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COMPRESSIBILITY FACTORS AND VIRIAL COEFFICIENTS

FOR THE HELIUM-NITROGEN SYSTEM BETWEEN

-160° AND -190°C UP TO 700 ATM

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SUBMITTED TO THE GRADUATE FACULTY

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degree of

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BY

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Norman, Oklahoma

1967

COMPRESSIBILITY FACTORS AND VIRIAL COEFFICIENTS
FOR THE HELIUM-NITROGEN SYSTEM BETWEEN
-160° AND -190°C UP TO 700 ATM

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ABSTRACT

The project was initiated in 1962 at the University of Oklahoma to measure compressibility factors of gases very accurately at high pressure and low temperature. The Burnett method was chosen for the experimental apparatus. The equipment as previously assembled was operable to 700 atmospheres and between $+50^{\circ}$ and -90°C .

Major modification of the temperature bath extended the range of applicability to -190°C and 700 atmospheres. The temperature control was $\pm 0.005^{\circ}\text{C}$ across the Burnett apparatus in the new configuration. A technique was also developed for employing valves completely immersed in the cryostat.

An extensive study of polynomial approximations for infinite series yielded a scheme for assigning realistic variances to the polynomial coefficients as compared with the series coefficients. This allows choice of optimal virial coefficients from the experimental compressibility data.

Finally, an optimal search routine was developed to reduce the Burnett data to the compressibility factors. This was essentially a problem in non-linear curve fitting. The results were very gratifying and seem to indicate that more accurate information could be expected from the data in this fashion than was possible with earlier techniques.

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COMPRESSIBILITY FACTORS AND VIRIAL COEFFICIENTS
FOR THE HELIUM-NITROGEN SYSTEM BETWEEN
-160° AND -190°C UP TO 700 ATM

CHAPTER I

INTRODUCTION

An apparatus based upon the method described by Burnett [4] has been used to study the volumetric behavior of the Helium-Nitrogen system at low temperatures and high pressures. A new procedure has been developed to reduce the data to compressibility factors, and a least-squares analysis is offered which enables choice of the optimal virial coefficients from the experimental data. The isotherms studied were -160° and -170°C for compositions of 100.00, 87.77, 75.29, 44.56, 30.13 and 0.00 percent helium balance nitrogen, and -190°C for compositions of 100.00, 87.77 and 75.29 percent helium. Compressibility factors are presented as a function of pressure under the experimental conditions, and the virial coefficients are reported for each mixture at all experimental temperatures.

The compositions were chosen to be those reported by Canfield [6]. Actually the mixtures were within 0.09 mole

percent of these compositions. These mixtures were chosen to facilitate calculation of thermodynamic properties using both sets of data.

The Burnett method is an experimental technique for determining the compressibility factors of gases without measuring the volume or mass of the sample under study. The apparatus is essentially two thermostated cells of unspecified volume connected by a valve. Initially one cell is filled with gas to some given pressure and the other cell is evacuated. When equilibrium is reached the pressure and temperature are recorded and the connecting valve is opened. After equilibration, the pressure and temperature are again recorded; the connecting valve is closed, and the second cell is reevacuated. This procedure is repeated until the pressure has reached a predetermined minimum, and the sequence of pressures constitutes a run. Usually the process is repeated, with a different starting pressure, a sufficient number of times to establish the isotherm adequately. While it is not necessary to maintain a constant temperature during a run, it was done in this study to allow a theoretical analysis of the data.

The apparatus was constructed to conform with the following analysis. Initially the equation of state is given by

$$P_0(V_a)_0 = Z_0 n_0 RT \quad (1)$$

and becomes, after the first expansion,

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

where V_a and V_b are the volumes of the two cells, the subscripts refer to the number of expansions associated with the subscripted quantity, $Z \equiv PV/nRT$ is the compressibility factor, n is the number of moles contained in the volume under consideration, R is the gas constant and T is the temperature. When the connecting valve is closed and V_b is evacuated, the equation becomes

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

Evidently, before the j^{th} expansion the relationship is

$$P_{j-1}(V_a)_{j-1} = Z_{j-1} n_{j-1} RT \quad (4)$$

and after the expansion becomes

$$P_j(V_a + V_b)_j = Z_j n_{j-1} RT \quad (5)$$

Dividing Equation 5 by Equation 4 gives

$$\frac{P_j(V_a + V_b)_j}{P_{j-1}(V_a)_{j-1}} \equiv \frac{P_j N_j}{P_{j-1}} = \frac{Z_j}{Z_{j-1}} \quad (6)$$

where the volume ratio is denoted as N_j and is referred to as the cell constant for the j^{th} expansion. Substitution

of subsequent values for j into this equation and multiplication reveal that

$$\frac{P_j (N_1 N_2 \dots N_j)}{P_0} = \frac{Z_j}{Z_0} \quad (7)$$

The N_j are related to N_∞ , the zero pressure cell constant, taking into account the Burnett cell dimensions and properties and the behavior of the differential pressure cells

$$N_j = N_\infty \frac{k_1 + k_2 P_j + k_3 P_j^2 + \dots}{m_1 + m_2 P_{j-1} + m_3 P_{j-1}^2 + \dots} \quad (8)$$

where the k_i and m_i are constants related to the pressure deformation of the cells (see Appendix A). Thus if N_∞ and the ratio Z_0/P_0 , the run constant, can be found, the compressibility factor is given by

$$Z_j = P_j \frac{Z_0}{P_0} N_\infty^j \prod_{i=1}^j \left(\frac{k_1 + k_2 P_i + k_3 P_i^2 + \dots}{m_1 + m_2 P_{i-1} + m_3 P_{i-1}^2 + \dots} \right) \quad (9)$$

and neither the volume nor the mass of the gas need have been measured.

Classically these constants were found by graphical extrapolation. Examination of Equations 6 and 7 reveals that in the limit as pressure approaches zero and the compressibility factor approaches unity

$$N_{\infty} = \lim_{P \rightarrow 0} \frac{P_{j-1}}{P_j} \quad (10)$$

$$\frac{P_0}{Z_0} = \lim_{P \rightarrow 0} P_j (N_1 N_2 \dots N_j) \quad (11)$$

Therefore, a plot of P_{j-1}/P_j vs. P_j should extrapolate to N_{∞} and a plot of $P_j (N_1 N_2 \dots N_j)$ vs. P_j should extrapolate to P_0/Z_0 . This extrapolation is usually performed by curve fitting and does produce reasonably accurate values for the constants. For example, from carefully taken data N_{∞} can usually be found within 1 part in 10000. If sufficiently accurate and abundant low pressure data were available, this method would give the proper values for the constants. Unfortunately, data meeting these requirements are very difficult to obtain.

A method is proposed in Chapter V for refining the estimated constants, in a least-squares sense, by establishing the minimum on a multidimensional response surface. The optimal virial coefficients are automatically recovered in this procedure by applying the least-squares analysis developed in Chapter IV. Interaction second and third virial coefficients are also calculated.

CHAPTER II

REVIEW OF PREVIOUS WORK

The Burnett method has been established recently as an acceptable and desirable means for measuring the compressibility factors of gases and gaseous mixtures. Concise reviews of work on this type of apparatus through 1965 have been presented by Mueller [23], Canfield [6] and Hoover [13]. Because of these compilations and because the method is accepted now, no specific review will be made for work on this type of apparatus. Furthermore, Canfield has presented a sufficiently complete review for work on helium, nitrogen and He-N₂ mixtures through 1962. This review is concentrated solely on the period 1962-present to avoid needless repetition.

P-V-T Behavior of Helium

Although the literature abounds with compressibility data (and, to a large degree, for that reason) for helium, work since 1962 has been relatively scarce. In fact, the majority of recent helium data has been taken in connection with a study of the helium-nitrogen system and is discussed below in that section.

Cook [9] has edited a book which offers a comprehensive review of the volumetric (and other) properties of helium. This work covers the period starting with the work by Ohnes through 1960.

Miller et al. [22] at the U. S. Bureau of Mines used the Burnett method to determine the compressibility factors of He. This work ranges up to 4000 psia between -10° and 130°F .

Various authors have noted that a large gap exists in helium data below 0°C and above 200 atm. Canfield has filled this gap substantially down to -140°C .

P-V-T Behavior of Nitrogen

Most of the recent reports on the volumetric properties of nitrogen have appeared in tabulations of thermodynamic properties by U. S. Government agencies. Little and Neel [19] in the Department of Commerce have tabulated the compressibility factor up to 10000 atm. between 100° and 1500°K . Hilsenrath and Klein [12] also at the Department of Commerce have extended this tabulation to include the range 2000° to 15000°K . Sewell [26] at the National Aeronautics and Space Administration presents compressibility factors and second virial coefficients between 2000° and $100,000^{\circ}\text{K}$ over a wide density range. Finally, Strobridge [28] at the National Bureau of Standards has tabulated thermodynamic properties, including the compressibility, up to 3000 psia between 114° and 540°R .

Meanwhile, Duclaux [10] has offered a distribution function approach for representing the compressibility up to 800°C and 400 atm. He then used the theory of progressive condensation to interpret the influence of temperature.

P-V-T Behavior of Helium-Nitrogen Mixtures

The most extensive study of this system is given by Canfield et al. [7]. Compressibility factors and virial coefficients are presented for helium, nitrogen and six mixtures between 0° and -140°C up to 500 atm.

At almost the same time, Witonsky and Miller [30] presented compressibilities and virial coefficients for helium, nitrogen, and seven mixtures between 175° and 475°C up to 100 atm.

Miller et al. at the U. S. Bureau of Mines presented compressibilities for helium, nitrogen and sixteen mixtures at 70°F up to 4000 psia in addition to their above mentioned helium data.

All three of the above investigations were made on Burnett-type apparatus. However, the range below -140°C above 100 atm. was left untouched.

Finally, Kielich [18] has calculated B_{12} by accounting for the tensorial forces acting on nondipolar molecules having a quadrupole or octapole moment. He calculates second virial coefficients for the helium-nitrogen system.

CHAPTER III

EXPERIMENTAL APPARATUS

The equipment used in this study as initially designed and constructed was operable between 50°C and -90°C up to 700 atm. Below -90°C excessive temperature gradients were encountered across the Burnett cells which introduced an intolerable uncertainty in measuring the absolute temperature. A major modification of the refrigeration system within the cryostat alleviated this condition and produced gradients of only a few thousandths of a degree. Because much of the apparatus has been described in detail by Blancett [2], only brief mention will be made of any unmodified equipment, and the reader is referred to the above work for additional information.

Cryostat

Figure 1 illustrates the essential features of the cryostat. Nitrogen in surging, two-phase flow enters the phase separator through a vacuum-insulated transfer line. A controlled liquid level is maintained within the separator to insure a constant refrigerating effect within the cryostat. The liquid leaves the separator through a metering valve

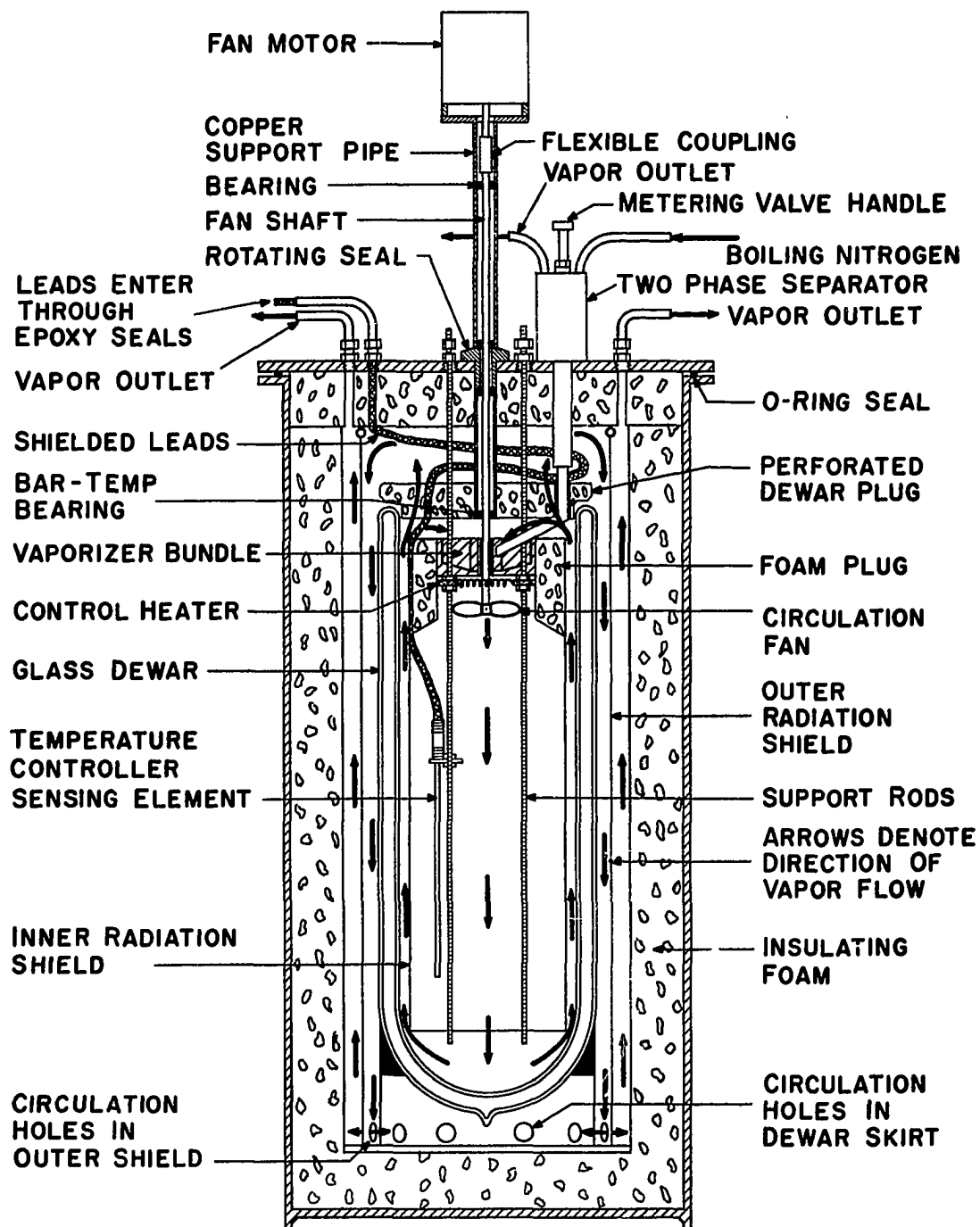


FIGURE 1. GAS BATH CRYOSTAT

and flows to the vaporizer bundle within a 1/2 in. thin-walled, stainless steel tube and delivers its sensible and latent heat to cool the bath. The metering valve is adjusted to allow a slight excess of refrigerant to enter the bundle which is offset by the control heater. A fan blows the vapor through the equipment space which contains the temperature-controller sensor. A combination radiation-shield and vapor-baffle establishes the indicated flow patterns.

The vaporizer bundle was designed based upon a 3°C approach to the boiling point of liquid nitrogen and required approximately 10 ft² of surface area. In addition, the dimensions were restricted to 5-1/2 in. diameter by 2 in. thick with sufficient capacity for holding a level of liquid nitrogen. This immediately suggested a home-made, finned surface.

The bundle was constructed about a piece of 1-5/8 in. I.D. copper water pipe fitted at one end with a 1/4 in. thick copper plug into which a 1/2 in. I.D. piece of water pipe had been soldered. The pieces of pipe were 2 in. long in keeping with the imposed dimensional restrictions. Brass spacer bars 2 in. long, 3/8 in. wide and 3/32 in. thick were then soldered in an eight point star to the outside wall of the outer water pipe. Two strips of 0.0125 in. thick by 2 in. wide pieces of copper strip were wrapped around the central structure adding more spacers each revolution until the

diameter of the bundle reached 5-1/2 in. One of the copper strips was corrugated to provide additional area. Prior to assembly the materials had all been coated with a thin layer of 50% Pb - 50% Sn solder and at this point were sweated together in an oven. Troughs, sloping toward the center, were then milled through the spacer bars into the central well. The slope would insure radial distribution of any liquid nitrogen build-up in the bundle. Liquid leaks were eliminated by coating the entire internal surface with low-melting indium solder. Figure 2 is an overall photograph of the bundle and Figure 3 presents a close-up view of one finned section. The irregular outside geometry of the final product was an accident of construction arising from the soldering operation. The effective surface area finally obtained was very nearly 10 ft² and idealized calculations indicated that the temperature on the fins was always at least 90% of the temperature at the wall.

The control heater was constructed by stringing 25 gage, coiled Nichrome wire within a 5 in. diameter phenolic frame. The wiring was installed in two sections to be used in either series or parallel connection. In series the wattage is variable between 10 and 170 watts by means of an external resistor. The series connection is used for control heat and is activated by a Hallikainen Model 1053A Thermotrol with proportional-plus-reset control. The controller sensor is a Rosemont Model 104N48AAC. The parallel

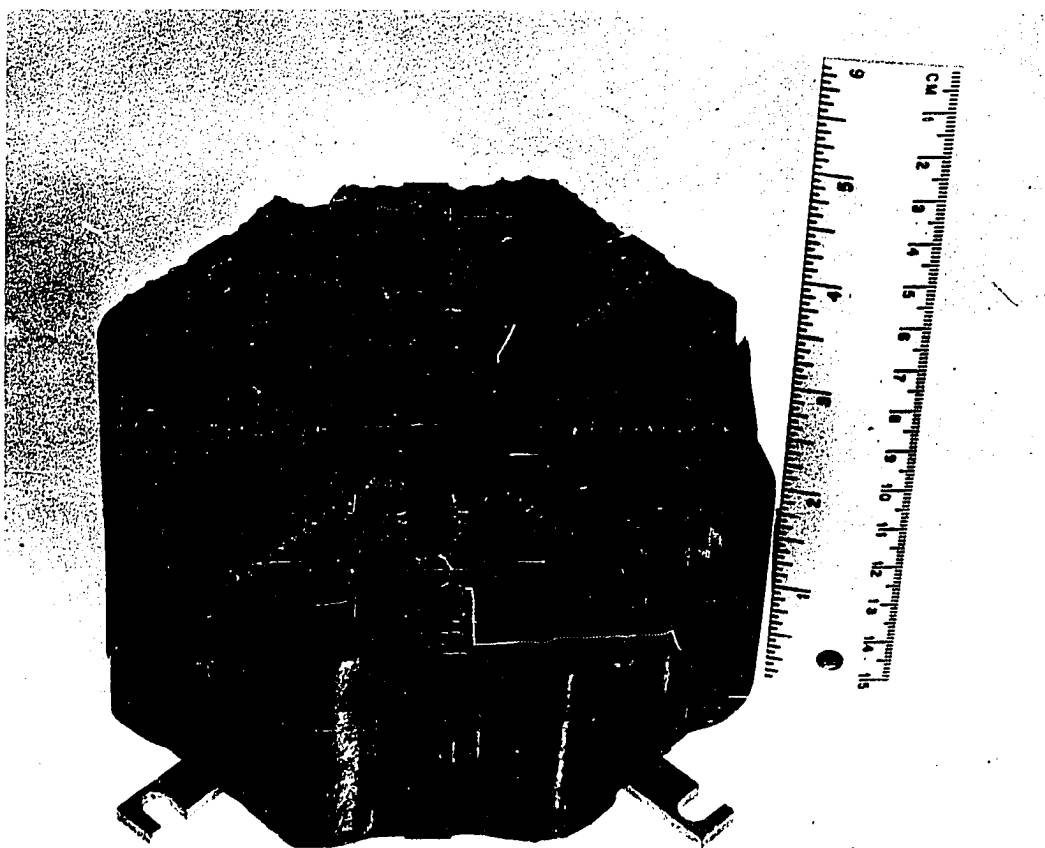


FIGURE 2. HEAT TRANSFER BUNDLE

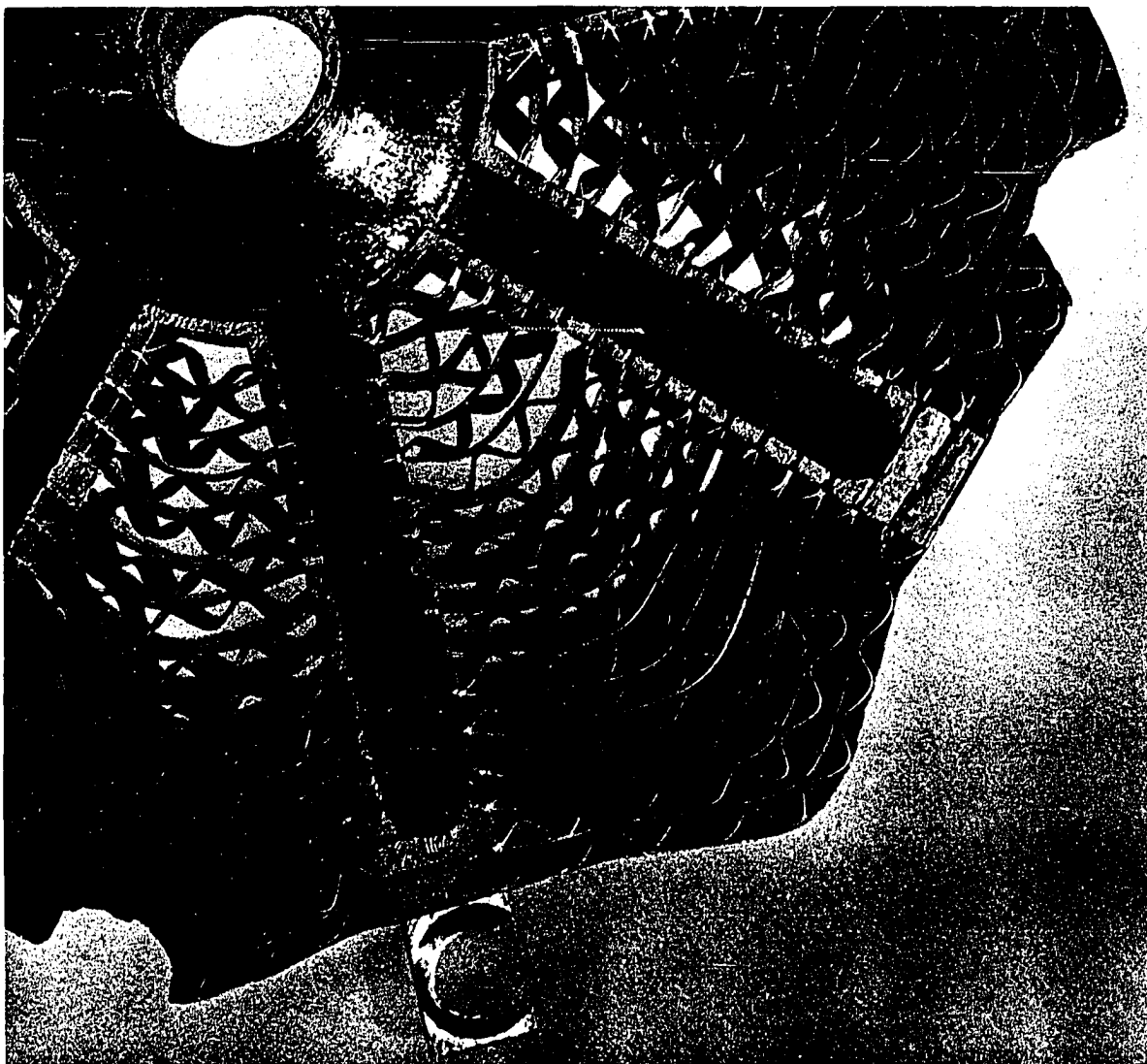


FIGURE 3. CLOSE-UP VIEW OF BUNDLE SECTION

connection is used for quick heat and generates 675 watts. To protect the bundle, the wiring was done in such a manner that the fan must be ON when the heater is operating.

The fan blade is 4 in. in diameter and has 10 vanes. It is driven by a 1750 rpm motor mounted on top of the cryostat and delivers approximately 120 cfm. The shaft enters the cryostat through a Materials Research Corp. V4-100 rotating vacuum seal and is held true at low temperatures by a Barden Bar-Temp bearing.

A styrofoam plug surrounds the vaporizer, heater and fan. This plug serves the twofold purpose of reducing back-mixing of the refrigerant vapor and supporting the radiation shield-vapor baffle. The plug is essential to close control of the gradients within the cryostat. Whereas the normal gradient was approximately 0.005°C , degeneration of the styrofoam caused an increase to about 0.025°C .

With the Burnett equipment in place, as shown in Figure 4, the nitrogen usage at steady state varies roughly between 1/5 liter/hr. at 0°C and 3 liters/hr. at -190°C . The minimum gradient observed across the Burnett cells was 0.000°C with careful adjustment of the equipment and was often less than 0.005°C . Several runs were made with gradients of about 0.025°C because the styrofoam plug had degenerated enough to disturb the flow patterns of the nitrogen vapor. This degeneration was actually melting caused by use of the quick heater.

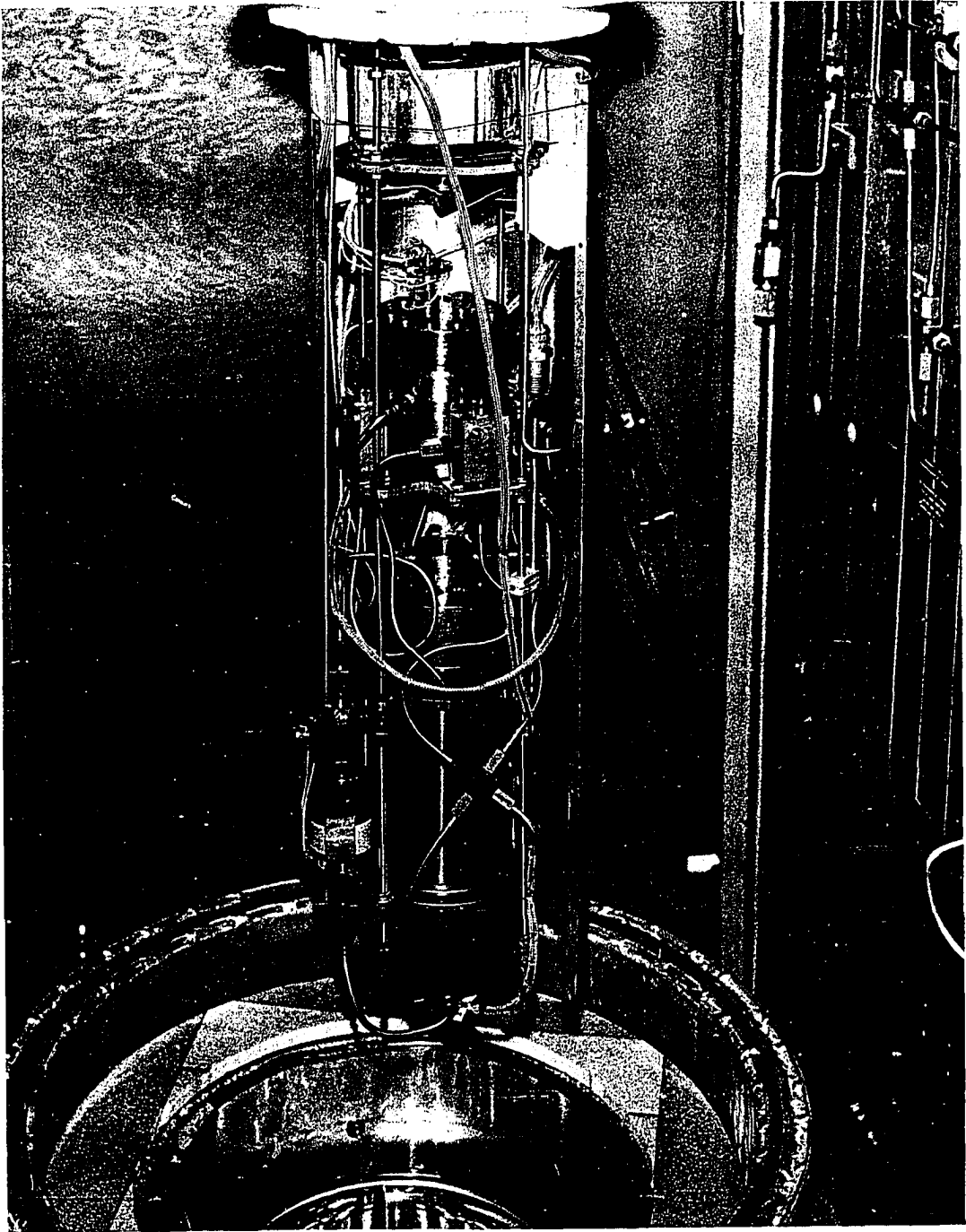


FIGURE 4. BURNETT APPARATUS AND CRYOSTAT

Burnett Cells and Magnetic Pump

The physical characteristics of these items have been thoroughly discussed by Blancett and by Canfield, Watson and Blancett [8]. Minor modifications were effected, however, and will be noted here.

The Burnett cells are jacketed to allow equal pressure to be applied on both the inside and outside. The cells and jacket are shown in rough detail in Figure 5. A thermometer well was provided in the outer section of each cell which would receive a Leeds and Northrup No. 8164 capsule platinum-resistance thermometer. In earlier work only one thermometer was available and a difference thermocouple, one junction embedded in each cell, was used in conjunction with the one available thermometer to indicate the approach of temperature equilibrium. For this work, an additional thermometer was used, and because the thermocouple was thereby rendered unnecessary, it was removed. Other than this the cells remain unchanged from the earlier work.

A magnetic pump is located in the line connecting the two Burnett cells. The purpose of this item is to speed equilibration by forced mixing of the gas from each chamber. The pump was especially useful when the more dense mixtures were being studied.

One difficulty associated with the magnetic pump is ascertaining whether or not it is operating properly. In their article, Canfield, Watson and Blancett suggest sensing

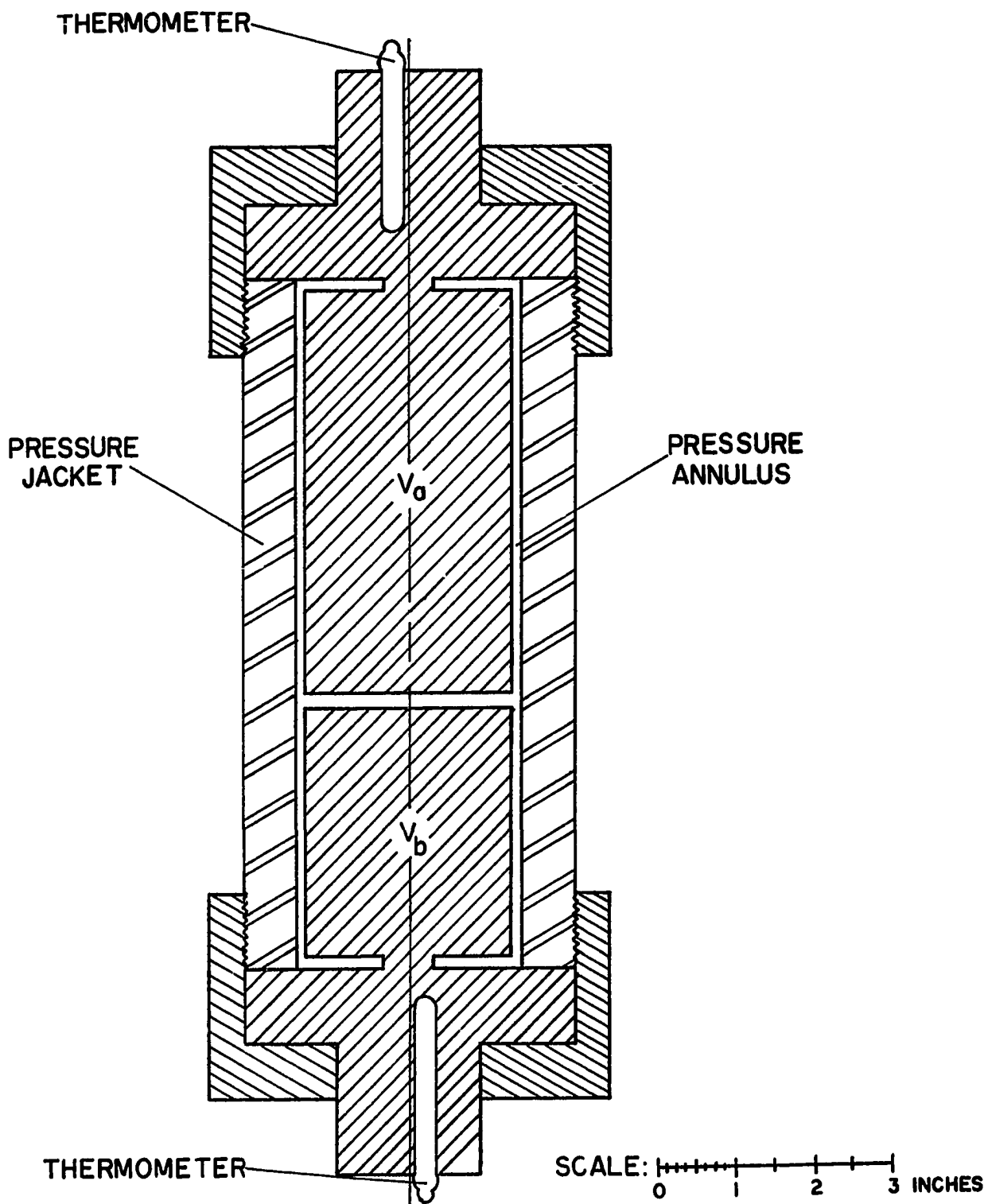


FIGURE 5. HIGH PRESSURE BURNETT CELL

the movement of a check ball which is pulsed by the surging gas. Their solution was to run an electrical lead to the check-ball seat which would deliver a signal whenever contacted by the ball. An intermittent signal would indicate proper operation. The lead was run into the pump through a magnesium oxide packed tube sealed at each end with epoxy resin. Unfortunately, when subjected to extreme temperature changes, the epoxy apparently loosened and allowed gas to leak out through the tube. Because this problem had been encountered before, it seemed advisable to seek a new procedure for detecting the operating condition of the pump.

This turned out to be a simple task. The pump produces audibly different sounds when operating properly or not, and they can be heard when an industrial stethoscope is touched to certain external parts of the cryostat. This may be checked with the pressure measuring instruments and will be mentioned in that section.

When this alternative proved satisfactory, the packed tube was discarded and the pump sealed. One other problem was noticed--the pump could not be left ON for too long a time or it would hinder rather than speed equilibration at low pressures. This was caused by too much energy dissipation which in turn caused the temperature to reach a higher equilibrium value than was desired.

Temperature and Pressure Measurements

The temperature of a run was taken to be the average value indicated by the two platinum resistance thermometers.

The resistance of these elements was measured on a Leeds and Northrup G-2 Mueller bridge. When properly calibrated and made consistent with the bridge, the thermometers were guaranteed to establish the temperature within $\pm 0.01^{\circ}\text{C}$ of the International Temperature Scale. The bridge calibration was checked prior to making any measurements and this calibration was used in lieu of that supplied by the manufacturer.

The thermometers had been calibrated by the National Bureau of Standards, one to the oxygen point the other to 12°K . Above -183°C a table of resistance versus temperature was prepared using the Callendar-Van Dusen equation. In order to make this table consistent with the available equipment the triple point was measured with each thermometer in this laboratory and the ice point calculated from this value was used in the equation rather than the ice point given by the National Bureau of Standards. The observed triple point resistances were 25.5522 ohms for thermometer #1617523 and 25.5341 ohms for thermometer #1665930. Below -183 the point-by-point values of the National Bureau of Standards were used for the calibrated thermometer and this temperature was taken as the system temperature. (This table was considered to be consistent with the bridge because the ice point observed in this laboratory agreed with the one reported by the National Bureau of Standards if no bridge correction were included and the correction at -190°C was only 0.00004 ohms.) The second thermometer was used only to indicate gradient in this region.

The system pressure was measured, primarily, by one of two Ruska Model 2400 dead weight gages used with two Ruska differential pressure cells and indicators. A set of accurately calibrated weights was supplied with the gages and were equivalent to Class "P" standard masses. The accuracy claimed for the gages by the manufacturer was $\pm 0.01\%$ of the reading or better.

Two gages were employed to allow measurements from 700 to 2 atm. without changing pistons. Consequently the "low pressure gage" was used up to 165 atm. and the "high pressure gage" beyond that. The two differential pressure cells were used for an entirely different reason.

One assumption in the Burnett analysis is that the gas be completely isothermal when its properties are measured. To insure this condition one of the cells was located inside the cryostat. Because of the extreme environment, this cell was specially designed and constructed by Ruska Instrument Corporation. The other cell, joined to the latter by an intermediate gas line, was used at room temperature. Both indicators had to be nulled simultaneously to obtain a correct pressure reading.

One characteristic of the indicators which had to be investigated in detail was the zero shift caused by pressure. This phenomenon resulted from a difference in reading for a "balanced" condition in the cell, that is a flat diaphragm with equal pressures on both sides, and a "nulled"

condition on the indicator. The manufacturer supplied information concerning the zero shift for both indicators, but their values were only used for the room-temperature device. The equation reported was

$$\Delta P_{ZSR} = 1.3 \times 10^{-7} P \quad (12)$$

where ΔP_{ZSR} is the zero shift in atmospheres and P is the system pressure in psia. Unfortunately, the zero shift of the cryogenic indicator was a function of temperature as well as pressure and had to be measured in this laboratory. Blancett described the technique employed and a method for correcting the measured values. The final equation used for this quantity was

$$\Delta P_{ZSC} = \frac{MZS}{1.0 - 0.0277 (\partial P / \partial \ln v)_T} \quad (13)$$

in which ΔP_{ZSC} is the zero shift in atmospheres, MZS is the measured zero shift in atmospheres and v is the molar volume cc/mole. Figure 6 is a plot of ΔP_{ZSC} versus P at the experimental temperatures.

A Welsh Model 122A marine barometer indicated the atmospheric pressure during a measurement. The resulting correction is given by

$$P_B = 0.0333902 (R-r) \quad (14)$$

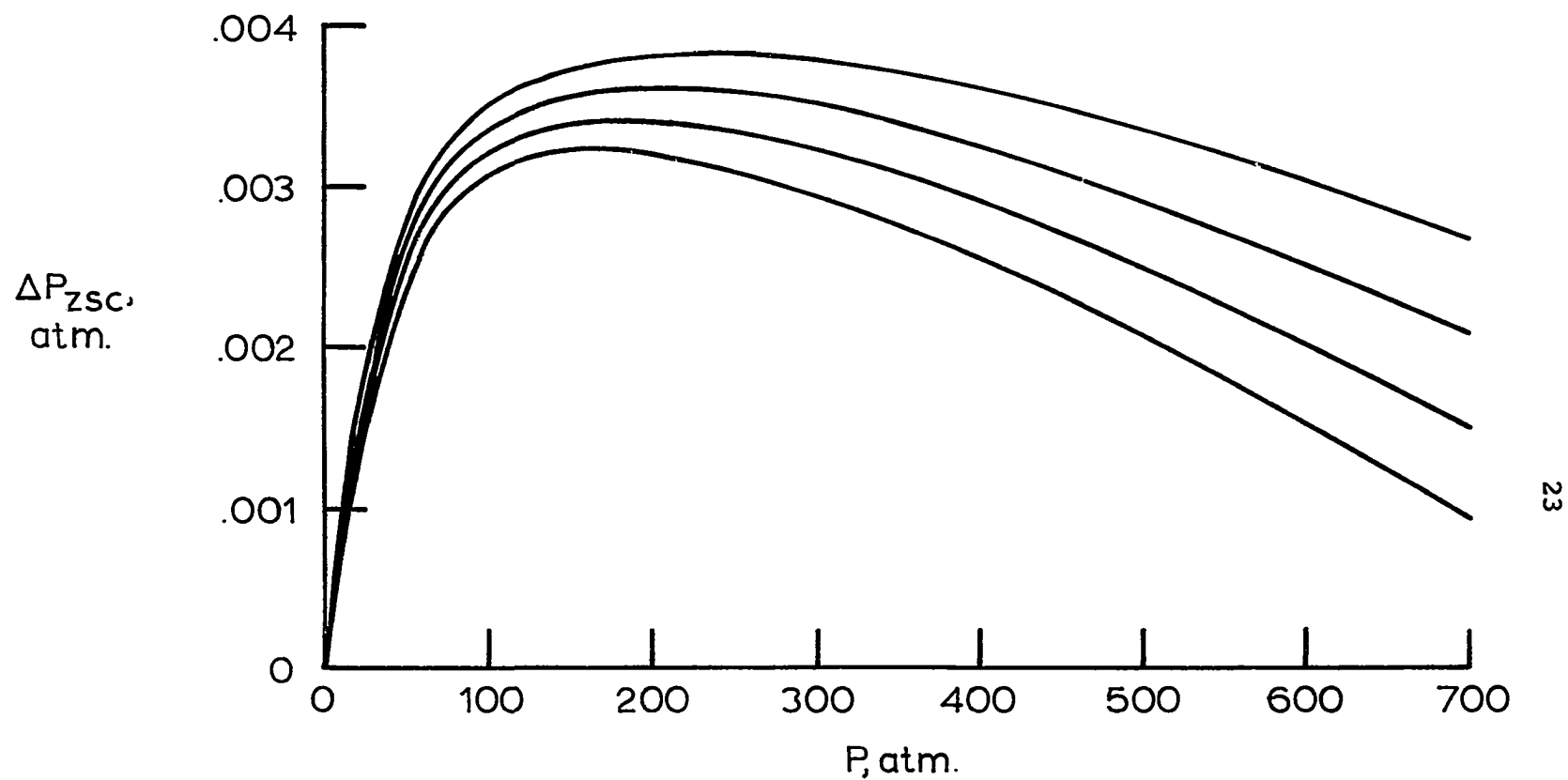


FIGURE 6. CORRECTED ZERO SHIFT CURVES FOR THE CRYOGENIC DIFFERENTIAL PRESSURE INDICATOR AT -160° , -170° , -180° , AND -190°C IN ORDER FROM TOP CURVE TO BOTTOM CURVE

where P_B is the barometric pressure in atmospheres, R is the barometer reading in inches of mercury, and r is a temperature correction.

Finally head corrections had to be applied to the gage reading. For the high-pressure gage this was

$$\Delta P_H = -0.00021 + (MW) [(-0.116) (\rho_g)_o + (h) (\rho_g)_i] \quad (15)$$

and for the low-pressure gage

$$\Delta P_H = -0.00057 + (MW) [(-0.116) (\rho_g)_o + (h) (\rho_g)_i] \quad (16)$$

where ΔP_H is the head correction in atmospheres, MW is the molecular weight of the gas, $(\rho_g)_o$ is the density of the gas in the system outside the cryostat, $(\rho_g)_i$ is the density of the gas in the system inside the cryostat and h is a multiplier with values of 0.0714 for the initial measurement of a run and 0.0747 for all successive measurements. The density units are moles/cc.

The gage pressure itself is, when corrected for temperature and pressure, for the low-pressure gage

$$P_G = \frac{0.521989 \Sigma(M_a)}{(1.0 + 1.7 \times 10^{-5} \Delta T) (1.0 - 4.8 \times 10^{-8} P)} \quad (17)$$

and for the high-pressure gage

$$P_G = \frac{2.610037 \Sigma(M_a)}{(1.0 + 1.7 \times 10^{-5} \Delta T) (1.0 - 3.6 \times 10^{-8} P)} \quad (18)$$

where P_G is the gage pressure in atmospheres, $\Sigma(M_a)$ is the sum of the weights used in pounds mass, ΔT is the temperature of the gage in $^{\circ}\text{C}$ less 25°C and P is the system pressure in psia. The actual pressure is then

$$P = P_G + P_B + \Delta P_H + \Delta P_{ZSR} + \Delta P_{ZSC} \quad (19)$$

This equation was programmed for a digital computer to speed the calculations and eliminate the chance of human error in the calculations.

Blancett has discussed the pressure measurement procedure in detail in his dissertation and it should be consulted for derivation of the above equations except for Equation 13 which has been modified by the present author.

Pressure Generation and Vacuum System

A Corblin #B2Cl000 single-stage diaphragm compressor was used to produce pressures above those in the gas cylinders. The diaphragm insured purity of the sample which was of primary concern in charging.

For pressures less than those contained in the sample cylinders, the gas was bled directly into the system and measured roughly by a Maxisafe bourdon tube gage. This gage was calibrated prior to use to insure that the system would not be charged above the dew point of any sample.

The vacuum system consisted of a two-stage oil-lubricated vacuum pump and a thermocouple gage to indicate

the pressure. The system was sufficiently tight that a 5 micron vacuum could be held for about 10 to 15 minutes when the pump was disconnected.

Valves and Tubing

With the exception of a short run of 1/2 in. copper pipe in the vacuum system, all the tubing was 3/16 in. O.D. stainless steel. The pressure rating was 15000 psi and a flare seal was used between tubing and fittings. The flared connections caused one problem--when tightened a large torque was set up in the tubing which tended to loosen some fittings. This was not too serious a problem, but the threat of a lengthy delay was always present should a fitting inside the cryostat begin to leak.

All the valves were High Pressure Inc. 30000 psi midget line with two-piece non-rotating stems. At room temperature they were provided with O-ring seals and performed admirably. At low temperatures the O-rings were unacceptable, however, and another packing had to be found.

Four valves were located within the cryostat and subjected to the very low temperatures of the experimental runs. Because the dead volume had to be kept to a minimum and the gas samples isothermal, the packing could not be removed from the cryostat. This constituted a major problem because all suitable packing materials shrink excessively with temperature and eventually begin to allow gas to leak past. This

condition was found to exist in the present work and had to be eliminated before any experimental runs were begun.

The final solution decided upon was to use some material with a very low coefficient of contraction as thrust washers for teflon packing, and to use the proper dimensions to assure that the packing could not shrink away from the stem or body of the valve. The dimensions were calculated by equating the volume change of the packing upon cooling with that of the packing cavity. To obtain the desired results Invar thrust washers were used and snugly fitted graphite washers were placed above and below the teflon to reduce extrusion. Both Invar and graphite contract very little with temperature. The equations used for the volume changes were

$$\Delta V_P = (3\pi/4) (D_B^2 - d_S^2) (\Delta L/L)_P L_P \quad (20)$$

and

$$\Delta V_C = (3\pi/4) L_P [D_B^2 (\Delta L/L)_B - d_S^2 (\Delta L/L)_S] + \quad (21)$$

$$+ (\pi/4) (D_B^2 - d_S^2) \{ [(\Delta L/L)_B - (\Delta L/L)_W] L_W + [(\Delta L/L)_B - (\Delta L/L)_G] L_G \}$$

where ΔV_P is the volume change of the packing from room temperature to -190°C , d_S is the diameter of the valve stem, $(\Delta L/L)$ is the change in length per length, D_B is the diameter of the cavity in the valve body and L is the length. The subscripts denote the following: S stem, P packing, B body,

W Invar washer, C cavity and G graphite. When the valves were assembled in this manner they held dead-tight against 700 atm and a vacuum at room temperature and between -160°C and -190°C . The system was thus ready to take data at the conditions desired. The final dimensions used were:

1/8 in. stem

1/4 in. O.D. x 1/8 in. I.D. x 5/16 in. upper
Invar washer

1/4 in. O.D. x 1/8 in. I.D. x 1/16 in. lower
Invar washer

1/4 in. O.D. x 1/8 in. I.D. x 1/32 in. graphite
washers

1/4 in. O.D. x 1/8 in. I.D. x .025 in. teflon packing.

CHAPTER IV

A GENERAL LEAST-SQUARES ANALYSIS APPLICABLE TO OPTIMAL RECOVERY OF VIRIAL COEFFICIENTS

Because of their theoretical importance, in the study of intermolecular forces for example, the coefficients of the virial equation

$$Z = \sum_{k=1}^{\infty} B_k \rho^{k-1} \quad (22)$$

are usually sought from compressibility data. This has been a rather perplexing problem because the equation is an infinite series and intractable by numerical methods. A number of techniques are used to approximate the virial coefficients and a few are mentioned below for comparison with the proposed procedure which is presented in detail.

Previous Methods

Possibly the first method which comes to mind is to apply a limiting behavior process to the equation. Rearrangement of Equation 22 reveals that

$$\left. \begin{aligned} B_1 &= 1 \\ B_2 &= \lim_{\rho \rightarrow 0} (Z-1/\rho) \\ B_3 &= \lim_{\rho \rightarrow 0} (Z-1/\rho^2 - B_2/\rho) \end{aligned} \right\} \quad (23)$$

and so on for as many coefficients as are desired. A serious disadvantage is that extremely accurate low density data are required to insure accuracy in the extrapolated values and, in general, such data are unavailable.

A more commonly used routine is to fit a polynomial approximation to the data and obtain the coefficients by requiring a "best fit." This is, by and large, a highly esoteric concept but quite often a least-squares analysis is employed.

This leaves the question as to which polynomial should be used. Many investigators prefer to use a pressure expansion in the form

$$Z = \bar{B}_1 + \bar{B}_2 P + \bar{B}_3 P^2 + \dots \quad (24)$$

for which the \bar{B} are related to the virial coefficients by

$$\left. \begin{aligned} B_1 &= \bar{B}_1 = 1 \\ B_2 &= RT\bar{B}_2 \\ B_3 &= (RT)^2 (\bar{B}_2^2 + \bar{B}_3) \end{aligned} \right\} \quad (25)$$

Still others (notably workers in The Netherlands) utilize Amagat data in which the ratio of actual volume to normal (0°C and 1 atm.) volume is measured. The Amagat compressibility factor is given by

$$P(V/V_N) = A_1 + A_2 (V_N/V) + A_3 (V_N/V)^2 + \dots \quad (26)$$

where V_N is the normal volume. The A_i are related to the virial coefficients by

$$\left. \begin{aligned} B_1 &= V_N A_1 / RT = 1 \\ B_2 &= (RT/A_1) (A_2/A_1) \\ B_3 &= (RT/A_1)^2 (A_3/A_1) \end{aligned} \right\} \quad (27)$$

A more direct method is simply to truncate the virial equation after a sufficient number of terms are judged to have been used.

The basic weakness in all these methods is that the coefficients obtained cannot be identified rigorously with the virial coefficients because their values will depend upon, among other things, the number of terms in the polynomial and the pressure range of the measurements. The polynomial coefficients could be used in theoretical work, however, if a good estimate were available for their variance from the infinite series coefficients.

Present Method

Michels et al. [21] have made a thorough investigation of this problem and have offered a criterion for choosing the best polynomial coefficients to approximate those of an infinite series. However, their approach has several shortcomings and a newer analysis has been developed based upon their work. The present approach is more satisfying and rigorous and is generally applicable to data reduction. Criteria are developed for choosing, in a least-squares sense, the best polynomial to approximate an infinite series and for picking the polynomial coefficients having a minimum variance from the series coefficients. To emphasize the generality of the method and to gain flexibility of expression, general nomenclature will be adopted throughout the remainder of this chapter.

Let $y_1, \dots, y_n, \dots, y_N$ be N experimental measurements at $x_1, \dots, x_n, \dots, x_N$ and assume that only random error exists in these measurements. Furthermore, assume that all the error is localized in the y_n , the x_n being exact. Admittedly, these assumptions are rather drastic but necessary for the ensuing analysis. They may be justified if care is taken to minimize systematic errors in the measurements and if it is understood that assuming localized error in a two variable experiment will magnify the error band of the random variable.

In general nomenclature the virial equation or any infinite series may be written

$$y_n^* = \sum_{k=1}^{\infty} \alpha_k f_k(x_n) \quad (28)$$

It is assumed that this is the functional form that the y_n vs. x_n data must fit and, therefore, that the y_n^* are exact, theoretical values. The $f_k(x_n)$ notation denotes any linearly independent set of functions of x_n ; for the virial equation it would be ascending powers of the density.

A "model function" was proposed by Michels et al. which would provide a measure of how closely an infinite series can be approximated by a polynomial derived from exact data. This proves to be an useful relationship and is given by

$$y_{mn} = \sum_{k=1}^m \alpha_{mk} f_k(x_n) \quad (29)$$

The values for y_{mn} would be established by placing a polynomial through N points on a y_n^* vs. x_n plot.

The function which will approximate the actual data is

$$u_{mn} = \sum_{k=1}^m a_{mk} f_k(x_n) \quad (30)$$

The a_{mk} will be found by a least-squares analysis and their variance from the α_k established. A brief review of the method of least-squares is in order then, if for no other reason than to introduce pertinent nomenclature.

Least Squares

The method of least squares places a polynomial approximation through a set of data points by minimizing the sum of the squares of the discrepancies defined by

$$\Delta_{mn} = y_n - u_{mn} = y_n - \sum_{k=1}^m a_{mk} f_{kn} \quad (31)$$

where f_{kn} is shorthand for $f_k(x_n)$. The requirement is that

$$\sum_{n=1}^N \Delta_{mn}^2 = \text{minimum} \quad (32)$$

The minimum is sought with respect to the a_{mk} and is obtained by differentiation

$$\partial/\partial a_{mk} \left[\sum_{n=1}^N \Delta_{mn}^2 \right] = \sum_{n=1}^N \Delta_{mn} f_{kn} = 0 \quad (33)$$

where k ranges from 1 to m .

The a_{mk} may be extracted from Equation 33 but this involves the solution of m simultaneous equations. However, if the f_{kn} are made orthonormal, this requisite is eliminated. Furthermore, employing orthonormal functions enables automatic recovery of the a_{mk} for all polynomials possessing fewer than some given, maximum number of parameters, M . These advantages are sufficiently enticing to motivate use of orthonormal functions in this application.

Orthonormalization of the f_{kn}

Orthonormal functions are vectors which are perpendicular and whose dot product is unity. The f_{kn} may be

converted to such functions by employing the Gram-Schmidt algorithm. Jones and Gallet [16] and Pfenning [25] have laid down the guide lines for application of this algorithm as it will be used below.

It will be necessary frequently to use the inner product of two vectors hereafter. This may be defined in terms of the f_{kn} as

$$(f_k, f_j) \equiv \sum_{n=1}^N f_{kn} f_{jn} \quad \begin{matrix} (k=1, \dots, M) \\ (j=1, \dots, M) \end{matrix} \quad (34)$$

The parentheses representation will be used often to simplify the notation.

The set of functions $\psi_{1n}, \psi_{2n}, \dots, \psi_{mn}$ are orthogonal (perpendicular) if

$$(\psi_k, \psi_j) = 0 \quad k \neq j \quad (35)$$

This condition will be satisfied by the set of functions generated from

$$\begin{aligned} \psi_{1n} &= f_{1n} & (k = 1) \\ \psi_{kn} &= f_{kn} + \sum_{r=1}^{k-1} C_{kr} \psi_{rn} & (k = 2, \dots, M) \end{aligned} \quad (36)$$

In this manner, N values of f_{kn} may be transformed into orthogonal ψ_{kn} . The set of constants C_{kr} are given by

$$C_{kr} = - (\psi_r, f_k) / (\psi_r, \psi_r) \quad (37)$$

when Equation 35 is applied to Equation 36.

Equation 36 is more useful in the analysis if put into the form

$$\psi_{kn} = \sum_{r=1}^k G_{kr} f_{rn} \quad (38)$$

The G_{kr} are functions of the C_{kr} and can be calculated from

$$\begin{aligned} G_{kk} &= C_{kk} = 1 & (k=1, \dots, M) \\ G_{kr} &= \sum_{j=r}^{k-1} G_{jr} C_{kj} & (k=2, \dots, M) \\ & & (r=1, \dots, k-1) \end{aligned} \quad (39)$$

This relationship arises when the ψ_{kn} calculated from Equation 36 are equated to those calculated from Equation 38 and the coefficients of like powers of f_{kn} are compared.

The ψ_{kn} are normalized by

$$\varphi_{kn} = \psi_{kn} / (\psi_k, \psi_k)^{1/2} \quad (40)$$

where $\varphi_{1n}, \varphi_{2n}, \dots, \varphi_{mn}$ are orthonormal functions. The defining equation for orthonormal functions is

$$\begin{aligned} (\varphi_k, \varphi_j) &= \delta_{kj} & (\delta_{kj} &= 0, k \neq j) \\ & & (\delta_{kj} &= 1, k = j) \end{aligned} \quad (41)$$

where δ_{kj} is the Kronecker delta. The φ_{kn} formed by Equation 40 can easily be shown to satisfy Equation 41 by forming the inner product of φ_{kn} and φ_{jn} .

Solution for Coefficients

The orthonormal ϕ_{kn} will now be used to recover the a_{mk} . Upon insertion of the proper coefficients, Equations 29 and 30 become

$$y_{mn} = \sum_{k=1}^m \alpha_{mk} f_{kn} = \sum_{k=1}^m \delta_{mk} \psi_{kn} = \sum_{k=1}^m \beta_{mk} \phi_{kn} \quad (42)$$

$$u_{mn} = \sum_{k=1}^m a_{mk} f_{kn} = \sum_{k=1}^m d_{mk} \psi_{kn} = \sum_{k=1}^m b_{mk} \phi_{kn} \quad (43)$$

where the d_{mk} and b_{mk} will be referred to as the orthogonal and orthonormal coefficients respectively. Equation 33 then becomes

$$(\Delta_m, f_k) = (\Delta_m, \psi_k) = (\Delta_m, \phi_k) = 0 \quad (k = 1, \dots, M) \quad (44)$$

This equation may be solved readily for the d_{mk} and b_{mk} because the normal equations are uncoupled by the property of orthogonality. Using the b_{mk} as an example

$$(\Delta_m, \phi_j) = (y, \phi_j) = (u_m, \phi_j) = (y, \phi_j) - \sum_{k=1}^m b_{mk} (\phi_k, \phi_j) = 0 \quad (45)$$

but by applying Equation 41 this reduces to

$$b_k = (y, \phi_k) \quad (46)$$

and because the b_{mk} are not functions of m they are written simply as b_k . Similarly, d_{mk} is found to be

$$d_k = (y, \psi_k) / (\psi_k, \psi_k) = b_k / (\psi_k, \psi_k)^{1/2} \quad (47)$$

If Equation 43 is expanded and the coefficients of like powers of f_{kn} compared, the a_{mk} are found to be

$$a_{mk} = \sum_{j=k}^m d_j G_{jk} = \sum_{j=k}^m b_j G_{jk} / (\psi_j, \psi_j)^{1/2} \quad (48)$$

The a_{mk} may be found most conveniently by constructing a matrix, T_{pk} , generated by

$$\begin{aligned} T_{1k} &= d_k G_{kk} & (k = 1, \dots, M) \\ T_{pk} &= T_{p-1,k} + T_{1,p+k-1} G_{p+k-1,k} & (p = 2, \dots, M) \\ & & (k = 1, \dots, M-p+1) \end{aligned} \quad (49)$$

In this matrix the a_{mk} are found at

$$\begin{aligned} a_{mk} &= T_{m-k+1,k} & (k = 1, \dots, m) \\ & & (m = 1, \dots, M) \end{aligned} \quad (50)$$

Therefore, instead of a single set of coefficients, the T_{pk} matrix contains M sets of coefficients corresponding to M polynomials. For example, if M were specified to be 4, the T_{pk} matrix would be

	T_{p1}	T_{p2}	T_{p3}	T_{p4}
T_{1k}	a_{11}	a_{22}	a_{33}	a_{44}
T_{2k}	a_{21}	a_{32}	a_{43}	
T_{3k}	a_{31}	a_{42}		
T_{4k}	a_{41}			

It is evident that this matrix effects a substantial reduction of time and effort compared with the solution for the a_{mk} by inversion procedures.

Cut-off Criteria

Two separate cut-off criteria will give an optimal set of parameters, a_{mk} , for the present problem. If the best fit of the data is required, the condition is

$$\sum_{n=1}^N \langle (u_{mn} - y_n^*)^2 \rangle = \text{minimum} \quad (51)$$

with respect to variation in m . If, however, coefficients are desired which are as near as possible in value to the exact coefficients, the requirement is that

$$\langle (a_{mk} - \alpha_k)^2 \rangle = \text{minimum} \quad (52)$$

with respect to variation in m for a given k . The number of parameters associated with the polynomial satisfying Equation 51 will be denoted as m^* .

Both criteria are of considerable importance, and must be developed into useful forms. Rigorous equations can and will be derived, but, because of the statistical nature of the analysis, they cannot be evaluated. Necessary approximations are available and can be justified by examples.

Before the criteria are expanded, a few basic relationships must be investigated. The experimental error

will necessarily have a role in this discussion. It is defined as

$$\epsilon_n \equiv y_n - y_n^* \quad (53)$$

and because only random error is allowed in the y_n

$$\langle \epsilon_n \rangle = 0 \quad (54)$$

where the brackets denote expected values. The errors are also assumed independent and then

$$\langle \epsilon_n \epsilon_s \rangle = \langle \epsilon_n \rangle \langle \epsilon_s \rangle = 0 \quad (55)$$

Also because $\langle y_n \rangle = y_n^*$ from Equations 53 and 54

$$\langle \epsilon_n^2 \rangle = \langle (y_n - y_n^*)^2 \rangle = \sigma^2 \quad (56)$$

where σ^2 is the variance of the data. Combining Equations 55 and 56

$$\langle \epsilon_n \epsilon_s \rangle = \delta_{ns} \sigma^2 \quad (57)$$

where δ_{ns} is the Kronecker delta. Another quantity which proves useful is the "model" error

$$h_{mn} \equiv y_n^* - y_{mn} \quad (58)$$

For both criteria, it is helpful to know some relationships between the various coefficients which have been introduced. One is established by taking the expected value

of the orthonormal coefficients defined by Equation 46

$$\langle b_k \rangle = \langle (y, \varphi_k) \rangle = (\langle y \rangle, \varphi_k) = (y^*, \varphi_k) \quad (59)$$

Here $\langle \varphi_{kn} \rangle = \varphi_{kn}$ because the error is localized in the y_n values. Had the "model" function, Equation 42, been used in a least-squares fit of N exact data points, the β_{mk} would be found (analogously to the b_k) to be

$$\beta_k = (y^*, \varphi_k) \quad (60)$$

Like the b_k , the β_k do not depend upon the number of parameters in the polynomial fit and the subscript m is dropped. Equations 59 and 60 reveal that

$$\langle b_k \rangle = \beta_k \quad (61)$$

In the case of the orthogonal coefficients, it can be shown easily that

$$\delta_{mk} \rightarrow \delta_k = \langle d_k \rangle = (y^*, \varphi_k) / (\psi_k, \psi_k)^{1/2} \quad (62)$$

From a development analogous to that for Equation 48, the α_{mk} are found to be

$$\alpha_{mk} = \sum_{j=k}^m \delta_j G_{jk} = \sum_{j=k}^m \beta_j G_{jk} / (\psi_j, \psi_j)^{1/2} \quad (63)$$

Examination of Equations 48, 61 and 63 establishes that

$$\langle a_{mk} \rangle = \alpha_{mk} \quad (64)$$

The necessary expressions are now available to develop more useful forms for the cut-off criteria. The best-fit criterion can be expanded using Equations 31, 53 and 57

$$\begin{aligned} \sum_{n=1}^N \langle (u_{mn} - y_n^*)^2 \rangle &= \sum_{n=1}^N \langle (y_n - y_n^* + u_{mn} - y_n)^2 \rangle = \sum_{n=1}^N \langle (\epsilon_n - \Delta_{mn})^2 \rangle = \\ &= \langle (\Delta_m, \Delta_m) \rangle + N \sigma^2 - 2 \sum_{n=1}^N \langle \epsilon_n \Delta_{mn} \rangle \end{aligned} \quad (65)$$

The third term in this equation reduces to

$$-2 \sum_{n=1}^N \langle \epsilon_n \Delta_{mn} \rangle = -2 \langle (y, \epsilon) \rangle + 2 \langle \sum_{k=1}^m b_k (\epsilon, \phi_k) \rangle \quad (66)$$

Equations 46, 53 and 60 indicate that

$$(\epsilon, \phi_k) = (y, \phi_k) - (y^*, \phi_k) = b_k - \beta_k \quad (67)$$

which when substituted into Equation 66 gives

$$\begin{aligned} -2 \sum_{n=1}^N \langle \epsilon_n \Delta_{mn} \rangle &= -2 \langle (y, \epsilon) \rangle + 2 \sum_{k=1}^m (\langle b_k^2 \rangle - \beta_k^2) = \\ &= -2 \langle (y, y) \rangle + 2 \langle (y^*, y^*) \rangle + 2 \sum_{k=1}^m (\langle b_k^2 \rangle - \beta_k^2) \end{aligned} \quad (68)$$

But, from earlier definitions it can be shown that

$$\begin{aligned} \langle (y, y) \rangle &= \langle (y^* + \epsilon, y^* + \epsilon) \rangle = \langle (y^*, y^*) \rangle + \\ &+ \sum_{n=1}^N \langle \epsilon_n^2 \rangle = \langle (y^*, y^*) \rangle + N \sigma^2 \end{aligned} \quad (69)$$

and

$$\begin{aligned}
 \langle b_k^2 \rangle &= \langle (y, \varphi_k)^2 \rangle = \sum_{n=1}^N \sum_{s=1}^N \langle y_n y_s \rangle \varphi_{kn} \varphi_{ks} = \\
 &= \sum_{n=1}^N \sum_{s=1}^N \langle (y_n^* + \epsilon_n)(y_s^* + \epsilon_s) \rangle \varphi_{kn} \varphi_{ks} = \sigma^2 + \beta_k^2 \quad (70)
 \end{aligned}$$

(This is equivalent to $\langle (b_k - \beta_k)^2 \rangle = \sigma^2$. Because σ^2 , the variance of the data, is a constant, this indicates that the calculated b_k are the best values automatically. Using these relationships, Equation 68 becomes

$$-2 \sum_{n=1}^N \langle \epsilon_n \Delta_{mn} \rangle = -2(N-m)\sigma^2 \quad (71)$$

and the criterion is

$$\sum_{n=1}^N \langle (u_{mn} - y_n^*)^2 \rangle = (2m-N)\sigma^2 + \langle (\Delta_m, \Delta_m) \rangle \quad (72)$$

for which $m = m^*$ at the minimum. This expression should be used in lieu of Gauss' criterion (see Kendall [17]) when the functional form which the data should fit is an infinite series, such as Equation 28.

The criterion for optimal coefficients also possesses a more useful form. Equation 52 may be expanded as follows

$$\begin{aligned}
 \langle (a_{mk} - \alpha_k)^2 \rangle &= \langle [(a_{mk} - \alpha_{mk}) + (\alpha_{mk} - \alpha_k)]^2 \rangle = \\
 &= \langle (a_{mk} - \alpha_{mk})^2 \rangle + \langle (\alpha_{mk} - \alpha_k)^2 \rangle + 2\langle (a_{mk} - \alpha_{mk})(\alpha_{mk} - \alpha_k) \rangle = \\
 &= \langle (a_{mk} - \alpha_{mk})^2 \rangle + (\alpha_{mk} - \alpha_k)^2 \quad (73)
 \end{aligned}$$

The first term in this expression is

$$\begin{aligned}
 \langle (a_{mk} - \alpha_{mk})^2 \rangle &= \langle \left(\sum_{j=k}^m (b_j - \beta_j) G_{jk} / (\psi_j, \psi_j)^{1/2} \right)^2 \rangle = \\
 &= \sum_{j=k}^m \sum_{i=k}^m \langle (b_j - \beta_j) (b_i - \beta_i) \rangle G_{jk} G_{ik} / \left[(\psi_j, \psi_j)^{1/2} (\psi_i, \psi_i)^{1/2} \right]
 \end{aligned} \tag{74}$$

From the definitions for b_k and β_k and Equation 57

$$\begin{aligned}
 \langle (b_j - \beta_j) (b_i - \beta_i) \rangle &= \langle (\epsilon, \varphi_j) (\epsilon, \varphi_i) \rangle = \sum_{n=1}^N \sum_{s=1}^N \langle \epsilon_n \epsilon_s \rangle \varphi_{jn} \varphi_{is} = \\
 &= \sum_{n=1}^N \sum_{s=1}^N \delta_{ns} \sigma^2 \varphi_{jn} \varphi_{is} = \sigma^2
 \end{aligned} \tag{75}$$

Substitution into Equation 74 gives

$$\langle (a_{mk} - \alpha_{mk})^2 \rangle = \sigma^2 \sum_{j=k}^m G_{jk}^2 / (\psi_j, \psi_j) \tag{76}$$

The second term of Equation 73 remains to be developed.

Equation 63 may be expanded using the definition of

β_k :

$$\begin{aligned}
 \alpha_{mk} &= \sum_{j=k}^m \beta_j G_{jk} / (\psi_j, \psi_j)^{1/2} = \sum_{j=k}^m \left[G_{jk} / (\psi_j, \psi_j)^{1/2} \right] \sum_{n=1}^N y_n^* \varphi_{jn} = \\
 &= \sum_{n=1}^N \sum_{i=1}^m \sum_{j=k}^m \left[G_{jk} \psi_{jn} / (\psi_j, \psi_j) \right] \alpha_{i f_{in}} + \sum_{n=1}^N \sum_{j=k}^m G_{jk} \psi_{jn} / (\psi_j, \psi_j) R_{mn}
 \end{aligned} \tag{77}$$

where $R_{mn} = \sum_{i=m+1}^{\infty} \alpha_{i f_{in}}$, the truncation error. For the time being, let Q represent the last term in this expression,

then because

$$f_{in} = \psi_{in} - \sum_{r=1}^{i-1} C_{ir} \psi_{rn}$$

Equation 77 becomes

$$\begin{aligned} \alpha_{mk} &= \sum_{n=1}^N \sum_{i=1}^m \sum_{j=k}^m \left[G_{jk} \psi_{jn} / (\psi_j, \psi_j) \right] \alpha_i (\psi_{in} - \sum_{r=1}^{i-1} C_{ir} \psi_{rn}) + Q = \\ &= \sum_{i=1}^m \alpha_i \sum_{j=k}^m G_{jk} (\psi_j, \psi_i) / (\psi_j, \psi_j) - \\ &- \sum_{i=1}^m \alpha_i \sum_{j=k}^m \sum_{r=1}^{i-1} G_{jk} C_{ir} (\psi_j, \psi_r) / (\psi_j, \psi_j) + Q = \\ &= \sum_{i=k}^m \alpha_i G_{ik} - \sum_{i=k+1}^m \alpha_i \sum_{r=k}^{i-1} G_{rk} C_{ir} + Q \end{aligned} \quad (78)$$

through use of the property of orthogonality. When Equation 39 is introduced, this relationship reduces to

$$\alpha_{mk} = \sum_{i=k}^m \alpha_i G_{ik} - \sum_{i=k+1}^m \alpha_i G_{ik} + Q = \alpha_k + Q \quad (79)$$

The difference between α_{mk} and α_k is Q or

$$\alpha_{mk} - \alpha_k = \sum_{j=k}^m G_{jk} (R_m, \varphi_j) / (\psi_j, \psi_j)^{1/2} \quad (80)$$

The inner product term may be expressed as

$$(R_m, \varphi_j) = (y^*, \varphi_j) - \sum_{i=1}^m \alpha_i (f_i, \varphi_j) \quad (81)$$

Therefore, the criterion for optimal coefficients is that

$$\begin{aligned} \langle (a_{mk} - \alpha_k)^2 \rangle &= \sigma_a^2 = \sigma^2 \sum_{j=k}^m G_{jk}^2 / (\psi_j, \psi_j) + \\ &+ \left\{ \sum_{j=k}^m \left[G_{jk} / (\psi_j, \psi_j)^{1/2} \right] \left[\beta_j - \sum_{i=1}^m \alpha_i (f_i, \phi_j) \right] \right\}^2 \end{aligned} \quad (82)$$

be a minimum with respect to m . It should be noted that this criterion may be satisfied at different values of m for different values of k .

Because σ^2 is essential to both criteria, it should also be put into a more convenient form. A good starting place is the sum of the squares of the deviations

$$\begin{aligned} \sum_{n=1}^N \Delta_{mn}^2 &= \sum_{n=1}^N (y_n - \sum_{k=1}^m b_k \phi_{kn})^2 = \\ &= \sum_{n=1}^N y_n^2 - 2 \sum_{n=1}^N y_n \sum_{k=1}^m b_k \phi_{kn} + \sum_{n=1}^N \sum_{k=1}^m \sum_{j=1}^m b_k b_j \phi_{kn} \phi_{jn} = \\ &= (y, y) - 2 \sum_{k=1}^m (y, \phi_k)^2 + \sum_{k=1}^m (y, \phi_k)^2 = (y, y) - \sum_{k=1}^m b_k^2 \end{aligned} \quad (83)$$

Taking the expected value of this equation produces

$$\begin{aligned} \langle (\Delta_m, \Delta_m) \rangle &= \langle (y, y) \rangle - \sum_{k=1}^m \langle b_k^2 \rangle = \\ &= (y^*, y^*) + N \sigma^2 - \sum_{k=1}^m \beta_k^2 - m \sigma^2 \end{aligned} \quad (84)$$

using Equations 79 and 80. If h_{mn} is substituted for Δ_{mn} in Equation 83, the result is

$$(h_m, h_m) = (y^*, y^*) - \sum_{k=1}^m \beta_k^2 \quad (85)$$

Therefore, the last two equations combine to give the desired expression for σ^2

$$\sigma^2 = \left[\langle (\Delta_m, \Delta_m) \rangle - (h_m, h_m) \right] / N-m \quad (86)$$

While Equations 72, 82 and 86 have been rigorously developed, they cannot be evaluated in their present form. In general, h_{mn} and all expected values will not be known, and must be approximated. Fortunately, good estimates are available and are presented in the next section.

Criteria Estimators

Because σ^2 is common to both criteria, it will be estimated first. The first term of Equation 86 is approximated by dropping the expected value operation

$$\langle (\Delta_m, \Delta_m) \rangle / N-m \approx (\Delta_m, \Delta_m) / N-m \equiv S^2 \quad (87)$$

This is an unbiased estimate of the term (which, incidentally, is the maximum value σ^2 may have).

The second term is more tedious. Examination of Equations 29, 30 and 64 reveals that

$$y_{mn} = \langle u_{mn} \rangle \quad (88)$$

therefore,

$$h_{mn} = y_n^* - y_{mn} = \langle y_n - u_{mn} \rangle = \langle \Delta_{mn} \rangle \quad (89)$$

and

$$(h_m, h_m) = \sum_{n=1}^N \langle \Delta_{mn} \rangle^2 \quad (90)$$

This may be expanded into

$$\begin{aligned} (h_m, h_m) &= \langle \Delta_{m1} \rangle^2 + \langle \Delta_{m2}^2 \rangle + \dots + \langle \Delta_{mN} \rangle^2 = \\ &= \langle \sum_{n=1}^N \Delta_{mn} \rangle^2 - 2 \sum_{n=1}^{N-1} \sum_{s=n+1}^N \langle \Delta_{mn} \Delta_{ms} \rangle \end{aligned} \quad (91)$$

and estimated by

$$(h_m, h_m) \approx \left[\sum_{n=1}^N \Delta_{mn} \right]^2 - 2 \sum_{n=1}^{N-1} \sum_{s=n+1}^N \Delta_{mn} \Delta_{ms} \equiv S^2_{(N-m)} \quad (92)$$

Unfortunately, this is a biased estimate, but it is the only available choice other than zero and will be used. The estimator for σ^2 is then

$$\sigma^2 \approx S^2 - \frac{\Lambda^2}{S} \quad (93)$$

The value calculated for σ^2 should be compared with an a priori estimate if possible. This will give some insight concerning the choice of f_{kn} establishing Equation 28 as the functional form fitting the data. If improper f_{kn} have been chosen the calculated and estimated values should be widely different.

The fact that S^2 is the maximum value for σ^2 is also an useful concept. If the Δ_{mn} are not randomly distributed, the value of \hat{S}^2 might be such that σ^2 will be estimated greater than S^2 . In this case, S^2 should be used for σ^2 . Experience has shown that this approximation does not introduce significant error because normally $S^2 \gg \hat{S}^2$.

The best fit criterion follows immediately

$$\sum_{n=1}^N \langle (u_{mn} - y_n^*)^2 \rangle \approx (2m-N) (S^2 - \hat{S}^2) + (\Delta_m, \Delta_m) \quad (94)$$

This is essentially unbiased because of the small magnitude of \hat{S}^2 . The criterion for optimal coefficients is a bit more difficult to estimate. The suggested form is

$$\begin{aligned} \sigma^2 \approx & (S^2 - \hat{S}^2) \sum_{j=k}^m G_{jk}^2 / (\psi_j, \psi_j) + \\ & + \left\{ \sum_{j=k}^m \left[G_{jk} / (\psi_j, \psi_j) \right]^{1/2} \left[b_j - \sum_{i=1}^m a_{m^*i} (f_i, \phi_j) \right] \right\}^2 \end{aligned} \quad (95)$$

This expression is statistically biased, but it possesses a definite advantage--it is available and computable. Replacing β_j with b_j is a very good approximation as indicated by Equations 61 and 70. Replacing α_i with a_{m^*i} is based upon experience with test cases. These examples indicated that the parameters associated with the m^* polynomial are generally fairly good approximations for the α_i . Of course, the values can be checked a posteriori. In the test cases run to check the procedure, the error incurred by this

approximation was not significant. Furthermore, the coefficients associated with the m^* polynomial satisfied Equation 95 in all cases.

Error Accumulation and Reorthonormalization

The involved computational requirements of this technique immediately suggest computer application. Care must be exercised, however, because in problems of this type, round-off error can easily accumulate and destroy all confidence in the values obtained. The most susceptible operation above is the orthonormalization step, but, fortunately, use of orthonormal functions provides a means for estimating this error.

The b_k were calculated from Equation 46 under the assumption that the ϕ_{kn} were orthonormal. Actually, because of round-off error the ϕ_{kn} might not be exactly orthonormal and Equation 45 should be used. Denoting the values obtained from Equation 45 as b_k^* , the following expression results

$$b_j = (y, \phi_j) = b_1^* (\phi_1, \phi_j) + \dots + b_j^* (\phi_j, \phi_j) + \dots \quad (96)$$

The difference between b_j and b_j^* in this equation is an indication of the effect of round-off error. The relative error is

$$(b_j^* - b_j) / b_j^* = 1 - \sum_{q=1}^m (b_q^* / b_j^*) (\phi_q, \phi_j) \quad (97)$$

The b_j^* are not necessarily known, but they may be approximated by the b_j

$$(b_j^* - b_j) / b_j^* \approx 1 - \sum_{q=1}^m (b_q / b_j) (\varphi_q, \varphi_j) \quad (98)$$

When this relative error exceeds some prescribed epsilon, it is reasonable to assume that round-off error has become significant. Experience has shown that unless epsilon is 10^{-6} or less; the results may not be accepted with confidence. One method for controlling this error is reorthonormalization.

Reorthonormalization of the set of functions, φ_{kn} , forms a new set φ'_{kn} which are more nearly orthonormal. The generating equation for the new orthogonal functions is

$$\psi'_{kn} = \sum_{r=1}^k G_{kr} \psi_{rn} \quad (99)$$

The G'_{kr} are found by merely substituting primed values into Equation 39 in which the C'_{kr} are given by

$$C'_{kr} = - (\psi'_r, \psi'_k) / (\psi'_r, \psi'_r) \quad (100)$$

The ψ'_{kn} are normalized by

$$\varphi'_{kn} = \psi'_{kn} / (\psi'_k, \psi'_k)^{1/2} \quad (101)$$

Following the earlier developments

$$b'_k = (y, \varphi'_k) \quad (102)$$

and

$$d_k' = b_k' / (\psi_k', \psi_k')^{1/2} \quad (103)$$

T_{pk}' is formed from

$$T_{1k}' = d_k' G_{kk}'$$

$$T_{pk}' = T_{p-1,k}' + T_{1,p+k-1}' \sum_{j=k}^{p+k-1} G_{p+k-1,j}' G_{jk}' \quad (104)$$

and the a_{mk}' are found in the same locations as in the T_{pk}' matrix. The variance of the coefficients is obtained by replacing G_{jk} in Equation 82 by

$$\sum_{i=k}^j G_{ji}' G_{ik}'$$

This procedure may be repeated as often as necessary to bring the relative round-off error within the tolerable limits. Of course, the expressions for T_{pk}' and σ_a^2' become increasingly more complex (see Hall and Canfield [11]).

Example

Several test cases were run on the computer to check the validity of the proposed technique. The most informative and stringent was the specially constructed function

$$g(x_n) = e^{-x_n} + 0.1 e^{x_n} + 0.01 x_n^5 + \epsilon_n \quad (105)$$

This function was chosen because it closely resembles a near-critical compressibility isotherm and has an infinite series representation for which the coefficients are known exactly.

The random error, ϵ_n , was included as follows. An average error of about 0.0005 was desired so a standard deviation of 0.001 was chosen and multiplied by the entries in a random-number sequence ($0.0 < n < 1.0$). This gave an average error of 0.00046. A second random-number sequence was used to determine the sign of the error which was then added to 30 discrete values of $g(x_n)$. The x_n were in the range $0.01 \leq x \leq 3.00$.

One reorthonormalization was required to control the relative round-off error to less than 3×10^{-10} using a 12 digit word. The coefficients for the first eight polynomials are given in Table 1 along with their standard deviations. The program chose $m^* = 6$ as the best fit which is correct. Also the coefficients for this polynomial have minimum variances. The exact coefficients are compared with the a_{6k} in Table 2. These coefficients are nearer in value to the α_k than any other coefficients in Table 1 as predicted. It should also be noted that, with few exceptions, all the coefficients in Table 1 are within their standard deviation of the exact coefficients.

These and similar results seem to substantiate the validity of the assumptions made when estimating the criteria.

TABLE 1
COEFFICIENTS OF $g(x_n)$ FOR VARIOUS POLYNOMIAL APPROXIMATIONS

m/k.	a_{mk}	σ_a		a_{mk}	σ_a
1/1	$3.8270(10^{-1})$	1.2824	2/1	-1.4305	$5.3077(10^{-1})$
			2	$7.9285(10^{-1})$	$2.4270(10^{-1})$
3/1	$-4.4191(10^{-1})$	$4.5778(10^{-1})$	4/1	$-9.6700(10^{-1})$	$6.7314(10^{-2})$
2	$-2.8840(10^{-1})$	$8.3856(10^{-1})$	2	$7.4613(10^{-1})$	$1.9598(10^{-1})$
3	$2.6607(10^{-1})$	$4.1856(10^{-1})$	3	$-3.2836(10^{-1})$	$1.7598(10^{-1})$
			4	$1.0408(10^{-1})$	$5.5800(10^{-2})$
5/1	$-8.9175(10^{-1})$	$8.2040(10^{-3})$	6/1	$-8.9970(10^{-1})$	$3.2869(10^{-3})$
2	$5.1532(10^{-1})$	$3.5282(10^{-2})$	2	$5.5016(10^{-1})$	$1.2571(10^{-2})$
3	$-1.0081(10^{-1})$	$5.1835(10^{-2})$	3	$-1.5238(10^{-1})$	$1.7481(10^{-2})$
4	$1.4357(10^{-2})$	$3.3986(10^{-2})$	4	$4.8283(10^{-2})$	$1.1159(10^{-2})$
5	$1.2284(10^{-2})$	$1.0232(10^{-2})$	5	$2.0553(10^{-3})$	$3.3204(10^{-3})$
			6	$1.1534(10^{-3})$	$3.7312(10^{-4})$
7/1	$-8.9844(10^{-1})$	$5.1072(10^{-3})$	8/1	$-8.9793(10^{-1})$	$7.3364(10^{-3})$
2	$5.4271(10^{-1})$	$2.6350(10^{-2})$	2	$5.3882(10^{-1})$	$4.8092(10^{-2})$
3	$-1.3707(10^{-1})$	$5.0757(10^{-2})$	3	$-1.2649(10^{-1})$	$1.2010(10^{-1})$
4	$3.3494(10^{-2})$	$4.7356(10^{-2})$	4	$1.9553(10^{-2})$	$1.5058(10^{-1})$
5	$9.3598(10^{-3})$	$2.2971(10^{-2})$	5	$1.9315(10^{-2})$	$1.0432(10^{-1})$
6	$-6.3323(10^{-4})$	$5.5720(10^{-3})$	6	$-4.5707(10^{-3})$	$4.0524(10^{-2})$
7	$1.7156(10^{-4})$	$5.3386(10^{-4})$	7	$9.8273(10^{-4})$	$8.2672(10^{-3})$
			8	$-6.7905(10^{-5})$	$6.8921(10^{-4})$

TABLE 2
COMPARISON OF a_{6k} WITH α_k

k	α_k	a_{6k}	σ_a
1	$-9.0000(10^{-1})$	$-8.9970(10^{-1})$	$3.2869(10^{-3})$
2	$5.5000(10^{-1})$	$5.5016(10^{-1})$	$1.2571(10^{-2})$
3	$-1.5000(10^{-1})$	$-1.5238(10^{-1})$	$1.7481(10^{-2})$
4	$4.5833(10^{-2})$	$4.8283(10^{-2})$	$1.1159(10^{-2})$
5	$2.5000(10^{-3})$	$2.0553(10^{-3})$	$3.3204(10^{-3})$
6	$1.5278(10^{-3})$	$1.1534(10^{-3})$	$3.7312(10^{-4})$

These criteria are the first impersonal, mathematical guides offered for obtaining optimal coefficients in this application and for obtaining best fits for infinite series. The program associated with this analysis was used in every phase of the data treatment in this project.

CHAPTER V

METHOD FOR REDUCTION OF BURNETT DATA TO COMPRESSIBILITY FACTORS AND VIRIAL COEFFICIENTS

The accuracy of compressibility factors obtained by the Burnett method depends to a large degree upon how well the constants N_∞ and P_0/Z_0 are established. Classically, they were found from graphical extrapolations using Equations 10 and 11, but, when demands for more accuracy emerged, several procedures for refining the graphical values were developed.

Some of these techniques are reviewed briefly below as background material. The bulk of this chapter, however, is devoted to an explanation of a new method for refinement of the constants which eliminates many major weaknesses of the previous schemes and introduces some added advantages. Use of the new method should produce results which reflect all the accuracy of present measuring capabilities.

Previous Methods for Refinement

While the errors in the extrapolated constants are not large (roughly 0.01% for N_∞ and 0.1% for P_0/Z_0), they must be reduced by at least an order of magnitude if the

results are truly to reflect the information available in the data. The major obstacle in this process lies in the fact that the constants appear non-linearly in the pertinent equations.

Some investigators, such as Pfefferle [24] and Silberberg et al. [27], propose linearization of the equations by various means and application of some iterative scheme to find corrections to be applied to the constants. Canfield [6] suggests that the low density linearity of a plot of $(Z-1)\rho$ vs. ρ is sensitive to the value of N_∞ and may be exploited to adjust this constant. Both methods suffer in that multiple runs for a given isotherm must be treated separately. This immediately restricts the amount of available information which may be extracted from the data.

Barieau and Dalton [1] have developed a rigorous, non-linear, least-squares technique which they have applied to Burnett data. Multiple runs may be treated with this method, but convergence problems would most likely appear when working with near critical isotherms. Hoover et al. [14] have proposed a "direct" method for establishing N_∞ and P_0/Z_0 along with the virial coefficients. This is an iterative technique based upon the Burnett analysis and establishes the constants with negligible error. However, the method is restricted to temperatures above $T_r > 0.75$ and to regions where the compressibility factor is given by

$$Z = 1 + B_2 \rho + B_3 \rho^2 \quad (106)$$

All the above methods assume N_∞ is a true apparatus constant for a given temperature and use a calibration value in their refining steps. While this is theoretically satisfying, data taken in this laboratory do not actually exhibit this behavior. Each run seems to have its own cell "constant" albeit this is, most likely, because of experimental error.

Present Method for Refinement

Upon reviewing these earlier treatments, it seemed desirable to devise a new method which would eliminate their major weaknesses and thereby increase the accuracy of the final results. In particular, a method was sought which would use all of the available information contained in the experimental data.

The useful information is: one or more sets of pressures for each isocomp-isotherm considered, the fact that the virial coefficients are identical for all sets of pressures along a given isocomp-isotherm and the Burnett analysis relating the pressures, N_∞ and P_0/Z_0 to the compressibility factors and to the virial coefficients (via Equation 22). Mathematically, a functional relationship exists of the form

$$F(j, P_j, T, N_\infty, P_0/Z_0, B_2, B_3, \dots) = 0 \quad (107)$$

in which j is the expansion number and for which there may be multiple sets of expansion numbers, pressures and Burnett constants. The function is non-linear in terms of the constants, but they may be recovered by constructing a multi-dimensional response surface which will exhibit a minimum when the proper values are inserted. This minimum may be searched out by well established procedures. In this work and in most other studies involving Burnett apparatus, two runs are used to establish an isotherm, so for the remainder of the discussion assume that

$$F(N_{\infty 1}, (P_0/Z_0)_1, N_{\infty 2}, (P_0/Z_0)_2, \dots) = 0 \quad (108)$$

where the expansion numbers, pressures, temperature and virial coefficients are understood.

The searching procedure requires initial values for the constants and virial coefficients. The extrapolation method (Chapter I) was implemented by placing an optimal least-squares polynomial through the appropriate data coordinates and then Equation 9 produced initial estimates for the compressibility factor. The technique proposed in Chapter IV then gave values for the virial coefficients consistent with the approximate values for the Burnett constants.

The particular form to be used for F must be established at this point. The difference between Equation 9 and Equation 22 is chosen because this function permits the fullest utilization of the development presented in Chapter IV and

because the virial coefficients are recovered automatically in the data treatment.

$$F = P_j \left(\frac{Z_0}{P_0} \right) N_\infty^j \xi_j - \sum_{k=1}^{\infty} B_k \rho_j^{k-1} \quad (109)$$

where j denotes an individual expansion and ξ_j and ρ_j are given by the following expressions.

$$\xi_j = \prod_{i=1}^j \frac{k_1 + k_2 P_i + k_3 P_i^2 + \dots}{m_1 + m_2 P_{i-1} + m_3 P_{i-1}^2 + \dots} \quad (110)$$

$$\rho_j = \frac{1}{RT \left(\frac{Z_0}{P_0} \right) N_\infty^j \xi_j} \quad (111)$$

The summation of F^2 over all the data points is minimized with respect to the Burnett constants treating both runs simultaneously i.e.

$$\begin{aligned} \sum F^2 &\equiv \sum_{j=1}^{J1} \left[P_j N_{\infty 1}^j \left(\frac{Z_0}{P_0} \right)_1 \xi_{j1} - \sum_{k=1}^{m^*} B_k \rho_{j1}^{k-1} \right]^2 + \\ &+ \sum_{j=1}^{J2} \left[P_j N_{\infty 2}^j \left(\frac{Z_0}{P_0} \right)_2 \xi_{j2} - \sum_{k=1}^{m^*} B_k \rho_{j2}^{k-1} \right]^2 = \\ &= \text{minimum} \end{aligned} \quad (112)$$

where J1 and J2 are the number of data points in the first and second runs respectively and m^* is (as in Chapter IV) the optimal number of parameters required to approximate the virial expansion for Z_j . In this expression the same set of B_k is used for each run.

Equation 112 possesses a major advantage and a major disadvantage in a least squares sense. Because the compressibility factors do not vary widely, a weighting factor is not absolutely necessary in the summation. On the other hand, the compressibility factor is a derived rather than observed quantity, and it must be used with care in this application. To be certain that the search is truly converging, a check is made employing the observable pressures. Equation 6 may be used by introducing the optimal values for the Burnett constants and virial coefficients to calculate

$$\begin{aligned}
 \text{CHK} = & \sum_{j=1}^{J1} \left[\frac{P_j}{P_{j-1}} - \frac{1}{N_{j1}} \frac{\sum_{k=1}^{m^*} B_k \rho_{j1}^{k-1}}{\sum_{k=1}^{m^*} B_k \rho_{j-1,1}^{k-1}} \right]^2 + \\
 & + \sum_{j=1}^{J2} \left[\frac{P_j}{P_{j-1}} - \frac{1}{N_{j2}} \frac{\sum_{k=1}^{m^*} B_k \rho_{j2}^{k-1}}{\sum_{k=1}^{m^*} B_k \rho_{j-1,2}^{k-1}} \right]^2 \quad (113)
 \end{aligned}$$

If CHK is small and within the range expected from experimental error, the search may be assumed to be converging.

The function, ΣF^2 , may be calculated from the various initial values now and the search for the minimum may commence. Many searching procedures have been proposed in the literature, but two sources collect most of the more useful ones into concise reviews. These references are a series of articles by Boas [3] and a text by Wilde [29]. The optimal method must be chosen to reflect the conditions of the problem in which it will be used.

Because the initial values of the Burnett constants can be found as accurately as they are, it seems safe to assume that the surface, ΣF^2 , will be unimodal and nearly quadratic in the region of interest. Under these conditions, the quadratic search outlined by Wilde should be employed immediately, although it is usually introduced only after having exhausted the usefulness of some linear search.

This particular search is performed by assuming that the ΣF^2 surface is quadratic and unimodal in $N_{\infty 1}$, $(Z_0/P_0)_1$, $N_{\infty 2}$, $(Z_0/P_0)_2$ - space. A Taylor's expansion then yields (defining ΣF^2 as S and Z_0/P_0 as A for simplicity)

$$\begin{aligned} \Delta S \approx & \left(\frac{\partial S}{\partial N_{\infty 1}} \right) \Delta N_{\infty 1} + \left(\frac{\partial S}{\partial A_1} \right) \Delta A_1 + \left(\frac{\partial S}{\partial N_{\infty 2}} \right) \Delta N_{\infty 2} + \left(\frac{\partial S}{\partial A_2} \right) \Delta A_2 + \\ & + \frac{1}{2} \left\{ \left(\frac{\partial^2 S}{\partial N_{\infty 1}^2} \right) (\Delta N_{\infty 1})^2 + \left(\frac{\partial^2 S}{\partial A_1^2} \right) (\Delta A_1)^2 + \left(\frac{\partial^2 S}{\partial N_{\infty 2}^2} \right) (\Delta N_{\infty 2})^2 + \right. \\ & \left. + \left(\frac{\partial^2 S}{\partial A_2^2} \right) (\Delta A_2)^2 \right\} + \left(\frac{\partial^2 S}{\partial N_{\infty 1} \partial A_1} \right) \Delta N_{\infty 1} \Delta A_1 + \left(\frac{\partial^2 S}{\partial N_{\infty 2} \partial A_2} \right) \Delta N_{\infty 2} \Delta A_2 + \end{aligned}$$

$$\begin{aligned}
& + \left(\frac{\partial^2 S}{\partial N_{\infty 1} \partial N_{\infty 2}} \right) \Delta N_{\infty 1} \Delta N_{\infty 2} + \left(\frac{\partial^2 S}{\partial N_{\infty 1} \partial A_2} \right) \Delta N_{\infty 1} \Delta A_2 + \\
& + \left(\frac{\partial^2 S}{\partial N_{\infty 2} \partial A_1} \right) \Delta N_{\infty 2} \Delta A_1 + \left(\frac{\partial^2 S}{\partial A_1 \partial A_2} \right) \Delta A_1 \Delta A_2
\end{aligned} \tag{114}$$

In this application the fourteen derivatives may be taken analytically (analytical and numerical values were compared to insure that taking the derivative of a least squares polynomial was valid under these conditions). The last four interaction are conveniently zero. Differentiation of Equation 114 with respect to each constant change produces four simultaneous equations which, when set equal to zero and solved, give corrections to be applied to the Burnett constants. When the corrected values of the constants are inserted into Equation 112, the minimum in the ΣF^2 surface should result. The fact that the surface may not be exactly quadratic requires that this procedure be iterated until the change in the constants from one iteration to the next is less than some prescribed epsilon. At this minimum, the compressibility factors, densities and virial coefficients will be the best (in a least squares sense) obtainable from the data. The virial coefficients are obtained in each iteration by calculating the Z_j and the ρ_j from the permuted Burnett constants and observable pressures, and then employing the technique of Chapter IV.

Unfortunately, there is a complication involved. Choice of a polynomial to approximate the virial equation again becomes the issue. The methods of Chapter IV will indicate the proper polynomial and best virial coefficients only after the refined compressibility factors have been used to establish them. It is necessary, therefore, to set up several surfaces, each using a different number of terms in this equation, and find the optimal values of the Burnett constants for each surface. Then the optimal compressibility factors, densities and virial coefficients are established for each surface.

Now the surface must be chosen which has yielded results which are most nearly consistent with the data. The first test which can be applied is Canfield's suggestion concerning the low density linearity of a plot of $(z-1)/\rho$ vs. ρ . Any surfaces whose results do not satisfy this condition are eliminated from consideration. The best remaining surface may be ferreted out by examining the standard deviation of the virial coefficients, the value of the best fit criterion, the deviations between observed and calculated compressibility factors and the sum of the squares of these deviations. Of these, the first two are emphasized. Ultimately, one surface will reveal superior behavior under this scrutiny, and may be considered to possess the optimal values for the desired quantities.

CHAPTER VI

DATA AND APPLICATIONS

After the pressures were corrected as outlined in Chapter III, they were treated by the methods described in Chapters IV and V to obtain compressibility factors and virial coefficients. The results are presented in Tables 3-17. In addition, interaction virial coefficients have been calculated.

Data

Each table presents the optimal results for one isocomp-isotherm as extracted from the computer program BURNOR (Appendix D). The apparatus constants, N_∞ and Z_0/P_0 , are presented at the top of the table. These are the optimal values and are consistent with the data presented. The experimental pressures in atmospheres are listed and all other quantities, reading across the page, correspond to these values. The compressibility factor is presented as calculated from the Burnett analysis (Equation 9) and as calculated from the virial equation. These latter values, labeled $Z(\text{Virial})$ should be considered the reported compressibilities with $Z(\text{Burnett})$ being additional information.

TABLE 3

EXPERIMENTAL AND CALCULATED RESULTS FOR
100.00% HELIUM AT -160°C

Run #1:		$N_{\infty} = 1.563311$	$Z_0/P_0 = 0.002657682$	
Run #2:		$N_{\infty} = 1.563360$	$Z_0/P_0 = 0.003186988$	
P(atm.)	Z(Burnett)	Z(Virial)	$Z_B - Z_V$	B_i and σ_{B_i}
701.449	1.86423	1.86423	-0.00000	$B_2 = 11.62527$ $\sigma = 0.01288$
347.045	1.44182	1.44177	0.00005	
191.860	1.24604	1.24606	-0.00002	
112.706	1.14425	1.14423	0.00002	$B_3 = 174.9200$ $\sigma = 1.9282$
68.5042	1.08723	1.08724	-0.00001	
42.4726	1.05377	1.05384	-0.00007	
26.6481	1.03356	1.03365	-0.00009	$B_4 = 814.5500$ $\sigma = 86.1629$
16.8416	1.02115	1.02121	-0.00006	
10.6906	1.01332	1.01344	-0.00011	
6.8060	1.00851	1.00854	-0.00003	$B_5 = 19134.01$ $\sigma = 1160.28$
4.3407	1.00552	1.00544	0.00008	
2.7715	1.00366	1.00347	0.00018	
517.434	1.64906	1.64906	-0.00000	$B_5 = 19134.01$ $\sigma = 1160.28$
270.051	1.34542	1.34548	-0.00006	
153.698	1.19707	1.19707	0.00000	
91.7634	1.11728	1.11720	0.00008	$B_5 = 19134.01$ $\sigma = 1160.28$
56.2974	1.07158	1.07155	0.00003	
35.0986	1.04441	1.04441	-0.00000	
22.0962	1.02789	1.02786	0.00003	$B_5 = 19134.01$ $\sigma = 1160.28$
13.9931	1.01765	1.01760	0.00004	
8.8948	1.01129	1.01117	0.00012	
5.6664	1.00716	1.00711	0.00005	$B_5 = 19134.01$ $\sigma = 1160.28$
3.6151	1.00453	1.00453	0.00000	
2.3082	1.00272	1.00289	-0.00017	
CHK = $3.83630(10^{-8})$			$\Sigma(Z_B - Z_V)^2 = 1.33668(10^{-7})$	
$\Sigma Z_B - Z_V = 1.31718(10^{-3})$			$(Z_B - Z_V)_{\text{AVE}} = 1.99488(10^{-6})$	

TABLE 4

EXPERIMENTAL AND CALCULATED RESULTS FOR
100.00% HELIUM AT -170°C

Run #1:	$N_{\infty} = 1.563277$		$Z_0/P_0 = 0.002789038$	
Run #2:	$N_{\infty} = 1.563311$		$Z_0/P_0 = 0.003332152$	
P(atm.)	Z(Burnett)	Z(Virial)	$Z_B - Z_V$	B_i and σ_{B_i}
697.208	1.94454	1.94455	-0.00000	$B_2 = 11.53950$ $\sigma = 0.00745$
337.723	1.47232	1.47230	0.00002	
184.843	1.25966	1.25964	0.00003	
108.053	1.15108	1.15108	-0.00000	$B_3 = 172.9100$ $\sigma = 1.0669$
65.5137	1.09099	1.09103	-0.00004	
40.5641	1.05597	1.05605	-0.00008	
25.4326	1.03496	1.03499	-0.00003	
16.0651	1.02199	1.02204	-0.00005	
10.1958	1.01394	1.01396	-0.00001	$B_4 = 1145.739$ $\sigma = 45.621$
6.4900	1.00895	1.00887	0.00008	
4.1383	1.00572	1.00565	0.00007	
2.6416	1.00359	1.00361	-0.00001	
512.059	1.70626	1.70624	0.00002	$B_5 = 18119.77$ $\sigma = 587.88$
262.786	1.36878	1.36887	-0.00008	
148.378	1.20817	1.20814	0.00003	
88.2355	1.12313	1.12306	0.00007	
54.0191	1.07489	1.07487	0.00001	
33.6389	1.04638	1.04639	-0.00000	
21.1626	1.02909	1.02907	0.00001	
13.3969	1.01842	1.01836	0.00007	
8.5123	1.01161	1.01164	-0.00004	
5.4222	1.00736	1.00741	-0.00005	
3.4594	1.00474	1.00472	0.00001	
CHK = $2.17787(10^{-8})$			$\Sigma(Z_B - Z_V)^2 = 4.64238(10^{-8})$	
$\Sigma Z_B - Z_V = 8.33166(10^{-4})$			$(Z_B - Z_V)_{\text{AVE}} = 1.27802(10^{-6})$	

TABLE 5

EXPERIMENTAL AND CALCULATED RESULTS FOR
100.00% HELIUM AT -190°C

Run #1: $N_{\infty} = 1.563218$ $Z_0/P_0 = 0.003100647$				
Run #2: $N_{\infty} = 1.563172$ $Z_0/P_0 = 0.003664451$				
P(atm.)	Z(Burnett)	Z(Virial)	$Z_B - Z_V$	B_i and σ_{B_i}
707.020	2.19222	2.19223	-0.00001	$B_2 = 11.05842$
321.708	1.55925	1.55928	-0.00003	
171.039	1.29584	1.29580	0.00004	$\sigma = 0.00938$
98.6461	1.16827	1.16815	0.00011	$B_3 = 184.4493$
59.4160	1.09994	1.09986	0.00009	
36.6613	1.06092	1.06093	-0.00001	
22.9425	1.03783	1.03781	0.00002	
14.4777	1.02376	1.02372	0.00001	$\sigma = 1.2035$
9.1823	1.01500	1.01499	-0.00001	
5.8422	1.00951	1.00951	-0.00000	$B_4 = 1315.162$
3.7245	1.00605	1.00605	0.00007	
2.3770	1.00370	1.00386	-0.00016	$\sigma = 46.199$
513.660	1.88228	1.88224	0.00004	$B_5 = 23733.74$
250.687	1.43591	1.43593	-0.00003	
138.255	1.23785	1.23792	-0.00007	$\sigma = 534.63$
81.3006	1.13782	1.13783	-0.00002	
49.4945	1.08275	1.08281	-0.00006	
30.7307	1.05085	1.05090	-0.00005	
19.3012	1.03169	1.03174	-0.00004	
12.2067	1.01992	1.01997	-0.00006	
7.7528	1.01258	1.01264	-0.00006	
4.9372	1.00798	1.00803	-0.00005	
3.1499	1.00524	1.00512	0.00012	
2.0112	1.00333	1.00326	0.00007	
CHK = $3.24424(10^{-8})$				$\Sigma(Z_B - Z_V)^2 = 9.67731(10^{-8})$
$\Sigma Z_B - Z_V = 1.19001(10^{-3})$				$(Z_B - Z_V)_{\text{AVE}} = -5.40438(10^{-6})$

TABLE 6

EXPERIMENTAL AND CALCULATED RESULTS FOR
87.77% HELIUM AT -160°C

Run #1:		$N_{\infty} = 1.562995$	$Z_0/P_0 = 0.005863029$		
Run #2:		$N_{\infty} = 1.562989$	$Z_0/P_0 = 0.006803262$		
P(atm.)	Z(Burnett)	Z(Virial)	$Z_B - Z_V$	B_i and σ_{B_i}	
218.759	1.28259	1.28259	0.00000	$B_2 = 9.62535$ $\sigma = 0.01358$	
125.751	1.15232	1.15227	0.00004		
75.9193	1.08731	1.08732	-0.00001	$B_3 = 229.8796$ $\sigma = 2.4505$	
46.9997	1.05206	1.05214	-0.00009		
29.4951	1.03191	1.03194	-0.00004		
18.6521	1.01992	1.01989	0.00004		
11.8480	1.01259	0.01250	0.00009	$B_4 = 4547.541$ $\sigma = 100.425$	
7.5459	1.00799	1.00791	0.00007		
4.8138	1.00506	1.00503	0.00003		
3.0739	1.00309	1.00320	-0.00011		
180.505	1.22802	1.22804	-0.00002	$\sigma = 100.425$	
105.881	1.12583	1.12581	0.00002		
64.5823	1.07327	1.07328	-0.00001		
40.1997	1.04414	1.04419	-0.00005		
25.3042	1.02724	1.02724	0.00000		
16.0298	1.01708	1.01702	0.00006		
10.1929	1.01083	1.01073	0.00010		
6.4960	1.00687	1.00680	0.00007		
4.1455	1.00429	1.00433	-0.00004		
2.6480	1.00265	1.00276	-0.00010		
CHK = $2.71052(10^{-8})$			$\Sigma(Z_B - Z_V)^2 = 7.26473(10^{-8})$		
$\Sigma Z_B - Z_V = 9.85699(10^{-4})$			$(Z_B - Z_V)_{\text{AVE}} = 3.24830(10^{-6})$		

TABLE 7

EXPERIMENTAL AND CALCULATED RESULTS FOR
87.77% HELIUM AT -170°C

Run #1: $N_{\infty} = 1.563050$ $Z_0/P_0 = 0.009346075$				
Run #2: $N_{\infty} = 1.563107$ $Z_0/P_0 = 0.01135285$				
P(atm.)	Z(Burnett)	Z(Virial)	$Z_B - Z_V$	B_i and σ_{B_i}
123.774	1.15680	1.15682	-0.00002	$B_2 = 8.63729$ $\sigma = 0.01699$
74.4737	1.08790	1.08786	0.00003	
46.0593	1.05162	1.05167	-0.00005	$B_3 = 234.6565$ $\sigma = 4.4250$
28.9002	1.03135	1.03135	-0.00000	
18.2763	1.01943	1.01940	0.00003	$B_4 = 5017.328$ $\sigma = 263.225$
11.6094	1.01215	1.01215	0.00000	
7.3951	1.00774	1.00767	0.00007	
4.7181	1.00495	1.00486	0.00008	
3.0126	1.00297	1.00309	-0.00012	
98.7404	1.12099	1.12095	0.00003	
60.2636	1.06938	1.06939	-0.00001	
37.5458	1.04139	1.04144	-0.00005	
23.6512	1.02538	1.02538	-0.00000	
14.9902	1.01583	1.01580	0.00003	
9.5350	1.00999	1.00993	0.00006	
6.0776	1.00627	1.00628	-0.00002	
3.8791	1.00391	1.00399	-0.00009	
2.4784	1.00261	1.00254	0.00006	
CHK = $3.98139(10^{-8})$			$\Sigma(Z_B - Z_V)^2 = 5.16134(10^{-8})$	
$\Sigma Z_B - Z_V = 7.65070(10^{-4})$			$(Z_B - Z_V)_{\text{AVE}} = 2.26539(10^{-6})$	

TABLE 8

EXPERIMENTAL AND CALCULATED RESULTS FOR
87.77% HELIUM AT -190°C

Run #1:	$N_{\infty} = 1.563012$	$Z_0/P_0 = 0.06014626$		
Run #2:	$N_{\infty} = 1.563063$	$Z_0/P_0 = 0.07192886$		
P(atm.)	Z(Burnett)	Z(Virial)	$Z_B - Z_V$	B_i and σ_{B_i}
16.8878	1.01574	1.01573	0.00000	$B_2 = 6.17366$ $\sigma = 0.02394$
10.7427	1.00990	1.00991	-0.00000	
6.8482	1.00624	1.00627	-0.00003	
4.3718	1.00403	1.00399	0.00005	
2.7929	1.00253	1.00254	-0.00001	
14.0841	1.01305	1.01306	-0.00000	$B_3 = 115.1844$ $\sigma = 12.3884$
8.9679	1.00824	1.00824	-0.00000	
5.7202	1.00522	1.00523	-0.00001	
3.6529	1.00338	1.00333	0.00005	
2.3340	1.00209	1.00212	-0.00003	
CHK = $9.00548(10^{-9})$		$\Sigma(Z_B - Z_V)^2 = 7.42261(10^{-9})$		
$\Sigma Z_B - Z_V = 2.05060(10^{-4})$		$(Z_B - Z_V)_{\text{AVE}} = 9.57850(10^{-7})$		

TABLE 9

EXPERIMENTAL AND CALCULATED RESULTS FOR
75.29% HELIUM AT -160°C

Run #1: $N_{\infty} = 1.563068$ $Z_0/P_0 = 0.008893446$				
Run #2: $N_{\infty} = 1.563026$ $Z_0/P_0 = 0.01106194$				
P(atm.)	Z(Burnett)	Z(Virial)	$Z_B - Z_V$	B_i and σ_{B_i}
124.032	1.10307	1.10306	0.00001	$B_2 = 2.84500$
75.4285	1.04849	1.04854	-0.00004	
47.1561	1.02455	1.02453	0.00001	$\sigma = 0.01260$
29.8361	1.01321	1.01318	0.00003	
18.9798	1.00744	1.00745	-0.00001	$B_3 = 394.2572$
12.1058	1.00437	1.00437	-0.00000	
7.7315	1.00262	1.00264	-0.00002	$\sigma = 3.4149$
4.9414	1.00161	1.00162	-0.00001	
3.1595	1.00103	1.00101	0.00002	
96.7873	1.07066	1.07068	-0.00002	$B_4 = 6070.033$
59.8381	1.03457	1.03449	0.00008	
37.6702	1.01796	1.01799	-0.00003	$\sigma = 211.771$
23.9100	1.00988	1.00992	-0.00004	
15.2348	1.00574	1.00572	0.00002	
9.7243	1.00338	1.00341	-0.00003	
6.2131	1.00203	1.00208	-0.00005	
3.9725	1.00138	1.00129	0.00009	
2.5400	1.00078	1.00081	-0.00002	
CHK = $2.63382(10^{-8})$ $\Sigma(Z_B - Z_V)^2 = 2.49561(10^{-8})$				
$\Sigma Z_B - Z_V = 5.33962(10^{-4})$ $(Z_B - Z_V)_{\text{AVE}} = -7.69060(10^{-7})$				

TABLE 10
EXPERIMENTAL AND CALCULATED RESULTS FOR
75.29% HELIUM AT -170°C

Run #1: $N_{\infty} = 1.562824$ $Z_0/P_0 = 0.02010412$				
Run #2: $N_{\infty} = 1.562812$ $Z_0/P_0 = 0.02536875$				
P(atm.)	Z(Burnett)	Z(Virial)	$Z_B - Z_V$	B_i and σ_{B_i}
50.7032	1.01934	1.01935	-0.00001	$B_2 = 1.09346$
32.1076	1.00877	1.00877	-0.00000	
20.4557	1.00438	1.00437	0.00001	$\sigma = 0.02601$
13.0628	1.00236	1.00235	0.00001	
8.3500	1.00133	1.00134	-0.00001	$B_3 = 249.0742$
5.3402	1.00083	1.00079	0.00004	
3.4158	1.00046	1.00048	-0.00002	$\sigma = 14.4485$
39.9181	1.01267	1.01265	0.00002	$B_4 = 21312.08$
25.3756	1.00603	1.00603	-0.00000	
16.1897	1.00307	1.00314	-0.00006	$\sigma = 1838.27$
10.3455	1.00173	1.00174	-0.00002	
6.6158	1.00111	1.00102	0.00009	
4.2312	1.00062	1.00061	0.00001	
2.7067	1.00035	1.00038	-0.00003	
CHK = $1.42202(10^{-8})$			$\Sigma(Z_B - Z_V)^2 = 1.71704(10^{-8})$	
$\Sigma Z_B - Z_V = 3.34930(10^{-4})$			$(Z_B - Z_V)_{\text{AVE}} = 1.57774(10^{-6})$	

TABLE 11
EXPERIMENTAL AND CALCULATED RESULTS FOR
75.29% HELIUM AT -190°C

Run #1: $N_{\infty} = 1.563541$ $Z_0/P_0 = 0.1287187$				
Run #2: $N_{\infty} = 1.563426$ $Z_0/P_0 = 0.1563508$				
P(atm.)	Z(Burnett)	Z(Virial)	$Z_B - Z_V$	B_i and σ_{B_i}
7.7087	0.99226	0.99228	-0.00000	$B_2 = -6.79800$ $\sigma = 0.02297$
4.9443	0.99506	0.99504	0.00001	
3.1680	0.99688	0.99682	0.00004	
2.0283	0.99791	0.99796	-0.00007	
6.3554	0.99367	0.99363	0.00004	
4.0741	0.99587	0.99591	-0.00005	
2.6097	0.99735	0.99738	-0.00004	
1.6709	0.99835	0.99832	0.00001	
CHK = $1.04443(10^{-8})$			$\Sigma(Z_B - Z_V)^2 = 1.32131(10^{-8})$	
$\Sigma Z_B - Z_V = 2.81047(10^{-4})$			$(Z_B - Z_V)_{\text{AVE}} = -6.75678(10^{-6})$	

TABLE 12
EXPERIMENTAL AND CALCULATED RESULTS FOR
44.56% HELIUM AT -160°C

Run #1: $N_{\infty} = 1.563421$ $Z_0/P_0 = 0.02118666$				
Run #2: $N_{\infty} = 1.563331$ $Z_0/P_0 = 0.02607363$				
P(atm.)	Z(Burnett)	Z(Virial)	$Z_B - Z_V$	B_i and σ_{B_i}
40.9855	0.86834	0.86834	0.00000	$B_2 = -32.2801$ $\sigma = 0.0231$
27.4286	0.90851	0.90853	-0.00001	
18.1222	0.93844	0.93844	0.00000	
11.8502	0.95938	0.95935	0.00003	$B_3 = 1312.275$ $\sigma = 14.884$
7.6910	0.97347	0.97347	-0.00001	
4.9664	0.98276	0.98282	-0.00005	
3.1966	0.98895	0.98892	0.00003	$B_4 = -11209.61$ $\sigma = 2192.50$
34.0672	0.88826	0.88826	-0.00000	
22.6603	0.92365	0.92366	-0.00001	
14.8956	0.94917	0.94913	0.00004	
9.7034	0.96662	0.96662	0.00000	
6.2815	0.97824	0.97830	-0.00005	
4.0498	0.98597	0.98598	-0.00000	
2.6037	0.99099	0.99097	0.00002	
CHK = $9.76740(10^{-9})$			$\Sigma(Z_B - Z_V)^2 = 1.00644(10^{-8})$	
$\Sigma Z_B - Z_V = 2.69523(10^{-4})$			$(Z_B - Z_V)_{\text{AVE}} = -1.06449(10^{-6})$	

TABLE 13

EXPERIMENTAL AND CALCULATED RESULTS FOR
44.56% HELIUM AT -170°C

Run #1: $N_{\infty} = 1.563044$ $Z_0/P_0 = 0.05475752$				
Run #2: $N_{\infty} = 1.563177$ $Z_0/P_0 = 0.06581494$				
P(atm.)	Z(Burnett)	Z(Virial)	$Z_B - Z_V$	B_i and σ_{B_i}
16.7706	0.91831	0.91832	-0.00000	$B_2 = -40.5956$
11.0577	0.94640	0.94638	0.00002	$\sigma = 0.0374$
7.2143	0.96510	0.96514	-0.00004	
4.6747	0.97747	0.97747	-0.00000	
3.0154	0.98551	0.98549	0.00002	$B_3 = 1268.757$
14.1492	0.93123	0.93121	0.00001	$\sigma = 21.898$
9.2827	0.95500	0.95505	-0.00006	
6.0376	0.97095	0.97086	0.00008	
3.9030	0.98117	0.98120	-0.00003	
2.5141	0.98792	0.98791	0.00001	
CHK = $2.12021(10^{-8})$			$\Sigma(Z_B - Z_V)^2 = 1.42277(10^{-8})$	
$\Sigma Z_B - Z_V = 2.78437(10^{-4})$			$(Z_B - Z_V)_{\text{AVE}} = 1.44322(10^{-6})$	

TABLE 14

EXPERIMENTAL AND CALCULATED RESULTS FOR
30.13% HELIUM AT -160°C

Run #1: $N_{\infty} = 1.563346$ $Z_0/P_0 = 0.02985032$				
Run #2: $N_{\infty} = 1.563378$ $Z_0/P_0 = 0.03673658$				
P(atm.)	Z(Burnett)	Z(Virial)	$Z_B - Z_V$	B_i and σ_{B_i}
27.3917	0.81765	0.81763	0.00002	$B_2 = -56.7904$
18.8174	0.87812	0.87815	-0.00002	
12.6102	0.91996	0.91993	0.00003	$\sigma = 0.0163$
8.3109	0.94786	0.94791	-0.00005	
5.4198	0.96634	0.96633	0.00002	$B_3 = 1730.987$
3.5098	0.97833	0.97831	0.00001	
				$\sigma = 5.752$
23.0927	0.84835	0.84838	-0.00003	
15.6634	0.89958	0.89959	-0.00000	
10.4071	0.93443	0.93437	0.00006	
6.8209	0.95744	0.95744	0.00000	
4.4316	0.97253	0.97254	-0.00002	
2.8633	0.98234	0.98234	-0.00000	
CHK = $1.29216(10^{-8})$			$\Sigma(Z_B - Z_V)^2 = 9.92392(10^{-9})$	
$\Sigma Z_B - Z_V = 2.74673(10^{-4})$			$(Z_B - Z_V)_{\text{AVE}} = 7.04968(10^{-7})$	

TABLE 15
EXPERIMENTAL AND CALCULATED RESULTS FOR
30.13% HELIUM AT -170°C

Run #1: $N_{\infty} = 1.563851$ $Z_0/P_0 = 0.06738365$				
Run #2: $N_{\infty} = 1.563683$ $Z_0/P_0 = 0.08590859$				
P(atm.)	Z(Burnett)	Z(Virial)	$Z_B - Z_V$	B_i and σ_{B_i}
13.0882	0.88193	0.88197	-0.00004	$B_2 = - 70.7607$ $\sigma = 0.0592$
8.7605	0.92316	0.92313	0.00003	
5.7665	0.95028	0.95028	0.00001	
3.7563	0.96804	0.96797	0.00007	
2.4301	0.97936	0.97943	-0.00007	
10.5516	0.90647	0.90640	0.00007	$B_3 = 1964.419$ $\sigma = 43.120$
6.9918	0.93923	0.93928	-0.00006	
4.5740	0.96078	0.96082	-0.00004	
2.9678	0.97477	0.97480	-0.00003	
1.9156	0.98387	0.98383	0.00004	
CHK = $2.29415(10^{-8})$ $\Sigma(Z_B - Z_V)^2 = 2.34610(10^{-8})$				
$\Sigma Z_B - Z_V = 4.39718(10^{-4})$ $(Z_B - Z_V)_{\text{AVE}} = - 2.08017(10^{-6})$				

TABLE 16

EXPERIMENTAL AND CALCULATED RESULTS FOR
100.00% NITROGEN AT -160°C

Run #1: $N_{\infty} = 1.562652$ $Z_0/P_0 = 0.04319787$				
Run #2: $N_{\infty} = 1.562557$ $Z_0/P_0 = 0.05351136$				
P(atm.)	Z(Burnett)	Z(Virial)	$Z_B - Z_V$	B_i and σ_{B_i}
16.3509	0.70632	0.70640	-0.00008	$B_2 = -121.2347$
11.9727	0.80819	0.80808	0.00010	$\sigma = 0.2865$
8.3061	0.87615	0.87630	-0.00015	
5.5856	0.92068	0.92068	-0.00000	$B_3 = -822.6764$
3.6860	0.94942	0.94923	0.00019	
14.2036	0.76006	0.75991	0.00015	$\sigma = 368.8199$
10.0974	0.84428	0.84437	-0.00009	$B_4 = 889607.3$
6.8866	0.89974	0.90000	-0.00026	
4.5850	0.93601	0.93594	0.00007	$\sigma = 108823.3$
3.0072	0.95926	0.95901	0.00025	
CHK = 2.45417(10 ⁻⁷)			$\Sigma(Z_B - Z_V)^2 = 2.46099(10^{-7})$	
$\Sigma Z_B - Z_V = 1.35995(10^{-3})$			$(Z_B - Z_V)_{\text{AVE}} = 1.98216(10^{-5})$	

TABLE 17

EXPERIMENTAL AND CALCULATED RESULTS FOR
100.00% NITROGEN AT -170°C

Run #1:		$N_{\infty} = 1.564732$	$Z_0/P_0 = 0.08969387$	
Run #2:		$N_{\infty} = 1.565250$	$Z_0/P_0 = 0.1104292$	
P(atm.)	Z(Burnett)	Z(Virial)	$Z_B - Z_V$	B_i and σ_{B_i}
8.9413	0.80198	0.80213	-0.00016	$B_2 = -161.8303$
6.2034	0.87068	0.87002	0.00066	
4.1691	0.91554	0.91549	0.00005	$\sigma = 0.6012$
2.7497	0.94483	0.94540	-0.00057	
7.5775	0.83677	0.83695	-0.00018	$B_3 = 8817.199$
5.1707	0.89375	0.89350	0.00025	$\sigma = 574.498$
3.4407	0.93087	0.93101	-0.00014	
2.2556	0.95519	0.95554	-0.00035	
CHK = $1.06099(10^{-6})$		$\Sigma(Z_B - Z_V)^2 = 1.02325(10^{-6})$		
$\Sigma Z_B - Z_V = 2.35647(10^{-3})$		$(Z_B - Z_V)_{\text{AVE}} = -5.44492(10^{-5})$		

Another listed quantity of interest is the discrepancy between $Z(\text{Burnett})$ and $Z(\text{Virial})$. It should be noted that the values for these discrepancies were calculated with more precision than reported for $Z(\text{Burnett})$ and $Z(\text{Virial})$ and quite often the difference in the reported compressibilities does not seem to equal the reported discrepancy. This is entirely a consequence of rounding-off the compressibility values. The last column contains the optimal virial coefficients and the standard deviation for each one.

Finally four quantities are listed which should offer some insight into the confidence with which the results may be viewed. They are the optimal value of the CHK function defined by Equation 113, the sum of the squares of the discrepancies between $Z(\text{Burnett})$ and $Z(\text{Virial})$, the average discrepancy and the sum of the absolute values of these discrepancies.

Appendix C contains a discussion of the expected experimental errors. The random error should be reduced to a negligible amount for all sets of data, but the maximum systematic error expected ranges from 0.55% for pure nitrogen at -160°C to 0.04% for helium rich mixtures at low pressure. The actual error would be much less than these maximum values.

The "goodness of fit" may be inferred from the CHK value. This quantity is a fair indication of the agreement between observed and calculated values for P_j/P_{j-1} and with the exception of 100% N_2 at -170°C is always less than

$5.5(10^{-8})$. The large value for this isotherm is a consequence of the fact that there simply are not enough data points to treat properly.

Interaction Virial Coefficients

Interaction second coefficients have been calculated from the mixture values. The equations relating mixture, interaction and pure component virial coefficients are

$$B_2 = \sum_{i=1}^2 \sum_{j=1}^2 B_{ij} x_i x_j \quad (115)$$

The coefficient $B_{\text{He-N}_2}$ can be found by applying the development of Chapter IV. The pure component coefficients may be inserted or calculated for comparison. The compositions are required and accuracy here is critical.

The U.S. Bureau of Mines supplied a mass spectrometer composition analysis with the samples. These values were checked by a molecular weight determination in this laboratory using a method similar to that described by Canfield [6]. The two sets of values are presented in Table 18 along with the composition of the mixtures used by Canfield. Finally the interaction second virial coefficients are presented for the -170°C and -160°C isotherms in Table 19.

TABLE 18
HELIUM-NITROGEN MIXTURE COMPOSITIONS

Canfield [6]	U.S. Bureau of Mines	Molecular Weight
87.68	87.60	87.77
75.23	75.20	75.29
44.56	44.50	44.56
30.06	30.11	30.13

All entries are mole per cent helium

TABLE 19
HELIUM-NITROGEN INTERACTION VIRIAL COEFFICIENTS

T	$B_{\text{He-N}_2}$
-160°C	11.26
-170°C	10.94

Second virial coefficient in cc/mol

CHAPTER VII

RESULTS AND CONCLUSIONS

A Burnett apparatus was available at the University of Oklahoma for very accurate determination of the compressibility factors of gases. As previously assembled, the equipment was operable to 700 atmospheres between 50°C and -90°C.

A major modification of the temperature bath extended the range of applicability to -190°C and 700 atmospheres. The temperature control was $\pm 0.005^\circ\text{C}$ across the Burnett apparatus in the new configuration. A technique was also developed which allowed use of valves completely immersed in the cryostat.

The helium-nitrogen system was studied at -160°C, -170°C and -190°C at maximum pressures ranging from near saturation for nitrogen bearing mixtures to 700 atmospheres for helium. The compressibility factors derived from the observed data should exhibit maximum errors ranging from 0.55% for nitrogen to 0.04% for helium.

An extensive study of polynomial approximations for infinite series yielded a scheme for assigning realistic variances to the polynomial coefficients as compared

with the series coefficients. This allowed choice of optimal virial coefficients from the experimental compressibility data.

Finally, an optimum search routine was developed to reduce the Burnett data to compressibility factors. This was essentially a problem in non-linear curve fitting. The results were very gratifying and seem to indicate that more accurate information could be extracted from the data in this manner than was possible with earlier techniques.

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APPENDIX A

SOME SPECIFIC INFORMATION CONCERNING THE EQUIPMENT

The following information was not considered vital to the main body of discussion, but it should prove useful to anyone working with this particular apparatus in the future and to anyone working with a similar piece of equipment. These specifics can be logically presented under the general headings of temperature measurement and pressure measurement.

Temperature Measurement

The Callendar-Van Dusen equation was used to relate the resistance of the thermometers to the absolute temperature above -182.97°C . The equation is

$$R_T = R_0 + \alpha R_0 \left[\frac{(1+\delta)}{10^2} T - \frac{\delta}{10^4} T^2 + \frac{\beta}{10^6} T^3 - \frac{\beta}{10^8} T^4 \right] \quad (\text{A-1})$$

where R_T is the resistance at $T^{\circ}\text{C}$, R_0 is the resistance in ohms at 0°C and α , β and δ are calibration constants. The values of these quantities are

Thermometer #1617523

Date of Calibration: May 17, 1963

Range: 444.6°C to -182.97°C

$$\alpha = 0.0039266_{19}$$

$$\beta = 0.110_{35} \text{ (below } 0^{\circ}\text{C)}$$

$$\delta = 1.491_{36}$$

$$R_0 \text{ (May 30, 1966) } = 25.5512 \, \Omega \text{ (ice point)}$$

Thermometer #1665930

Range: 444.6°C to -261.15°C

Date of Calibration: March 9, 1966

$$\alpha = 0.003926145$$

$$\beta = 0.11054 \text{ (below } 0^{\circ}\text{C)}$$

$$\delta = 1.49154$$

$$R_0 \text{ (May 30, 1966) } = 25.5331 \, \Omega \text{ (ice point)}$$

Only #1665930 was used to measure the temperature below -182.97°C . Because the Callendar-Van Dusen equation does not hold in this region, the point-by-point calibration supplied by the National Bureau of Standards was employed to relate the resistance to temperature.

The G-2 Mueller bridge was set up with equal ratio arms to insure that the true resistance of the thermometers would be the averages of normal and reverse readings. As an added precaution the resistance of the thermometer leads was equalized within a few ten-thousands of an ohm to render any imperfection in the adjustment of the ratio arms negligible.

Pressure Measurement

The elements involved in pressure measurement are the dead-weight gages, the weights and the differential pressure indicators. Some particulars should be mentioned for each item.

Ruska Instrument Corporation provides a list of instrument constants with each dead-weight gage. These constants are (for the gages in this laboratory)

	<u>High Pressure Gage</u>	<u>Low Pressure Gage</u>
Effective Area at 25°C and 1 atm, in. ²	0.0260430	0.130220
Coefficient of Superficial Thermal Expansion, (°C) ⁻¹	1.7×10^{-5}	1.7×10^{-5}
Fraction Change of Area per Unit Pressure Change, (psi) ⁻¹	-3.6×10^{-8}	-4.8×10^{-8}
Resolution	< 5 PPM	< 5 PPM
Plane of Reference	0.04 in. below line on sleeve weight	0.10 in. below line on sleeve weight

The weights furnished by the manufacturer were precisely machined stainless steel masses which were calibrated against a set of Class S standards. The results of this calibration are given in Table A-1. In addition, a set of Class C standard weights up to 500 mg were used for fine balancing.

The manufacturer's specifications for accuracy and sensitivity of the differential pressure indicators are:

Accuracy: $\pm 1\text{-}1/2$ scale divisions at null

Sensitivity: 0.0001 psi/scale division, maximum

Blancett measured the sensitivity of the indicators in situ and found that the room temperature indicator exhibited 0.00005 psi/division while at -183°C the cryogenic indicator exhibited 0.0004 psi/division. These values were not re-measured and his results were taken as indicative of the behavior under the conditions experienced in this work.

TABLE A-1

CALIBRATION DATA FOR WEIGHTS

Letter Designation	Apparent Mass vs. Brass, Pounds
A	26.03576
B	26.03564
C	26.03567
D	26.03569
E	26.03575
F	26.03500
G	26.03511
H	26.03504
I	26.03513
J	26.03543
K	26.03552
L	13.01812
M	5.20716
N	5.20718
O	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
<u>X</u>	0.01302
<u>A</u>	0.00521
<u>A</u>	0.00521
<u>B</u>	0.00260
<u>C</u>	0.00130
Tare High	0.78104
Tare Low	0.78107

The zero shift of the indicators (described in Chapter III) has a bearing on the values of the constants k_i and m_i in Equations 8 and 9. These constants were derived taking into account the pressure deformation of the Burnett cells, the cryogenic valves, the magnetic pump, the connecting tubing and the cryogenic differential pressure cell. However, another factor had to be considered--the fact that a zero shift indicated that the position of the diaphragm in the differential pressure cell was a function of pressure at the electronic null and would therefore contribute to the pressure effect on the cell constant (see Figure 6). When all these factors are combined the following results were obtained (see Blancett for detailed analysis):

TABLE A-2

CONSTANTS FOR PRESSURE EFFECT ON THE CELL CONSTANT

$T^{\circ}\text{C}$	k_1	k_2	k_3	k_4	k_5	k_6
-160.00	1.0	$1.25(10^{-6})$	$-6.56(10^{-9})$	$2.03(10^{-11})$	$-2.87(10^{-14})$	$1.48(10^{-17})$
-170.00	1.0	$1.19(10^{-6})$	$-6.10(10^{-9})$	$1.86(10^{-11})$	$-2.60(10^{-14})$	$1.34(10^{-17})$
-180.00	1.0	$1.16(10^{-6})$	$-5.86(10^{-9})$	$1.78(10^{-11})$	$-2.47(10^{-14})$	$1.26(10^{-17})$
-190.00	1.0	$1.15(10^{-6})$	$-5.32(10^{-9})$	$1.57(10^{-11})$	$-2.15(10^{-14})$	$1.09(10^{-17})$
$T^{\circ}\text{C}$	m_1	m_2	m_3	m_4	m_5	m_6
-160.00	1.0	$1.67(10^{-6})$	$-9.81(10^{-9})$	$3.04(10^{-11})$	$-4.29(10^{-14})$	$2.21(10^{-17})$
-170.00	1.0	$1.60(10^{-6})$	$-9.12(10^{-9})$	$2.79(10^{-11})$	$-3.89(10^{-14})$	$2.01(10^{-17})$
-180.00	1.0	$1.54(10^{-6})$	$-8.76(10^{-9})$	$2.66(10^{-11})$	$-3.69(10^{-14})$	$1.88(10^{-17})$
-190.00	1.0	$1.46(10^{-6})$	$-7.96(10^{-9})$	$2.35(10^{-11})$	$-3.22(10^{-14})$	$1.63(10^{-17})$

APPENDIX B

EXPERIMENTAL PROCEDURE AND PROBLEMS

The experimental procedure is designed to be as consistent as possible with the Burnett analysis. In particular, a constant temperature is sought for the period before an expansion and after re-equilibration. Also the amount of gas in V_a before an expansion should be equal to the amount in V_a and V_b after the expansion (i.e., no leaks). Finally, the amount of gas in V_a should be the same before and after closing the expansion valve during a measurement.

Pre-charging Procedure

In the most general case, the apparatus had to be brought from ambient temperature and pressure containing air to the experimental temperature and pressure containing the desired mixture. This alteration proceeded in the following manner.

The room-temperature differential pressure indicator was zeroed. Then the vacuum pump was turned ON and the liquid-nitrogen transfer line and the phase separator were evacuated to 10μ Hg. These were then closed off and the rest of the system (except for that section used exclusively

in charging) was opened to the pump. A pressure of three to four psi was then applied to the liquid-nitrogen transfer dewar which caused the nitrogen to flow via the phase separator into the cryostat. The thermotrol was adjusted to the appropriate setting for the desired temperature and the control heater was set to pulse at 25-30 watts with about 1/4 ON time. The liquid-nitrogen metering valve was opened several turns and cool-down was under way.

The bath would reach any of the experimental temperatures (-160° , -170° , and -190°C) in about three hours. The apparatus within the cryostat equilibrated much slower, however, requiring from eight hours at -160°C to twelve hours at -190°C . During this period the system pressure would easily reach $5\mu\text{ Hg}$, and the charging system, including the compressor, could be purged repeatedly (minimally three times at 100 atm and 3 times at 10 atm) with the desired mixture.

When the temperature was within a few tenths of a degree of the desired value, an adjustment had to be made on the circuitry of the cryogenic differential pressure indicator while the system was at low pressure. This was necessary because temperature had a very strong effect upon the operating characteristics of this instrument. The adjustment was made on a "trim pot" inside the indicator with a corresponding change of the zero control until a minimum deflection of the indicator needle occurred about the null

position when the sensitivity control was rotated through its full range. When this was done the maximum variation in null position was specified by the manufacturer as $\pm 1\text{--}1/2$ scale divisions. This adjustment caused a severe upset in the behavior of the indicator which usually required from 30 min. to several hours to stabilize. When the spasmodic lurching of the indicator needle ceased, the sensitivity knob was again rotated through its full range to check the behavior. If necessary the adjustment was repeated until the indicator exhibited the desired properties (usually the secondary adjustments caused very little upset to the circuitry and it stabilized quickly). With the pressure indicator operating properly, the temperature controller was adjusted, if necessary, to bring the temperature within $\pm 0.004^{\circ}\text{C}$ of the desired value.

Purging and Charging the System

The entire system was purged three times using the following procedure. First the cold trap (consisting of pure alcohol) was frozen by passing liquid nitrogen through the cooling coil. Then about 10 atm of the desired gas was bled into the system. This was done very slowly while simultaneously adjusting the piston gage hand pumps to avoid overpressuring the differential pressure indicators. This gas was then vented at various points and the entire system was evacuated to 10μ Hg. The cryogenic differential pressure indicator was zeroed at the desired temperature and 10μ Hg, and the system was ready to charge.

A sufficient number of weights was loaded upon the proper piston gage and the pressure was slowly brought up to the desired initial value. Again the hand pumps were adjusted to avoid overpressuring the pressure indicators. If cylinder pressure was not enough, the compressor was used to attain the required pressure. However, in the event the compressor was turned on, the charge and feed valves were only slightly opened and acted as snubbers for the pressure surges. The gas was then allowed to soak until it equilibrated at the desired temperature.

Measurements and Expansions

When the temperature remained constant at the desired value, the cells were isolated and a 5μ Hg vacuum was pulled on the rest of the system. The pressure was then monitored and equilibrium was assumed when it remained constant for 10-15 min. The facts that the pressure remained constant and the vacuum held at 5μ Hg were taken to indicate that the system was leak tight. At this point one of the expansion valves connecting the two cells was closed and the other necked down until it was only 1/8 turn open. (For the initial measurement both valves were closed because only the upper cell, V_a , contained any gas.) The pressure was very carefully measured at this point by nulling both differential pressure indicators simultaneously while the weights were floating at the proper level on the piston gage.

As soon as the nulling operation was complete, the cracked expansion valve was closed tight while the weights and indicator needles were balanced. This was done to proportion the gas properly between the two cells. Next the barometric pressure was recorded followed by the system temperature. Finally, the weights on the gage were recorded and double checked and the temperatures at the gage and in the room were noted.

Up to this point, the operation was usually trouble-free, barring freak accidents and operator bungling. However, when an expansion was made several undesirable things could (and often did) happen.

An expansion was effected by venting the lower cell, V_b (as slowly as practical to avoid undue upset of the equilibrium temperature). Then a 5μ Hg vacuum was pulled on this cell--this required 20-30 min. depending upon composition and pressure. This waiting period did serve to allow the temperature to return to the equilibrium value after the venting. When the evacuation was complete, the cell was isolated and one of the expansion valves was cracked to allow the gas to fill the lower cell. This was done as slowly as possible to avoid large temperature upsets and possible condensation of some of the mixtures. While the expansion was in progress, the differential pressure indicators were maintained in an approximately nulled position to avoid large overpressures. This was a rather touchy manipulation

requiring simultaneous adjustment of the hand pump in the oil system, venting of the intermediate gas system and several adjustments of the expansion valve to maintain a reasonably constant decrease in pressure. A pitfall in this operation was operating too quickly. If the expansion were rapid, there was a good chance that the intermediate gas would be vented fast enough to cause an overpressure from the bottom in the differential pressure cells--precisely the effect which was to be avoided.

At this point the system was again allowed to soak, and presumably would return to the set temperature. This was seldom the case. Usually, 2-4 hours were required for the temperature to equilibrate and, usually, the value was on the order of $\pm 0.02^{\circ}\text{C}$ different from the set temperature. This required an adjustment of the thermotrol after each expansion and necessitated an additional 30-45 min. wait for the desired equilibrium temperature.

A run was finished when the system pressure dropped below 2.0 atm. When this occurred the remaining pressure was vented and the zeroes on the differential pressure indicators checked. If necessary, they were re-zeroed before starting another run.

Some mechanical difficulties were noticed (possibly the understatement of this whole report) regarding the fan assembly and the cryogenic valves. Although the low temperature bearing was specified usable down to the boiling

point of nitrogen, it seemed to deteriorate quite rapidly at -190°C . While this could have been because of improper mounting (the bearings will only support a small axial loading, for example) it seemed to behave quite well at -160°C and slightly less well at -170°C . Extreme care should be used when mounting this bearing in future work to remove this variable in its operation.

The cryogenic valves also had to be mounted carefully. If they were not very nearly vertical and aligned very well with the stem extension, there was a good chance the stem would break in use. Furthermore, when shipped the threads and two-piece stem assembly were lubricated with MoS_2 grease. This had to be completely removed and replaced with dry MoS_2 to avoid freezing. The threads could be cleaned by washing directly with benzene and acetone, but it was more satisfactory to heat the two-piece stem assembly over a low flame prior to washing with the solvents. This caused the grease to flow out of a quite restricted volume and allowed its complete removal.

It was also noticed that these valve stem threads tended to gall after extended use. This could be minimized by carefully rounding the leading edge of the threads on the stem followed by working them in with MoS_2 powder. A very good bond of MoS_2 could be obtained with about 30 min. work and might save several hours by prolonging the valve life.

When the valves were first assembled, it was felt that the tip should be highly polished and worked in with MoS_2 before a satisfactory seal could be effected. In retrospect this does not seem to have made any real difference.

APPENDIX C

ERRORS

The errors inherent in a Burnett-type experiment are those associated with the measurement of temperature and pressure and those arising from inconsistencies between the experimental procedure and the analysis.

The measurement errors are those intrinsic to the instruments used and human error in their implementation. The inconsistencies are caused by incomplete evacuation of the lower cell before an expansion, temperature variation during a run and incorrect proportioning of the gas between the two cells.

Mueller [23], Canfield [6] and Blancett [2] have thoroughly discussed these factors and their developments will not be repeated here. However, the final equations used should be noted for the sake of consistency.

The above authors have shown that incomplete evacuation of the lower cell introduces negligible error and that the error due to incorrect proportioning can be included in the values for the Burnett constants. The effect of temperature and pressure uncertainties are reflected in the error defined by

$$\Delta Z_j \approx \frac{N_j^j \Delta P_j + j P_j N_j^{j-1} \Delta N - Z_j \Delta(P_0/Z_0)}{P_0/Z_0} + (\partial Z/\partial T)_P \Delta T \quad (C-1)$$

where it has been assumed that $N_1 = N_2 = \dots = N_j$ and that differentials may be replaced by Δ quantities defined as "true less calculated" values. It should be noted that this equation is simpler than that used by the previous authors although it is based upon their reasoning. The simplification was made possible because good estimates for ΔN and $\Delta(P_0/Z_0)$ are readily available from the searching procedure of the computer program presently used in the data treatment. The Δ quantities may be taken as the difference in two successive values of the constants as the minimum is approached. The maximum error caused by a temperature variation of ± 0.005 during the experimental runs was 0.012% at -190°C , 0.010% at -170°C and 0.009% at -160°C . The quantity P is given by

$$\Delta P_j = (P_j \times 10^{-4} + 3 \times 10^{-4}) \text{ atm} \quad (C-2)$$

The value of ΔT is always 0.01 while $\Delta N = \Delta(P_0/Z_0) = 5 \times 10^{-6}$. The partial derivative of Z with T was estimated from the experimental data for each isocomp-isotherm. Thus the maximum error is the sum of the value given by Equation C-2 and the temperature variation uncertainty.

Table C-1 is a list of the maximum errors for each isocomp-isotherm. The error is entered as a percentage. The actual error in the compressibility factors should be much less than these maximum values.

TABLE C-1

MAXIMUM EXPERIMENTAL ERRORS IN Z

Comp.	Temp. ($^{\circ}\text{C}$)	P (atm.)	ΔZ (%)	P (atm.)	ΔZ (%)
100% He	-160	700	0.04	2	0.04
100% He	-170	700	0.04	3	0.04
100% He	-190	700	0.05	2	0.04
88% He	-160	220	0.17	3	0.04
88% He	-170	125	0.11	3	0.04
88% He	-190	9	0.04		
75% He	-160	125	0.22	3	0.04
75% He	-170	50	0.11	3	0.03
75% He	-190	4	0.03		
45% He	-160	40	0.17	3	0.06
45% He	-170	9	0.05		
30% He	-160	16	0.53		
30% He	-170	7	0.27		
0% He	-160	8	0.55		
0% He	-170	5	0.39		

APPENDIX D

COMPUTER PROGRAMS

The following computer programs were used in the data treatment. The first program, PCALC, is written in Fortran II [15] and calculates the corrected pressures from the observables. The second program, BURNOR is written in extended ALGOL [5] and is the main data treatment routine which reduces the corrected pressures to compressibility factors, densities and virial coefficients. The final program is a general calling program for the ORNOR procedure of the data treatment program. This routine is written in ALGOL and produces a least-squares fit of data based upon the methods of Chapter IV and was useful in calculating interaction virial coefficients.

COMMENT PCALC PROGRAM

```

40KFORTTRANRUN
DIMENSION PAL(30),FMAL(30),PAH(30),FMAH(30),J(30)
READ 301,(FMAL(I),PAL(I),FMAH(I),PAH(I),I=1,29)
301  FORMAT(4F12.6)
101  PRINT 777
777  FORMAT(1H1,20HPRESSURE CALCULATION)
READ 100, DELT,RR,FMW,RHOG0,RHOG1,HCHB
READ 200, DPZSC, DELTA, KHL
100  FORMAT (F11.6,5F12.6)
200  FORMAT(2F11.6,13)
PRINT 701
701  FORMAT(1X,////28H INPUT VALUES ARE AS FOLLOWS)
PRINT 702, DELT
702  FORMAT(1X,13HDELTA TEMP = F12.6)
PRINT 703, RR, FMW
703  FORMAT(1X,6HR-R = F12.6/1X,19HMOLUCULAR WEIGHT = F12.6)
PRINT 704,RHOG0,RHOG1
704  FORMAT(1X,16HDENSITY SUB 0 = F12.6/1X,16HDENSITY SUB 1 = F12.6)
PRINT 705,HCHB
705  FORMAT(1X,8HHC-HB = F12.6)
PRINT 706,DPZSC,DELTA
706  FORMAT(1X,8HDPZSC = F12.6/1X,8HDELTA = F12.6)
READ 105,N,(J(L),L=1,N)
105  FORMAT(110,10X,30I2)
SUMA = 0.0
SUPA = 14.1
IF(KHL)51,55,61
C SUM OF LOW PRESSURES AND WEIGHTS
51  DO 6 L = 1, N
    I = J(L)
    SUMA = SUMA & FMAL(I)
    SUPA = SUPA & PAL(I)
    GO TO 53
C SUM OF HIGH PRESSURES AND WEIGHTS
61  DO 7 L = 1, N
    I = J(L)
    SUMA = SUMA & FMAH(I)
    SUPA = SUPA & PAH(I)
    GO TO 63
C PRINTING LOW PRESSURES AND WEIGHTS USED
53  DO 52 L = 1, N
    I = J(L)
    PRINT 800, PAL(I),FMAL(I)
    PRINT 801, SUPA, SUMA
    GO TO 76
C PRINTING HIGH PRESSURES AND WEIGHTS USED
63  DO 62 L = 1, N
    I = J(L)
    PRINT 800, PAH(I), FMAH(I)
    PRINT 801, SUPA, SUMA
800  FORMAT(16X,F11.5,28X,F11.5)
801  FORMAT(1X,15HSUM OF PRESS = F11.5,12X,17HSUM OF WEIGHTS = F11.5)
76  PB = 0.0333902*RR
    DPZSR = 0.130E-06*SUPA
    IF(KHL)50,55,60
    55  PRINT 500
    500 FORMAT(1X,22HKHL VALUE IS INCORRECT)
    GO TO 101
C CALCULATION OF PG, DPH FOR HIGH PRESSURE
60  PG=(2.61004*(SUMA&DELTA))/((1.0&(1.7E-05)*DELT)*(1.0-(3.6E-08)*SUP
    1A))
    DPH=(-0.00021 )&FMW*((-0.116)*RHOG0&HCHB&RHOG1)
    GO TO 75
C CALCULATION OF PG, DPH FOR LOW PRESSURE

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50 PG=(0.521989*(SUMA&DELTA))/((1.0&(1.7E-05)*DELT)*(1.0-(4.8E-08)*SU
    1PA))
    DPH =(-0.00057 )&FMW*((-0.116)*RHOG0&HCHB*RHOGI)
75 PCOR = PG&PB&DPH&DPZSR&DPZSC
802 PRINT 707
707 FORMAT(1X,32HCALCULATED VALUES ARE AS FOLLOWS)
    PRINT 708, PB
708 FORMAT(1X,22HBAROMETRIC PRESSURE = F11.5)
    PRINT 709, DPZSR
709 FORMAT(1X,8HDPZSR = F11.5)
    PRINT 710, PG, DPH
710 FORMAT(1X,16HGAGE PRESSURE = F11.5/1X,11HDELTA PH = F11.5)
    PRINT 400, PCOR
400 FORMAT(1X,7/22H CORRECTED PRESSURE = F11.5)
    GO TO 101
END

```

COMMENT BURNOR PROGRAM

```

00:35 AM      JULY 08, 1967      *****      DICK HALL      CSC
BEGIN
COMMENT THE PLOTTER PACKAGE IS NOT LISTED BUT GOES HERE;
PROCEDURE DPOW(X,XL,Y,YL,K);
  VALUE X,XL,K;
  REAL X,XL,Y,YL;
  INTEGER K;
  BEGIN
    LABEL DW;
    INTEGER I;
    Y+1.0; YL+0.0;
    IF K<1 THEN GO TO DW ELSE
      FOR I+1 STEP 1 UNTIL K DO
        DOUBLE(X,XL,Y,YL,X,+,Y,YL);
    DW: END OF DPOW;
  PROCEDURE DSQRT(X1,XL,Y1H,Y1L) ;
  VALUE      X1,XL ;
  REAL      X1,XL,Y1H,Y1L ;
  BEGIN
    INTEGER      T ;
    REAL      X,Y ;
    REAL ARRAY  CON[0:7] ;
    LABEL      L1,RETURN ;
    IF X1 = 0 THEN GO TO L1 ;
    CON[0] + 0.0000026973988 ;
    CON[1] + 0.000001603883 ;
    CON[2] + 0.0000076294 ;
    CON[4] + 2.137099#23 ;
    CON[3] + 0.000004536465 ;
    CON[5] + 1.270727#23 ;
    CON[6] + 7.555786#22 ;
    CON[7] + 4.482697#22 ;
    X + X1 * 1.0 ;
    T + 0 ;
    T + X.[8:2] ;
    T.[45:1] + X.[2:1] ;
    Y + X ;
    Y.[3:6] + Y.[2:6] ;
    Y + Y * CON[T] ;
    Y + (X/Y + Y) * 0.5 ;
    Y + (X/Y + Y) * 0.5 ;
    Y + (X/Y + Y) * 0.5 ;
    Y + (X/Y + Y) * 0.5 ;
    DOUBLE(X1,XL,Y,0,/,Y,0,-,0.5,X,Y,0,+,Y1H,Y1L) ;
    GO TO RETURN ;
    Y1H + Y1L + 0 ;
  L1:
  RETURN:  END;
  REAL TOM,TOML, HAM,HAML;
  LABEL L60;
  REAL LOWDDXI,DBDUM;
  INTEGER IXQ;  BOOLEAN ARRAY SLON[0:100];
  COMMENT PROGRAM 200;
  DEFINE FORNQ=FUR NQ +1,NQ+1 WHILE NQS#,
    FORR=FOR R+1,R+1 WHILE RS#, FORI=FOR I+1,I+1 WHILE IS #,
    FORK=FOR K+1,K+1 WHILE KS      #;
  DEFINE FORIXQ = FOR IXQ+1 STEP 1 UNTIL #;

```

```

      INTEGER AMT,IND;      REAL R, EPSILON;
BEGIN
  INTEGER I,J;
  INTEGER ARRAY INDICES[0:100];
  FOR I=0 STEP 1 UNTIL 100 DO SLON[I]+FALSE;
  READ(CR,/,      FOR I=0,1 STEP 1 WHILE INDICES[I-1]≥0 DO INDICES[I]);
  FOR I=0 STEP 1 WHILE (J+INDICES[I])≥0 DO SLON[J]+TRUE;
END;
  READ(CR, /, AMT, EPSILON, R);  IND + 1;
L60: BEGIN
  INTEGER N,M;
  READ(CR,/,N,M);
  SLON[5]+TRUE;
  BEGIN
    REAL TEMP, COMP;  INTEGER NQ,K,NN,NUMRUN,MIN;
    COMMENT IND =I.  NQ = LOWER CASE N;
    ARRAY F[0:M,0:N], Y,X[0:N], A[0:M,0:M], BFF[0:M];
    ARRAY FL[0:M,0:N], AL[0:M,0:M], BFFL[0:M], XL[0:N];
  ARRAY TEMPXA,TEMPYA,TEMPXC,TEMPY [0:N+1];
  ARRAY TEMPXB,TEMPXC,TEMPYB,TEMPYC[0:N+1];
  FORMAT FM15 (  /"FINAL FIT OF Z VS RHO");
  FORMAT FM10(  /"Y(N)"/ ), FM12(  /"X(N)"/ );
  PROCEDURE DRAWIT(X,Y,N1,N2);  VALUE N1,N2;  INTEGER N1,N2;
  ARRAY X,Y[0];
  BEGIN
    ARRAY XNAME,YNAME[0:5];
    INTEGER I,N;
    REAL YMIN,DY,XMIN,DX;
  XNAME[0]+ "DENSIT";  XNAME[1]+ "Y      ";  YNAME[0]+ "(Z-1)V";
  N+N1+N2;
  PLOT(0,.5,-5);
  X[N+1]+0.0;
  IF ABS(Y[1]-Y[N]) < 0=4 THEN BEGIN  YMIN+ ENTIER(Y[1])-5;
  DY+1;  SCALES(Y,N, YMIN,DY,1)  END  ELSE
  SCALE(Y,N,8,YMIN,DY,1);
  SCALE(X,N+1,8,XMIN,DX,1);
  AXIS(0,0,XNAME,-7,8,0,XMIN,DX);
  AXIS(0,0,YNAME,6,8,90,YMIN,DY);
  FOR I=1 STEP 1 UNTIL N1 DO SYMBOL(X[I],Y[I],.08,XNAME,0,-5);
  FOR I=N STEP -1 WHILE I>N1 DO SYMBOL(X[I],Y[I],.08,XNAME,0,-9);
  PLOT(1,-.5,-3);
END OF DRAWIT;

      COMMENT PROCEDURES URNOR, INVERT PERMUTE AND CALFY,
      OR THEIR EQUIVALENTS INSERTED HERE;
PROCEDURE INVERSE(N,A,EPS,SINGULAR);VALUE N,EPS;INTEGER N;REAL EPS;REAL
ARRAY A[0,0];LABEL SINGULAR;BEGIN INTEGER I,J,K,II,N1,K2,L;REAL BIG,TEMP
,DIAG,Q;INTEGER ARRAY F[0:N];LABEL I2,I3,I4,I5,I6,SK3;I2:FOR I=1STEP 1UN
TIL N DO BEGIN II+I-1;FOR J=1 STEP 1UNTIL N DO BEGIN Q=0;FOR K=1STEP 1UN
TIL II DO Q+A[J,K]*A[K,I]+Q;A[J,I]+A[J,I]-Q END;BIG=0;K2+I;I3:FOR K=I ST
EP 1UNTIL N DO BEGIN IF ABS(A[K,I])>BIG THEN BEGIN BIG=ABS(A[K,I]);K2=K
END END;IF BIG=EPS THEN GO TO SINGULAR;F[I]+K2;IF K2#I THEN I4:FOR K=1ST
EP 1UNTIL N DO BEGIN TEMP+A[I,K];A[I,K]+A[K2,K];A[K2,K]+TEMP END;DIAG+A[
I,I];FOR J=I+1STEP 1UNTIL N DO BEGIN Q=0;FOR K=1STEP 1UNTIL II DO Q+A[I,
K]*A[K,J]+Q;A[I,J]+(A[I,J]-Q)/DIAG END END;I5:FOR I=1STEP 1UNTIL N DO BE
GIN II+I-1;DIAG+A[I,I];FOR J=1STEP 1UNTIL I DO BEGIN IF I=J THEN A[I,J]+

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1/DIAG ELSE BEGIN Q+Q;FOR K+J STEP 1UNTIL II DO Q+A[I,K]*A[K,J]+Q;A[I,J]
+Q/DIAG END END;N1+N-1;FOR I+N1 STEP-1UNTIL 100 BEGIN II+I+1;FOR J+
N STEP-1UNTIL II DO BEGIN Q+Q;L+J-1;FOR K+II STEP 1UNTIL L DO Q+A[I,K]*A
[K,J]+Q;A[I,J]+A[I,J]-Q END END;FOR I+1STEP 1UNTIL N1 DO FOR J+1STEP 1U
NTIL N DO BEGIN Q+Q;IF I≥J THEN BEGIN FOR K+I+1STEP 1UNTIL N DO Q+A[I,K]
*A[K,J]+Q;A[I,J]+A[I,J]+Q END ELSE BEGIN FOR K+J STEP 1UNTIL N DO Q+A[I,
K]*A[K,J]+Q;A[I,J]+Q END END;I6;FOR J+N STEP-1UNTIL 100 BEGIN K2+K+1;IF
F[J]=J THEN GO TO SK3;FOR K+1STEP 1UNTIL N DO BEGIN TEMP+A[K,K2];A[K,K2]
+K+K,J;A[K,J]+TEMP END;SK3;END END;
DEFINE INVERT=INVERSE;

COMMENT PROGRAM 201;
PROCEDURE ORNOR(N,M,EPSILON,Y,F,FL,A,AL,BFF,BFFL,MIN);
REAL EPSILON; INTEGER N,M,MIN; ARRAY Y,BFF[0],F,A[0,0];
ARRAY BFFL[0],AL,FL[0,0];
BEGIN
REAL SUM,SSQMIN,ARG,BF,YPROD;
INTEGER NQ,K,R,I,J,Q,NOORTH0,MINA,MINB,MN;
ARRAY G1,G2,G3,G4,G5[0:M,0:M], RTPSI,B,D,SSD,SSQ,RELERR[0:M],
PSI,PHI,FSUB[0:M,0:N];
ARRAY BF2[0:M];
REAL SUML,SSQMINL,ARGL,BFL,YPRODL;
ARRAY G1L,G2L,G3L,G4L,G5L[0:M,0:M],RTPSIL,BL,DL,SSDL,SSQL,RELERRL[0
:M],PSIL,PHIL,FSUBL[0:M,0:N];
ARRAY BF2L[0:M];
FORMAT FM1( /"B(K)"/ ), FM2(5(E17.10,X5) ),
FM3( /"SUM OF SQUARES OF DEVIATIONS"/ ),
FM4( /"S SQUARED"/ ),
FM5( /"MINIMUM S SQUARED FIT="I3),
FM6( /"RELATIVE ROUND-OFF ERROR"/ ),
FM8( /"D(K)"/ ),
FM7( /"DAMN-IT, ROUND-OFF ERROR IS STILL GREATER "
"THAN EPSILON"), FM15( /"EST. BEST FIT="I3),
FM13( /"REORTHONORMALIZATION" ),
FM14( /"BEST FIT CRITERION"/ );
LABEL ORTHO;
LABEL FINALPT;
LABEL L63,L33,L34;
NOORTH0+1; ARG+ARGL+0.0;
FOR NQ+1,NQ+1 WHILE NQSN DO DOUBLE(ARG,ARGL,Y[NQ],0,Y[NQ],0,x,+,+,A
RG,ARGL); DOUBLE(ARG,ARGL,+,YPROD,YPRODL);
ORTH0;
BEGIN
LABEL L1,L2,L3,L4,L5, FINORT,L6,L7;
REAL SUMQ,IPPSI,IPPSIF;
ARRAY C,G[0:M,0:M];
REAL SUMQL,IPPSIL,IPPSIFL; ARRAY CL,GL[0:M,0:M];
SWITCH GCALC+L1,L2,L3,L4,L5;
FORMAT F2(5(E17.10,X5) ),
F3( /"PSI(K,N)"/ ), F4( /"G(K,R)"/ ),
F5( /"PHI(K,N)"/ ), F6( /"ROOT INNER PRODUCT PSI"/ );
FORNQ N DO DOUBLE(F[1,NQ],FL[1,NQ],+,PSI[1,NQ],PSIL[1,NQ]);
IF SLON[15] THEN BEGIN WRITE(LP,F3);
WRITE(LP,F2,FOR IXQ+1STEP 1 UNTIL N DO PSI[1,IXQ]);END;
IF M=1 THEN GO TO FINORT;
FOR K+2,K+1 WHILE K≤M DO

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BEGIN      FORNQ N DO
  BEGIN    SUMQ+SUMQL+0;  FOR R+1,R+1 WHILE R<K DO
  BEGIN    IPPSI+IPPSIL+IPPSIF+IPPSIFL+0;  FORI N DO
  BEGIN    DOUBLE(IPPSI,IPPSIL,PSI[R,I],PSIL[R,I],PSI[R,I],PSIL[R,I],x,+,
            +,IPPSI,IPPSIL);
            DOUBLE(IPPSIF,IPPSIFL,F[K,I],FL[K,I],PSI[R,I],PSIL[R,I],x,+,+,IPPSI
F,IPPSIFL);
  END;      DOUBLE(-IPPSIF,-IPPSIFL,IPPSI,IPPSIL,/,+,C[K,R],CL[K,R]);
            DOUBLE(C[K,R],CL[K,R],PSI[R,NQ],PSIL[R,NQ],x,SUMQ,SUMQL,+,+,SUMQ,SU
MQL);
  END;      DOUBLE(F[K,NQ],FL[K,NQ],SUMQ,SUMQL,+,+,PSI[K,NQ],PSIL[K,NQ]);
  END;      IF SLON[15] THEN
            WRITE(LP,F2,FOR IXQ+1 STEP 1 UNTIL N DO PSI[K,IXQ]);
  END;      IF SLON[15] THEN WRITE(LP,F4);
  FINORT;   FORK M DO
  BEGIN    IF K=1 THEN GO TO L6;
            FOR R+1,R+1 WHILE R<K DO
  BEGIN    ARG+ARGL+0,0;  FOR J+R,J+1 WHILE J<K DO DOUBLE(G[J,R],GL[J,R],
            C[K,J],CL[K,J],x,ARG,ARGL,+,+,ARG,ARGL);
            DOUBLE(ARG,ARGL,+,G[K,R],GL[K,R]);
  END;
  L6:      DOUBLE(1,0,+,G[K,K],GL[K,K]);  IF SLON[15] THEN WRITE(LP,F2,F
ORIXQ K DO
            G[K,IXQ]);
  END;      FORK M DO FORR K DO
  BEGIN    GO TO GCALC[NOORTH0];
  L1:      DOUBLE(G[K,R],GL[K,R],+,G1[K,R],G1L[K,R]);  GO TO L7;
  L2:      DOUBLE(G[K,R],GL[K,R],+,G2[K,R],G2L[K,R]);  GO TO L7;
  L3:      DOUBLE(G[K,R],GL[K,R],+,G3[K,R],G3L[K,R]);  GO TO L7;
  L4:      DOUBLE(G[K,R],GL[K,R],+,G4[K,R],G4L[K,R]);  GO TO L7;
  L5:      DOUBLE(G[K,R],GL[K,R],+,G5[5,R],G5L[K,R]);  GO TO L7;
  L7:
  END;      IF SLON[15] THEN WRITE(LP, F5);
            FORK M DO
  BEGIN    FORNQ N DO
  BEGIN    ARG+ARGL+0,0;
            FORI N DO DOUBLE(PSI[K,I],PSIL[K,I],PSI[K,I],PSIL[K,I],x,ARG,ARGL,+,
            +,ARG,ARGL);
            DSQRT(ARG,ARGL,TOM,TOML);  RTPSI[K]+TOM;  RTPSIL[K]+TOML;
            DOUBLE(PSI[K,NQ],PSIL[K,NQ],RTPSI[K],RTPSIL[K],/,+,PHI[K,NQ],PHIL[K
,NQ]);
  END;      IF SLON[15] THEN WRITE(LP,F2,FORIXQ N DO PHI[K,IXQ]);
  END;      IF SLON[15] THEN BEGIN WRITE(LP,F6);
            WRITE(LP,F2,FORIXQ M DO RTPSI[IXQ] )  END ;
  END;
  FORK M DO
  BEGIN    ARG+ARGL+0,0;
            FORI N DO DOUBLE(Y[I],0,PHI[K,I],PHIL[K,I],x,ARG,ARGL,+,+,ARG,ARGL)
;
            DOUBLE(ARG,ARGL,+,B[K],BL[K]);
            DOUBLE(B[K],BL[K],RTPSI[K],RTPSIL[K],/,+,D[K],DL[K]);
  END;      IF SLON[14] THEN
  BEGIN    WRITE(LP,FM1); WRITE(LP,FM2, FORIXQ M DO B[IXQ ]);

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WRITE(LP,FM8);      WRITE(LP,FM2,FORIXQ M DO D[IXQ]);
END;
DOUBLE(YPROD,YPRODL,B[1],BL[1],B[1],BL[1],X,-,+,SSD[1],SSDL[1]);
DOUBLE(SSD[1],SSDL[1],N-1,0,/,+,SSQ[1],SSQL[1]);
IF M=1 THEN GO TO L63;
FOR K+2,K+1 WHILE KSM DO
BEGIN
  DOUBLE(SSD[K-1],SSDL[K-1],B[K],BL[K],B[K],BL[K],X,-,+,SSD[K],SSDL[K]);
  DOUBLE(SSD[K],SSDL[K],N-K,0,/,+,SSQ[K],SSQL[K]);
END;
L63: IF SLON[5] THEN BEGIN
  WRITE(LP,FM3); WRITE(LP,FM2,FORIXQ M DO SSD[IXQ]);
  WRITE(LP,FM4); WRITE(LP,FM2, FORIXQ M DO SSQ[IXQ]); END;
  FORK M DO
  BEGIN
    IF K=M THEN BEGIN MINA+M; GO TO L33 END;
    IF ABS(SSQ[K]) < ABS(SSQ[K+1]) THEN BEGIN MINA+K; K+M END;
  L33:
  END;
  IF SLON[5] THEN WRITE(LP,FM5,MINA);
  FORK M DO DOUBLE(SSD[K],SSDL[K],SSQ[MINA],SSQL[MINA],2*X-N,0,X,+,+,
    BFF[K],BFFL[K]);
  FORK M DO
  BEGIN
    IF K=M THEN BEGIN MIN+M; GO TO L34 END;
    IF ABS(BFF[K]) < ABS(BFF[K+1]) THEN BEGIN MIN+K; K+M END;
  L34:
  END;
  IF SLON[5] THEN BEGIN
    WRITE(LP,FM14); WRITE(LP,FM2,FORIXQ M DO BFF[IXQ]);
    WRITE(LP,FM15,MIN); END;
    MN+ IF MINA < MIN THEN MIN ELSE MINA;
    MINB+ IF MN+2SM THEN MN+2 ELSE MN;
    FORK MN DO
  BEGIN
    SUM+SUML+0,0; FOR Q+1,Q+1 WHILE QSMN DO
  BEGIN
    ARG+ARGL+0,0; FORI N DO DOUBLE(ARG,ARGL,PHI[K,I],PHIL[K,I],PHI[Q,I],
      PHIL[Q,I],X,+,+,ARG,ARGL);
    DOUBLE(SUM,SUML,ARG,ARGL,B[Q],BL[Q],X,+,+,SUM,SUML);
  END;
  DOUBLE(1,0,SUM,SUML,B[K],BL[K],/, -, +, RELERR[K],RELEHRL[K]);
  END;
  IF MN < M THEN FOR K+MN+1,K+1 WHILE KSMINB DO
  BEGIN
    SUM+SUML+0,0; FOR Q+1,Q+1 WHILE QSK DO
  BEGIN
    ARG+ARGL+0,0; FORI N DO DOUBLE(ARG,ARGL,PHI[K,I],PHIL[K,I],
      PHI[Q,I],PHIL[Q,I],X,+,+,ARG,ARGL);
    DOUBLE(SUM,SUML,ARG,ARGL,B[Q],BL[Q],X,+,+,SUM,SUML);
  END;
  DOUBLE(1,0,SUM,SUML,B[K],BL[K],/, -, +, RELERR[K],RELEHRL[K]);
  END;
  IF SLON[5] THEN BEGIN
    WRITE(LP,FM6); WRITE(LP,FM2,FORIXQ MINB DO RELEHRL[IXQ]); END;
    FORK MN DO
  BEGIN
    IF EPSILON < ABS(RELEHRL[K]) THEN
  BEGIN
    IF NUORTHU=5 THEN BEGIN
      IF SLON[5] THEN WRITE(LP,FM7); GO TO FINALPT END;
      FORI M DO FORNQ N DO
  BEGIN
    IF NUORTHU=1 THEN DOUBLE(F[I,NQ],FL[I,NQ],+,FSUB[I,NQ],FSUBL[I,NQ]);
    DOUBLE(PSI[I,NQ],PSIL[I,NQ],+,F[I,NQ],FL[I,NQ]);
  END;
  NUORTHU+NUORTHU+1; IF SLON[5] THEN WRITE(LP,FM13); GO TO UORTHU;
  END;
  END;

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FINALPT :
BEGIN      REAL TFAC,SD2,FAC1,FAC2,FAC3,FAC4,SUMDEV,SUMABSD,SUMDSQ,
           YCALC,DELTA,SD22,SIGSQ;  INTEGER P,L;
REAL TFACL,SD2L,FAC1L,FAC2L,FAC3L,FAC4L,SUMDEVL,SUMABSDL,SUMDSL,YCALCL,
DELTAEL,SD22L,SIGSQL,FACL;
INTEGER ST;      ARRAY SD,S2D[1:M],T[1:M,1:M],DELTA[1:N];
ARRAY SUL,S2DL[1:M],TL[1:M,1:M],DELTAL[1:N];
REAL FAC;
FORMAT FS1( /"R="I4/), FS2(5(E17.10,X5) ),
FS3( /"COEFFICIENTS"/ ),
FS5( /"STANDARD DEVIATION OF COEFFICIENTS FIRST SET "
     "BASED UPON SIGMA SQUARED NEXT SET UPON S SQUARED."/
     "IF THE ABOVE DELTAS ARE RANDOM, THEN THE FIRST "
     "SET SHOULD BE USED OTHERWISE THE SECOND SET"/),
FS7( X10,E17.10,X5,E17.10,X5,E17.10 ),
FS6( /X15 "Y(OBS)"X7="-X7"Y(CALC)"X6="X7"DELTA"/ ),
FS8( /"SUM OF DELTAS="E17.10,X5"SUM OF ABS(DELTA)="
     E17.10/"AVERAGE DELTA="E17.10,X5"SUM OF DELTA SQUARED="
     E17.10), FS9( /"SIGMA SQUARED="E17.10),
FS10( /"BEST FIT BASED UPON SIGMA SQUARED"/ ),
FS11( /"BEST FIT=" I3);
LABEL L10,L11,L12,L13,L14,L20,L21,L22,L23,L24,L15,L16,L30,L35,L25;
LABEL L26;
SWITCH TCALC + L10,L11,L12,L13,L14;
SWITCH SDCALC + L20,L21,L22,L23,L24;
FORR M DO FORK (M=R+1) DO
BEGIN      IF R=1 THEN BEGIN DOUBLE(D[K],DL[K],+,T[1,K],TL[1,K]);GO TO L1
6 END;
GO TO TCALC[NDORTHO];
L10:      DOUBLE(G1[R+K-1,K],G1L[R+K-1,K],+,TFAC,TFACL); GO TO L15;
L11:      TFAC+TFACL+0.0;      FOR J+K,J+1 WHILE JS(R+K-1) DO
      DOUBLE(TFAC,TFACL,G1[J,K],G1L[J,K],G2[R+K-1,J],G2L[R+K-1,J],x,+,+,T
FAC,TFACL);      GO TO L15;
L12:      TFAC+TFACL+0.0;      FOR J+K,J+1 WHILE JS(R+K-1) DO
BEGIN      FAC2+FAC2L+0.0;
      FOR I+K,I+1 WHILE ISJ DO DOUBLE(FAC2,FAC2L,G1[I,K],G1L[I,K],G2[J,I]
,G2L[J,I],x,+,+,FAC2,FAC2L);
      DOUBLE(TFAC,TFACL,FAC2,FAC2L,G3[R+K-1,J],G3L[R+K-1,J],x,+,+,TFAC,TF
ACL);
END;
GO TO L15;
L13:      TFAC+TFACL+0.0;      FOR J+K,J+1 WHILE JS(R+K-1) DO
BEGIN      FAC2+FAC2L+0.0;      FOR I+K,I+1 WHILE ISJ DO
BEGIN      FAC3+FAC3L+0.0;      FOR P+K,P+1 WHILE PSI DO
      DOUBLE(FAC3,FAC3L,G1[P,K],G1L[P,K],G2[I,P],G2L[I,P],x,+,+,FAC3,FAC3
L);
      DOUBLE(FAC2,FAC2L,G3[J,I],G3L[J,I],FAC3,FAC3L,x,+,+,FAC2,FAC2L);
END; DOUBLE(TFAC,TFACL,FAC2,FAC2L,G4[R+K-1,J],G4L[R+K-1,J],x,+,+,TFAC,TF
ACL);
END;
GO TO L15;
L14:      TFAC+TFACL+0.0;      FOR J+K,J+1 WHILE JS(R+K-1) DO
BEGIN      FAC2+FAC2L+0.0;      FOR I+K,I+1 WHILE ISJ DO
BEGIN      FAC3+FAC3L+0.0;      FOR P+K,P+1 WHILE PSI DO
BEGIN      FAC4+FAC4L+0.0;      FOR Q+K,Q+1 WHILE QSP DO
      DOUBLE(FAC4,FAC4L,G1[Q,K],G1L[Q,K],G2[P,Q],G2L[P,Q],x,+,+,FAC4,FAC
4L);
      DOUBLE(FAC3,FAC3L,FAC4,FAC4L,G3[I,P],G3L[I,P],x,+,+,FAC3,FAC3L);

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END; DOUBLE(FAC2,FAC2L,FAC3,FAC3L,G4[J,I],G4L[J,I],x,+,+,FAC2,FAC2L);
END; DOUBLE(TFAC,TFACL,FAC2,FAC2L,G5[R+K-1,J],G5L[R+K-1,J],x,+,+,TFAC,TF
ACL);
END;
L15: DOUBLE(T[R-1,K],TL[R-1,K],T[1,R+K-1],TL[1,R+K-1],TFAC,TFACL,x,+,+,T
[ R,K],TL[R,K]);
L16:
END; IF SLON[5] THEN WRITE(LP,FS3);      FORR M DO
BEGIN IF SLON[5] THEN WRITE(LP,FS1,R); FORK R DO DOUBLE(T[R-K+1,K],TL[R-
K+1,K],+,A[R,K],AL[R,K]);
IF SLON[5] THEN WRITE(LP, FS2, FORIXQ R DO A[R,IXQ]);
END; IF SLON[5] THEN WRITE(LP,FS6);
ST+ IF MINA<MN-2 THEN MINA=2 ELSE IF MIN<MN-2 THEN MIN=2
ELSE MN=2; IF ST<1 THEN ST+1;
FOR R+ST,R+1 WHILE R<MINB DO
BEGIN SUMDEV+SUMDEVL+SUMABSD+SUMABSOL+SUMDSQ+SUMDSL+0.0;
IF SLON[5] THEN WRITE(LP, FS1, R);
FORNQ N DO
BEGIN YCALC+YCALCL+0.0; IF NOURTHU=1 THEN
BEGIN FORI R DO DOUBLE(YCALC,YCALCL,A[R,I],AL[R,I],F[1,NQ],FL[I,NQ],
x,+,+,YCALC,YCALCL); GO TO L30;
END; FORI R DO DOUBLE(YCALC,YCALCL,A[R,I],AL[R,I],FSUB[I,NQ],FSUBL[I,NQ]
,x,+,+,YCALC,YCALCL);
L30: DOUBLE(Y[NQ],0,YCALC,YCALCL,-,+,DELTA[NQ],DELTAL[NQ]);
IF SLON[5] THEN WRITE(LP,FS7,Y[NQ],YCALC,DELTA[NQ]);
DOUBLE(SUMDEV,SUMDEVL,DELTA[NQ],DELTAL[NQ],+,+,SUMDEV,SUMDEVL);
DOUBLE(ABS(DELTA[NQ]),ABS(DELTAL[NQ]),SUMABSD,SUMABSOL,+,+,SUMABSD,
SUMABSOL);
DOUBLE(SUMDSQ,SUMDSL,DELTA[NQ],DELTAL[NQ],DELTA[NQ],DELTAL[NQ],x,+,
+,SUMDSQ,SUMDSL);
END; DOUBLE(SUMDEV,SUMDEVL,N,0,/,+,DELTAVE,DELTAVL);
IF SLON[5] THEN WRITE(LP,FS8,SUMDEV,SUMABSD,DELTAVE,
SUMDSQ); IF R=MINA THEN
BEGIN FAC1+FAC1L+0.0; FOR P+1,P+1 WHILE P<N DO
BEGIN FAC2+FAC2L+0.0; FOR Q+1,Q+1 WHILE Q<N DO DOUBLE(DELTA[Q],
DELTAL[Q],FAC2,FAC2L,+,+,FAC2,FAC2L);
DOUBLE(FAC1,FAC1L,FAC2,FAC2L,DELTA[P],DELTAL[P],x,+,+,FAC1,FAC1L);
END; DOUBLE(SUMDEV,SUMDEVL,SUMDEV,SUMDEVL,x,FAC1,FAC1L,2.0,x,-,N-MINA,0
,/,+,FAC,FACL);
DOUBLE(SSQ[MINA],SSL[MINA],FAC,FACL,-,+,SIGSQ,SIGSQL);
END
END; IF SLON[5] THEN WRITE(LP,FS9,SIGSQ);
FORK M DO DOUBLE(SSQ[K],SSL[K],SIGSQ,SIGSQL,2*x-K-N,0,x,+,+,BF2[K],B
F2L[K]); FORK M DO
BEGIN IF K=M THEN
BEGIN MIN+M; GO TO L35
END; IF ABS(BF2[K])<ABS(BF2[K+1]) THEN BEGIN MIN+K; K+M END;
L35:
END;
IF SLON[5] THEN BEGIN
WRITE(LP,FS10); WRITE(LP,FS2, FORIXQ M DO BF2[IXQ]);
WRITE(LP,FS11,MIN); WRITE(LP,FS5); END;
FORR M DO
BEGIN FORK R DO
BEGIN SD2+SD2L+SD22+SD22L+0.0;
FOR J+K,J+1 WHILE J<R DO

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BEGIN      GO TO SOCALC(NDORTHO);
L20: DOUBLE(G1[J,K],G1L[J,K],+,FAC1,FAC1L); GO TO L25;
L21: FAC1=FAC1L+0.0;   FOR I=K,I+1 WHILE ISJ DO
      DOUBLE(FAC1,FAC1L,G1[I,K],G1L[I,K],G2[J,I],G2L[J,I],x,+,+,FAC1,FAC
1L);
      GO TO L25;
L22: FAC1=FAC1L+0.0;   FOR P=K,P+1 WHILE PSJ DO
BEGIN      FAC2=FAC2L+0.0;   FOR I=K,I+1 WHILE ISP DO
      DOUBLE(FAC2,FAC2L,G1[I,K],G1L[I,K],G2[P,I],G2L[P,I],x,+,+,FAC2,FAC2
L);
      DOUBLE(FAC1,FAC1L,FAC2,FAC2L,G3[J,P],G3L[J,P],x,+,+,FAC1,FAC1L);
END;
      GO TO L25;
L23: FAC1=FAC1L+0.0;   FOR Q=K,Q+1 WHILE QSJ DO
BEGIN      FAC2=FAC2L+0.0;   FOR P=K,P+1 WHILE PSQ DO
BEGIN      FAC3=FAC3L+0.0;   FOR I=K,I+1 WHILE ISP DO
      DOUBLE(FAC3,FAC3L,G1[I,K],G1L[I,K],G2[P,I],G2L[P,I],x,+,+,FAC3,FAC3
L);
      DOUBLE(FAC2,FAC2L,G3[Q,P],G3L[Q,P],FAC3,FAC3L,x,+,+,FAC2,FAC2L);
END;
      DOUBLE(FAC1,FAC1L,G4[J,Q],G4L[J,Q],FAC2,FAC2L,x,+,+,FAC1,FAC1L);
END;
      GO TO L25;
L24: FAC1=FAC1L+0.0;   FOR L=K,L+1 WHILE LSJ DO
BEGIN      FAC2=FAC2L+0.0;   FOR Q=K,Q+1 WHILE QSL DO
BEGIN      FAC3=FAC3L+0.0;   FOR P=K,P+1 WHILE PSQ DO
BEGIN      FAC4=FAC4L+0.0;   FOR I=K,I+1 WHILE ISP DO
      DOUBLE(FAC4,FAC4L,G1[I,K],G1L[I,K],G2[P,I],G2L[P,I],x,+,+,FAC4,FAC4
L);
      DOUBLE(FAC3,FAC3L,FAC4,FAC4L,G3[Q,P],G3L[Q,P],x,+,+,FAC3,FAC3L);
END;
      DOUBLE(FAC2,FAC2L,FAC3,FAC3L,G4[L,Q],G4L[L,Q],x,+,+,FAC2,FAC2L);
END;
      DOUBLE(FAC1,FAC1L,FAC2,FAC2L,G5[J,L],G5L[J,L],x,+,+,FAC1,FAC1L);
END;
L25: DOUBLE(SD2,SD2L,FAC1,FAC1L,FAC1,FAC1L,x,RTPSI[J],RTPSI[J],RTPSI[J],
      ,RTPSI[J],x,/,+,+,SD2,SD2L);
      FAC=FACL+0.0; FOR I R DO
BEGIN      ARG=ARGL+0.0; IF NDORTHO=1 THEN
BEGIN      FORN= N DO DOUBLE(ARG,ARGL,PHI[J,NQ],PHIL[J,NQ],F [I,NQ],F
      [I,NQ],x,+,+,ARG,ARGL); GO TO L26;
END; FORN= N DO DOUBLE(ARG,ARGL,PHI[J,NQ],PHIL[J,NQ],FSUB[I,NQ],FSUBL[I,
      NQ],x,+,+, ARG,ARGL);
L26: DOUBLE(FAC,FACL,ARG,ARGL,ALMIN,I),AL[MIN,I],x,+,+,FAC,FACL);
END;
      DOUBLE(SD22,SD22L,B[J],BL[J],FAC,FACL,-,FAC1,FAC1L,x,RTPSI[J],RTPSI
      L [J],/,+,+,SD22,SD22L);
END;
      DOUBLE(SIGSQ,SIGSQL,SD2,SD2L,x,SD22,SD22L,SD22,SD22L,x,+,+,ARG,ARGL
      );
      DOUBLE(SSQ[MINA],SSQL[MINA],SD2,SD2L,x,SD22,SD22L,SD22,SD22L,x,+,+,
      SSQMIN,SSQMINL);
      DSQRT(SSQMIN,SSQMINL,TOM,TOML); S2D[K]+TOM; S2DL[K]+TOML;
      DSQRT(ARG,ARGL,TOM,TOML); S0[K]+TOM; S0L[K]+TOML;
END;
      IF SLUN[5] THEN BEGIN
      WRITE(LP,FS1,R);WRITE(LP,FS2,FORIXQ R DO SD [IXQ]);
      WRITE(LP,FS1,R); WRITE(LP,FS2,FORIXQ R DO S2D[IXQ]); END;
END
END
END OF PROCEDURE UPNR;

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      COMMENT PROGRAM 202;
PROCEDURE CALFY(N,M,N1,N2,NUMRUN,FIT,K1,K1L,K2,K2L,AK1,AK1L,AK2,AK2L,P,P

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P,XI,XIL,XXI,XXIL,X,XL,Y,F,FL);
  INTEGER N,M,N1,N2,NUMRUN,FIT;
  REAL K1,K2,AK1,AK2;
  REAL K1L,K2L,AK1L,AK2L;
  ARRAY P,PP,XI,XXI,X,Y (0),F(0,0);
  ARRAY XIL,XXIL,XL(0),FL(0,0);
BEGIN
  LABEL NX10,NX11,NX13,NX12,NX14,NX15;
  LABEL NX20;
  INTEGER I,K; COMMENT I CORRESPONDS TO ORIGINAL "LITTLE N";
  Y[1]+P[1]*AK1;
  IF NUMRUN#1 THEN GO TO NX10;
  FOR I+2,I+1 WHILE I#N1 DO Y[I]+P[I]*AK1*K1*(I-1)*XI[I-1];
  GO TO NX11;
NX10:  Y[N1+1]+PP[1]*AK2;
  FOR I+2,I+1 WHILE I#N1 DO Y[I]+P[I]*AK1*K1*(I-1)*XI[I-1];
  FOR I+2,I+1 WHILE I#N2 DO Y[N1+I]+PP[I]*AK2*K2*(I-1)*XXI[I-1];
NX11:  IF FIT#1 THEN GO TO NX12; IF NUMRUN#1 THEN GO TO NX13;
  FORI N1 DO DOUBLE(1.0,+,F[1,I],FL[1,I]); IF M=1 THEN GO TO NX20;
  FOR K+2,K+1 WHILE K#M DO FORI N1 DO BEGIN
    TOM+X[I]; TOML+XL[I];
    DPOW(TOM,TOML,HAM,HAML,K-1);
    F[K,I]+HAM; FL[K,I]+HAML;
  END;
  GO TO NX20;
NX13:  FORI N DO DOUBLE(1.0,+,F[1,I],FL[1,I]); IF M=1 THEN GO TO NX
20;
  FOR K+2,K+1 WHILE K#M DO FORI N1 DO BEGIN HAM+X[2*I-1];
    HAML+XL[2*I-1]; DPOW(HAM,HAML,TOM,TOML,K-1);
    F[K,I]+TOM; FL[K,I]+TOML; END;
  FOR K+2,K+1 WHILE K#M DO FORI N2 DO BEGIN HAM+X[2*I]; HAML+XL[2*I
  ]; DPOW(HAM,HAML,TOM,TOML,K-1); F[K,N1+I]+TOM; FL[K,N1+I]+TOM
  L;
  GO TO NX20;
NX12:  FORI N1 DO Y[I]+Y[I]-1.0; IF NUMRUN=1 THEN GO TO NX14;
  FORI N2 DO Y[N1+I]+Y[N1+I]-1.0;
NX14:  IF NUMRUN#1 THEN GO TO NX15;
  FORK M DO FORI N1 DO BEGIN HAM+X[I]; HAML+XL[I];
    DPOW(HAM,HAML,TOM,TOML,K); F[K,I]+TOM; FL[K,I]+TOML; END;
  GO TO NX20;
NX15:  FORK M DO FORI N1 DO BEGIN HAM+X[2*I-1]; HAML+XL[2*I-1];
    DPOW(HAM,HAML,TOM,TOML,K); F[K,I]+TOM; FL[K,I]+TOML; END;
  FORK M DO FORI N2 DO BEGIN HAM+X[2*I]; HAML+XL[2*I];
    DPOW(HAM,HAML,TOM,TOML,K); F[K,N1+I]+TOM; FL[K,N1+I]+TOML;
  END;
NX20:
END OF CALFY ;

LABEL BURNETT;
  READ(CR,/,TEMP,CUMP,NUMRUN);
  BURNETT: BEGIN
    INTEGER NN,MMM,N1,N2,FIT,WH,WH1,I,DN;
    REAL TOL,SS1,SS2,SS3,SS4,SS5,SSK1,SSK2,SSK3,SSK4,SSK5,SSK6;
    REAL SS1L,SS2L,SS4L,SS3L,SS5L,SSK1L,SSK2L,SSK3L,SSK4L,SSK5L,SSK6L;
    REAL A1,A2,A3,A4,A5,A6,B1,B2,B3,B4,B5,B6;
    READ(CR,/,NN,MMM,N1,N2,TOL);
    READ(CR,/,FIT,WH,WH1,A1,A2,A3,A4,A5,A6,B1,B2,B3,

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      B4,B5,B6));
WRITE(LP,PAGE));
WRITE(LP,<9("*****") " INPUT DATA " 9("*****")>);
WRITE(LP,<"* X118 *">);
WRITE(LP,<"* X3 *EPSILON                                =" E10.3 ,X77 "*">,EPSILON)
;
WRITE(LP,<"* X3 *GAS CONSTANT                                =" F10.4 ,X77 "*">,R);
WRITE(LP,<"* X3 *NO. OF DATA PUINTS                        =" I10 ,X77 "*">,N);
WRITE(LP,<"* X3 *NO. OF PARAMETERS                          =" I10 ,X77 "*">,M);
WRITE(LP,<"* X3 *TEMPERATURE                                =" F10.4 ,X77 "*">,TEMP);
WRITE(LP,<"* X3 *CUMPOSITION                                =" F10.4 ,X77 "*">,COMP);
WRITE(LP,<"* X3 *NO. OF RUNS IN DATA SET                    =" I10 ,X77 "*">,NUMRUN);
WRITE(LP,<"* X3 *NO. OF POINTS EXTRAPOLATED                 =" I10 ,X77 "*">,NN);
WRITE(LP,<"* X3 *NO. OF PARAMS. IN EXTRAP.                  =" I10 ,X77 "*">,MMM);
WRITE(LP,<"* X3 *POINTS IN FIRST RUN                        =" I10 ,X77 "*">,N1);
WRITE(LP,<"* X3 *POINTS IN SECOND RUN                       =" I10 ,X77 "*">,N2);
WRITE(LP,<"* X3 *TOLERANCE                                  =" E10.3 ,X77 "*">,TOL);
WRITE(LP,<"* X3 *TYPE OF FIT                                =" I10 ,X77 "*">,FIT);
WRITE(LP,<"* X3 *INPUT CONTROL                              =" I10 ,X77 "*">,WH);
WRITE(LP,<"* X3 *INITIAL SURFACE PARAMETER                  =" I10 ,X77 "*">,WH1);
WRITE(LP,<"* X3 *A1 = A6                                    =" 6(E10.3,X2),X15,"*">,A1,
A2,A3,A4,A5,A6);
WRITE(LP,<"* X3 *R1 = B6                                    =" 6(E10.3,X2),X15,"*">,B1,
B2,B3,B4,B5,B6);
      IF N2=0 THEN N2+2;
BEGIN
  REAL XIQ;
  REAL XIQL;
  REAL K1,K2, AK1,AK2,AN1,AN2,KK,AK, RT,SUM,ZETA0,ZETA1,ZETA2,
    ZETA3,ZETA4,ZETA5,ZETA6,ZETA7,ZETA8,ZETA9,ZETA10,ZETA11,
    ZETA12,ZETA13,ZETA14,UK1,UA1,D2K1,D2A1,D2K1A1,DK2,DA2,D2K2,
    D2A2,D2K1K2,D2K1A2,D2A1K2,D2A1A2, D2K2A2;
  REAL K1L,K2L,AK1L,AK2L,AN1L,AN2L,KKL,AKL,RTL,SUML;
  REAL DK2L,DA2L,D2K2L,D2A2L,D2K1K2L,D2K1A2L,D2A1K2L,D2A1A2L,D2K2A2L;
  REAL ZETA0L,ZETA1L,ZETA2L,ZETA3L,ZETA4L,ZETA5L,ZETA6L,ZETA7L,
    ZETA8L,ZETA9L,ZETA10L,ZETA11L,ZETA12L,ZETA13L,ZETA14L;
  REAL DK1L,DA1L,D2K1L,D2A1L,D2K1A1L;
  REAL K10,A10,K20,A20,ST0;
  REAL K10L,A10L,K20L,A20L,ST0L;
  INTEGER NNN,MM,KNT,J;
  ARRAY P[0:N1],PP[0:N2],PRAT,X1,ZT1[0:N1-1],PPRAT,XXI,ZT2[0:N2-1],
    ZV,PN,DUM1,TEST,P1,DUM[0:N], CHG,DVEC[0:4],DMIX[0:4,0:4];
  ARRAY PRATL,X1L[0:N1-1],PPRATL,XXIL[0:N2-1],
    ZVL,PNL,DUM1L,TESTL,P1L,DUML[0:N],CHGL,DVECL[0:4],DMTXL[0:4,0:
4];
  ARRAY ZT1L[0:N1-1], ZT2L[0:N2-1];
  ARRAY KK1,AAK1,KK2,AAK2[0:M], TBF[0:20,0:M];
  ARRAY KK1L,AAK1L,KK2L,AAK2L[0:M],TBF1[0:20,0:M];
  COMMENT REAL PROCEDURE DOXI GOES HERE;

  REAL PROCEDURE DOXI(N1F,N2F,MF,FF,AF,AFL,PF,PPF,XF,XFL);
  VALUE N1F,N2F,MF,FF) INTEGER N1F,N2F,MF,FF;
  ARRAY AF,AFL[0,0],PF,PPF,XF,XFL[0];
  BEGIN
    LABEL NX50;
    REAL SUMH,SUML,SUM1H,SUM1L,SUM2H,SUM2L;

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      INTEGER N,K;
      REAL TAH,TBH,TCH,TDH,TAL,TBL,TCL,TDL;
      SUMH+SUML+0.0;
      FOR N+2 STEP 1 UNTIL N1F DO
    BEGIN
      IF FF=1 THEN
    BEGIN
      SUM1H+SUM1L+SUM2H+SUM2L+0.0;
      TAH + IF NUMRUN=1 THEN XF[N] ELSE XF[2*N-1]; TBH+1.0;
      TAL+IF NUMRUN=1 THEN XFL[N] ELSE XFL[2*N-1];
      TCH + IF NUMRUN=1 THEN XF[N-1] ELSE XF[2*N-3]; TDH+1.0;
      TCL+IF NUMRUN=1 THEN XFL[N-1] ELSE XFL[2*N-3];
      TBL+TDL + 0.0;
      FOR K+1 STEP 1 UNTIL MF DO
    BEGIN
      DOUBLE(AF[MF,K],AFL[MF,K],TBH,TBL,x,SUM1H,SUM1L,+,+,SUM1H,SUM1L);
      DOUBLE(TAH,TAL,TBH,TBL,x,+,+,TBH,TBL);
      DOUBLE(AF[MF,K],AFL[MF,K],TDH,TDL,x,SUM2H,SUM2L,+,+,SUM2H,SUM2L);
      DOUBLE(TCH,TCL,TDH,TDL,x,+,+,TDH,TDL);
    END
      END ELSE
    BEGIN
      SUM1H + SUM2H+1.0; SUM1L+SUM2L+0.0;
      TAH + IF NUMRUN=1 THEN XF[N] ELSE XF[2*N-1]; TBH+TAH;
      TAL+IF NUMRUN=1 THEN XFL[N] ELSE XFL[2*N-1];
      TCH + IF NUMRUN=1 THEN XF[N-1] ELSE XF[2*N-3]; TDH+TCH;
      TCL+IF NUMRUN=1 THEN XFL[N-1] ELSE XFL[2*N-3];
      TBL+TAL; TDL+TCL;
      FOR K+1 STEP 1 UNTIL MF DO
    BEGIN
      DOUBLE(AF[MF,K],AFL[MF,K],TBH,TBL,x,SUM1H,SUM1L,+,+,SUM1H,SUM1L);
      DOUBLE(TAH,TAL,TBH,TBL,x,+,+,TBH,TBL);
      DOUBLE(AF[MF,K],AFL[MF,K],TDH,TDL,x,SUM2H,SUM2L,+,+,SUM2H,SUM2L);
      DOUBLE(TCH,TCL,TDH,TDL,x,+,+,TDH,TDL);
    END
      END;
      DOUBLE(PF[N],0,PF[N-1],0,/,SUM1H,SUM1L,A6,0,PF[N],0,x,A5,0,+,PF[N],0,
        x,A4,0,+,PF[N],0,x,A3,0,+,PF[N],0,x,A2,0,+,PF[N],0,x,A1,0,+,
        B6,0,PF[N-1],0,x,B5,0,+,PF[N-1],0,x,B4,0,+,PF[N-1],0,x,B3,0,+,
        PF[N-1],0,x,B2,0,+,PF[N-1],0,x,B1,0,+,/,SUM2H,SUM2L,x,K1,0,x,/,
        =,+,TAH,TAL);
      DOUBLE(TAH,TAL,TAH,TAL,x,SUMH,SUML,+,+,SUMH,SUML);
    END;
      IF NUMRUN=1 THEN GO TO NX50;
      FOR N+2 STEP 1 UNTIL N2F DO
    BEGIN
      IF FF=1 THEN
    BEGIN
      SUM1H+SUM1L+SUM2H+SUM2L+0.0;
      DOUBLE(XF[2*N],XFL[2*N],+,TAH,TAL); TBH+1.0;
      DOUBLE(XF[2*N-2],XFL[2*N-2],+,TCH,TCL); TDH+1.0;
      TBL+TDL+0.0;
      FOR K+1 STEP 1 UNTIL MF DO
    BEGIN
      DOUBLE(AF[MF,K],AFL[MF,K],TBH,TBL,x,SUM1H,SUM1L,+,+,SUM1H,SUM1L);
      DOUBLE(AF[MF,K],AFL[MF,K],TDH,TDL,x,SUM2H,SUM2L,+,+,SUM2H,SUM2L);
    END
    END
      END
    END
  
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      DOUBLE(TAH,TAL,TBH,TBL,X,+,TBH,TBL);
      DOUBBLE(TCH,TCL,TDH,TDL,X,+,TDH,TDL);
END
END ELSE
BEGIN
  SUM1H+SUM2H+1.0;      SUM1L+SUM2L+0.0;
  TAH+TBH+XF[2*N];      TCH+TDH+XF[2*N-2] ;
  TAL+TBL+XFL[2*N];      TCL+TDL+XFL[2*N-2];
  FOR K+1 STEP 1 UNTIL MF DO
  BEGIN
    DOUBLE(AF[MF,K],AFL[MF,K],TBH,TBL,X,SUM1H,SUM1L,+,+,SUM1H,SUM1L);
    DOUBBLE(AF[MF,K],AFL[MF,K],TDH,TDL,X,SUM2H,SUM2L,+,+,SUM2H,SUM2L);
    DOUBLE(TAH,TAL,TBH,TBL,X,+,TBH,TBL);
    DOUBBLE(TCH,TCL,TDH,TDL,X,+,TDH,TDL);
  END
END;
DOUBLE(PPF[N],0,PPF[N-1],0,/,SUM1H,SUM1L,A6,0,PPF[N],0,X,A5,0,+,PPF[N],
0,X,A4,0,+,PPF[N],0,X,A3,0,+,PPF[N],0,X,A2,0,+,PPF[N],0,X,A1,0,
+,B6,0,PPF[N-1],0,X,B5,0,+,PPF[N-1],0,X,B4,0,+,PPF[N-1],0,X,B3,
0,+,PPF[N-1],0,X,B2,0,+,PPF[N-1],0,X,B1,0,+,/,SUM2H,SUM2L,X,K2,
0,X,/,+,TAH,TAL);
DOUBLE( TAH,TAL,TAH,TAL,X,SUMH,SUML,+,+,SUMH,SUML);
END;
NX50:      DD XI+SUMH;
           LOWDDXI+SUML;
END OF DD XI;

PROCEDURE CALCX(N1F,N2F,RTF,RTFL,K1F,K1FL,K2F,K2FL,A1F,A1FL,A2F,A2FL,XIF
,XIFL,XXF,XXFL,XFF,XFFL);
  REAL RTF,K1F,K2F,A1F,A2F;  INTEGER N1F,N2F;  ARRAY XIF,XXF,XFF[0];
  REAL RTFL,K1FL,K2FL,A1FL,A2FL;  ARRAY XIFL,XXFL,XFFL[0];
BEGIN
  REAL ANN;  INTEGER I;
  REAL ANNL ;
  DOUBLE(1.0,RTF,RTFL,A1F,A1FL,X,/,+,XFF[1],XFFL[1]);
  DOUBLE(1.0,RTF,RTFL,A2F,A2FL,X,/,+,XFF[2],XFFL[2]);
  FOR I+2, I+1 WHILE I≤N1F DO
  BEGIN
    OPDW(K1F,K1FL,TOM,TOML,I-1);  DOUBLE(XIF[I-1],XIFL[I-1],TUM,TOML,A1F,A
1FL,X,+,+,ANN,ANNL);
    DOUBLE(1.0,RTF,RTFL,ANN,ANNL,X,/,+,XFF[2*I-1],XFFL[2*I-1]);
  END;
  FOR I + 2, I+1 WHILE I≤N2F DO
  BEGIN
    OPDW(K2F,K2FL,TOM,TOML,I-1);
    DOUBLE(XXF[I-1],XXFL[I-1],TUM,TOML,A2F,A2FL,X,+,+,ANN,ANNL);
    DOUBLE(1.0,RTF,RTFL,ANN,ANNL,X,/,+,XFF[2*I],XFFL[2*I]);
  END
END;

FORMAT  FH1(      /"APPROX. CELL CONST. 1ST RUN=" E17.10),
        FR2(5(E17.10,X5) ),
        FB10(      /"EXTRAPOLATION FOR CELL CONSTANT"),
        FR3(      /"APPROX. CELL CONST. 2ND RUN=" E17.10),
        FB4(      /"APPROX. RUN CONST. 1ST RUN=" E17.10),
        FB5(      /"APPROX. RUN CONST. 2ND RUN=" E17.10),

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FB13( /*RELATIVE DIFFERENCE IN Z*/ ),
FB6( /*Z(APPROX) VS RHO(APPROX)*/ ),
FB12( /*NEXT TO LAST FIT IS OPTIMAL FOR Z VS RHO*/ ),
FB8( /*X6*P(N)*X17*Z(N)*X16*RHO(N)*X16*(Z-1)*X14*P(N0...)*/
/ ),
FB16( /*SUM OF (P RATIO - Z*RHO RATIO)= E17.10),
FB17( /*DERIVATIVE MATRIX*/ ), FB18(4(E17.10,X5)/),
FR20( /*DERIVATIVE VECTOR*/ ),
FB21( /*CHANGE VECTOR*/ ),
FB22( /*MATRIX IS SINGULAR*/ ),
FB11( /*EXTRAPOLATION FOR KUN CONSTANT*/);
LABEL L97,NX1,L71,NX2,L37,L31,L45,L96,L47,L43,NX33,NX30,L89,
DWT,L40,L41,NX3,SINGUL,UN,NX4,L42,L44,L94,L95,PLT;
LABEL L77,L88,L46;
IF NUMRUN=1 THEN READ(CR,/, FOR IXQ+1 STEP 1 UNTIL N1 DO P[IXQ])
ELSE READ(CR,/,FOR IXQ+1STEP 1 UNTIL N1 DO P[IXQ],
FOR IXQ+ 1 STEP 1 UNTIL N2 DO PP[IXQ]);
WRITE(LP[NQ],<X4 "PRESSURES FOR FIRST RUN =">);
WRITE(LP,<"* X31, 6(F10.5,X2), X15 "*">, FOR IXQ+1 STEP 1 UNTIL N1 DO
P[IXQ]);
IF NUMRUN=2 THEN BEGIN
WRITE(LP[NQ],<X4 "PRESSURES FOR SECOND RUN =">);
WRITE(LP,<"* X31, 6(F10.5,X2), X15 "*">, FOR IXQ+1 STEP 1 UNTIL N2 DO
PP[IXQ]); END;
WRITE(LP,<"* X118 "*">);
WRITE(LP[PAGE],<20("*****")>);
COMMENT EXTRAPOLATION FOR FIRST CELL CONSTANT;
NNN+N; MM + M; N + NN; M + MMM;
IF WH#1 THEN GO TO NX1;
READ(CR,/,K10,A10); IF NUMRUN=1 THEN GO TO L97;
READ (CR,/,K20, A20);
L97: GO TO L31;
NX1: IF WH#2 THEN GO TO NX2;
READ(CR,/,K10); IF NUMRUN = 1 THEN GO TO L77;
READ(CR,/,K20); L77: GO TO L37;
NX2: FOR NQ+2,NQ+1 WHILE NQSN1 DO DOUBLE(P[NQ],0,P[NQ-1],0,/,+,PRAT[NQ-1],
PRATL[NQ-1]);
FOR NQ+1,NQ+1WHILE NQSN DO
BEGIN DOUBLE(1,0,+,F[1,NQ],FL[1,NQ]); Y[NQ]+PRAT[N1-NN+NQ-1];
END;
FOR K + 2,K+1 WHILE KSM DO FOR NQ+1,NQ+1 WHILE NQSN DO
BEGIN HAM+P[N1-NN+NQ]; DPOW(HAM,0,TUM,TUML,K-1);
F[K,NQ]+TUM; FL[K,NQ]+TUML; END;
WRITE(LP,FB10);
ORND(N,M,EPSILON,Y,F,FL,A,AL,BFF,BFFL,MIN);
DOUBLE(1,0,A[MIN,1],AL[MIN,1],/,+,K1,K1L); WRITE(LP,FB1,K1); IF
NUMRUN=1 THEN GO TO L37;
DOUBLE(K1,K1L,+,K10,K10L);
COMMENT EXTRAPOLATION FOR 2ND CELL CONSTANT;
FOR NQ+2,NQ+1 WHILE NQSN2 DO DOUBLE(PP[NQ],0,PP[NQ-1],0,/,+,PPRAT[NQ-1],
PPRATL[NQ-1]);
FOR NQ + 1,NQ+1 WHILE NQSN DO
BEGIN F[1,NQ]+1,0; Y[NQ]+ PPRAT[N2-NN+NQ-1] ;
FL[1,NQ]+0,0;
END;
FOR K+2,K+1 WHILE KSM DO FOR NQ+1,NQ+1 WHILE NQSN DO

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      BEGIN      HAM=PP[N2-NN+NQ];      DPOW(HAM,0,TOM,TOML,K-1);
      F[K,NQ]+TOM;      FL[K,NQ]+TOML; END;
      WRITE(LP,FB10);
      ORNOR(N,M,EPSILON,Y,F,FL,A,AL,BFF,BFFL,MIN);
      DOUBLE(1.0,A[MIN,1],AL[MIN,1],/,+,K2,K2L);      WRITE(LP,FB3,K2);
      K20+K2;      K20L+K2L;
      DOUBLE(K1,K1L,K2,K2L,+,2.0,/,+,K2,K2L);      K10+K20+K1+K2;
      K10L+K20L+K1L+K2L;
L37: IF WH=2 THEN DOUBLE(K10,K10L,+,K1,K1L);      IF NUMRUN=2 THEN
      DOUBLE(K20,K20L,+,K2,K2L);
      COMMENT EXTRAPOLATION FOR FIRST RUN CONSTANT ;
      BEGIN      DEFINE SEGMENTBUMP =0#;
      XIQ+1.0;
      XIQL+0.0;      XI[0]+ZT1[0]+1.0;
      XIL[0]+ZT1L[0]+0.0;
      FOR NQ+2,NQ+1 WHILE NQ≤N1 DO
      BEGIN
      DOUBLE(P[NQ],0,A6,0,x,A5,0,+,P[NQ],0,x,A4,0,+,P[NQ],0,x,A3,0,+,P[NQ],
      0,x,A2,0,+,P[NQ],0,x,A1,0,+,P[NQ-1],0,B6,0,x,B5,0,+,P[NQ-1],
      0,x,B4,0,+,P[NQ-1],0,x,B3,0,+,P[NQ-1],0,x,B2,0,+,P[NQ-1],0,x,
      B1,0,+,/,+,ZT1[NQ-1],ZT1L[NQ-1]);
      DOUBLE(XIQ,XIQL,ZT1[NQ-1],ZT1L[NQ-1],x,+,XIQ,XIQL);
      DOUBLE(XIQ,XIQL,+,XI[NQ-1],XIL[NQ-1]);
      END;
      FOR NQ+1,NQ+1 WHILE NQ ≤ N DO
      BEGIN      Y[NQ] + P[N1-NN+NQ]*K1*(N1-NN+NQ-1) * XI[N1-NN+NQ-1];
      F[1,NQ]+1.0;
      FL[1,NQ]+0.0;
      END;
      FOR NQ+2,NQ+1 WHILE NQ≤N1 DO BEGIN DPOW(K1,K1L,TOM,TOML,NQ-1);
      DOUBLE(P[NQ],0,TOM,TOML,XI[NQ-1],XIL[NQ-1],x,+,PN[NQ],PNL[NQ
      ]);      END;
      PN[1]+P[1];
      PNL[1]+0.0;
      FOR K+2,K+1 WHILE K≤M DO FOR NQ+1,NQ+1 WHILE NQ≤N DO
      BEGIN HAM+P[N1-NN+NQ];      DPOW(HAM,0,TOM,TOML,K-1);
      F[K,NQ]+TOM;      FL[K,NQ]+TOML; END;
      WRITE(LP,FB11);
      ORNOR(N,M,EPSILON,Y,F,FL,A,AL,BFF,BFFL,MIN);
      DOUBLE(1.0,A[MIN,1],AL[MIN,1],/,+,AK1,AK1L);
      WRITE(LP,FB4,AK1);
      DOUBLE(AK1,AK1L,+,A10,A10L);
      END;
      IF NUMRUN=1 THEN GO TO L31;
      COMMENT EXTRAPOLATION FOR 2ND RUN CONSTANT;
      BEGIN      DEFINE SEGMENTBUMP =0#;
      XIQ+1.0;
      XIQL+0.0;      XXI[0]+ZT2[0]+1.0;
      XXIL[0]+ZT2L[0]+0.0;
      FOR NQ+2,NQ+1 WHILE NQ≤N2 DO BEGIN
      DOUBLE(PP[NQ],0,A6,0,x,A5,0,+,PP[NQ],0,x,A4,0,+,PP[NQ],0,x,A3,0,+,
      PP[NQ],0,x,A2,0,+,PP[NQ],0,x,A1,0,+,PP[NQ-1],0,B6,0,x,B5,0,+,
      PP[NQ-1],0,x,B4,0,+,PP[NQ-1],0,x,B3,0,+,PP[NQ-1],0,x,B2,0,+,
      PP[NQ-1],0,x,B1,0,+,/,+,ZT2[NQ-1],ZT2L[NQ-1]);
      DOUBLE(XIQ,XIQL,ZT2[NQ-1],ZT2L[NQ-1],x,+,XIQ,XIQL);
      DOUBLE(XIQ,XIQL,+,XXI[NQ-1],XXIL[NQ-1]);

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END;
FOR NQ+1,NQ+1 WHILE NQ≤N DO
BEGIN
  Y[NQ]← PP[N2-NN+NQ]*K2*(N2-NN+NQ-1)* XXI[N2-NN+NQ-1] ;
  F[1,NQ]←1.0; FL[1,NQ]←0.0;
END;
FOR NQ ← 2,NQ+1 WHILE NQ ≤ N2 DO
BEGIN
  DPOW(K2,K2L,TOM,TOML,NQ-1);
  DOUBLE(P[NQ],0,TUM,TUML,XXI[NQ-1],XXIL[NQ-1],*,*,+,PN[N1+
    NQ],PNL[N1+NQ]);
  PNL[N1+1]←PP[1]; PNL[N1+1]←0.0;
  FOR K←2,K+1 WHILE K≤N DO FOR NQ+1,NQ+1 WHILE NQ≤N DO
  BEGIN
    HAM←PP[N2-NN+NQ]; DPOW(HAM,0,TOM,TOML,K-1);
    F[K,NQ]←TOM; FL[K,NQ]←TOML;
  END;
  WRITE(LP,FB11);
  ORNOR(N,M,EPSILON,Y,F,FL,A,AL,BFF,BFFL,MIN);
  DOUBLE(1.0,A[MIN,1],AL[MIN,1],/,*,AK2,AK2L);WRITE(LP,FB5,AK2);
  DOUBLE(AK2,AK2L,*,A20,A20L);
END;
L31: N←NNN; M←MM;TEMP←TEMP+273.15;DOUBLE(TEMP,0,R,0,*,*,RT,RTL);
  COMMENT CALCULATION OF Z(APPROX) AND RHO(APPROX);
  NNN←WH1; MM←M;
L45: FOR J←WH1 STEP 1 UNTIL MM DO
BEGIN
  K1L←K10L; AK1L←A10L;
  K1←K10; AK1←A10; IF NUMRUN=1 THEN GO TO L47; K2←K20; AK2←A20;
  K2L←K20L; AK2L←A20L;
L47: NN←0;
L43: NN←NN+1;
  WRITE(LP,FB1,K1); WRITE(LP,FB4, AK1);
  IF NUMRUN=1 THEN GO TO NX33; WRITE(LP,FB3,K2); WRITE(LP,FB5,AK2);
NX33: CALCX(N1,N2,RT,RTL,K1,K1L,K2,K2L,AK1,AK1L,AK2,AK2L,XI,XIL,XXI,
  XXIL,X,XL);
  CALFY(N,J,N1,N2,NUMRUN,FIT,K1,K1L,K2,K2L,AK1,AK1L,AK2,AK2L,P,PP,XI,
  XIL,XXI,XXIL,X,XL,Y,F,FL);
  IF FIT=2 THEN FOR NQ+1,NQ+1 WHILE NQ≤N DO Y[NQ] ← Y[NQ] + 1.0;
  IF NUMRUN=1 THEN GO TO NX30;
  FOR NQ+1,NQ+1 WHILE NQ≤N DO DOUBLE(X[NQ],0,*,DUM1[NQ],DUM1L[NQ]);
  FOR NQ+1,NQ+2 WHILE NQ≤N DO X[(NQ+1)DIV 2]←DUM1[NQ];
  FOR NQ+2,NQ+2 WHILE NQ≤N DO X[N1 + NQ DIV 2] ← DUM1[NQ];
NX30: COMMENT CALCULATION OF (Z-1)V AND Z(APPROX) VS RHO(APPROX);
  BEGIN
    DEFINE SEGMENTBUMP =0;
    WRITE(LP,FB8);
    FOR NQ+1,NQ+1 WHILE NQ≤N DO DOUBLE(Y[NQ],0,1.0,*,X[NQ],0,/,*,ZV[NQ],
      ZVL[NQ]);
  ]
  FOR NQ+1,NQ+1 WHILE NQ≤N DO WRITE(LP,FB2,P[NQ],Y[NQ],X[NQ],
    ZV[NQ], PNL[NQ]);
  FOR NQ ← 1,NQ+1 WHILE NQ≤N2 DO
    WRITE(LP,FR2, PP[NQ], Y[N1+NQ],X[N1+NQ],ZV[N1+NQ],PN[N1+NQ]);
  COMMENT FIRST SAVE FOR PLOTTING;
  FOR NQ ← 1 STEP 1 UNTIL N DO
  BEGIN
    TEMPXA[NQ]← X[NQ];
    TEMPYA[NQ]← ZV[NQ];
  END;
  IF FIT=2 THEN FOR NQ+1,NQ+1 WHILE NQ≤N DO Y[NQ]←Y[NQ]-1.0;
  ORNOR(N,J,EPSILON,Y,F,FL,A,AL,BFF,BFFL,MIN);DOUBLE(BFF[J],BFFL[J],*

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      ,TBF[NN,J],TBF[NN,J]);
END;
COMMENT PERTURBATION OF A AND N;
IF FIT=1 THEN
  BEGIN
    FOR NQ+1,NQ+1 WHILE NQ≤N1 DO
    BEGIN
      SUM+SUML+0.0;
      FOR K+1,K+1 WHILE K≤J DO
      DOUBLE(X[NQ]*(K-1),0,A[J,K],AL[J,K],X,SUM,SUML,+,+,SUM,SUML);
      Y[NQ]+SUM; DOUBLE(SUM,SUML,,1.0,-,X[NQ],0,/,+,ZV[NQ],ZVL[NQ]);
    END;
    IF NUMRUN=1 THEN GO TO L89;
    FOR NQ+1,NQ+1 WHILE NQ≤N2 DO
    BEGIN
      SUM+0.0;
      SUML+0.0;
      FOR K+1,K+1 WHILE K≤J DO DOUBLE(X[N1+NQ]*(K-1),0,A[J,K],AL[J,K],X,SUM,SUML,+,+,SUM,SUML);
      Y[N1+NQ]+SUM; DOUBLE(SUM,SUML,,1.0,-,X[N1+NQ],0,/,+,ZV[N1+NQ],ZVL[N1+NQ]);
    END; L89;
  END ELSE
  BEGIN
    FOR NQ+1,NQ+1 WHILE NQ≤N1 DO
    BEGIN
      SUM + 1.0;
      SUML+0.0;
      FOR K+1,K+1 WHILE K≤J DO DOUBLE(X[NQ]*K,0,A[J,K],AL[J,K],X,SUM,SUML,+,+,SUM,SUML);
      Y[NQ]+SUM; DOUBLE(SUM,SUML,,1.0,-,X[NQ],XL[NQ],/,+,ZV[NQ],ZVL[NQ]);
    Q]
    END;
    IF NUMRUN=1 THEN GO TO L88;
    FOR NQ+1,NQ+1 WHILE NQ≤N2 DO
    BEGIN
      SUM+1.0;SUML+0.0;FOR K+1,K+1 WHILE K≤J DO DOUBLE(SUM,SUML,A[J,K],AL[J,K],X[N1+NQ]*K,0,X,+,+,SUM,SUML);
      Y[N1+NQ]+SUM; DOUBLE(SUM,SUML,,1.0,-,X[N1+NQ],0,/,+,ZV[N1+NQ],ZVL[N1+NQ]);
    END;L88;
  END;
  WRITE(LP,F88);
  FOR NQ+1,NQ+1 WHILE NQ≤N1 DO WRITE(LP,F82,P[NQ],Y[NQ],X[NQ],ZV[NQ],PN[NQ]); FOR NQ+1,NQ+1 WHILE NQ≤N2 DO
  WRITE ( LP,F82,PP[NQ],Y [N1+NQ],X[N1+NQ],ZV[N1+NQ],PN[N1+NQ])
;
  BEGIN DEFINE SEGMENTBUMP =0;
  COMMENT FIRST SAVE FOR PLOTTING SECOND GRAPH;
  FOR NQ+1 STEP 1 UNTIL N DO
  BEGIN
    TEMPXB[NQ]+X[NQ]; TEMPYB[NQ]+ ZV[NQ];
  END
  ;
  IF NUMRUN=2 THEN
  BEGIN
    FOR NQ+1,NQ+1 WHILE NQ≤N1 DO
    BEGIN
      DUM1[NQ] + P[NQ]; P1[2*NQ-1] + DUM1[NQ] ;
      DUM1L[NQ]+0.0;P1L[2*NQ-1]+0.0;
    END;
    FOR NQ+1,NQ+1 WHILE NQ≤N2 DO
    BEGIN
      DUM1[NQ]+PP[NQ]; P1[2*NQ]+DUM1[NQ];
      DUM1L[NQ]+0.0; P1L[2*NQ]+0.0;
    END
  END;
  CALCX(N1,N2,RT,RTL,K1,K1L,K2,K2L,AK1,AK1L,AK2,AK2L,XI,XIL,XXI,XXIL,X,XL);
  ZETA0+DDXI(N1,N2,J,FIT,A,AL,P,PP,X,XL); WRITE(LP,F816,ZETA0);

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ZETAOL ←LOWDDXI;
COMMENT 2ND SAVE FOR PLOTTING;
FOR NQ←1 STEP 1 UNTIL N DO
BEGIN
  TEMPXC[NQ]←TEMPXA[NQ];
  TEMPY[NQ]←TEMPYA[NQ];
  TEMPXC[NQ]←TEMPXB[NQ];  TEMPYC[NQ]←TEMPYB  [NQ];

  END;
END OF SEGMENTBUMP;
COMMENT FORMATION OF DERIVATIVES;
L40: CALCX(N1,N2,RT,RTL,K1,K1L,K2,K2L,AK1,AK1L,AK2,AK2L,XI,XIL,XXI,XXIL,
      X,XL);
CALFY(N,M,N1,N2,NUMRUN,FIT,K1,K1L,K2,K2L,AK1,AK1L,AK2,AK2L,P,PP,XI,
      XIL,XXI,XXIL,X,XL,Y,F,FL);
SLONC5J←FALSE;
ORNORCN,J,EPSILON,Y,F,FL,A,AL,BFF,BFFL,MIN);
SLONC5J←TRUE;
BEGIN
  DEFINE SEGMENTBUMP =0;
  SS1←SS2+SS3←SS4+SS5+SSK6+0.0;
  SS1L←SS2L+SS3L+SS4L+SS5L+SSK6L+0.0;
  FOR NQ←1 STEP 1 UNTIL N1 DO BEGIN
    SSK1←SSK2←SSK3←SSK4←SSK5+0.0;
    SSK1L←SSK2L←SSK3L←SSK4L+SSK5L+0.0;
    HAM←XL2×NQ-1; HAML←XL[2×NQ-1];
    FOR K←1 STEP 1 UNTIL J DO BEGIN
      DPUMCHAM,HAML,10M,10ML,K);
      DOUBLE(TOM,TUML,A[J,K],AL[J,K],X,+,ZETA1,ZETA1L);
      DOUBLE(ZETA1,ZETA1L,SSK1,SSK1L,+,+,SSK1,SSK1L);
      DOUBLE(NQ-1,0,K,0,X,+,1,+,K,0,X,ZETA1,ZETA1L,X,SSK3,SSK3L,+,+,SSK3,
        SSK3L);
      DOUBLE(1+K,0,K,0,X,ZETA1,ZETA1L,X,SSK4,SSK4L,+,+,SSK4,SSK4L);
      DOUBLE(K,0,K,0,X,ZETA1,ZETA1L,X,SSK5,SSK5L,+,+,SSK5,SSK5L)

      END OF SUM OVER K LOOP;
      DPOM(K1,K1L,ZETA2,ZETA2L,NQ-1);
      DPOM(K1,K1L,ZETA3,ZETA3L,NQ-2);
      DPOM(K1,K1L,ZETA4,ZETA4L,NQ-3);
      DOUBLE(P[NQ],0,AK1,AK1L,X,ZETA2,ZETA2L,X,XI[NQ-1],XIL[NQ-1],X,+,1.0,
        SSK1,SSK1L,+,+,SSK6,SSK6L);
      XIL[NQ-1],X,NQ-1,0,SSK2,SSK2L,X,K1,K1L,/,+,SSK6,SSK6L,X,SS1,
        SS1L,+,+,SS1,SS1L);
      DOUBLE(P[NQ],0,ZETA2,ZETA2L,X,XI[NQ-1],XIL[NQ-1],X,SSK2,SSK2L,AK1,
        AK1L,/,+,SSK6,SSK6L,X,SS2,SS2L,+,+,SS2,SS2L);

      SS3←SS3+(SSK6×((NQ-1)×(NQ-2)×P[NQ]×AK1×K1+(NQ-3)×XI[NQ-1]-(NQ-1)×
        SSK3/(K1×2)))+(CNQ-1)×P[NQ]×AK1×K1+(NQ-2)×XI[NQ-1]-(NQ-1)×SSK2/
        K1)×2);
      SS4←SS4+(SSK6×(-SSK4/(AK1×2)))+(P[NQ]×K1+(NQ-1)×XI[NQ-1]+SSK2/AK1)×2
        );
      SS5←SS5+(SSK6×((NQ-1)×P[NQ]×K1+(NQ-1)×XI[NQ-1]-(NQ-1)×SSK5/(AK1×K1)
        )+((NQ-1)×P[NQ]×AK1×K1+(NQ-2)×XI[NQ-1]-(NQ-1)×SSK2/K1)×(P[NQ]×
        K1+(NQ-1)×XI[NQ-1]+SSK2/AK1)
      END OF SUM OVER NQ LOOP;
      DOUBLE(SS1,SS1L,2.0,X,+,DK1,DK1L);

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DOUBLE(SS2,SS2L,,2.0,x,+,DA1,DA1L);
DOUBLE(SS3,SS3L,,2.0,x,+,D2K1,D2K1L);
DOUBLE(SS4,SS4L,,2.0,x,+,D2A1,D2A1L);
DOUBLE(SS5,SS5L,,2.0,x,+,D2K1A1,D2K1A1L);
SS1+SS2+SS3+SS4+SS5+SSK6+0.0;
SS1L+SS2L+SS3L+SS4L+SS5L+SSK6L+0.0;
FOR NQ+1 STEP 1 UNTIL N2 DO BEGIN
SSK1+SSK2+SSK3+SSK4+SSK5+0.0;
SSK1L+SSK2L+SSK3L+SSK4L+SSK5L+0.0;
HAM+X[2*NQ]; HAML+XL[2*NQ];
FOR K+1 STEP 1 UNTIL J DO BEGIN
DPOW(HAM,HAML,TOM,TOML,K);
DOUBLE(TOM,TOML,A[J,K],AL[J,K],x,+,ZETA1,ZETA1L);
DOUBLE(ZETA1,ZETA1L,SSK1,SSK1L,+,+,SSK1,SSK1L);
DOUBLE(ZETA1,ZETA1L,K,0,x,SSK2,SSK2L,+,+,SSK2,SSK2L);
DOUBLE(NQ-1,0,K,0,x,,1,+,K,0,x,ZETA1,ZETA1L,x,SSK3,SSK3L,+,+,SSK3,
SSK3L);
DOUBLE(1+K,0,K,0,x,ZETA1,ZETA1L,x,SSK4,SSK4L,+,+,SSK4,SSK4L);
DOUBLE(K,0,K,0,x,ZETA1,ZETA1L,x,SSK5,SSK5L,+,+,SSK5,SSK5L)
END OF SUM OVER K LOOP;
DPOW(K2,K2L,ZETA2,ZETA2L,NQ-1);
DPOW(K2,K2L,ZETA3,ZETA3L,NQ-2);
DPOW(K2,K2L,ZETA4,ZETA4L,NQ-3);
DOUBLE(PP[NQ],0,AK2,AK2L,x,ZETA2,ZETA2L,x,XXI[NQ-1],XXIL[NQ-1],x,,
1.0,SSK1,SSK1L,+,+,SSK6,SSK6L);
DOUBLE(NQ-1,0,PP[NQ],0,x,AK2,AK2L,x,ZETA3,ZETA3L,x,XXI[NQ-1],
XXIL[NQ-1],x,NQ-1,0,SSK2,SSK2L,x,K2,K2L,/,+,SSK6,SSK6L,x,SS1,
SS1L,+,+,SS1,SS1L);
DOUBLE(PP[NQ],0,ZETA2,ZETA2L,x,XXI[NQ-1],XXIL[NQ-1],x,SSK2,SSK2L,
AK2,AK2L,/,+,SSK6,SSK6L,x,SS2,SS2L,+,+,SS2,SS2L);

SS3+SS3+((SSK6*((NQ-1)*(NQ-2)*PP[NQ]*AK2*K2*(NQ-3)*XXI[NQ-1]-(NQ-1)*
SSK3/(K2*2)))+(NQ-1)*PP[NQ]*AK2*K2*(NQ-2)*XXI[NQ-1]+(NQ-1)*SSK2
/K2*2);
SS4+SS4+((SSK6*(-SSK4/(AK2*2)))+(PP[NQ]*K2*(NQ-1)*XXI[NQ-1]+SSK2/AK2)
*2);
SS5+SS5+((SSK6*((NQ-1)*PP[NQ]*K2*(NQ-1)*XXI[NQ-1]+(NQ-1)*SSK5/(AK2*
K2)))+(NQ-1)*PP[NQ]*AK2*K2*(NQ-2)*XXI[NQ-1]+(NQ-1)*SSK2/K2)*
(PP[NQ]*K2*(NQ-1)*XXI[NQ-1]+SSK2/AK2))

END OF SUM OVER NQ LOOP;
DOUBLE(SS1,SS1L,,2.0,x,+,DK2,DK2L);
DOUBLE(SS2,SS2L,,2.0,x,+,DA2,DA2L);
DOUBLE(SS3,SS3L,,2.0,x,+,D2K2,D2K2L);
DOUBLE(SS4,SS4L,,2.0,x,+,D2A2,D2A2L);
DOUBLE(SS5,SS5L,,2.0,x,+,D2K2A2,D2K2A2L);
D2K1K2+D2K1A2+D2A1K2+D2A1A2+0.0;
D2K1K2L+D2K1A2L+D2A1K2L+D2A1A2L+0.0;
END OF SEGMENTBUMP;
COMMENT SOLUTION FOR DELTA A AND DELTA N;
L41: IF NUMRUN=1 THEN
BEGIN
DOUBLE(D2K1A1,D2K1A1L,DA1,DA1L,x,D2A1,D2A1L,DK1,DK1L,x,-,
D2K1,D2K1L,D2A1,D2A1L,x,D2K1A1,D2K1A1L,D2K1A1,D2K1A1L,x,-,/,
+,CHG[1],QBDM);
DOUBLE(D2K1A1,D2K1A1L,DK1,DK1L,x,D2K1,D2K1L,DA1,DA1L,x,-,

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      D2K1,D2K1L,D2A1,D2A1L,x,D2K1A1,D2K1A1L,D2K1A1,D2K1A1L,x,-,/,
      +,CHG[2],DBDUM);
    GO TO L42;
END;
  DMTX[1,1]+D2K1; DMTX[1,2]+D2K1A1; DMTX[1,3]+D2K1K2; DMTX[1,4]+
    D2K1A2; DMTX[2,1]+D2K1A1; DMTX[2,2]+D2A1;
  DMTX[2,3]+D2A1K2; DMTX[2,4]+D2A1A2; DMTX[3,1]+D2K1K2;
  DMTX[3,2]+D2A1K2; DMTX[3,3]+D2K2; DMTX[3,4]+D2K2A2; DMTX[4,1]+
  D2K1A2; DMTX[4,2]+D2A1A2; DMTX[4,3]+D2K2A2; DMTX[4,4]+D2A2;
  DMTXL[1,1]+D2K1L; DMTXL[1,2]+D2K1A1L; DMTXL[1,3]+D2K1K2L; DMTXL[1,4]+
  D2K1A2L; DMTXL[2,1]+D2K1A1L; DMTXL[2,2]+D2A1L; DMTXL[2,3]+D2A1K2L; DMTXL[2,4]+
  D2A1A2L; DMTXL[3,1]+D2K1K2L; DMTXL[3,2]+D2A1K2L; DMTXL[3,3]+D2K2L; DMTXL[3,
  4]+D2K2A2L; DMTXL[4,1]+D2K1A1L; DMTXL[4,2]+D2A1A2L; DMTXL[4,3]+D2K2A2L; DMTX
  L[4,4]+D2A2L;
  SLON[12]+TRUE;
  IF NOT SLON[12] THEN GO TO NX3;
  WRITE(LP,FB17); WRITE(LP,FB18, FOR I=1,I+1 WHILE I≤4 DO
    FOR K=1,K+1 WHILE K≤4 DO DMTX[I,K]);
NX3: INVERT(4,DMTX, @-6,SINGUL); GO TO ON;
SINGUL: WRITE(LP,FB22);
ON: DVEC[1]+=-DK1; DVEC[2]+=-DA1; DVEC[3]+=-DK2; DVEC[4]+=-DA2;
  DVECL[1]+=-DK1L; DVECL[2]+=-DA1L; DVECL[3]+=-DK2L; DVECL[4]+=-DA2L;
  IF NOT SLON[12] THEN GO TO NX4;
  WRITE(LP,FB17);
  WRITE(LP,FB18, FOR I=1 STEP 1 UNTIL 4 DO FOR K=1 STEP 1 UNTIL 4
    DO DMTX[I,K]);
  WRITE(LP,FB20); WRITE(LP,FB18, FOR I=1 STEP 1 UNTIL 4 DO DVEC[I]);
NX4: FOR I=1 STEP 1 UNTIL 4 DO
  BEGIN
    KK+0.0; KKL+0.0; FOR K=1 STEP 1 UNTIL 4 DO
      DOUBLE(DMTX[I,K],DMTXL[I,K],DVEC[K],DVECL[K],x, KK, KKL, +, +, KK, K
      KL);
    CHG[I]+ KK;
    CHGL[I]+KKL;
  END;
  IF NOT SLON[12] THEN GO TO L42;
  WRITE(LP, FB21); WRITE(LP,FB18, FOR I=1 STEP 1 UNTIL 4 DO CHG[I]);
L42: DOUBLE(CHG[1],CHGL[1],K1,K1L,+,+,K1,K1L);
  DOUBLE(CHG[2],CHGL[2],AK1,AK1L,+,+,AK1,AK1L);
  IF NUMRUN#1 THEN
  BEGIN
    DOUBLE(CHG[3],CHGL[3],K2,K2L,+,+,K2,K2L);
    DOUBLE(CHG[4],CHGL[4],AK2,AK2L,+,+,AK2,AK2L);
  END;
  IF NN=1 THEN GO TO L43;
  GO TO IF NN=3 THEN PLT ELSE L43;
OWT: WRITE(LP,FB12);
PLT: IF NOT SLON[25] THEN DRAWIT(TEMPX,TEMPY,N1,N2);
  IF NOT SLON[25] THEN DRAWIT(TEMPXC,TEMPYC,N1,N2);
L94: END;
L95: END END END END;
  IF IND<AMT THEN
  BEGIN
    ARRAY LAIRD[0:5];
    FILL LAIRD[*] WITH "00END OF00 DATA 00SET ";
    SYMBOL(0,4.5,.21,LAIRD,-90,15);
    PLOT(3,0,-5);
    IND+IND+1;
  END;

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      GO TO L60;
    END;
    IF NOT SLOW[25] THEN
  BEGIN
    ARRAY LAST[0:5];
    FILL LAST[*] WITH "00PLOTTIOONG FINOOISHED ";
    SYMBOL ( 1,8.5,.49, LAST,-90,17);
    PLOT(4,0,-3);
  END;
  WRITE(LP[PAGE]);
  WRITE ( LP, <"I/O TIME =" F7.2 " SEC."// "PROC. TIME=" F7.2 " SEC.">
    , TIME(3)/60 , TIME(2)/60 );
  END OF PRUGRAM.
  ARCTAN IS SEGMENT NUMBER 0079,PRT ADDRESS IS 0117
  COS IS SEGMENT NUMBER 0080,PRT ADDRESS IS 0075
  EXP IS SEGMENT NUMBER 0081,PRT ADDRESS IS 0072
  LN IS SEGMENT NUMBER 0082,PRT ADDRESS IS 0071
  SIN IS SEGMENT NUMBER 0083,PRT ADDRESS IS 0076
  OUTPUT(W) IS SEGMENT NUMBER 0084,PRT ADDRESS IS 0045
  BLOCK CONTROL IS SEGMENT NUMBER 0085,PRT ADDRESS IS 0005
  INPUT(W) IS SEGMENT NUMBER 0086,PRT ADDRESS IS 0144
  X TO THE I IS SEGMENT NUMBER 0087,PRT ADDRESS IS 0073
  GO TO SOLVER IS SEGMENT NUMBER 0088,PRT ADDRESS IS 0065
  ALGOL WRITE IS SEGMENT NUMBER 0089,PRT ADDRESS IS 0014
  ALGOL READ IS SEGMENT NUMBER 0090,PRT ADDRESS IS 0015
  ALGOL SELECT IS SEGMENT NUMBER 0091,PRT ADDRESS IS 0016
  COMPILATION TIME = 208 SECONDS.
  NUMBER OF ERRORS DETECTED = 000. LAST ERROR ON CARD #
  NUMBER OF SEQUENCE ERRORS COUNTED = 0.
  NUMBER OF SLOW WARNINGS = 0.
  PRT SIZE= 470; TOTAL SEGMENT SIZE= 6389 WORDS.
  DISK STORAGE REQ.= 360 SEGS.; NO. SEGS.= 92.
  ESTIMATED CORE STORAGE REQUIREMENT = 29335 WORDS.

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Program 200; Comment ORNOR CALL;

Begin Integer AMT, I: READPT(AMT); I 1;

L60:Begin Integer N,M; READPT(N,M);

Begin Real A0,AT,epsilon,Temp; Integer n,k,comp,NN,MIN;

Array F 1:M,1:N,Y,X 1:N, a 1:M,1:M, BFF 1:M;

Format FM10(5(J1), 'Y(N)',2(J1)),FM12(5(J1),'X(N)',2(J1)),
      FM11(J7, 'TEMPERATURE=',F5.2,S5,'PER CENT HELIUM=',
      F5.2,S5,'NO. OF DATA POINTS=', I3,S5,'M=',I3),
      FM9(5(R10,S5),J1);

Mc Procedure ORNOR(201,1,10);

READPT(Temp,comp,epsilon);

READPT(Y 1, ..., Y N, X 1, ..., X N);

PRINT(FM11,Temp,comp,N,M); PRINT(FM10); PRINT(FM9,Y 1, ...,Y N);

      PRINT(FM12); PRINT(FM9,X 1, ...,X N);

For n←1,n+1 While n ≤ N Do F[1,n]←1.0;

For k←2,k+1 While k ≤ M Do For n←1 While n≤N Do F[k,n]←X[n]
      ↑k-1; (or any function of X n desired)

ORNOR(N,M, epsilon,Y,F,a,BFF,MIN);

End End;

If I < AMT Then Begin I←I+1;

Goto L60 End End;

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