*ETA\*EXDIV\*(XDIV\*AETA+BETA)+X3\*CETA\*\*2+ 16.0\*ETA\*CETA\*X2+18.0\*XDIV\*ETA\*\*2-12.0\*ETA\*BETA FNUMER=X4\*EXDIV\*(XDIV\*DETA+BETA\*\*2) FDENOM=GDENOM++2 FXETA=FNUMER/FDENOM GXETA=GNUMER/GDENOM IF (K-1) 9,8,9 8 Y(I)=XINV2+FXETA+XFI GO TO 13 9 IF (K-2) 11,10,11 10 Y(I)=XINV2+FXETA+XFJK GO TO 13 IF (K-3) 13,12,13 11 12 Y(I)=XINV2+GXETA+XFJK 13 CONTINUE IF (J-1) 14,14,15 14 J=J+1N=M1+INC2 M=M2 INC=INC2 GO TO 6 IF (J-2) 16,16,17 15 16 J=J+1N=M2+INC3 M=M3 INC=INC3 GO TO 6 17 IF (J-3) 18,18,19 18 J=J+1N=M3+INC4 M=M4-INC4INC=INC4 GO TO 6 19 CONTINUE GO TO 34 20 M1 = 10M2=200 M3=500 M4=1000 INC1=10INC2=1- INC3=5 INC4=25

J=1 N=INC1 M=M1 INC=INC1 I=0 21 DO 28 L=N, M, INC AL=L X = AL/1000.0I = [+]XDIY=(1.0-X)/XX2=XD[V\*\*2 X3 = X2 + XDIVX4=X2\*X2 X6=X4\*X2 X10=X6\*X4X4V = X4/V(1)X10V = X10/V(2)DO 22 MX=1,3 22 X6V0V(MX)=X6+V(MX)/V(MX+1) XFI=X4V+(C6+X6V0V(1)-1.0) XFJK=X10V\*(1.0+X6VDV(2)\*(C12\*X6VDV(3)-2.0\*C6)) XINV2=1.0/X\*\*2 EXDIV=1.0/DEXP(XDIV) GNUMER=XDIV\*EXDIV\*(XDIV\*AETA+BETA) GDENDM=12.0\*ETA\*EXDIV\*(XDIV\*AETA+BETA)+X3\*CETA\*\*2+ 16.0\*ETA\*CE1A\*X2+18.0\*XDIV\*ETA\*\*2-12.0\*ETA\*BETA FNUMER=X4\*EXDIV\*(XDIV\*DETA+BETA\*\*2) FDENOM=GDENOM++2 FXETA=FNUMER/FDENDM GXETA=GNUMER/GDENOM IF (K-1) 24,23,24 Y{I)=XINV2\*FXETA\*XFI 23 GO TO 28 IF (K-2) 26,25,26 24 Y(I)=XINV2\*FXETA\*XFJK 25 GO TO 28 IF (K-3) 28,27,28 26 27 Y(I)=XINV2\*GXETA\*XFJK -----28 CONTINUE IF (J-1) 29,29,30 29 J=J+1N=M1+INC2 M=M2 INC=INC2 GO TO 21 30 IF (J-2) 31,31,32 31 J=J+1 N=M2+INC3 M=M3 INC=INC3 GO TO 21

32	IF (J-3) 33,33,34
33	J=J+1
	N=M3+INC4
	M=M4-INC4
34	CUNIINUE
C	STEP SIZE AND NUMBER OF STEPS
	IF (K-1) 35,37,35
35	IF (K-2) 36,38,36
36	IF (K-3) 40,38,40
37	N1=2
	N2=140
	N3=60
	H3=U.005
	H4=0.025
	GO TO 39
38	N1=1
	N2=190
	N3=60
	N4=20
	$H_{2=0,00}$
20	
23	NJ=N1+N2
	N/=N6+N4
	H1=0.01
40	CONTINUE
	DO 59 J=1,4
	IF (J-1) 41,45,41
41	1F (J-2) 42,46,42
42	1F (J-3) 43,47,43
43	IF (J-4) 44,48,44
44	CONTINUE
45	$Y_0 = 0$
	VN = V(N)
	M-1
	N=N1 CO TO (0
	GU 18 49
46	YU=Y(NL)
-	¥N=Y(N5)
	H=H2
	M=N1+1
	N=N5
	GO TO 54
47	¥0≠¥(N5)
• -	YN=Y(NG)

```
H=H3
      M=N5+1
      N=N6
      GO TO 54
48
      YO = Y(N6)
      YN=0_0
      H=H4
      M=N6+1
      N=N7
      GO TO 54
C
      SIMPSONS RULE FOR CALCULATING VALUE OF INTEGRALS
49
      IF (J-1) 54.50.54
50
      IF (K-1) 51,57,51
51
      IF (K-2) 52,58,52
52
      IF (K-3) 53,58,53
53
      CONTINUE
54
      YODD(J)=0.0
      DO 55 [=M.N.2
55
      YODD(J) = YODD(J) + Y(I)
      YEVEN(J)=0.0
      MM = M+1
      NN=N-1
      DO 56 I=MM.NN.2
56
      YEVEN(J) = YEVEN(J) + Y(I)
      SUM(J)=(H/3.0)*(Y0+4.0*Y00D(J)+2.0*YEVEN(J)+YN)
      GO TO 59
57
      SUM(1) = (H/2.0) * (Y0+2.0*Y(1)+Y(2))
      GO TO 59
58
      SUM(1) = (H/2.0) * (Y0+Y(1))
59
      CONTINUE
      VALUE(K) = SUM(1) + SUM(2) + SUM(3) + SUM(4)
60
      CONTINUE
      DETERMINATION OF CALCULATED PRESSURES
C
      PHS=((1.0+ETA+ETA++2)/(1.0-ETA)++3)+RHOKT
      COEFI=(48.0*ETA*C6*EPDVK)/T
      COEFJK=(96.0*ETA*C12*EPOVK**2)/(T**2)
      ETAJ=(CETA**4)/GETA
      ETAK1=(4.0*ETA*(CETA**3))/GETA
      ETAK2=(4.0*ETA*BETA*(CETA**4))/(GETA**2)
      PI=COEFI*RHOKT*VALUE(1)
      PJ=COEFJK*RHOKT*ETAJ*VALUE(2)
      PK=COEFJK+RHOKT+(ETAK1+ETAK2)+VALUE(3)
      PC2=-P+PHS+PI-PJ+PK
      RETURN
      END
      SUBROUTINE HINT (C1,C2,FA,FB,P,T,RHO,IT,CX,FX)
      DOUBLE PRECISION C1,C2,FA,FB,P,T,RHO,EP,EPS,CX(50),
     1FX(50), DEL(50), DELIT, FX1, CX1
      EP=0.1
```

	EPS=0.00001
	IT=0
	WRITE (6.15)
	WRITE (6.14)
1	
-	IF (11-20) 2.2.12
2	$C_{X}(1T) = (C_{1+}C_{2})/2.0$
2	
	CALL DCALC (EV1.CV1.T.D.DHO)
	CHEE FOHEG (FALIGEALIIFFIKHU) Evitti-evi
	TALIJJ=FAL Hotte (4 13) It (viit) evity)
	WK17E (0+137 11+6X(1))+FX(11)
-	$\frac{1}{1} \frac{1}{1} \frac{1}{2} \frac{1}$
5	UEL([]]=(FX(]])-FX([]-[])/(GX(]])-GX([]-[])
	1 + (11 - 3) + 4 + 4
4	DELIT=DABS(DEL(IT)-DEL(IT-1))
_	IF (DABS(DELIT/DEL(IT))-EP) 11,11,5
5	IF (FX(IT)) 6,12,7
6	IF ((FX(IT)/P)+EPS) 8,12,12
7	IF ((FX(IT)/P)-EPS) 12,12,8
8	IF (FX(IT)*FA) 9,12,10
9	C2=CX(IT)
	FB=FX(IT)
	GO TO 1
10	C1=CX(IT)
	FA=FX(IT)
	GO TO 1
11	CONTINUE
	CALL NRS (CX.FX.P.T.RHD.IT)
12	
	BETHEN
13	FORMAT (16.2020.10)
14	FORMAT {//.T5.11T1.T19.1(Y1.T27.15Y1.//)
16	COPNAT(//.T2. (STADT OF WALE THTEDVAL CEADOWS //)
15	FURNATIVITISTARI UF HALF INTERVAL SEAKUN #//J
	ENU
	CHREATENE MAC ICY EV A T ANA ITA
	SUDKUUTINE NKS (CAFFAFFIFKNUFIT) DOUDLE DDECISION SYLEAD SKIEAD DIE DUD SDC SDIFF
	DUDDLE PRECISION CX(DU);PX(DU);P;1;KHU;EPS;CUIFF;
	WKITE (6,6)
-	EPS=0.00001
L	CDIFF=CX(IT)-CX(IT-1)
	FDIFF=FX(IT)-FX(IT-1)
	CHECK=DABS(FX(IT)/P)
	IF (CHECK-EPS) 4,4,2
2	IT=IT+1
	CX(IT)=CX(IT-1)-(FX(IT-1)*CDIFF)/FDIFF
	CALL PCALC (FX(IT),CX(IT),T,P,RHD)
	WRITE (6,5) IT,CX(IT),FX(IT)
	IF (IT-20) 3,4,4
3	GO TO 1

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- 4 CONTINUE WTFAC=FDIFF/CDIFF WRITE (6,7) WTFAC RETURN
- 5 FORMAT (16,2020.10)

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FORMAT(//,T3,\*UNNORMALIZED (DP/DC)=\*,D20.10,//) FORMAT(//,T3,\*START OF NEWTON-RAPHSON\*,//) 7

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- 6
  - END

THIS PROGRAM USED TO DETERMINE COEFFICIENTS IN-С C EXPANSION FOR CUTOFF PARAMETER DOUBLE PRECISION T.P.F(16,205),CD(205),RHOGM,A(16,16), LW(205), SLON(3) COMMON F.CD.A.W.SLON EPS=0.000001 SLON(1) = 0.0SLON(2) = 0.0SLON(3) = 1.0NT=205 N=16 WRITE (6.3) DO 1 N=1.NT READ (5,2) (T,P,RHOGM,CD(N)) WRITE (6,2) (T,P,RHOGM,CD(N)) F(1,N)=1.0 F(2,N)=TF(3,N)=RHOGM F(4,N)=RHOGM+T F(5,N)=RH0GM++2 F(6,N)=T+RHDGM++2 F(7,N)=T++2 F(8,N)=RH0GM\*T\*\*2 F(9,N)={T++2}+{RHOGM++2} F(10,N)=RH0GM++3 F(11,N)=T\*RHOGM\*\*3 F{12,N}=(T\*\*2)\*(RHDGM\*\*3) F{13,N}=T\*\*3 F(14,N)=RHOGM\*T\*\*3 F{15,N}=(RH0GM++2)+(T++3) F(16,N)=(RH0GM\*\*3)\*(T\*\*3) CONTINUE 1 WRITE (6,4) READ (5,5) (W(I),I=1,NT) WRITE (6,5) (W(I),I=1.NT) CALL ORNOR (NT, M, MIN, EPS) STOP 2 FORMAT (4020.10) 3 FORMAT(//, T8, \*TEMP\*, T26, \*PRESSURE\*, T48, \*RHOGM\*, T70, 1°CD',//) 4 FORMAT(//,T3, WEIGHTING FACTORS',//) 5 FORMAT (D20.10) END

SUBROUTINE ORNOR (NT,M,MIN,EPS) INTEGER NT,M,MIN,NOR,N,K,R,I,J,MINA,P,KM1,RPKM1 DOUBLE PRECISION F(16,205),Y(205),YP,S1,S2,S3,S4,S5, 1S6,D(16),B(16),SIGSQ,PSI(16,205),C(16,16),G(16,16), 2G1(16,16),PHI{16,205},RTP(16),G2(16,16),G3(16,16), 3SSQ(16),SSD(16),RE(16),BFF(16),T(16,16),G4(16,16),

4G5(16,16), DEL(205), SDB(16), FSUB(16,205), A(16,16), 5W(205), SLON(3) COMMON F,Y,A,W,SLON С BEGINNING OF PROGRAM WRITE (6,93) NOR=1C NOR IS NUMBER REORTHONORMALIZATION YP=0. DO 1 N=1,NT YP=YP+(Y(N)+Y(N)+W(N))1 CONTINUE C BEGIN ORTHOGONALIZATION OF FUNCTION F TO PSI 2 CONTINUE DO 3 N=1.NT PSI(1,N) = F(1,N)3 CONTINUE IF (SLON(3).EQ.0.) WRITE (6,94) IF (M.EQ.1) GO TO 8 DO 7 K=2,M DO 6 N=1.NT S1=0.0 KM1=K-1 DO 5 R=1,KM1 S2=0.0 \$3=0.0 DO 4 I=1,NT S2=S2+PS1(R,I)\*PSI(R,I)\*W(1) S3=S3+PS[(R, [] +F(K, [] +W(1) 4 CONTINUE C(K,R) = -S3/S2S1=S1+C(K,R)\*PS1(R,N) 5 CONTINUE PSI(K,N)=S1+F(K,N)CONTINUE 6 IF (SLON(3).EQ.O.) WRITE (6,95) (PSI(K,I),I=1,NT) 7 CONTINUE C CONVERSION OF C(K,R) TO G(K,R) . IF (SLON(3).EQ.O.) WRITE (6,96) 8 CONTINUE DO 12 K=1.M IF (K.EQ.1) GO TO 11 KM1=K-1 DO 10 R=1,KM1 S1=0.0 DO 9 J=R,KM1 S1=S1+(G(J,R)+C(K,J))9 CONTINUE G(K,R)=S110 CONTINUE 11 G(K.K)=1.0 IF (SLON(3).EQ.O.) WRITE (6,95) (G(K,I),I=1,K) 

12 CONTINUE ICT=NOR DD 19 K=1.M DO 19 R=1,K S2=G(K,R)GO TO (13,14,15,16,17), ICT 13 G1(K,R)=S2GO TO 18 G2(K,R)=S214 GO TO 18 15 G3(K,R)=S2GO TO 18 G4(K,R)=S216 GO TO 18 17 G5(K,R)=S2 CONTINUE 18 NORMALIZATION OF FUNCTION PSI TO PHI C 19 CONTINUE IF (SLON(3).EQ.0.) WRITE (6,97) 00 22 K=1,M 00 21 N=1.NT S1=0.0 DO 20 I=1,NT 20 S1=S1+PSI(K,I)\*PSI(K,I)\*W(I)RTP(K)=DSQRT(S1)  $PHI(K \cdot N) = PSI(K \cdot N)/RTP(K)$ 21 CONTINUE IF (SLON(3).EQ.0.) WRITE (6,95) (PHI(K,I),I=1,NT) 22 CONTINUE IF (SLON(3).EQ.0.1 WRITE (6,98) IF (SLON(3).EQ.0.) WRITE (6,95) (RTP(I),I=1,M) CALCULATION OF ORTHONORMAL AND ORTHOGONAL COEFFICIENTS C DO 24 K=1.M S1=0.0 DO 23 N=1,NT 23 S1=S1+Y(N) + PHI(K,N) + W(N) B(K)=S1D(K) = S1/RTP(K)24 CONTINUE IF (SLON(3).NE.O.) GO TO 25 WRITE (6,99) WRITE (6,95) (B(1),I=1,M) WRITE (6,100) WRITE (6,95) (D(I),I=1,M) 25 CONTINUE CALCULATION OF THE SUM OF THE SQUARES OF THE ERRORS AND С C GAUSS PARAMETERS SSD(1) = YP - B(1) + B(1)SSQ(1) = SSD(1) / (NT - 1)IF (M.EQ.1) GD TO 27 DD 26 K=2,M

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	SSD(K)=SSD(K-1)-B(K)+B(K)
	SSQ(K) = SSD(K) / (NT - K)
26	CONTINUE
27	CONTINUE
<b>C</b> 1	TE (SIGNIZ) NE A 1 JUITE (6.301)
	IF ISLUNIZIANEAUAI WRITE IS AEA /CCA/IN 1-1 WA
	IF (SLUN(S) NE 0 + NOITE (( 103) (SSU(1))[*1)M
	IF (SLUN(2).NE.U.) WRITE (6,102)
_	IF (SLUN(2).NE.O.) WRITE (6,95) (SSQ(1),1=1,M)
C	ESTABLISHMENT OF THE BEST FIT
	DO 30 K=1,N
	IF (K.NE.M) GO TO 28
	MENA=M
	GO TO 30
28	CONTINUE
	IF (DABS(SSQ(K)).GE.DABS(SSQ(K+1))) GD TO 29
	MINA=K
	K=M
29	CONTINUE
30	CONTINUE
30	IE (SIGN(2),EQ.Q.) WRITE (6,103) MINA
	DD 31 K=1.M
	266// V-134/-NTV4660/MENAV4660//VV
2.	DFF (N/~ (4+N~N) /+334(H]NA/+33D(N) CANTINGE
21	CUNTINUE
	UU 34 N=197
	IF (K.NE.M) GU IU 32
	GU TO 34
32	CONTINUE
	IF (DABS(BFF(K)).GE.DABS(BFF(K+1))) GO TO 33
	N IN=K
	K=M
33	CONTINUE
34	CONTINUE
	IF (SLON(2).NE.O.) GO TO 35
	WRITE (6,104)
	WRITE (6,95) (BFF(I),I=1,M)
	WRITE (6,105) MIN
35	CONTINUE
C	CALCULATION OF THE RELATIVE ROUND OFF ERRORS
•	DO 38 K=1.M
	S1=0.0
	DO 37 J=1.M
	S2=0.0
	S2=S2+PHI(.1.N) + PHI(K_N) + W(N)
26	CONTINUE
27	51-51+51+52 FANTENHE
	PE(K)=1 $O=C1/R(K)$
29	~~~~**********************************
30	CURTINUE 15 /610N/20 60 0 1 UDITE /4 10/1
	IF IJLUNICIOCYOUOJ WKIIE IO91UDJ

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	IF (SIGN(2)_FO.O.) WRITE (6.95) (PE(1)_I=).W)
	DO 43 K=1.M
	IE (EPS.GE.DARS(RE(K))) GD TD 42
	$IF (NOR_NE_5) GO TO 40$
	WRITE (6.107)
	HOITE (A.QA)
	DO 39 J=1.M
	WRITE (6.95) (PSI(1.1), 1=1.NT)
20	CONTINUE
40	CONTINUE
10	
	$D\Omega 41 N=1.NT$
	IF $(NOR, FO_1)$ FSUB $(I_1N) = F(I_2N)$
	$F(I_0N) = PSI(I_0N)$
41	CONTINUE
	NOR=NOR+1
	WRITE (6.108)
	GO TO 2
42	CONTINUE
43	CONTINUE
C	RECOVERY OF DESIRED COEFFICIENTS
44	DØ 45 K=1,M
	T{1+K}=D{K}
45	CONTINUE
	DO 62 R=2,M
	MMRP1=M-R+1
	DO 62 K=1,MMRP1
	ICT1=NOR
_	GD TO (46,47,49,52,56), ICT1
46	RPKM1=R+K-1
	S1=G1(RPKM1,K)
	GO TO 61
41	RPKM1=K+K-1
	$UU = 48 J = K_1 KPKM1$
10	51=51+621KPKM1+J)+61(J+K)
40	CONTINUE CO TO 41
60	GU 10 GL S1-0 0
47	31-0.0 31-0.0
	NG 5) 1=K.PDKM1
	$S_{2=0,0}$
	DD 50 I=K.J
	$S2=S2+G2\{1,1\}+G1\{1,K\}$
50	CONTINUE
	S1=S1+G3(RPKM1.J)*S2
51	CONTINUE
	GO TO 61
52	<b>S1=0.</b> 0
	RPKM1=R+K-1

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00 55 J=K, RPKN1 S2=0.0 DO 54  $I = K_{+}J$ S3=0.0 DO 53  $P=K_{*}I$ S3=S3+G2(I,P)+G1(P,K) 53 CONTINUE S2=S2+G3(J,I)\*S3 CONTINUE 54 S1 = S1 + G4(RPKM1 + J) + S255 CONTINUE GO TO 61 56 S1=0.0 RPKM1=R+K-1DO 60 J=K.RPKN1 S2=0.0 DO 59  $I = K_{*}J$ S3=0.0 DO 58 P=K,1 S4=0.0 DO 57 N=K,P S4=S4+G2(P,N)+G1(N,K) 57 CONTINUE S3=S3+G3([,P]\*S4 58 CONTINUE \$2=\$2+G4(J,I)\*\$3 59 CONTINUE S1=S1+G5(RPKN1, J) +S2 60 CONTINUE 61 · RPKM1=R+K-1 T(R,K) = T(R-1,K) + T(1,RPKM1) + S162 CONTINUE IF (SLON(1).EQ.0) WRITE (6,109) DO 64 R=1, MIF (SLON(1).EQ.0) WRITE (6,110) R DO 63 K=1,RRMKP1=R-K+1A(R,K) = T(RMKP1,K)63 CONTINUE IF (SLON(1).EQ.0) WRITE (6,95) (A(R,I),I=1,R). 64 CONTINUE С CALCULATION OF Y(OBS)-Y(CAL)=DELTA IF (SLON(1).EQ.0) WRITE (6,111) DO 70 R=1,M S1=0.0 S2=0.0 \$3=0.0 \$5=0.0 S6≈0.0 IF (SLON(1).EQ.0) WRITE (6,110) R DO 69 N=1,NT

S4=0.0 IF (NOR.NE.1) GD TO 66 DD 65 I=1.R S4=S4+A(R, I)+F(I,N) 65 CONTINUE GO TO 68 66 CONTINUE 00 67 l=1,RS4=S4+A(R,[)+FSUB([,N) 67 CONTINUE DEL(N) = Y(N) - S468 IF (SLON(1).EQ.0) WRITE (6,112) Y(N), S4, DEL(N) S1=S1+DEL(N)S2=S2+DABS(DEL(N)) S3=S3+DEL(N)+DEL(N) S5=S5+W(N)+DEL(N)+DEL(N) S6=S6+DSORT(W(N)) + DEL(N)69 **CONTINUE** S4=S1/NT IF (SLON(1).EQ.0) WRITE (6,113) S1, S2, S4, S3, S5 С CALCULATION OF SIGNA SQUARED IF (R.EQ.MIN) SIGSQ=(S5-S6+S6)/(NT-MIN) 70 CONTINUE IF (SLON(2).NE.0.) GO TO 92 WRITE (6,114) SIGSQ DO 71 K=1.H BFF(K]=(2\*K-NT)\*SIGSQ+SSD(K) 71 CONTINUE WRITE (6,115) WRITE (6,95) (BFF(I),I=1,M) С CALCULATION OF THE STANDARD DEVIATION OF THE COEFFICIENTS С WRITE (6,116) DO 91 R=1.M DO 90 K=1.R S1=0.0 S2=0.0DO 89 J=K.R ICT2=NOR GO TO (72,73,75,78), [CT2 72  $S3=G1(J\cdot K)$ GO TO 82 73 \$3=0.0 DD 74 I=K,J 74 S3=S3+G2(J,I)\*G1(I,K) GO TO 82 75 S3=0.0 DO 77 P=K,J S4=0.0 DO 76 I=K,P S4=S4+G2(P,[)+G1([,K)

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76	CONTINUE
	S3=S3+G3(J,P)*S4
77	CONTINUE
	GO TO 82
78	\$3=0.0
	D0 81 N=K.J
	S4=0_0
	DD 80 P=K-N
	\$5=0.0
	DD 79 I-K D
	DU 17 1-NJF 65-6640910 11+0111 V1
70	37-374024F917+01419K7
13	
~~	34=34+63(N+F)+33
80	
	5,3=53+64(J+N)=54
81	LUNIINUE
	GU TU 82
82	\$2=\$2+\$3*\$3/(RTP(J)*RTP(J))
	\$5=0 <b>.</b> 0
	DO 88 I=1,R
	\$6=0 <b>.</b> 0
	IF (NOR.NE.1) GO TO 84
	DO 83 N=1,NT
	S6=S6+F(I,N)*PHI(J,N)*W(N)
83	CONTINUE
	GO TO 86
84	CONTINUE
	DO 85 N=1,NT
	\$6=\$6+F\$UB(I,N)*PHI(J,N)*W{N}
85	CONTINUE
86	IF (R.LE.MIN) GO TO 87
	\$5=\$5+A(R,1)*\$6
	GO TO 88
87	\$5=\$5+A(MIN.I)*\$6
88	CONTINUE
	S1=S1+S3+(B{J}-S5)/RTP(J)
89	CONTINUE
	S4=SSQ(MINA)*S2+S1*S1
	SDB(K)=DSQRT(S4)
90	CONTINUE
	WRITE (6.95) (SOB(1), $I=1,R$ )
91	
02	CONTINUE
76	DETIDN
03	FROMATE ///0 RECTN ODNOD OUTDUTE//1
7 <i>7</i> 94	FORMATE /// DEUEN URNUR UUTPUT*/// Endwate // Deuen urnur uutput*///
96	FORMATINE TOTAL TOTAL CONTROL CONTRACTION TO TAR TOTAL TOTA
77 96	FURRAL LOLELOSLUSTANT MEED TO OBTHOROMALIZE THE
70	TONTATE / UNINING CONSTANT USED TO UKINUGUNALIZE THE
07	ECONATI / DUILV NI THE ODTHOCONALIZED CAN NAME
71	FURMAIL /* PHILKONI-THE UKTHUGUNALIZED F(KON)*/)

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- 99 FORMAT( /\* B{K}- COEFFICIENT TO BE USED WITH THE ORTHO INORMAL FUNCTIONS, PHI(K,N)\*/)
- 100 FORMAT( /\* D(K)- CDEFFICIENT TO BE USED WITH ORTHO INORMAL FUNCTIONS, PSI(K, N)\*/)
- 101 FORMAT(/\* THE SUM OF THE SQUARE OF DISCREPANCIES 1BETWEEN Y OBSERVED AND Y CALCULATED\*/)
- 102 FORMATI /\* GAUSS PARAMETER S SQUARED THE SUM OF THE 1SQUARES OF THE DISCREPANCIES DIVIDED BY THE NUMBER OF 2DEGREES OF FREEDOM\*//)
- 103 FORMAT( /\* THE MINIMUM S SQUARED POLYNOMIAL IS THE 10NE WITH \*,13,\* PARAMETERS\*/)
- 104 FORMAT( //\* CRITERION FOR CHOOSING THE BEST POLYNOMIAL 1TO FIT AN INFINITE SERIES\*/)
- 105 FORMAT( //' THE BEST POLYNOMIAL HAS', I3, PARA 1METERS'/)
- 106 FORMAT( // THE RELATIVE ROUNDOFF ERROR FOR EACH 1POLYNOMIAL '/)
- 107 FORMATI //\* THE RONND OFF ERROR IS STILL GREATER THAN 1EPSILON AFTER FOUR ORTHONORMALIZATIONS\*,//,\* READ THE 2FOLLOWING VALUES OF PSI(K,N) IN AS F(K,N) AND RERUN 3THE PROGRAM\*/)
- 108 FORMAT( ///\* REORTHONORMALIZATIONS THE ROUNDOFF 1ERROR IS TOO LARGE FOR ONE OF THE REQUIRED POLYNOMIALS 2\*/)
- 109 FORMAT( // COEFFICIENT FOR THE M DESIRED 1POLYNOMIALS\*/)
- 110 FORMAT (/\*R=\*,I4,/)
- 111 FORMAT( /16X, "Y(DBS)", 7X, "-", 7X, "Y(CALC)", 7X, "=", 7X," 1DELTA"/)
- 112 FORMAT (10X,E17.10,5X,E17.10,5X,E17.10)
- 113 FORMAT( /' SUN OF DELTAS =',E17.10,5X, SUM OF ABS{DEL 1TA) = ',E17.10,//' AVERAGE DELTA = ',E17.10,5X, SUM 20F DELTA SQUARED = ',E17.10,//' SUM OF WEIGHTED DELTA 3SQUARED = ',E17.10,//)
- 114 FORMAT( // SIGMA SQUARED ESTIMATED VARIANCE IN 1DATA = ',E17.10)
- 115 FORMAT( //\* BEST FIT CRITERION BASED UPON SIGMA ISQUARED\*/)
- 116 FORMATE //\* STANDARD DEVIATION OF THE COEFFICIENTS\*/) END

C THIS PROGRAM USED WITH SUBROUTINE PCALC ABOVE TO С CALCULATE PERCENT ERROR IN DENSITY DOUBLE PRECISION AVNUM, BMW, C, EPS, RHO, T, P, RHOGNX(400), lpc(400).Dpc.DrHugm.CHECK.CrHu.DIFF.Errur.Rhugm.fx N=400 DO 6 JJ=1,NREAD (5,7) T,P,RHOGMX(1) WRITE (6,10) WRITE (6,7) T,P,RHOGMX(1) AVNUM=0.602295D+24 BMW=16.043 EPS=0.000001 WRITE (6,8) DO 4 I=1,10RHO=(RHOGMX([)\*AVNUM)/BMW RHOGM=RHOGMX(I) C EXPRESSION FOR CUTOFF PARAMETER C DETERMINED FROM ORNOR FIT REPLACES THIS CARD С CALL PCALC (FX,C,T,P,RHO) PC(I)=FXWRITE (6,9) I,RHOGM,PC(I) IF (I-2) 1.2.2 1 RH0GMX([+1]=1.0001+RH0GMX(]) GO TO 4 DPC=PC(I)-PC(I-I)2 DRHOGM=RHOGMX(I)-RHOGMX([-1) RHOGMX(I+1)=RHOGMX(I)-(PC(I)+DRHOGM)/DPC IF (I-3) 4,4,3 3 CHECK=DABS(DRHOGM/RHOGMX(1)) IF (CHECK-EPS) 5,5,4 4 CONTINUE 5 CRHO=RHOGMX(I) WRITE (6.11) I WRITE (6,12) CRHO DIFF=RHOGMX(1)-CRHO ERROR=(100.0\*DIFF)/RHOGMX(1) WRITE (6,13) DIFF WRITE (6,14) ERROR WRITE (6,15) CONTINUE 6 7 FORMAT (3020.10) FORMAT (//, T4, "I', T17, "RHOGM", T37, "FX", //) 8 FORMAT (14,2020.10) 9 10 FORMAT(//,T11,\*TEMP\*,T29,\*PRESSURE\*,T48,\*RHO(GM/CC) 1..//) 11 FORMAT(//,T3,"CONVERGED WHEN I=",I2) FORMAT(T3, \*FOR RHO(GM/CC) = \*, D20.10, //) 12 13 FORMAT (T3, \*RHO(EXP)-RHO(CALC)=\*,D20.10,//) 14 FORMAT(T3, \*PERCENT ERROR=\*, D20.10,//)

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