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THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

LIQUID DENSITY AND EXCESS VOLUME OF LIGHT HYDROCARBON MIXTURES AT -165.0°C AND AT SATURATION PRESSURE

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

BY

MOHAMMED YOUSUF SHANA'A

Norman, Oklahoma

1966

LIQUID DENSITY AND EXCESS VOLUME OF

LIGHT HYDROCARBON MIXTURES AT

-165.0°C AND AT SATURATION PRESSURE

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Joyce, Bianca and Najiya

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LIQUID DENSITY AND EXCESS VOLUME OF LIGHT HYDROCARBON MIXTURES AT -165.0°C AND AT SATURATION PRESSURE

CHAPTER I

INTRODUCTION

This thesis is a report on the development of a low temperature experimental apparatus for the determination of the density of cryogenic liquids. This apparatus was successfully used to measure the liquid densities of pure components and mixtures of liquefied petroleum gases. All the measurements were made at around -165°C and at subatmospheric pressures. The limits of the absolute accuracy of the experimental results were established for each individual system as shown in Appendix E.

The need for such data is easily established. For example, the several sources of data for the density of pure liquid methane[9,12,16,25] show disagreement of about one percent. In addition, accurate density data of liquid mixtures such as methane + ethane, methane + propane, etc. are not to our knowledge available in the literature.

The systems selected for study included 1) the pure

components methane, ethane and propane, 2) the binary mixtures methane + ethane, methane + propane and ethane + propane (complete composition range), 3) the binary mixtures methane + n-butane and ethane + n-butane (each at one composition), and 4) the ternary system methane + ethane + propane at two different compositions.

The pycnometer method was chosen for the experimental work. The liquid density was determined by condensing the component gases from high pressure weighing bombs into a 30 cc fused quartz pycnometer. The mass of each gas condensed was determined by direct differential weighing of the pressure bomb containing the gas. The composition of the resulting mixture was calculated from the known masses of each component and the resulting total mass of the mixture. The volume of the pycnometer at room temperature was determined by direct differential weighings with distilled water. Then by using the thermal expansion data for fused quartz, the volume of the pycnometer at the temperature of operation was calculated. The thermal expansion data for fused quartz were measured by the National Bureau of Standards. The pycnometer was placed in a cryostat controlled to $\pm$ 0.002°C. The cryostat temperature was measured with a platinum resistance thermometer in conjunction with a Leeds and Northrup G-2 Mueller resistance bridge.

The operating temperature of -165°C was chosen for this study. Because of the difficulty in bringing the temperature of

the cryostat to exactly -165°C, the liquid density was measured as a function of temperature in a range that included -165°C. Then, the density at the operating temperature was read directly from the smoothed data of the experimental results.

The experimental density values were used to calculate the excess volume of the binary mixtures methane + ethane, methane + propane and ethane + propane, and of the two ternary systems.

The calculated excess volume results were used to test the applicability of the principle of congruence which was introduced by Bronsted and Koefoed[6]. According to these authors, the thermodynamic properties of a mixture of n-alkanes are determined by an average chain-length,

$$n = \Sigma_i n_i x_i \qquad (1)$$

where n_i is the number of carbon atoms in a molecule of the ith species, and x_i the mole fraction of that species in the mixture. Mixtures of the same average chain-length are said to be congruent. Thus for example, if n is integral, all mixtures with average chain-length n are congruent with the pure substance C_nH_{2n+2}.

The validity of the principle of congruence was confirmed for straight chain hydrocarbon mixtures with components having 5 carbon atoms or more[20,21,22,23,24]. The results of this investigation did not conform to this principle. This finding led

to the conclusion that the principle of congruence should not be used to describe the thermodynamic properties of mixtures containing liquid methane. The invalidity of this principle to such mixtures could be attributed to the difference in molecular structure of methane and that of other hydrocarbons.

CHAPTER II

REVIEW OF PREVIOUS WORK

A review of previous work on the density and excess volume of cryogenic liquids is presented in this chapter. This review served a two-fold purpose, (a) to aid in the selection of the experimental method, and (b) to obtain data for comparison with the results of this study. A summary of this review is presented below.

Keyes, Taylor and Smith[25] used a 1.5798 cc volumenometer to determine the liquid density of methane in a temperature range of 100°K to 191°K. The mass of the condensed gas was calculated from a knowledge of the methane equation of state[26]. These authors made two series of density measurements. The agreement between the different measurements was satisfactory on the whole, although in some instances, the authors reported a difference of 1 part in 230. However, they claimed an average reproducibility of 1 part in 1500.

Dana, Jenkins, Burdick and Timm[11] used the pycnometer method to determine the liquid densities of n-butane, isobutane and propane. They reported an accuracy of 0.5% in their density results.

Mass and Wright[29] used the pycnometer method to measure

the liquid densities of propane and ethane. The density of propane was measured in a temperature range of -78°C to -24°C, and that of ethane was determined in a range of -108°C to -74°C. Their reported accuracy was 1 part in 2000.

Heizberg[19] determined the effective density of boiling liquid oxygen in a tank 30 feet tall and 10 feet in diameter. He utilized the equation of fluid statics relating pressure, density and vertical distance in fluid media.

Arnett, Millhiser and Probert[1] measured the bulk density of boiling liquid oxygen using a cylindrical aluminum tank 16 feet tall and 2 feet in diameter. After calibrating the volume of the tank, these investigators determined the weight of liquid oxygen needed to fill the tank to a specified volume by differential weighing using a 5000 lb. capacity balance.

Shupert[37] used a 262.71 cc pycnometer to determine the liquid density of oxygen in a steady state condition. A 1500 gram capacity balance and the pycnometer were placed in an environmental chamber in which the pressure was controlled to attain equilibrium between the liquid and the vapor.

Saji and Okuda[36] measured the density of cryogenic liquids indirectly by converting the buoyancy effect on a quartz sphere into a proportional electrical signal. A balance between the buoyancy effect and a torsion wire determines the position of a core within a differential transformer which generates the readout

signal. Initial calibration of the instrument with the known density of oxygen as a function of temperature allows it to be used to determine the density of mixtures. The composition of the mixture was calculated from the density measurements on the basis of the theoretical value of the excess volume to be computed by means of Prigogine's[35] average potential model.

Morlet[31] determined the liquid specific gravity of the methane + ethane system and of the methane + ethane + propane mixtures. The method consisted of condensing a known volume of each component into a pyrex tube graduated in 0.1 cc increments. The number of moles of each condensed gas was determined by making use of the ideal gas law.

Fuks, Legros and Bellemans[16] used a 0.64824 cc pyrex bulb surmounted by a calibrated capillary to determine the molar volume of methane and deuteromethane. These authors made their measurements in a temperature range of 98°K to 112°K. The reported values were one percent larger than those of Keyes[25]. A relative accuracy of about 2×10^{-4} cc/cc mol^{-1} was claimed by these investigators.

Mathot, Staveley, Young and Parsonage[28] determined the excess volume of methane + carbon monoxide mixtures at the methane triple point by measuring the amount required to fill a 0.8 cc pycnometer. The number of moles of mixture condensed into the pycnometer was determined to 0.05 percent by measuring the pressure

change of a known volume of gas mixture at a constant temperature. Corrections for non-ideality of the gas mixture were made by using the reduced second virial coefficient correlation of Guggenheim and McGlashan[17]. When the excess volumes so obtained are plotted as a function of composition, the average and maximum deviation from a smooth curve through the points are about 5% and 20% respectively. In a more recent paper, Pool and Staveley[34] determined the excess volume data for argon + oxygen at 83.8 and 90°K and for argon + nitrogen at 83.8°K. By increasing the volume of the pycnometer to 2.3 cc and by increasing the accuracy of the pressure measurements on which the determination of the amount of each component in the pycnometer depended, they were able to reduce the average deviation to about 3% with a maximum deviation of about 7%.

Blagoi and Rudenko[5] determined the liquid density of nitrogen + oxygen and oxygen + argon mixture. They used the pycnometer method in much the same way as Mathot, et al[28]. These authors quoted an accuracy of 0.1%.

Croll and Scott[9] measured the excess volume for methane + tetrafluoromethane mixtures at 110°K. They used several pairs of dilatometers which ranged in bulb capacity from 0.07 cc to 2.0 cc. They reported an average deviation of 2% in the experimental excess volume data.

Knaap, Knoester and Beenakker[27] measured the excess

volume for oxygen + nitrogen and oxygen + argon mixtures. These authors employed a different technique for determining the excess volume. They observed the change in volume when the two pure liquids were mixed at constant temperature and pressure by noting the meniscus level difference in a capillary attached to the volume in which the mixing occurred.

Davenport, Rowlinson and Saville[12] determined the molar volume of methane in a temperature range of 115°K to 153°K. They used a 0.6 cc bulb to which was attached a precision-bore capillary tube of 15 cm length and 1 mm internal diameter.

CHAPTER III

DESCRIPTION OF EXPERIMENTAL APPARATUS

The experimental apparatus used in this work is presented graphically in Figure 1. The main components of the apparatus are 1) the cryostat, 2) high pressure weighing bomb, 3) pycnometer, 4) temperature measurement equipment, 5) refrigeration and temperature control equipment, 6) weighing equipment, 7) vacuum equipment, 8) pressure measurement equipment, 9) analytical equipment and 10) transfer tubing between the weighing bomb and the pycnometer. These components are described separately as follows:

The Cryostat

The cryostat as presented in Figure 1, consisted of two strip-silvered glass Dewar vessels which were constructed by H. S. Martin and Son. The Dewar flasks were mounted concentrically similar to the arrangement of the cryostat described by Din and Cockett[14]. The annulus between both vessels was used to store the refrigerant. The inside of the inner Dewar flask was the working space and consequently was used to house the bath fluid.

The inner Dewar vessel was 20 inches deep, 6 inches in

inside diameter and 7 1/2 inches in outside diameter. In order to mount this flask, it was linked to a 3 1/2-inch glass pipe joint similar to the one described on page D60, catalog 70 of H. S. Martin and Son. This glass joint was attached to a mounting metal flange. The walls of the inner Dewar flask were equipped with a vacuum outlet. This arrangement provided a good means to adjust and control the thermal conductivity of the medium between the refrigerant and the bath fluid. If the desired temperature of the cryostat is high relative to the temperature of the refrigerant, the space between the walls of the vessel is evacuated. For other lower temperatures, the space is filled with sufficient dry gas such as helium to provide an appropriate heat transfer medium between the refrigerant and the bath fluid.

The top of the inner Dewar flask was sealed by a 3/8-inch brass plate fitted with a Viton O-ring. A 2-inch thick piece of urethane was attached to the bottom of the brass plate to help minimize the heat leak between the bath fluid and the surrounding atmosphere.

The outer Dewar flask (23 inches deep, 10-1/2 inches in inside diameter and 12 inches in outside diameter) was mounted in a wooden box which was placed in a steel vessel that served as a reservoir to collect the bath fluid in case of failure of the glass Dewar flasks. The space between this vessel and the inner Dewar was sealed by a 2-1/2-inch thick styrofoam piece. Silicon

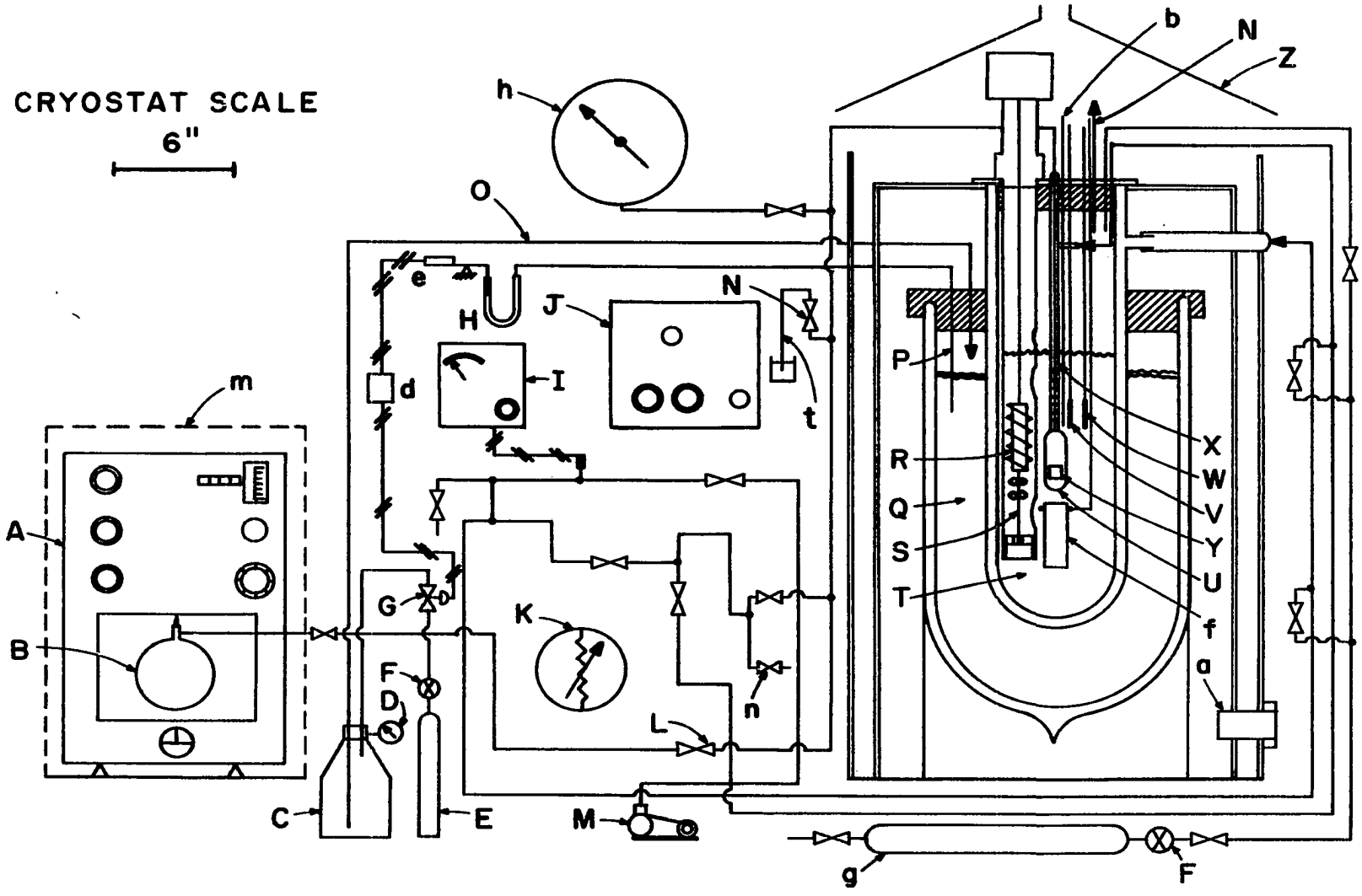


FIGURE I. SCHEMATIC DIAGRAM OF THE EXPERIMENTAL APPARATUS

LEGEND FOR FIGURE 1

A	Analytical Balance
B	Weighing Bomb
C	Liquid Nitrogen Dewar
D	Pressure Gauge
E	Nitrogen Gas Cylinder
F	Pressure Regulator
G	Solenoid Valve
H	Manometer for Liquid Nitrogen Level Control
I	Vacuum Gauge
J	Temperature Controller
K	Control Heater Rheostat
L	Metering Valve
M	Vacuum Pump
N	Pressure Relief Valve
O	Liquid Nitrogen Transfer Line
P	Liquid Level Control Sensor
Q	Liquid Nitrogen in Cryostat
R	Control Heater
S	Stirrer
T	Bath Fluid (propane)
U	Fused Quartz Pycnometer
V	Resistance Thermometer

LEGEND FOR FIGURE 1

(continued)

W	Temperature Control Sensor
X	Pycnometer Vacuum Jacket
Y	Nickel Stirrer in Pycnometer
Z	Venting Hood
h	Fused Quartz Pressure Gauge, 0-100 psia.
g	Dry Helium Gas Cylinder
m	Pressure Barricade
n	Vacuum Valve to Chromatograph
t	Water Valve
f	Pycnometer Heater
a	Air Blower
b	Pycnometer Horseshoe Magnet
d	Electrical Relay
e	Mercury Switch

rubber cement was used to fill the cavities between the styrofoam piece and the walls of both Dewar vessels.

In order to prevent the condensation of moisture on the outside wall of the outer Dewar flask, a 3/4-inch copper tubing was mounted through the styrofoam piece. This copper tubing served as a vent for the nitrogen vapor from the outer vessel directly to the atmosphere. In addition, an air blower was mounted as shown in Figure 1, to provide circulation of the air continuously in the space between the Dewar and the wooden box.

A hood was securely mounted above the cryostat to provide a vent for any unexpected leak of hydrocarbon vapor from the inner vessel to the atmosphere.

The cryostat proved to be of great precision and flexibility. In using liquid nitrogen as the refrigerant, the cryostat can be operated successfully at any temperature between $77^{\circ}K$ and $273^{\circ}K$. In this work at about $-165^{\circ}C$, temperature variaticns of the order of $\pm 0.002^{\circ}C$ were obtained for several hours.

High Pressure Weighing Bomb

Previous investigators[13,16,26,28,31] determined the mass of a condensed gas by employing the ideal or the non-ideal gas laws; the latter being corrected by using the compressibility factor or the second virial coefficient.

In this work, based on the results of an error analysis,

and in order to obtain the most accurate experimental results, it was decided to weigh the component gases. This led to the construction of the high pressure weighing bombs which were used throughout this investigation.

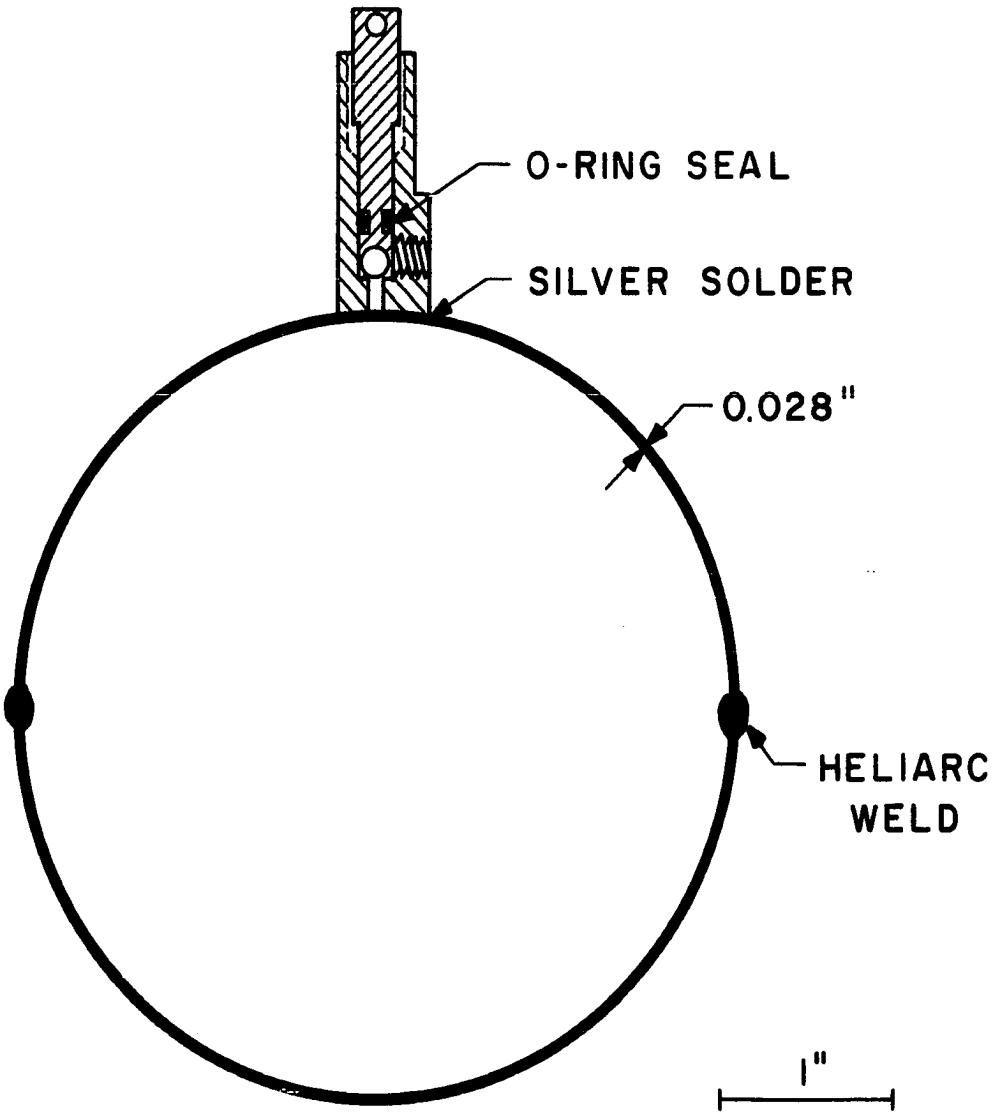
The following factors were considered in constructing the high pressure weighing bomb:

1. As a consequence of the availability of a 300 gram capacity Right-A-Weigh analytical balance, the total weight of the bomb including the required connections must not exceed a maximum weight of 275 grams.

2. The weighing bomb must have a capacity of at least 20 grams methane at a safe operating pressure.

3. The construction material of the weighing bomb must be resistant to corrosion to avoid contamination of the pure gases under study and to prevent any weight change due to oxidation.

With these specifications in mind, the weighing bomb with a specially designed light-weight (35 grams) valve (see Figure 2) was constructed by welding together two 2-inch radius hemispheres hydroformed from flat sheets (0.028 inches thick) of PH 15-7 Mo stainless steel manufactured by Armco Steel Corp. This particular steel has an excellent corrosion resistance. The weight of the bomb including the valve is only 215 grams. Yet, it is capable of containing 20 grams of methane at 750 psia with an operational safety factor of 4.75.



SPECIFICATIONS

VALVE MATERIAL — TYPE 303 S.S.
SPHERE MATERIAL — PH 15-7 MO S.S.
TOTAL WEIGHT — 215 GRAMS
INSIDE DIAMETER — 4 INCHES
WORKING PRESSURE — 750 psi

FIGURE 2. WEIGHING BOMB

The light-weight valve was constructed from AISI 303 stainless steel. It was silver-soldered to the weighing bomb.

In order to accurately determine the air buoyance effect in weighing the hydrocarbon gases, the change in the volume of the weighing bomb must be known as a function of pressure. This was experimentally determined using the apparatus shown in Figure 3. This apparatus consisted of the following elements:

1. Pyrex Glass Flask: It was used to boil the distilled water to free it from air before storing it in container A.
2. Air-Free Water Reservoirs: The two reservoirs, A and B, were constructed from Plexi-glas pipe, 4 inches in inside diameter, 1/8 inch thick and 8 inches long. The ends were sealed with aluminum plates fitted with neoprene gaskets. The plates were supported with six equally spaced 3/16-inch threaded steel rods.

Reservoir A was used only to store the air-free distilled water. The top plate in reservoir B is equipped with a thermometer and a 1/8 inch inside diameter precision bore capillary tube. The first was used to measure the temperature of the water and the latter to measure the change in the volume of the weighing bomb by noting the change in the height of the water level in the capillary tube with change of pressure in the bomb. The change of the water level in the capillary tube was determined by using a cathetometer.

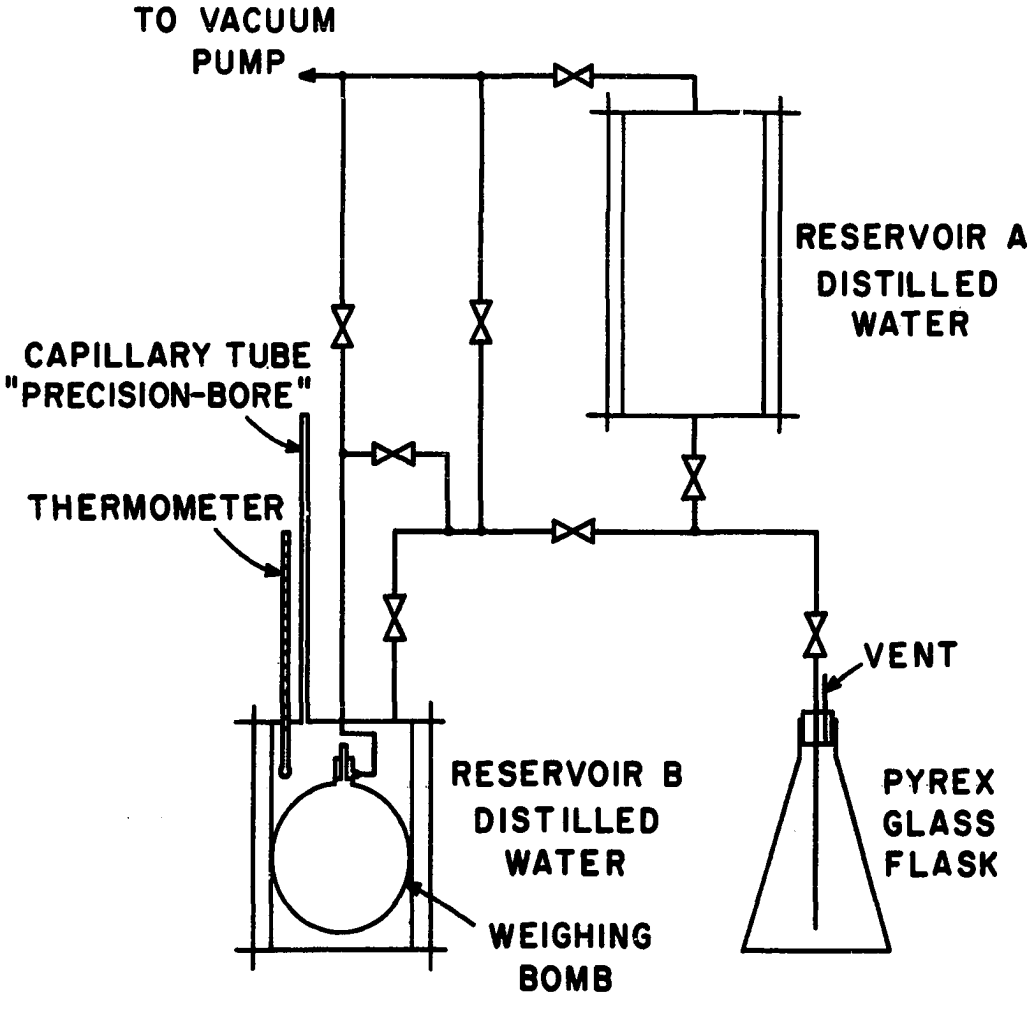


Figure 3. EXPERIMENTAL APPARATUS FOR CALIBRATION OF THE VOLUME OF THE WEIGHING BOMB AS A FUNCTION OF PRESSURE.

Fused Quartz Pycnometer

The desired accuracy in the results of any experimental investigation is generally the main factor that must be considered and examined with extreme care before any decision is reached in selecting the experimental method.

As a result of a careful examination of existing low temperature techniques and some suitable high temperature methods with particular attention being focused on the effect of the various variables affecting the accuracy of the liquid density results, the pycnometer method was selected.

The pycnometer method has been widely used for similar investigations[11,16,25,28,29,37]. Gases with known compositions are liquefied and placed in a pycnometer whose volume is predetermined as a function of temperature.

The pycnometer used in this investigation, presented in Figure 4, was constructed from fused quartz. Its volume is approximately 30 cubic centimeters.

In the process of constructing the pycnometer, the following factors concerning the selection of the material was considered:

1. The pycnometer must be transparent for visual observation.

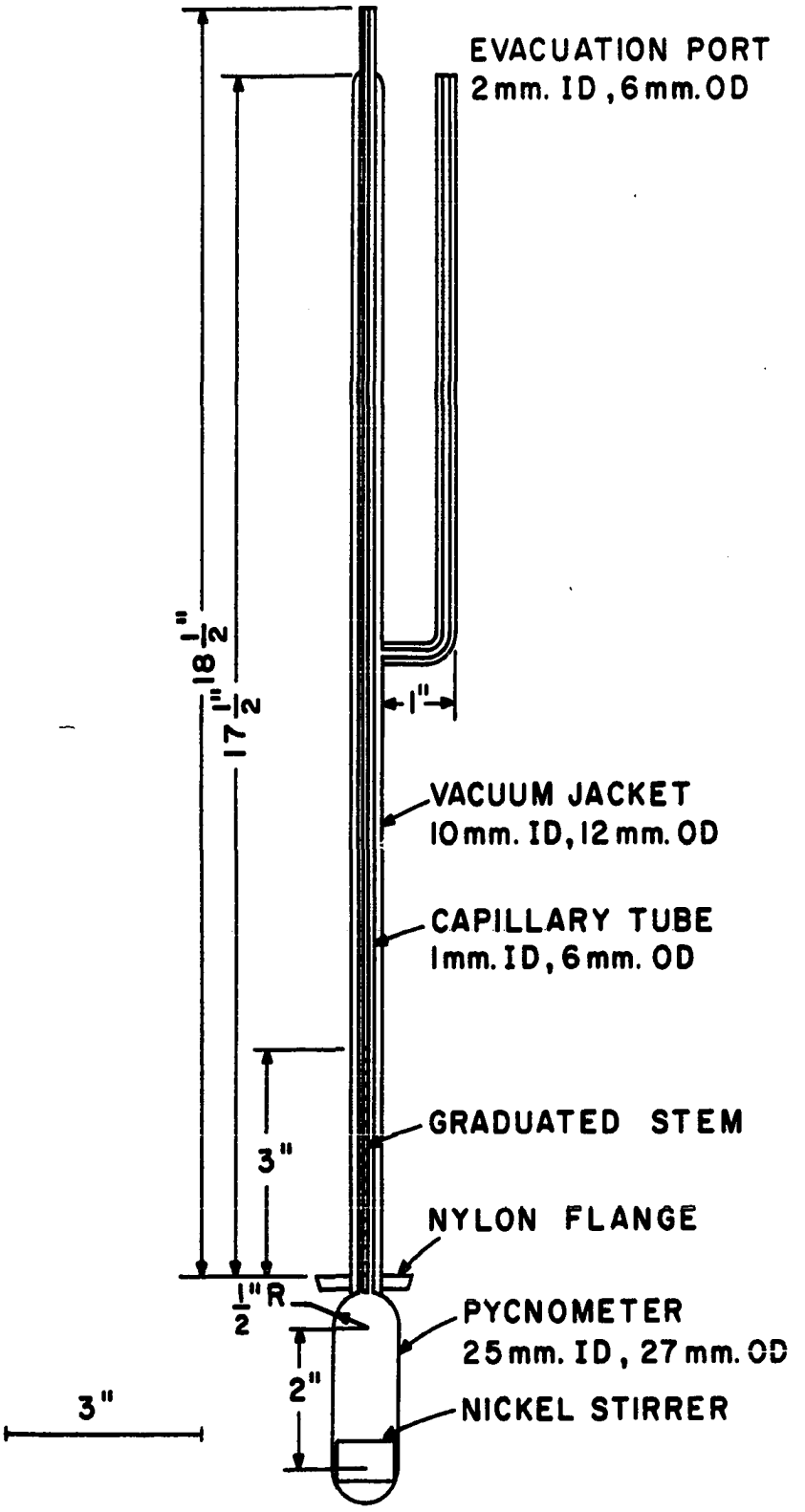


FIGURE 4. SCHEMATIC DIAGRAM OF FUSED QUARTZ PYCNOMETER.

2. The thermal expansion coefficient of the material must be as small as possible and at the same time, must be accurately known as a function of temperature in the operating range.

As a result of a careful examination of the properties of different kinds of glass, fused quartz was selected.

The thermal expansion coefficient of fused quartz is quite sensitive to composition. Therefore, in order to construct a pycnometer with all of its components having similar thermal expansion properties, several different sizes of General Electric fused quartz tubing from the same batch (Type 204) were acquired. The thermal expansion data of this material were experimentally determined as a function of temperature by the National Bureau of Standards in Washington, D. C. A copy of their experimental results is shown in Appendix A.

In order to facilitate reading accurately the volume of the condensed gases in the pycnometer, the following provisions were made:

1. A 7 cm portion of the pycnometer stem was graduated into 70 approximately equal divisions.

2. The volume of the pycnometer was experimentally determined as a function of these divisions. This was accomplished by differential weighing against distilled water with impurities stated to be less than 2 parts per million.

3. A cathetometer was used for interpolation between the divisions.

A stirrer was constructed from Nickel A and then placed inside the pycnometer. Nickel A was selected because of the availability of its thermal expansion data[2] as a function of temperature in the experimental range. These data aided in correcting for the change in the volume of the stirrer at the operating temperature and consequently for the change in the pycnometer volume at the same temperature. In addition, Nickel A is magnetic and therefore, the stirrer was manually raised or lowered by means of a horseshoe magnet which was placed externally around the pycnometer.

The pycnometer stem was surrounded by a vacuum jacket which was made from 1/2 inch fused quartz tubing. The purpose of having a vacuum jacket was to prevent condensation of the gas in the capillary tube while filling the pycnometer.

The vapor pressure of some of the hydrocarbon materials under study such as propane and n-butane is extremely small at -165.0°C. Consequently, in order to facilitate evacuating the pycnometer at the end of a run, it must be heated in order to raise the vapor pressure of the condensed gases. This was accomplished by mounting a resistance heater inside a Teflon casing, 2 inches in outside diameter, 3/8 inches thick and 3 3/4 inches long. The bottom of this casing was sealed by a Teflon plug. The heater

was made from 20 feet of 30 gauge Nichrome wire which had a resistance of 6.82 ohms per foot. The heater assembly was raised or lowered by means of a 1/8 inch steel rod. The lower end of the rod was attached to the top of the Teflon casing by means of a brass collar, and the upper end extended through a Swagelok connection fitted to the top brass plate. This connection was equipped with Teflon ferrules to permit raising or lowering the heater and at the same time to keep the cryostat free from leakage to or from the atmosphere.

When the heater assembly was raised, the top was sealed by means of a nylon flange permanently placed around the pycnometer stem. The nylon flange was machined to match exactly the top of the heater casing. This arrangement resulted in isolating the pycnometer from the bath fluid. Therefore, when the heater was turned on, it heated mainly the fluid surrounding the pycnometer and consequently the liquid inside the pycnometer. The walls of the Teflon piece served as an insulator.

The volume of the pycnometer at room temperature was determined by direct differential weighing with distilled water using the Right-A-Weigh analytical balance. The volume at any other temperature was calculated by making use of the known thermal expansion data which were determined by the National Bureau of Standards. Correction was made for the change in the volume of the stirrer inside the pycnometer.

Temperature Measurement Equipment

The bath temperature was measured with a Leeds and Northrup Model 8164 capsule-type platinum resistance thermometer used in conjunction with a Leeds and Northrup G-2 Mueller bridge and galvanometer. The thermometer was calibrated by the National Bureau of Standards at the oxygen boiling point, the ice point, the steam point, and the sulfur boiling point. The temperature interpolation equations used are presented in Appendix C.

The platinum resistance thermometer was mounted in a piece of 0.5" x 0.02" stainless steel tubing 22" long. The bottom section of this mounting support was constructed from a piece of magnetic stainless steel. The thermometer leads were soldered to four 18-gauge copper wires. These four wires were supported and separated from each other by 18 nylon spacers which were placed in the stainless steel tubing approximately one inch apart. A brass fitting equipped with a Viton O-ring was used to seal the top of the stainless steel tubing from the atmosphere.

A number of 1/4" holes were drilled in the tubing to allow free circulation of the bath fluid past the thermometer. The tubing served to protect the thermometer from accidental breakage and to shield the thermometer from the moving magnetic field created by the pycnometer agitation magnet.

Refrigeration and Temperature Control Equipment

Liquid nitrogen was used as the refrigerant in all phases of the entire experimental work. The liquid nitrogen was purchased from a local dealer through the Research Institute at the University of Oklahoma. It was acquired in 110 and 160 liter Dewar flasks pressurized to 25 psi.

The temperature was controlled by a Hallikainen Model 1053A thermotrol with proportional plus reset control. The power output from the thermotrol leads to a bare wire control heater which was mounted above the propellers of the stirrer.

The following considerations were found to be extremely important in maintaining close temperature control:

1. Constant Refrigeration Effect:

A constant refrigeration effect in practice means keeping constant the level of the liquid nitrogen in the outer dewar flask. In order to run the cryostat properly, it was found that this level must be kept constant to $\pm$ 1 cm. This requirement was achieved by means of a simple level indicator presented graphically in Figure 5.

The level indicator consisted of a dip tube connected to a manometer which contained water. The dip tube is made of copper so that the heat leak from the surroundings is capable of evaporating the liquid nitrogen at a sufficient rate to keep the dip tube filled with nitrogen gas. Preliminary experimental

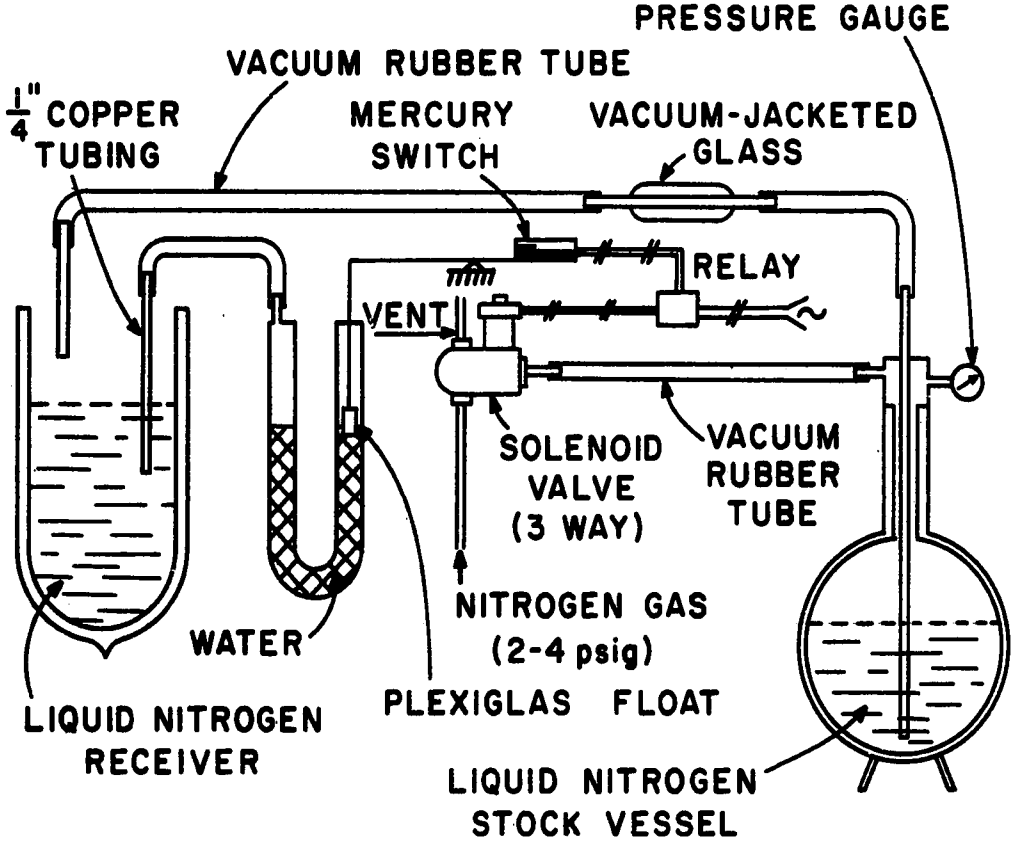


Figure 5. AUTOMATIC CONTROL OF THE LIQUID NITROGEN LEVEL.

investigation showed that the pressure drop due to evaporation of the liquid nitrogen in the copper tube depended linearly on the immersed length of the dip in the liquid. In addition, it showed that the pressure drop was independent of the size of the copper tube. The manometer thus indicated the depth of the immersion of the dip in the liquid nitrogen.

The manometer was equipped with a hollow Plexi-glas float. The float was connected to one end of a 3/16 threaded steel rod while a mercury switch was mounted on the other end of the rod. The rod was supported in the middle and equipped with several steel nuts to be used for balancing the mercury switch against the Plexi-glas float. The mercury switch was included in an electrical circuit with a relay which was connected to a three-way solenoid valve. As the level of the liquid nitrogen in the outer Dewar vessel falls, the hydrostatic head diminishes and thus causes the float to be lowered. As a result of lowering the float, the mercury switch will tilt making a contact and consequently closing the electrical circuit through the relay.

A 50-liter Dewar vessel of liquid nitrogen, was fitted with a gas inlet and a liquid transfer tube, the latter reaching to the cryostat outer Dewar flask. Nitrogen gas at about 2 to 4 psig was brought from a nitrogen gas cylinder to one side of the solenoid valve which was also connected to the gas inlet in the

liquid nitrogen container. When the electrical circuit through the relay is completed by the mercury switch, the solenoid valve opens permitting nitrogen gas to flow to the stock vessel and thereby forcing liquid nitrogen to flow into the outside Dewar flask in the cryostat. When the liquid level is brought back to the required point, the hydrostatic head forces the float to rise which in turn causes the mercury switch to come back to its original horizontal level and therefore breaking the circuit. This closes the solenoid valve and consequently shuts off the nitrogen gas supply to the liquid nitrogen stock vessel, which in turn prevents the flow of liquid nitrogen. In addition, the solenoid valve will serve as a vent to the nitrogen vapor from the liquid nitrogen tank.

2. Control Heater:

In any experimental work where precise temperature control is involved, it is essential to employ a control heater with a low total heat capacity so that the heating effect will not lag the need for such an effect appreciably. The most effective design to meet this requirement is a bare wire electrical resistance heater immersed in the bath fluid. Therefore, the control heater used in the cryostat was made from 30 feet of 30 gauge Nichrome wire with a resistance of 6.82 ohms per foot. The wire was wound around a 5-inch long frame consisted of four threaded 5/16-inch phenolic tubing. These

tubings were mounted on 3/16-inch brass rods which were supported by two similar nylon circular disks. The heater was mounted directly above the propellers in the two-inch stainless steel pipe. This arrangement assured good contact between the bath fluid circulated by the stirrer and the bare wire control heater. The power dissipated by the heater was adjustable from 10 to 70 watts by a 350 ohm external rheostat.

The heater leads were made from a 20 gauge copper wire insulated by Teflon spaghetti tubing. These two leads were brought out through separate Swagelok connectors ($\frac{1}{8}$" x $\frac{1}{16}$"). These Swagelok fittings were connected to $\frac{1}{8}$ copper tubings. The copper tubings were soldered to the fitting connecting the 2-inch stainless steel tubing and the brass plate on top of the cryostat. The heater leads were then connected directly to the thermotrol.

3. Stirring of the Bath Fluid:

The stirrer used in this work consisted of two 1.5-inch stainless steel 3-bladed propellers mounted on a 5/16 shaft. The shaft was housed in a 2-inch thin walled stainless steel tube. This tube extended from near the bottom of the inside Dewar flask through the top brass plate of the cryostat. Two 2-inch openings were machined in the stainless steel tube. The first was positioned near the bottom and the second was machined approximately 1 inch below the liquid level of the bath

fluid. The top opening was machined so that when the stirrer was placed in its final position, the opening would face the pycnometer. This arrangement and the fact that the bare wire control heater was mounted directly above the propellers, ensured good heat transfer between the heater and the temperature sensor in the bath fluid. This caused all temperature changes in response to control signals to occur promptly and therefore these changes were very small.

The stirrer was driven by an induction motor operating at 1750 rpm. The motor shaft was connected to the shaft of the stirrer by means of a $\frac{3}{8}$ - inch flexible metal bellow coupling.

Weighing Equipment

The weighing equipment used in the experimental part of this work consisted of the following units:

1. Analytical Balance

A 300 gram capacity Right-A-Weigh analytical balance was used. It was manufactured by Wm. Ainsworth and Sons, Inc. Its sensitivity was 0.1 milligram.

The balance was enclosed in a pressure barricade to protect the operator against failure of the high pressure weighing bomb. In addition, it served to shield the balance from any air current caused by changes in the surrounding conditions.

In the process of weighing any of the component gases and in order to ensure maximum accuracy in determining its mass, the weighing bomb after being placed in the pressure barricade was handled remotely. The bomb was moved into and from the analytical balance by means of an aluminum fork which was constructed to fit around the end of the stem of the weighing bomb's valve. This fork was placed horizontally through a hole in the right hand side of the barricade. The valve of the weighing bomb was turned on by means of a specially made connection to fit the top of the valve's stem. The handle of this connection extended vertically through a hole in the top of the barricade. The edges of the hole were covered with felt material to prevent any chipping of the metal of the barricade while opening and or closing the valve of the weighing bomb.

A Beckman differential thermometer was placed inside the pressure barricade to measure the change in temperature to within $\pm$ 0.01^{o}C. This information together with the change of the barometric pressure was needed to calculate the change in the density of air while making an experimental run. Knowledge of the change in the density of the air was required to accurately calculate the effect of air buoyance on the mass of the gas being weighed.

2. Standard Masses

The analytical balance was calibrated against a set of

class M standards which were calibrated by the National Bureau of Standards. A copy of their certification is presented in Appendix D.

Vacuum Equipment

A schematic diagram of the vacuum system was presented in Figure 1 in conjuction with other parts of the experimental apparatus. An oil-lubricated vacuum pump capable of producing a shut-off pressure of 0.05 micron of mercury was used in this work. The pump was connected to the remainder of the vacuum system by means of a 3/8-inch copper tube flare joint. The tubing used in the vacuum system consisted of 3/8, 1/4 and 1/8-inch copper tubing. Swagelok brass connections and Whitey valves were used in this system.

The pressure in the system was measured by a thermocouple vacuum gauge, type GTC 100, which was manufactured by Consolidated Vacuum Corporation. The gauge was capable of measuring the pressure in the range 1,000 to 0 micron mercury. It was calibrated against a swing-type McLeod gauge.

The vacuum pump was used mainly to evacuate:

1. the weighing pressure bomb before filling it with the gas under study

2. the pycnometer and the transfer tubing from the weighing pressure bomb to the pycnometer before and after each

experimental run

3. the vacuum jacket of the pycnometer

4. the annulus between the walls of the inner Dewar flask

5. the sampling valve in the chromatograph

Pressure Measuring Equipment

In making a complete experimental run, it was necessary to measure 1) the pressure of the pycnometer and the transfer line, 2) the pressure in the weighing bomb when being charged with any gas, and 3) the barometric pressure at the start and at the end of each individual run.

The absolute pressure in the pycnometer was measured by means of a Fused Quartz Pressure Gage, model 140, which was manufactured by Texas Instruments Incorporated. Its operating range was from 0 psia to 100 psia. The absolute accuracy was 0.015% of reading plus 0.002% of Standard Readout. The gage was connected to the pycnometer and to the rest of the system as shown in Figure 1.

The pressure in any weighing bomb when charged with any of the component gases was measured by means of a Maxisafe, AISI 316 tube pressure gage. This gage was calibrated against a Heise pressure gage which in turn was calibrated by Heise Bourdon Tube Co. The same gage was used in determining the effect of pressure

on the volume of the weighing bombs.

The barometric pressure was determined by a Welch Fixed Cistern Barometer manufactured by Welch Scientific Co. Correction for the effect of temperature on the indicated pressure was made.

Transfer Line Between the Weighing Bomb and the Pycnometer

The transfer line between the weighing bomb when placed in the pressure barricade surrounding the analytical balance and the pycnometer in the cryostat is schematically presented in Figure 1 in conjunction with the rest of the experimental apparatus. It consisted mainly of 1/8-inch copper tubing equipped with appropriate valves as follows:

The first valve coming from the pressure barricade was a Whitey needle valve. Then the next valve in line was a metering valve. These two valves were used to regulate the flow of the gas from the weighing bomb to the pycnometer to prevent sudden increase in pressure which may result in breaking the quartz pycnometer or over-pressuring the pressure gauge. For additional safety, a 5 psi pressure relief valve was installed in the line. In addition, three other valves were installed in the transfer line; the first connected the transfer line to the vacuum system, the second isolated the pressure gauge from the rest of the system, and the third separated the pycnometer from

the transfer tubing.

In order to account for the amount of gas trapped in the transfer line while filling the pycnometer, the volume of this line was determined. This was achieved as follows:

(1) The pycnometer with its volume known was filled with air at a known temperature and pressure. The pressure was determined by the Texas Instruments pressure gauge.

(2) With the transfer line connected to the weighing bomb, the line including the pressure gauge, was evacuated to approximately 0.002 mm Hg.

(3) The air from the pycnometer was expanded to the line and the final pressure and temperature were recorded.

(4) By knowing the initial and final conditions and assuming that the amount of air was constant, the volume of the transfer line was accurately calculated. It was equal to 36.306 ml.

Analytical Equipment

All the research grade hydrocarbons (methane, ethane, propane and n-butane) were analyzed by making use of an F and M chromatograph, model 810R-29. A thermal conductivity detector was used to analyze the non-flammable impurities such as air. A flame ionization detector was used to identify the hydrocarbon impurities in each component. Results of these analyses and those

supplied by Phillips Petroleum Company are presented in Chapter IV.

A 9 foot column was used to analyze all the component gases. The column was packed with Analab Silica gel 1-1/2% Apiezon L.

CHAPTER IV

MATERIALS USED

All the hydrocarbon materials used in the experimental work were supplied by Phillips Petroleum Company. These materials which consist of the bath fluid and the research grade hydrocarbons are described in the following sections.

BATH FLUID

At the early stages of initiation of this work, a study searching for a bath fluid suitable for operating the cryostat at around -160°C was made. Based on the results of this study, it was decided to use the eutectic solution of isopentane-pentane. This solution (14% pentane) has a eutectic temperature of approximately -163°C and a viscosity of 0.0042 cp at -141°C.

The eutectic solution was prepared using technical grade pentane and isopentane. The inner Dewar flask was charged with this mixture. The temperature of the cryostat was successfully controlled at -142°C to $\pm$ 0.002°C. The cryostat was cooled until the solution froze at approximately -162°C.

This solution is liquid at room temperature.

Consequently, it is easier to handle than other bath fluids such as liquid propane. Therefore, it is strongly recommended for use in cryostats to be operated at around -142°C.

Because the desired operating temperature in this work was -165°C, liquid propane was used as the bath fluid. Propane gas was condensed by feeding it to the cryostat at a pressure of 2 psig. It should be pointed out that condensing the required amount of approximately 12 pounds of propane was a time consuming process. It took 11 hours to do the job. Nevertheless, this method is recommended whenever safe operation is desired. In shutting down the cryostat, the propane was vented to the atmosphere.

It was decided first to use technical grade propane (95% purity). After condensing this propane, the cryostat became cloudy. This made the pycnometer, when placed in the inner Dewar flask, invisible to the operator. Because it was essential to observe the pycnometer visually, the use of this quality propane was abandoned. The visibility problem was successfully solved by using instrument grade propane with 99.5% purity.

Research Grade Hydrocarbons

All the hydrocarbon gases studied in the experimental part of this work were research grade hydrocarbons which were

supplied by Phillips Petroleum Company. They were used without any further purification. Analyses of these gases were also supplied by Phillips Petroleum Co. It was stated[18] that usually some air or moisture is picked up while transferring these gases from one container to the other. Therefore, an attempt was made in this laboratory to analyze all the gases for air and moisture impurities. The analyses were made using an F and M research chromatograph, Model 810R-29. The results of these analyses together with those supplied by Phillips Petroleum Company are presented for the individual components as follows:

1. Methane Gas		Method of Analysis
CH_4	99.99 mol %	Mass Spec., Gas
H_2O	less than 10 ppm	Chromatograph and
Air	less than .01 mol %	CEC moisture monitor
C_2H_6	less than .01 mol %	

2. Ethane Gas		
C_2H_6	99.99 Wt %	Infrared and Gas
C_2H_4	Less than .01 Wt %	Chromatograph
C_3H_6 + C_3H_8	Less than .01 Wt %	
Air	Less than 25 ppm	

3. Propane Gas		Method of Analysis
C_3H_8	99.97 Wt %	Gas Chromatograph
C_2H_6	Less than .01 Wt %	
C_3H_6	Less than .02 Wt %	
Air	Less than 30 ppm	
Heavy Components not detected		

4. n-Butane Gas		
nC_4H_{10}	99.96 Wt %	Gas Chromatograph
trans-butane-2	0.03 Wt %	
isobutane	probably 1 ppm	
Air	less than 20 ppm	

CHAPTER V

EXPERIMENTAL PROCEDURE

The experimental procedure can most conveniently be presented by describing separately (1) charging the cryostat with the bath fluid, (2) controlling the temperature of the cryostat, and (3) condensing the gases into the pycnometer.

Charging the Cryostat with the Bath Fluid

The inner Dewar flask was purged with dry helium gas several times to drive all the air out. This was done to avoid having an air-propane mixture and to eliminate any moisture condensation on the inside walls of the Dewar flask. The pressure was then held constant at 2 psig. Then the space between the walls of this vessel was evacuated and charged with dry helium at 2 psig. During this process, the cryostat was checked for possible leaks. The helium gas was dried by means of a specially made trap which was immersed in liquid nitrogen during the drying process. The dry gas was stored in a small cylinder at a pressure of 100 psig. The cylinder was equipped with a regulator set at 2 psig from which the helium was allowed to flow

to three separate valves leading to the walls of the inside Dewar flask, to the pycnometer vacuum jacket, and to the working space in the inside Dewar vessel.

The cryostat was then cooled to approximately -280°F. This was accomplished by filling the outer Dewar flask with liquid nitrogen to the desired level and then controlling it at that level by making use of the mechanism described previously.

The system was allowed to stabilize with the pressure in the space between the walls of the inside Dewar vessel being held constant at 2 psig to ensure good heat transfer. Then, the valve of an instrument grade propane cylinder, which was equipped with a regulator set at 2 psig, was opened and the propane gas was permitted to flow into the working space in the inner Dewar flask where condensation took place immediately. This process was continued until the level of liquid propane reached approximately 1 inch above the upper opening in the stirring mechanism. It took approximately 11 hours to condense the required amount of the bath fluid.

Controlling the Temperature of the Cryostat

As pointed out previously, good temperature control depends on maintaining constant refrigeration effect in the cryostat, adequate stirring of the bath fluid, and the use of a control heater with minimum time lag. In addition to these

general requirements, in order to keep the bath fluid at a given constant temperature, an equally important factor is to determine the appropriate pressure which must be maintained in the space between the walls of the inner Dewar flask. This pressure is determined in such a way that the resulting heat transfer medium will have the proper thermal conductivity to permit sufficient heat transfer between the bath fluid and liquid nitrogen. This will balance the heat supplied by the control heater, generated by the stirring mechanism, and gained by heat leaks.

As a starting point, the space between the walls of the inner Dewar vessel was maintained at a constant pressure between 0 and 1 atmosphere. Sufficient time was allowed for the thermotrol to stabilize. Then, depending on the resulting condition, the pressure in the walls was either increased, by addition of helium, or decreased by evacuation. This process was repeated until the desired condition was achieved. It should be pointed out that the heat dissipated by the control heater was kept as small as possible to minimize the temperature gradient in the bath fluid.

Charging the Pycnometer with the Condensed Gases

In this section, a brief summary of the experimental procedure followed in charging the pycnometer with the condensed

gases and in reading the instruments involved is presented.

Throughout the experimental part of this work, it was desired to determine the isothermal liquid densities of the systems studied at -165.0°C. As shown in Appendix A, the volume of the pycnometer was determined as a function of the divisions on the graduated portion of the stem. Therefore, the amounts of gases condensed must be sufficient to fill the pycnometer at -165.0°C to a level somewhere between the 0 and 70 divisions on the capillary stem. The procedure followed can best be presented by describing separately the functional units comprising 1) determination of the mass of the condensed gases, 2) condensation of the gases in the pycnometer, and 3) determination of the volume of the condensed gases.

1. Determination of the Mass of the Condensed Gases

The mass of each condensed gas was determined by direct differential weighing of the pressure bomb with the analytical balance. Corrections were made for the air buoyancy effect and for the amount of gas trapped in the transfer line between the weighing pressure bomb when placed in the pressure barricade and the pycnometer in the cryostat. The mass of any mixture in the pycnometer was the sum of the masses of the individual condensed gases. The weighing procedure was as follows:

The pressure bomb was filled with the gas by making use of the apparatus presented schematically in Figure 6. The

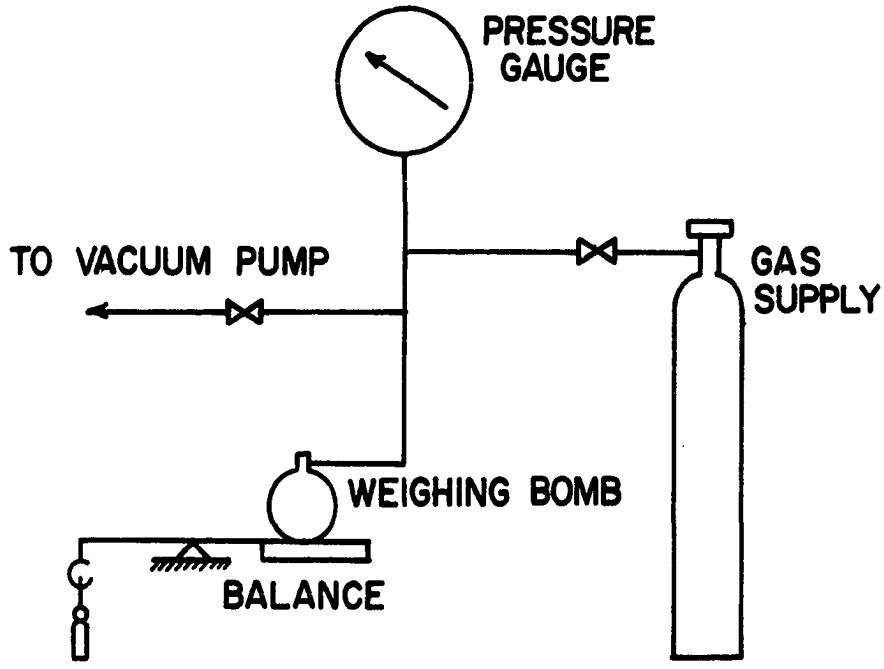


Figure 6. APPARATUS FOR FILLING THE WEIGHING BOMB WITH THE GAS.

weighing bomb and the entire transfer line including the pressure gauge between the gas cylinder and the bomb were evacuated to 0.002 mm Hg. The valve of the cylinder was then opened and the gas was permitted to flow into the bomb. In filling the bomb with propane and n-butane, the cylinder was immersed in hot water to raise the vapor pressure of these components and consequently to increase the flow of the gas into the bomb. The final pressure in the bomb was read directly from the pressure gauge in the system. The balance shown in Figure 6 was used to approximate the amount of gas in the bomb while charging it.

The full bomb was connected to the analytical balance and its weight was determined. The temperature and barometric pressure together with the reading on the differential thermometer were read and recorded.

The bomb was then removed from the balance casing using the aluminum fork and then placed on a felt covered stand. It was connected to the transfer line to start condensing the gas into the pycnometer as explained later.

At the end of the experimental run, the bomb was disconnected from the transfer line. Its final weight, the temperature and the barometric pressure were determined and recorded. The actual change in temperature between both weighings was indicated to within $\pm$ 0.01^{o}C by means of the differential thermometer.

2. Condensation of the Gases in the Pycnometer

The component gases of all the different systems studied except those containing n-butane were condensed at a temperature a few tenths of a degree lower than -165°C. Condensation of the n-butane systems was started at around -130°C.

In describing the condensation process, it will be assumed that the cryostat was maintained at the desired temperature and that the full pressure bomb was weighed, removed from the balance and then connected to the transfer line.

The flow of all the gases from the weighing bomb through the transfer line was regulated to avoid any over-pressuring of the system and thus to avoid breaking the pycnometer and or damaging the fused quartz pressure gauge. This was accomplished as described below.

First, the system was evacuated to 0.002 mm Hg and the pressure gauge was balanced for absolute pressure measurements. Then, all the valves in the transfer line except those leading to the pycnometer and the pressure gauge were closed. The pycnometer vacuum jacket was continuously being evacuated to prevent any condensation in the pycnometer stem. The valve of the weighing bomb was then opened by using the specially made fitting extending through the top of the pressure barricade. Then, the first valve away from the weighing bomb was slightly opened to allow the gas to fill the transfer line up to the metering

valve. Immediately after that, the metering valve was opened $\frac{1}{10}$ th of a complete turn and the gas was permitted to flow to the pycnometer. The metering valve was constantly adjusted in such a way that the pressure indicated by the fused quartz gauge did not exceed one atmosphere. This process was continued until sufficient amount of the gas was condensed in the pycnometer.

In order to check any possible leak through the pressure relief valve, it was connected to a 1/4 inch glass tubing. The end of this glass tubing was immersed in a beaker filled with water. The liquid level of the water in the glass tubing was maintained approximately one inch above the water level in the beaker. This arrangement permitted the immediate detection of any gas leak regardless of its size.

Description of the actual condensation process in the pycnometer can most conveniently be presented by describing separately the different processes involving the condensation of pure component systems, binary and ternary systems without n-butane, and binary systems containing n-butane.

The pure component systems were those of methane, ethane and propane. In order to determine the density of each of these pure components, a sufficient amount of the gas was condensed at a temperature a few tenths of a degree lower than -165°C so that whenever the cryostat was heated to -165°C, the liquid level of the condensed gas was raised to a point somewhere on the graduated

portion of the capillary stem of the pycnometer.

The binary systems without n-butane were methane + ethane, methane + propane and ethane + propane. The ternary systems included all these three components. The densities of the binary systems were determined over the entire range of composition while those of the ternary systems were determined at two fixed compositions only. In determining the density of any of these systems, for any desired composition, the amount of each component was estimated. In the process of filling the pycnometer, the component with the higher boiling point was condensed first. The mixture was continuously stirred by manually raising and lowering the pycnometer stirrer while the lighter component was being condensed. When sufficient amount of the last gas was condensed, the temperature of the cryostat was lowered approximately 25-30 degrees centigrade. When the temperature was stabilized, the entire mixture was thoroughly mixed to achieve homogeneity. Then, the cryostat was heated up to a temperature high enough to cause the liquid level of the condensed gases to rise to the first few divisions on the graduated portion.

Extreme care should be exercised to prevent any vapor from being trapped between the liquid in the pycnometer and that in its capillary stem especially in the space surrounded by the nylon flange which was used to seal the top of the pycnometer heater.

The binary systems with n-butane were those of methane + n-butane and ethane + n-butane. The liquid densities of each of these two systems were determined at one composition. N-butane was condensed at around -130°C. For the ethane + n-butane, ethane was then condensed at the same temperature. Then the cryostat was slowly cooled to -165°C. During the cooling period, the mixture was continuously stirred to avoid any possible freezing of the n-butane in the pycnometer. Although this was a time consuming process, no major difficulities were encountered in bringing the temperature down to -165°C.

For the methane + n-butane system, the n-butane again was condensed near -130°C. Then, methane was allowed to flow into the pycnometer at the same temperature. The cryostat was then slowly cooled down. Even though the system was continuously being stirred, the n-butane froze. The temperature was brought down to just slightly lower than the boiling point of methane. At this point, the methane was condensed at a fast rate. Steady stirring was continued for at least 10 hours after which all the n-butane was completely dissolved in the methane liquid. After that, the temperature of the cryostat was slowly lowered a few tenths of a degree below -165°C. With the cryostat being cooled down, methane was continuously condensed until the final liquid level of the mixture at -165°C, was like all other mixtures somewhere on the graduated portion of the capillary stem of the pycnometer.

It should be mentioned that for all the systems, whenever the heavy component was condensed, all the valves in the transfer line were turned to the same position as used in determining the volume of the transfer line. When equilibrium was achieved, the pressure indicated by the fused quartz pressure gauge and the room temperature were read and recorded. This information was used to correct for the amount of gas trapped in the transfer line. At this point, the pycnometer was isolated from the rest of the system by turning off the valve closer to the pycnometer. The rest of the system was then evacuated to two microns pressure before starting to condense the next component.

3. Determination of the Volume of the Condensed Gases

The volume of the condensed gases was measured as a function of temperature in a range that corresponded to expanding the liquid to approximately fill the graduated portion of the pycnometer's stem. This was accomplished as follows:

In order to describe the procedure conveniently, the following two conditions are assumed to hold:

a) The cryostat was maintained at few tenths of a degree lower than the desired operating temperature of -165°C.

b) The pycnometer was charged with sufficient amount of liquefied gases as described in the previous section.

By making use of the fine dial on the thermotrol, the

temperature of the cryostat was adjusted in such a way that the liquid level in the pycnometer assembly was raised to a point somewhere within the lower few divisions on the graduated portion of the capillary stem. Adequate time was allowed for the temperature to stabilize. Then, the temperature of the cryostat, the pressure in the pycnometer, the liquid level in the capillary stem and the room temperature were determined.

The temperature of the cryostat was measured with platinum resistance thermometer in conjunction with the G-2 Mueller bridge. The resistance was read directly from the bridge and then was converted to the appropriate temperature.

The pressure of the liquefied gases in the pycnometer was read directly from the fused quartz pressure gauge in degrees and then converted to the appropriate pressure units. Before reading the pressure, the valves in the transfer line were set at exactly the same positions used while calibrating the volume of the transfer line between the pycnometer and the high pressure weighing bomb.

The information concerning the pressure of the liquefied gases together with the appropriate room temperature valve were used to account for the amount of gas trapped in the transfer tubing between the pycnometer and the weighing bomb.

The liquid level in the capillary stem was determined by reading the appropriate division on the graduated scale of

the capillary stem. A properly leveled cathetometer was used for interpolation between the different divisions. With this information and by making use of the calibration curve of the pycnometer, the volume of the condensed gases was accurately calculated.

This process of raising the temperature of the cryostat and consequently raising the liquid level in the capillary stem was repeated several times until the liquid expanded to the upper end of the graduated portion of the stem. Readings of the temperature, pressure and liquid level at the end of each expansion were made and recorded. Extreme care was exercised to allow sufficient time for the temperature to be controlled before taking any reading. In general, a minimum of 50-60 minutes was needed for temperature stabilization. On several occasions, after the temperature was controlled, the liquid level was observed during a 20-25 minutes period. This served two purposes: first to check the temperature stability and second to check the pressure indicated by the fused quartz pressure gauge.

From the resulting experimental volumetric data, the density of the system under study in each run was calculated as a function of temperature in a range that included the desired operating temperature of -165°C.

CHAPTER VI

ACCURACY OF RESULTS AND EXPERIMENTAL TECHNIQUES

The main variables that affect the accuracy of the density values are temperature, pressure, mass, volume and composition. In order to achieve the maximum possible accuracy, the effect of each of these variables must be kept to a minimum. The limits of the absolute accuracy of the results have been established as shown in Appendix E. In this chapter, a brief summary of some of the experimental techniques which must be observed to ensure the desired accuracy is described.

Temperature Measurement

An extremely important factor is to adequately control the temperature and keep it constant long enough until the condensed gases in the pycnometer achieve thermal equilibrium with the bath fluid. In addition, the bath fluid must be continuously stirred to avoid appreciable temperature gradients.

As explained previously, to achieve good temperature control, it was essential to determine the appropriate value of the pressure in the walls of the inner Dewar flask and the proper

setting of the control heater. This was accomplished by varying both conditions and observing the resulting temperature until the desired value was achieved. After the cryostat was brought into equilibrium, and in order to check the temperature control, the cryostat was left for a two day period during which the temperature was continuously observed. During that time, the temperature appeared to remain constant to within $\pm$ 0.002°C.

In order to check the temperature gradient in the bath fluid, the platinum resistance thermometer holder was constructed in such a way that it could be manually raised or lowered. After the temperature of the bath fluid was stabilized and a good control was achieved ($\pm$ 0.002°C), the thermometer was raised approximately 1 inch. The corresponding temperature was determined. This process was repeated until the thermometer was raised 7 1/2 inches. With the thermometer placed at its highest position, it was decided to reverse the process by lowering the thermometer back to its original position. The thermometer was lowered at approximately 2-inch increments and the corresponding temperatures were determined and recorded. The temperature difference between any two points covered in this test did not exceed 0.002°C.

Another equally important point that must be carefully observed is to allow sufficient time during which the temperature of the condensed gases in the pycnometer can achieve thermal

equilibrium with the bath fluid. Usually, a period of 45-60 minutes was allowed.

Mass Measurement

In the process of making an experimental run, the entire system must be leak-free. In addition, extreme care must be exercised to avoid any gas bubbles in the pycnometer especially in the portion that is surrounded by the nylon flange.

In general, this was a tricky problem to cope with. First, sufficient amount of gases were condensed. Then, with the vacuum jacket being continuously evacuated, the pycnometer was heated slowly until the liquid level in the capillary stem was raised several inches. While the pycnometer was being heated, the pressure in the system was carefully monitored and was never allowed to exceed atmospheric pressure. The pycnometer was then cooled and thus bringing back the liquid level in the pycnometer stem to the lower section of the graduated portion. While cooling the pycnometer and whenever the liquid level was few inches above the graduated section, dry helium gas was introduced to the vacuum jacket. This process of heating and cooling was repeated as many times as needed to ensure the absence of any trapped gas bubbles.

It should be pointed out that this problem was termed "tricky" because of the fact that filling the pycnometer with

the condensed gases was not always a one time job. In other words, whenever the pycnometer was charged with what appeared to be sufficient amount of condensed gases, it was heated and then cooled. Then, in most cases, it was necessary to condense some more gases which of course necessitated the heating and cooling process again.

Another important factor that should be re-emphasized is the fact that the transfer line between the weighing bomb and the pycnometer was calibrated with the different valves being set at one specified position. Consequently, in making any run and before taking any pressure reading, all the valves included in the transfer line must be set at these specified positions.

Volume Measurement

In addition to the precautions which were taken while calibrating the volume of the pycnometer, an equally important factor was the ability to accurately determine the liquid level height in the graduated capillary stem of the pycnometer.

As stated previously, a cathetometer was used to aid in determining the right location of the liquid level. This cathetometer was leveled before taking any reading.

Whenever the temperature of the system was stabilized at the desired value, and before taking any final reading, the

liquid level in the pycnometer capillary stem was observed and recorded. After a period ranging from 10 to 25 minutes, the liquid level height was again read and recorded. An experimental point was recorded whenever both readings agreed with each other. Otherwise more time was allowed until both readings came to an agreement.

The consistency of the volume readings was also verified in another way. After the liquid was allowed to expand enough to fill the graduated portion, the temperature of the pycnometer was lowered few tenths of a degree. The liquid level and the corresponding temperature were then measured. These two measurements formed a new experimental point which was compared with the readings observed as indicated above.

CHAPTER VII

DISCUSSION OF RESULTS

The experimental liquid density results for the systems studied in this work are presented in this chapter. The absolute accuracy in these data is established as shown in Appendix E. These results are compared with comparable values reported in the literature.

As stated previously, the goal of this work was to determine the liquid density for all the systems at -165°C. It was very difficult to bring the temperature of the cryostat to exactly -165°C for each individual run. Therefore, in order to avoid such difficulty, the liquid density was measured as a function of temperature in a small temperature range that included -165°C. The magnitude of the range for each system was approximately equal to a temperature increase which would cause the liquid in the pycnometer to expand about 0.05 cc. This volume change is approximately equal to the volume of the graduated portion of the pycnometer's capillary stem. The experimental liquid density results are presented in Tables 1 through 7.

TABLE 1

SATURATED LIQUID DENSITY OF THE PURE COMPONENTS

METHANE, ETHANE AND PROPANE, GM/ML

Component	Temperature	Pressure, psia	Density, gm/ml
Methane "Run No. 1"	-165.020	10.925	0.427560
	-164.983	10.977	0.427519
	-164.895	11.051	0.427406
	-164.820	11.114	0.427323
	-164.765	11.172	0.427232
	-164.677	11.246	0.427122
Methane "Run No. 2"	-165.135	10.792	0.427704
	-165.041	10.891	0.427582
	-164.893	11.050	0.427390
	-164.751	11.175	0.427220
	-164.615	11.287	0.427044
Ethane	-165.061	.012	0.632335
	-164.947	.013	0.632215
	-164.712	.016	0.631982
	-164.556	.020	0.631823

TABLE 1

(continued)

Component	Temperature	Pressure, psia	Density, gm/ml
	-164.423	.024	0.631694
	-164.329	.033	0.631603
	-164.118	.042	0.631397
Propane	-165.160	.009	0.709941
	-165.099		0.709872
	-164.845		0.709629
	-164.680		0.709462
	-164.493		0.709293
	-164.372		0.709168

TABLE 2

SATURATED LIQUID DENSITY OF THE BINARY MIXTURE

METHANE + ETHANE

CH_4 Mole Fraction	Temperature °C	Pressure psia	Density gm/ml
0.19015	-165.586	2.931	0.604181
	-165.364	2.949	0.603949
	-165.105	2.955	0.603692
	-164.920	2.967	0.603487
	-164.740	2.897	0.603284
	-164.608	2.912	0.603148
0.34264	-165.345	4.600	0.578504
	-165.172	4.617	0.578305
	-164.997	4.638	0.578120
	-164.796	4.668	0.577896
	-164.567	4.709	0.577643
0.54540	-165.020	6.067	0.539981
	-164.983	6.042	0.539931
	-164.848	6.160	0.539772
	-164.647	6.300	0.539542
	-164.419	6.465	0.539266
	-164.239	6.886	0.539047

TABLE 2
(continued)

SATURATED LIQUID DENSITY OF THE BINARY MIXTURE

METHANE + ETHANE

CH_4 Mole Fraction	Temperature °C	Pressure psia	Density gm/ml
0.67674	-165.443	7.596	0.512862
	-165.212	7.704	0.512542
	-165.040	7.795	0.512309
	-164.907	7.873	0.512132
	-164.820	7.957	0.511949
0.86677	-165.093	9.328	0.465166
	-164.969	9.441	0.465004
	-164.830	9.570	0.464835
	-164.649	9.728	0.464586
	-164.535	9.834	0.464425

TABLE 3

SATURATED LIQUID DENSITY OF THE BINARY MIXTURE

METHANE + PROPANE

CH_4 Mole Fraction	Temperature °C	Pressure psia	Density gm/ml
0.25750	-165.627	4.478	0.666985
	-165.435	4.496	0.666800
	-165.243	4.680	0.666629
	-165.032	4.699	0.666422
	-164.788	4.209	0.666196
	-164.576	4.730	0.666001
0.40679	-165.471	6.035	0.636100
	-165.259	6.039	0.635865
	-165.048	6.055	0.635658
	-164.827	6.084	0.635422
	-164.613	6.117	0.635197
0.55042	-165.315	7.377	0.600588
	-165.175	7.419	0.600323
	-165.100	7.461	0.600185
	-164.977	7.483	0.599961
	-164.776	7.502	0.599593

TABLE 3
(continued)

SATURATED LIQUID DENSITY OF THE BINARY MIXTURE

METHANE + PROPANE

CH_4 Mole Fraction	Temperature °C	Pressure psia	Density gm/ml
0.69239	-165.102	8.692	0.557346
	-165.306	8.605	0.557569
	-164.918	8.774	0.557159
	-164.765	8.901	0.556978
	-164.601	9.028	0.556805
0.84839	-165.585	9.622	0.500080
	-165.447	9.690	0.499925
	-165.266	9.909	0.499696
	-165.112	9.998	0.499521
	-164.989	10.070	0.499376
	-164.910	10.107	0.499283

TABLE 4

SATURATED LIQUID DENSITY OF THE BINARY MIXTURE

ETHANE + PROPANE

C_2H_6 Mole Fraction	Temperature °C	Pressure psia	Density gm/ml
0.26189	-165.399	0.004	0.696228
	-165.182	0.005	0.696036
	-164.972	0.005	0.695863
	-164.779	.006	0.695704
	-164.540	0.006	0.695475
	-164.311	0.007	0.695266
0.41202	-165.885	0.005	0.687819
	-165.666	0.007	0.687614
	-165.362	0.008	0.687340
	-165.190	0.010	0.687171
	-164.983	0.011	0.686982
0.58516	-165.231	0.004	0.675277
	-165.027	0.005	0.675085
	-164.818	0.005	0.674892
	-164.600	0.006	0.674675
	-164.388	0.007	0.674458
	-164.107	0.008	0.674212

TABLE 4

(continued)

SATURATED LIQUID DENSITY OF THE BINARY MIXTURE

ETHANE + PROPANE

C_2H_6 Mole Fraction	Temperature °C	Pressure psia	Density gm/ml
0.70365	-165.885	0.004	0.666869
	-165.645	0.008	0.666625
	-165.418	0.009	0.666404
	-165.222	0.009	0.666207
	-165.007	0.010	0.666013
	-164.852	0.011	0.665863
0.80869	-165.038	0.008	0.655561
	-164.796	0.009	0.655321
	-164.564	0.009	0.655095
	-164.361	0.009	0.654893
	-164.137	.010	0.654680

TABLE 5

SATURATED LIQUID DENSITY OF THE BINARY MIXTURES

METHANE + N-BUTANE AND ETHANE + N-BUTANE

Methane + n-Butane

CH_4 Mole Fraction	Temperature °C	Pressure psia.	Density gm/ml
0.88426	-165.003	10.925	0.506146
	-164.851	11.079	0.505967
	-164.661	11.272	0.505734
	-164.481	11.455	0.505518
	-164.288	11.700	0.505286

Ethane + n-Butane

C_2H_6 Mole Fraction	Temperature °C	Pressure psia.	Density gm/ml
0.88332	-165.016	.016	0.657287
	-164.842	.0250	0.657122
	-164.653	.033	0.656949
	-164.396	.038	0.656700
	-164.138	.041	0.656449

TABLE 6

LIQUID DENSITY OF THE TERNARY MIXTURE

METHANE + ETHANE + PROPANE

CH_4 Mole Fraction	C_2H_6 Mole Fraction	Temperature °C	Pressure psia	Density gm/ml
0.38842	0.32159	-165.102	5.664	0.606799
		-164.914	5.715	0.606607
		-164.708	5.772	0.606401
		-164.537	5.813	0.606228
		-164.328	5.867	0.606002
0.72383	0.16678	-165.013	8.920	0.521196
		-164.854	8.988	0.521009
		-164.674	9.056	0.520808
		-164.508	9.111	0.520622
		-164.337	9.168	0.520424

By employing the least square curve fit, a functional linear relationship between the liquid density of each system and the temperature was determined. A digital computer was used for this purpose. The functions obtained from the least square technique were of the form:

$$\rho = a + b\,t \qquad (2)$$

where:

ρ = liquid density, gm/ml

t = temperature, ^{o}C

a and b are constants, characteristics of each system.

The constants a and b obtained for each system are tabulated in Table 7.

TABLE 7

SATURATED DENSITIES OF LIQUEFIED PETROLEUM GASES

X_{C1} = Methane Mole Fraction, X_{C2} = Ethane Mole Fraction

$\rho = a + bt$, where t is in degrees centigrade; gm/ml

Component	a x 10	$-bx10^4$	Temperature Range From (°C)	To (°C)	Deviation* Maximum $x10^5$	Minimum $x10^6$
Methane						
Run No. 1	2.15968	12.82254	-165.02	-164.68	1.395	0.788
Run No. 2	2.18958	12.64077	-165.14	-164.62	0.558	0.171
Runs No. 1 and 2	2.18804	12.65030	-165.02	-164.62	1.583	0.117
Ethane	4.68286	9.93837	-165.06	-164.12	-0.508	0.520
Propane	5.49277	9.72744	-165.16	-164.37	-0.658	-0.088
Methane + Ethane						
X_{C1}						
0.19015	4.28919	10.58467	-165.58	-164.61	1.434	-2.801
0.34264	3.96126	11.02998	-165.35	-164.57	-0.545	-0.136
0.54540	3.43799	11.88823	-165.02	-164.24	0.646	1.508
0.67674	2.76515	14.28624	-165.44	-164.82	-3.207	0.908
0.86677	2.46666	13.23529	-165.09	-164.54	1.221	-2.758

TABLE 7

(continued)

Component	a x 10	$-bx10^4$	Temperature Range From (°C)	To (°C)	Deviation* Maximum $x10^5$	Minimum $x10^6$
Methane + Propane						
X_{C1}						
0.25750	5.11825	9.36795	-165.63	-164.58	-0.403	-1.451
0.40679	4.62842	10.47037	-165.47	-164.61	-0.893	0.388
0.55042	2.96015	18.42357	-165.32	-164.78	0.404	-0.240
0.69239	3.78273	10.84636	-165.10	-164.60	0.973	-0.444
0.84839	3.03815	11.85293	-165.59	-164.91	0.693	0.005
Ethane + Propane						
X_{C2}						
0.26189	5.50566	8.80705	-165.40	-164.31	1.671	-1.798
0.41202	5.33917	9.27764	-165.89	-164.98	0.601	-0.208
0.58516	5.17222	9.56582	-165.23	-164.11	-1.467	-0.465
0.70365	5.05742	9.71275	-165.89	-164.85	-0.872	-3.510
0.80869	4.93979	9.79045	-165.04	-164.14	-0.337	-0.119
Methane + n-Butane						
X_{C1}						
0.88426	3.07293	12.05154	-165.00	-164.29	0.276	0.261

TABLE 7

(continued)

Component	a x 10	$-bx10^4$	Temperature Range From (°C)	To (°C)	Deviation* Maximum $x10^5$	Minimum $x10^6$
Ethane + n-Butane						
X_{C2}						
0.88332	4.99923	9.53644	-165.02	-164.14	-0.564	-1.599
Methane + Ethane + Propane						
X_{C1} = 0.38842	X_{C2} = 0.32159					
	4.37557	10.25091	-165.10	-164.33	0.594	-1.52
X_{C1} = 0.72383	X_{C2} = 0.16678					
	3.33556	11.37105	-165.01	-164.34	-0.384	-0.161

*Deviation = Experimental Density Value - Calculated Density Value

The equations tabulated in Table 7 were utilized to compute the liquid density for each system at -165.0°C. Then, with the availability of the density values, the molar volume of the different systems was calculated. The density values and the molar volume data are presented in Tables 8 and 9.

TABLE 8

SATURATED LIQUID DENSITY AND MOLAR VOLUME

OF THE PURE COMPONENTS METHANE, ETHANE

AND PROPANE AT -165.0°C

Component	Density, gm/ml	Molar Volume, ml/gm-mol
Methane	0.427535	37.5221
Ethane	0.632269	47.5557
Propane	0.709780	62.1235

TABLE 9

SATURATED LIQUID DENSITY AND MOLAR VOLUME OF LIGHT HYDROCARBON MIXTURES AT -165.00°C

System	Mole Fraction CH_4	Mole Fraction C_2H_6	Density gm/ml	Molar Volume ml/gm-mol
Methane + Ethane				
	0.19015		0.603566	45.3988
	0.34264		0.578121	43.6970
	0.54540		0.539955	41.5190
	0.67674		0.512238	40.1695
	0.86677		0.465048	38.5142
Methane + Propane				
	0.25750		0.666396	55.3288
	0.40679		0.635603	51.4202
	0.55042		0.600004	47.7560
	0.69239		0.557238	44.2744
	0.84839		0.499388	40.6403
Ethane + Propane				
		0.26189	0.695882	58.0857
		0.41202	0.686998	55.7722
		0.58516	0.675058	53.1613
		0.70365	0.666002	51.3882
		0.80869	0.655521	49.9623

TABLE 9

(continued)

System	Mole Fraction CH_4	C_2H_6	Density gm/ml	Molar Volume ml/gm-mol
Methane + n-Butane				
	0.88426		0.506143	41.3132
Ethane + n-Butane				
		0.88332	0.657274	50.7272
Methane + Ethane				
	0.38842	0.32159	0.606697	47.2851
+ Propane	0.72383	0.16678	0.521185	41.1568

The liquid density values shown in Table 9 for the binary mixtures methane + ethane, methane + propane and ethane + propane were presented graphically as shown in Figures 7, 8 and 9 respectively.

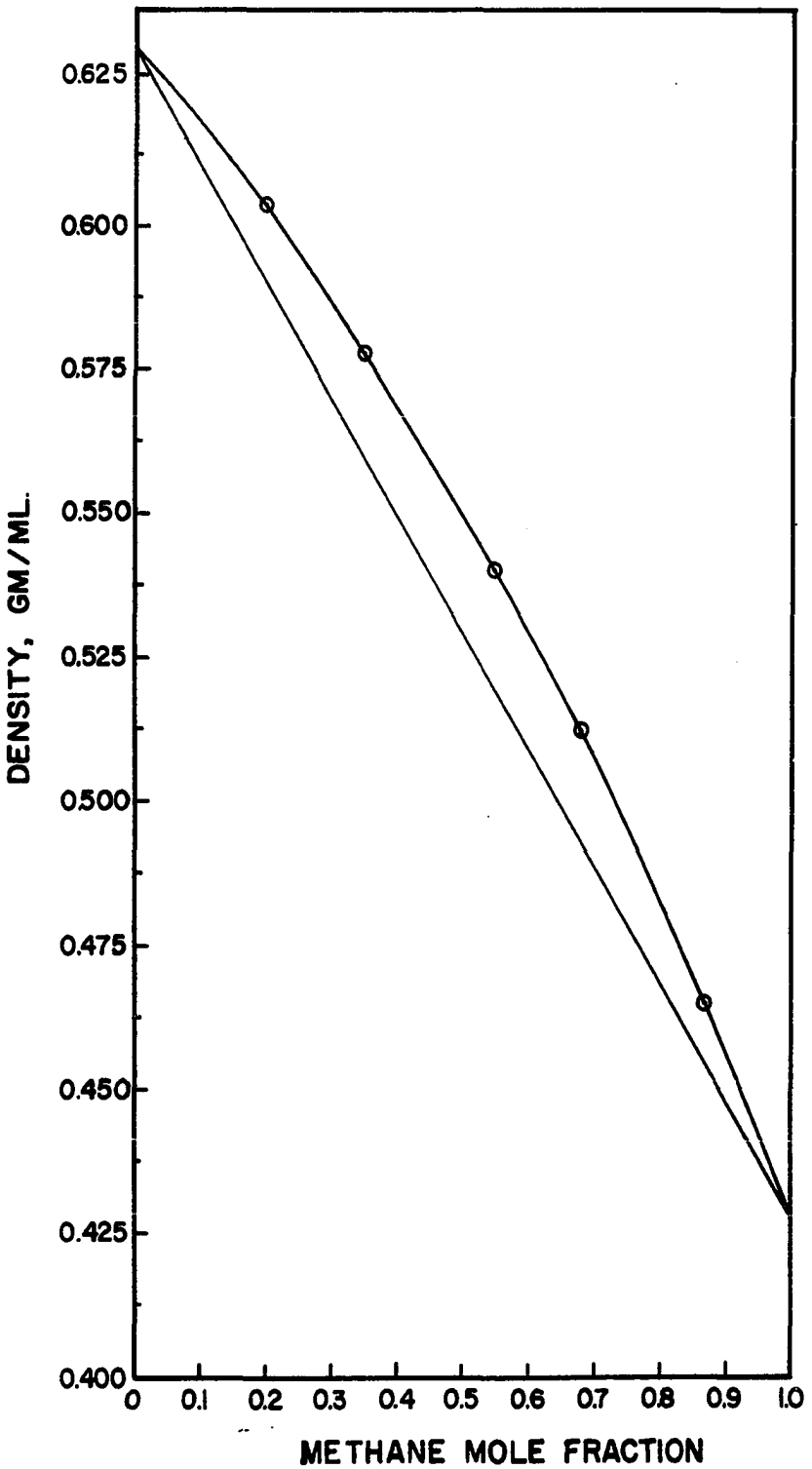


Figure 7. SATURATED LIQUID DENSITY OF METHANE+ETHANE MIXTURE AT -165.0°C

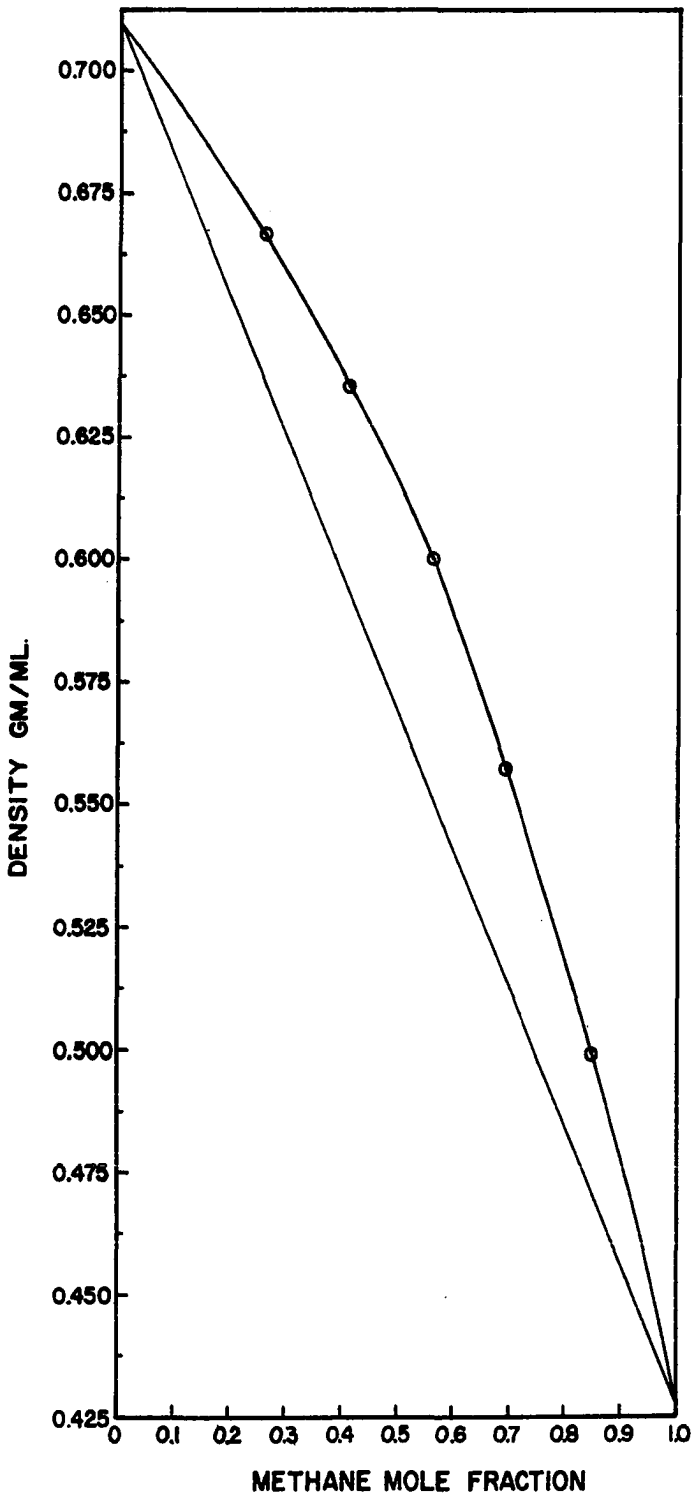


Figure 8. SATURATED LIQUID DENSITY OF METHANE+ PROPANE MIXTURE AT -165.0°C.

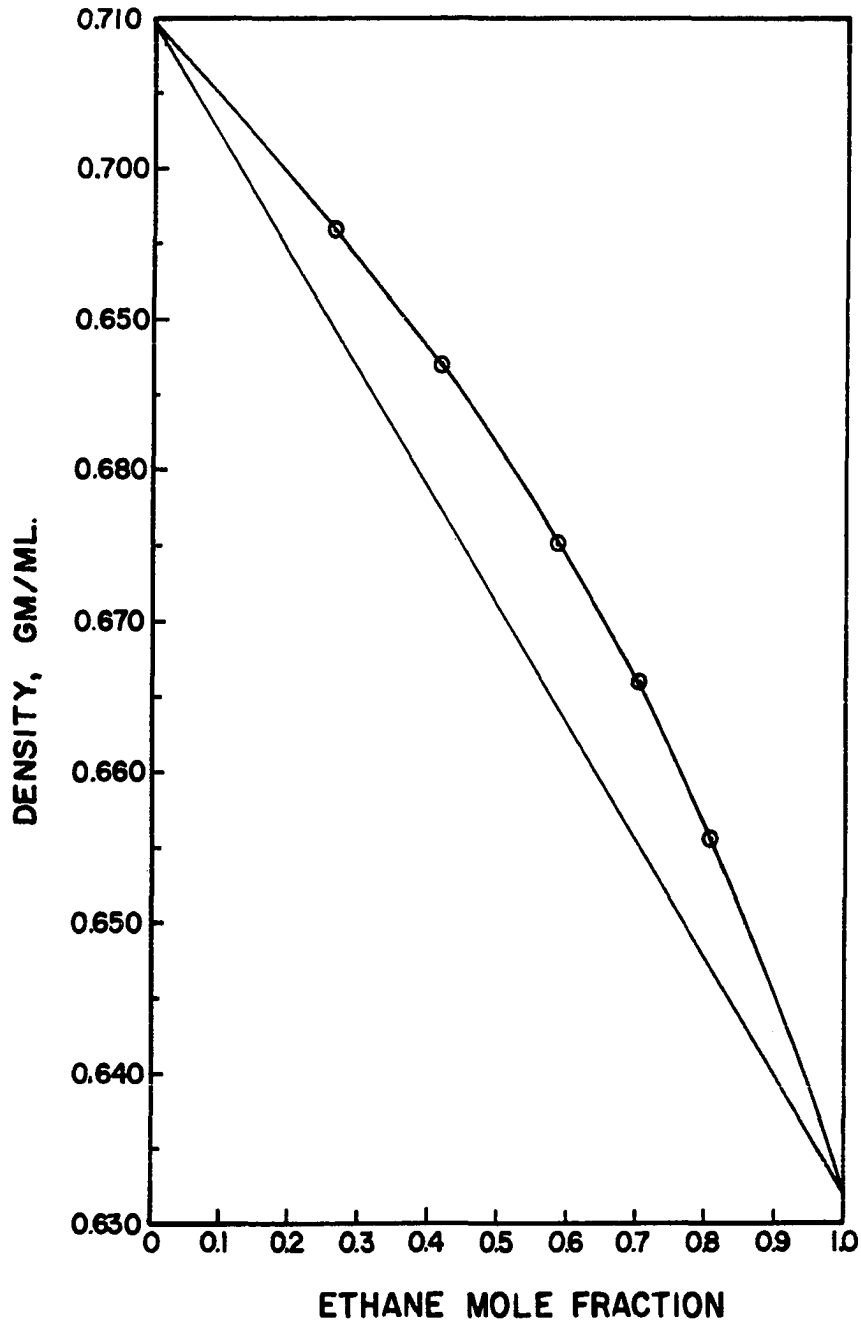


Figure 9. SATURATED LIQUID DENSITY OF ETHANE+ PROPANE MIXTURE AT -165.0°C.

Accuracy of the Experimental Results

The limits of the absolute accuracy of the experimental results were established by means of a complete error analysis as shown in Appendix E. For the binary mixtures methane + ethane, methane + propane and ethane + propane, the accuracy values listed in Table E-6 indicate the maximum and minimum errors in the density results. The accuracy of the experimental density results of any of these three binary mixtures other than those included in the error analysis calculation is smaller than the maximum and larger than the minimum.

It should be pointed out that even though the experimental results are accurate only to within few parts in 100,000, they were reported to six significant figures. Similarly, the temperature was reported to a $0.001^{\circ}C$ even though it was accurate to $\pm 0.01^{\circ}C$. This was done to provide accurate means to calculate the change in density with the change in temperature in the experimental range. In other words, if the density and temperature data were reported to within their indicated accuracy, the calculated values of the change in density may be misleading. In addition, because the temperature range was small, the smoothness of the experimental

results if reported to only five significant figures may be distorted.

Because of the limited range covered by the literature data for similar systems used in this investigation, the reliability of the present experimental data must be judged mainly by 1) the reproducibility of the data, 2) the smoothness of the resulting values, and 3) the inherent errors in the experimental apparatus used.

In order to check the reproducibility of the data, two runs were made to determine the liquid density of methane. The agreement between both runs was excellent. The density of liquid methane at -165.0°C was computed by means of the equations presented in Table 7. The difference in the results of both runs was less than 1×10^{-5} gm/ml.

Because the temperature range in this work was small, the density of the different systems would be expected to be a linear function of the temperature. This was verified as shown in Table 7. The magnitude of the deviation reported in Table 7 revealed the smoothness of the data.

The effect of the inherent errors in the equipment was thoroughly investigated by means of the error analysis presented in Appendix E.

As a final check on the accuracy of the present data,

the liquid density values of methane were compared with comparable data in the literature.

The density value of the smoothed data reported by Keyes, Taylor and Smith[25] was about 0.3% larger than the value obtained in this investigation. The liquid density value reported by Fuks, Legros and Bellemans[16] was approximately 0.6% lower than the present value. On the other hand, the density data reported by Davenport, Rowlinson and Saville[12] when extrapolated seem to have excellent agreement with our experimental results.

It is of interest to point out that all the above investigating groups used essentially the same method employed in this work. The volumes of their pycnometers ranged from 1.5798 cc to 0.6 cc in comparison to a 30 cc pycnometer used in this work. This indicates that for the same error to occur in measuring the mass or the volume while determining the density, the minimum error in the results will correspond to the present investigation. In fact, the resulting error in this work will be several fold less than in the other methods.

It is concluded from this discussion that the reliability of the data reported in this thesis is firmly established. Therefore, we strongly believe that our data should be worthy of consideration by present and future investigators.

CHAPTER VIII

APPLICATION OF RESULTS

This chapter is devoted to the application of the liquid density results at -165.0°C which were presented in Tables 8 and 9. These values were used 1) to calculate the excess volume, and 2) to check the validity of the principle of congruence.

Calculation of the Excess Volume

The excess volume is defined by Equation (3):

$$V^{E}_{T,P} = Vm - \sum_{i} X_i V_i^{o} \qquad (3)$$

where:

$V^{E}_{T,P}$ = excess volume at constant temperature and pressure, ml/gm-mol.

V_m = molar volume of the mixture at the same temperature and pressure, ml/gm-mol.

X_i = mole fraction of component i in the mixture.

V_i^{o} = molar volume of pure component i at the same temperature and pressure of the mixture, ml/gm-mol.

The excess volume values of the mixtures methane + ethane, methane + propane, ethane + propane, and methane + ethane + propane were calculated as shown in Appendix F. The results were tabulated in Table 10. In addition, the calculated excess volume data for the three binary mixtures $CH_4 + C_2H_6$, $CH_4 + C_3H_8$ and $C_2H_6 + C_3H_8$ were presented graphically in Figures (10), (11) and (12) respectively.

It should be pointed out that in calculating the excess volume data presented in Table 10, the effect of the pressure variation was assumed negligible. The validity of this assumption was verified in Appendix F.

TABLE 10

EXCESS VOLUME OF LIQUEFIED PETROLEUM

GASES AT -165.0°C

Mixture	CH_4 Mole Fraction	C_2H_6 Mole Fraction	Excess Volume V^E ml/gm-mole
$CH_4+C_2H_6$	0.19015		-.2495
	0.34264		-.4213
	0.54540		-.5648
	0.67674		-.5965
	0.86677		-.3450
$CH_4+C_3H_8$	0.25750		-.4598
	0.40679		-.6957
	0.55042		-.8265
	0.69239		-.8155
	0.84839		-.6119
$C_2H_6+C_3H_8$		0.26189	-.2227
		0.41202	-.3492
		0.58516	-.4380
		0.70365	-.4850
		0.80869	-.3808
$CH_4+C_2H_6+C_3H_8$	0.72383	0.16678	-.7304
	0.38842	0.32159	-.5982

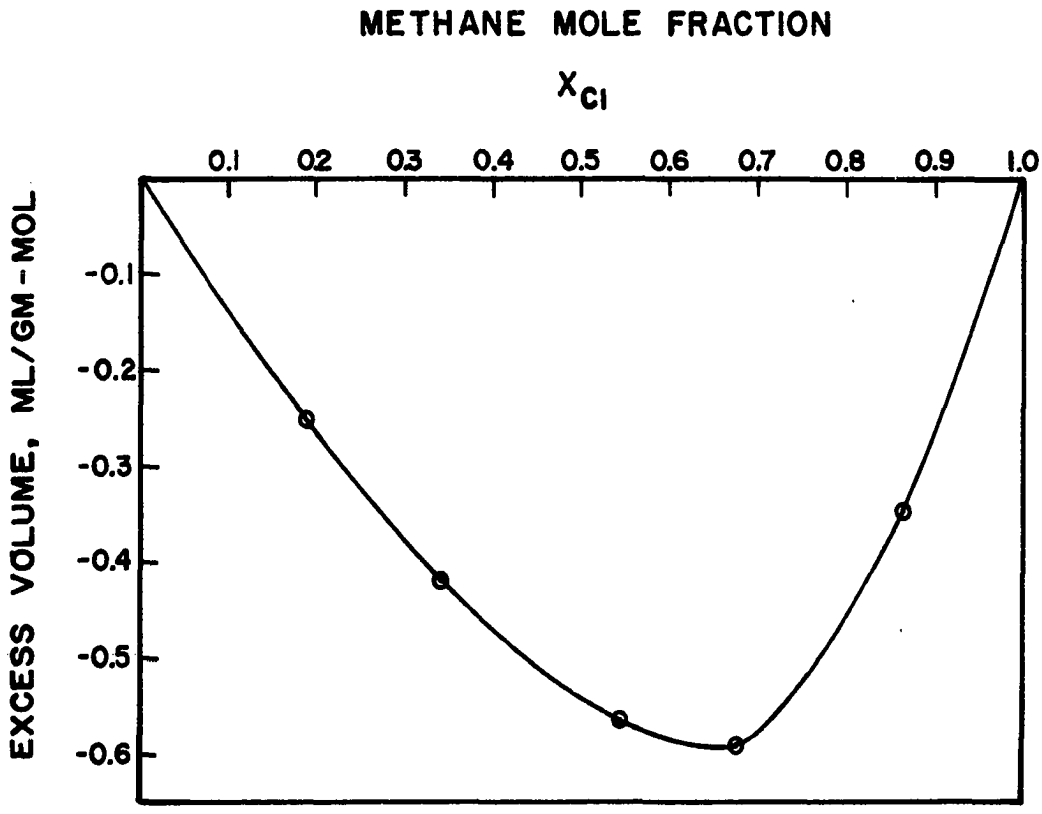


Figure 10. EXCESS VOLUME OF METHANE+ETHANE MIXTURE AT -165.0°C.

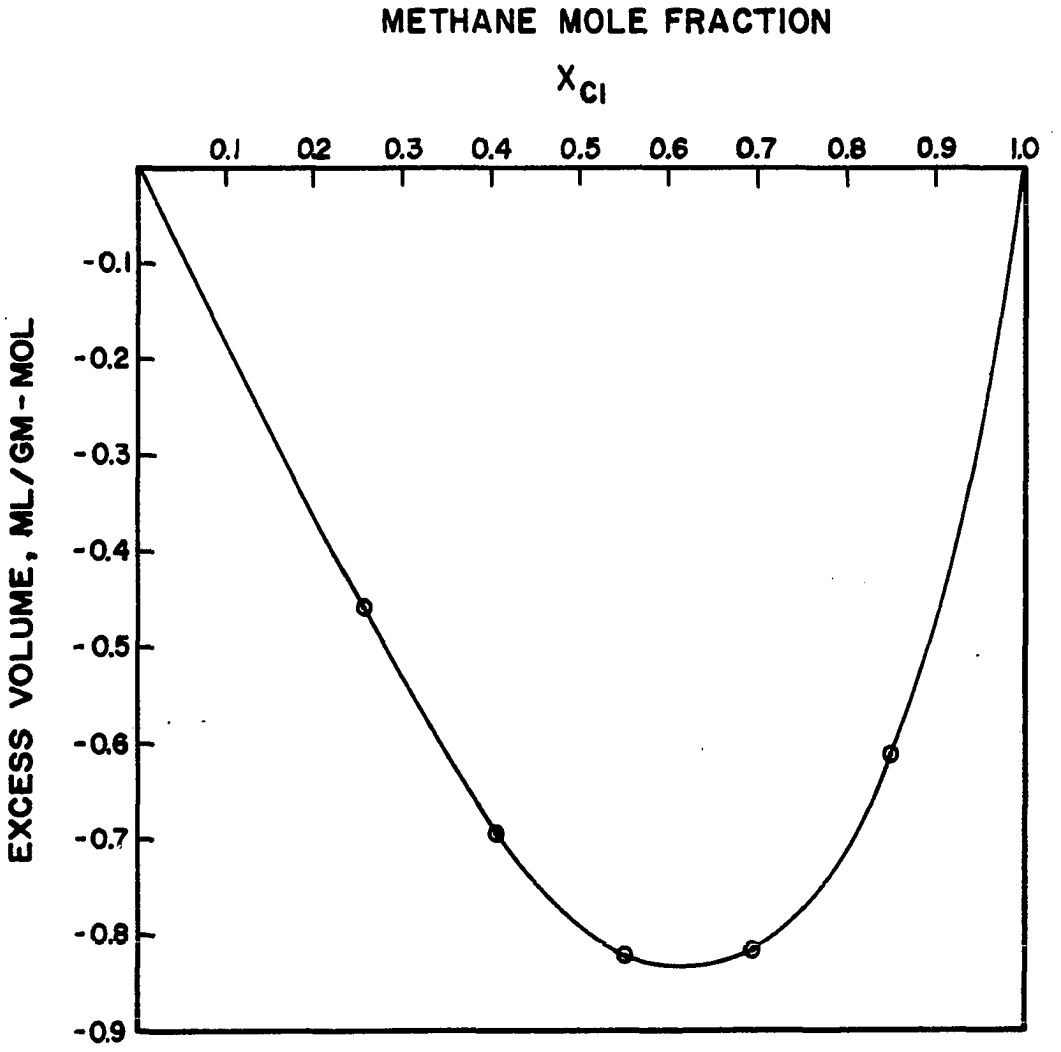


Figure 11. EXCESS VOLUME OF METHANE+PROPANE MIXTURE AT -165.0°C.

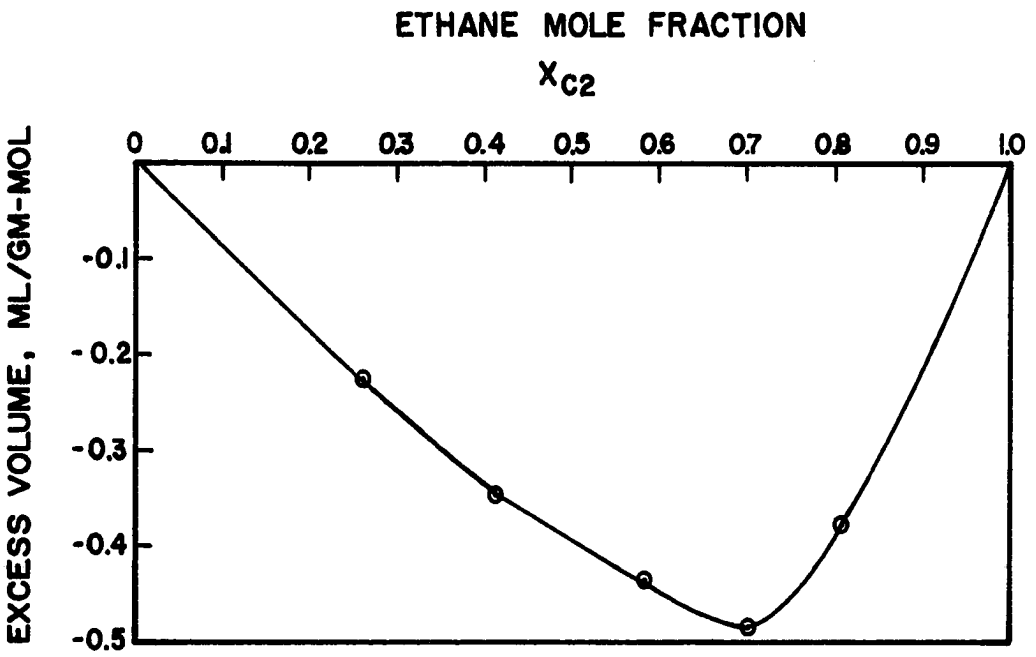


Figure 12. EXCESS VOLUME OF ETHANE+PROPANE MIXTURE AT -165.0°C.

Checking the Validity of the Principle of Congruence

The principle of congruence was introduced by Bronsted and Koefoed[6]. According to these authors, the thermodynamic properties of a mixture of n-alkanes are determined by an average chain-length defined by Equation (1)

$$n = \sum_i n_i x_i \qquad (1)$$

Hijmans[20] reported that if the excess volume of a binary n-alkane mixture is plotted as a function of the average chain length n, then the excess volume of two n-alkanes having chain-lengths n_1 and n_2 should be represented by the difference in height between this curve and the straight line.

$$V^{id} = \frac{n_2 - n}{n_2 - n_1} V^{E1} + \frac{n - n_1}{n_2 - n_1} V^{E2} \qquad (4)$$

where:

V^{E1} = excess volume of a mixture with average chain-length n_1.

V^{E2} = excess volume of a mixture with average chain-length n_2.

V^{id} = ideal volume.

The excess volume of the binary mixture methane + propane was plotted as a function of the chain-length as shown in Figure 13.

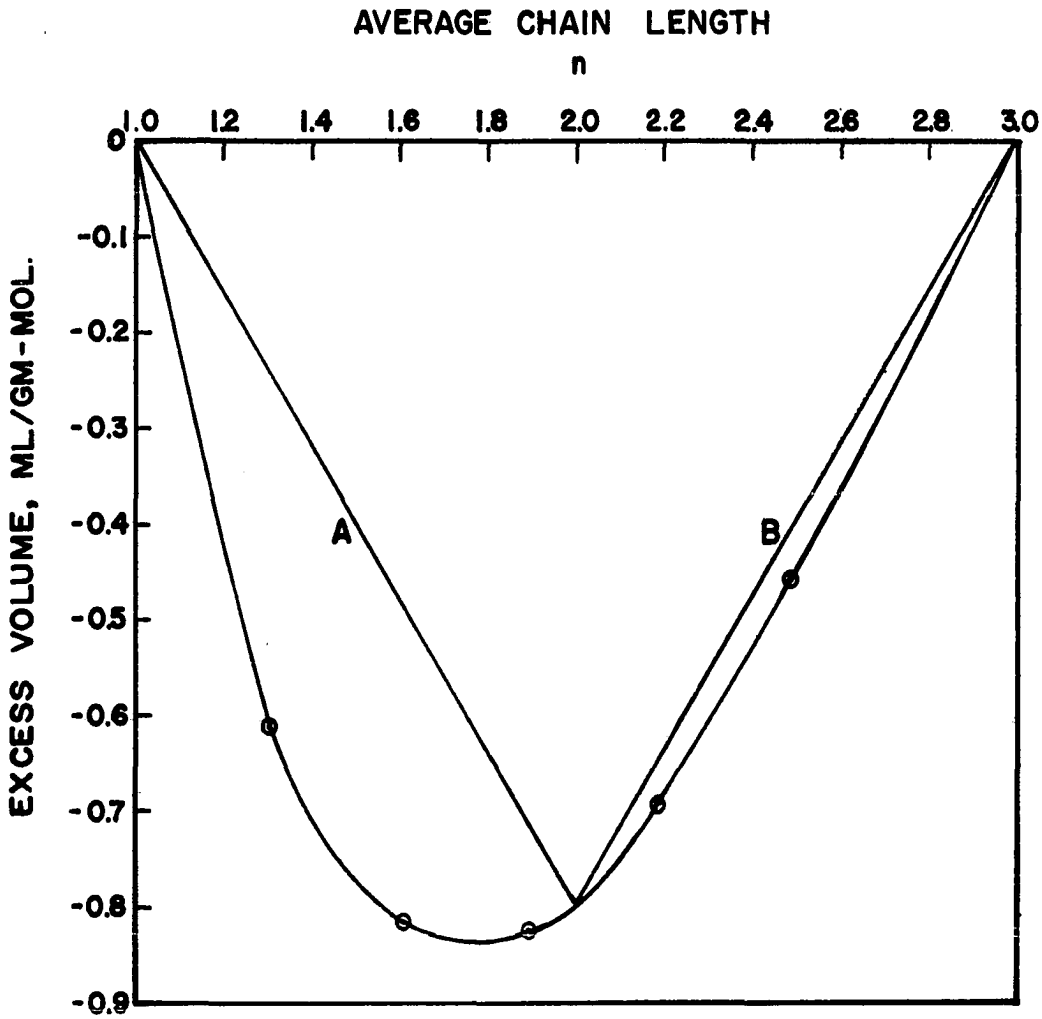


Figure 13. EXCESS VOLUME OF METHANE + PROPANE MIXTURE AT -165.0°C VS. AVERAGE CHAIN LENGTH

Then the two lines A and B were drawn. Line A connected the points $n = 0$ and $n = 2$. Line B connected the points $n = 2$ and $n = 3$. Now, for the principle of congruence to hold, the excess volume of the binary mixture ethane + propane must be represented by the difference in height between the excess volume curve of the methane + propane mixture and line B. For the mixture methane + ethane, the excess volume should be the difference between line A and the curve.

The values calculated in this manner are compared with the experimental points as shown in Table 11.

TABLE 11

COMPARISON BETWEEN THE THEORETICAL AND THE EXPERIMENTAL EXCESS VOLUME DATA

X_{C1} = Methane Mole Fraction, X_{C2} = Ethane Mole Fraction, n = Average chain-length, V^{EE} = Experimental Excess Volume, V^{EC} = Theoretical Excess Volume

System	X_{C1}	X_{C2}	n	$-V^{EE}$	$-V^{EC}$
Methane+Ethane	0.1902		1.81	0.2495	0.18
	0.8677		1.13	0.3450	0.14
Ethane + Propane		0.2619	2.77	0.2227	.03
		0.8087	2.19	0.3808	0.04

The results tabulated in Table 11 indicate that the principle of congruence is not applicable to the systems studied in this work. This finding could be attributed to the effect of the difference in molecular structure between methane and the other hydrocarbons.

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APPENDIX A

CALIBRATION OF THE VOLUME OF THE PYCNOMETER

The volume of the pycnometer was measured at room temperature by differential weighing with distilled water. Then, by making use of the known thermal expansion data of fused quartz, the volume of the pycnometer at the operating temperature of -165°C was calculated. In addition, a correction for the change in the volume of the nickel stirrer in the pycnometer was made.

Volume of the Pycnometer at Room Temperature

The volume of the pycnometer at room temperature was determined by measuring the amount of distilled water required to fill the pycnometer at a certain known temperature. The method followed to achieve this can best be presented by describing the separate units comprising 1) constant temperature bath, 2) filling the pycnometer with distilled water, 3) determination of the mass of the distilled water, and 4) measurement of the pycnometer's volume at room temperature.

1. Constant Temperature Bath

The apparatus used for the constant temperature bath consisted of two concentric vessels. Both were filled with

water which was used as the bath fluid. The inside vessel was sealed by a 1-inch thick styrofoam piece. The bath fluid was stirred by a 2-inch propeller. The stirrer was driven by a 1500 rpm electrical motor which was equipped with a speed adjusting mechanism. The temperature was controlled by a Hallikainen Model 1053A Thermotrol with proportional plus reset control. The power output from the Thermotrol led to a 125 watts immersion heater. The bath temperature was measured with a Leeds and Northrup Model 8164 capsule-type platinum resistance thermometer used in conjunction with a Leeds and Northrup G-2 Mueller bridge and galvanometer. The thermometer was calibrated by the National Bureau of Standards. This thermometer was mounted in a stainless steel tubing as described in Chapter III. The stainless steel tubing was placed inside a copper cylinder, 3/4 inch in inside diameter. The copper cylinder was filled with vacuum oil and then placed inside the inner vessel. With this apparatus the bath temperature was controlled to $\pm$ 0.002°C.

The pycnometer, filled with distilled water was placed in the inside vessel. The main body of the pycnometer was completely immersed in the bath fluid. The main portion of the graduated portion of the capillary stem was above the styrofoam piece.

2. Filling the Pycnometer with Distilled Water

The water used in this calibration was distilled at the

laboratory of the School of Chemical Engineering and Materials Science at the University of Oklahoma. It was analyzed using an AC Conductivity Apparatus which was manufactured by Barnstead Demineralizer Company. The results indicated the impurities to be less than 2 parts per million.

One of the major difficulties in filling the pycnometer was preventing the formation of air bubbles. This was achieved by using a hypodermic needle equipped with a stainless steel capillary tubing. This tubing was 20 inches long with an outside diameter of 0.05 centimeter.

In order to fill the pycnometer, the hypodermic needle was filled with the distilled water. Then, with the stainless steel capillary tubing extending throughout the length of the pycnometer stem, water was slowly fed to the pycnometer. This was repeated until the pycnometer was filled to the desired level on the graduated portion of the capillary stem.

After the pycnometer was filled, the stainless steel capillary tubing was connected to a vacuum system. Then this tubing was placed in the pycnometer stem with the free end just few millimeters above the liquid level in the pycnometer. The vacuum system was turned on for few hours. This helped to circulate the air through the pycnometer stem which in turn helped to dry the walls of the stem.

3. Determination of the Mass of the Distilled Water

The pycnometer was weighed using the Right-A-Weigh analytical balance under the conditions; first filled with air and second filled with distilled water. The mass of the water in the pycnometer was equal to the difference between the second and the first weighings plus the mass of the air in the pycnometer. The mass of the air was calculated from knowledge of the atmospheric pressure and the temperature of the analytical balance surroundings while weighing the pycnometer filled with air.

The full pycnometer was weighed before placing it in the constant temperature bath and also at the end of the calibration run. This was done to check the amount of water lost by evaporation through the pycnometer stem. The results did not show any difference between both weighings. This of course meant that the calibration of the volume of the pycnometer was not affected by this process.

4. Measurement of the Volume of the Pycnometer at Room Temperature

After the full pycnometer was placed in the constant temperature bath and the temperature was controlled to $\pm$ 0.002^{o}C, the liquid level in the pycnometer capillary stem was read and recorded together with the corresponding temperature of the bath. The liquid level was determined by making use of a cathetometer. The temperature was measured by reading the resistance indicated

by the G-2 Mueller bridge and then determining the corresponding temperature. Then, the thermotrol settings were readjusted to cause a temperature rise just sufficient to raise the liquid level in the stem approximately 2 millimeters. Sufficient time, usually 45-60 minutes, was allowed for temperature stabilization. The liquid level and temperature were then read and recorded.

This process was repeated until the liquid in the pycnometer expanded enough to fill the entire graduated portion of the fused quartz capillary stem.

Now, from the known density of distilled water as a function of temperature and the measured mass of the distilled water, the volume of the pycnometer corresponding to each liquid level reading was calculated.

FUSED QUARTZ THERMAL EXPANSION DATA

The thermal expansion data for annealed fused quartz from which the pycnometer was constructed, were experimentally determined by the National Bureau of Standards, Washington, D.C. The preliminary smoothed data[32] reported by the National Bureau of Standards are presented in Table A-1.

TABLE A-1

LINEAR THERMAL EXPANSION DATA OF ANNEALED FUSED QUARTZ (GE TYPE 204)

Temperature T, °K	Linear Thermal Expansion $\frac{(L_T - L_{293})\ 10^6}{L_{293}}$
320	+ 11.47
300	+ 2.87
293	0
280	- 5.35
260	- 12.76
240	- 19.36
220	- 24.51
200	- 28.15
180	- 30.15
160	- 30.08
140	- 27.90
120	- 22.69
100	- 13.80
80	+ 6.10

The precision of each value shown above was reported to be approximately $\pm$ 0.3×10^{-6}.

With the availability of these thermal expansion data, and the experimentally determined volume at room temperature, the volume of the pycnometer was calculated at the operating temperature of -165°C. This was achieved by first calculating the change in the volume as indicated by Equation (A-1):

$$\Delta V = \frac{3V_{TO} \ (L_T - L_{TO})}{L_{TO}} \qquad \text{(A-1)}$$

where:

ΔV = Change in volume between T_0 and T.

V_{TO} = Volume at Reference temperature.

TO = Reference temperature.

T = Operating Temperature

$\frac{L_T - L_{TO}}{L_{TO}}$ = Linear Thermal Expansion

It is clear that the change in volume is also equal to the difference between the volume at the operating temperature, V_T, and that at the reference temperature, V_{TO}. Mathematically, this can be represented by Equation (A-2):

$$\Delta V = V_T - V_{TO} \qquad \text{(A-2)}$$

Combining Equations (A-1) and (A-2) and solving for V_T, one finds that Equation (A-3) gives the desired relationship between the volume of the pycnometer at the operating temperature and at room temperature:

$$V_T = V_{TO} \left(1 + 3 \left(\frac{L_T - L_{TO}}{L_{TO}} \right)\right) \qquad \text{(A-3)}$$

Calculation of the Volume of the Nickel Stirrer

The mass of the nickel stirrer was determined at room temperature by weighing it on the Right-A-Weigh analytical balance. The volume of the stirrer at room temperature was calculated by dividing its mass by its known density[30].

The change in the volume of the stirrer at the operating temperature of -165°C was calculated by making use of equation (A-1). The linear thermal expansion data for Nickel A were determined by Arp, Wilson and Winrich[2].

Calculation of the Actual Pycnometer's Volume at the Operating Temperature

The actual volume of the pycnometer at the operating temperature was calculated by adding the volume of the pycnometer obtained by making use of Equation (A-3) to the change in the volume of the nickel stirrer calculated above. The final results showing the volume of the pycnometer as a function of the

divisions on the graduated portion of the capillary stem, were presented in Table A-2. A sample calculation is presented later in this Appendix.

TABLE A-2

VOLUME OF THE PYCNOMETER AT -165°C

Division on Graduated Portion of Capillary Stem	Volume, ml
6.2	30.1268
8.1	30.1284
11.7	30.1312
13.9	30.1331
16.9	30.1354
19.6	30.1374
22.0	30.1394
24.5	30.1413
27.2	30.1433
29.5	30.1452
32.1	30.1472
34.0	30.1488
35.8	30.1503
37.8	30.1518
41.6	30.1549
43.8	30.1564
45.6	30.1575
48.1	30.1597
50.0	30.1612

TABLE A-2
(continued)

Division on Graduated Portion of Capillary Stem	Volume, ml
51.8	30.1627
53.6	30.1643
55.9	30.1658
57.5	30.1672
59.2	30.1686
61.9	30.1706
63.9	30.1723
66.2	30.1739
67.7	30.1753
69.7	30.1770

Sample Calculation of the Volume of the Pycnometer

1. Volume of the Pycnometer at Room Temperature

Empty Pycnometer Data

Weight of Pycnometer filled with air as indicated by the analytical balance = M_{pa} = 223.8481 gm

Temperature during weighing process = 70.5°F

Differential thermometer reading 4.23

Barometric pressure 29.210 in Hg

Temperature of barometer 75.0°F

Pressure Correction 0.122 in Hg

Corrected Pressure 29.088 in Hg

Standard Masses used to balance

$M_{pa} = M_{sa}$ = 223.8363 gm

Temperature while using Standard Masses 69.5°F

Barometric Pressure 29.106 in Hg

Temperature of barometer 74.5°F

True Mass of Pycnometer filled with

air = M_{PE} = 223.8379

"Determined as shown in Appendix D"

Full Pycnometer Data

Weight of Pycnometer filled with distilled water as indicated by the analytical balance = M_{pw} = 253.7983 gm

Temperature during weighing process 21.14°C

Differential thermometer reading 3.98

Barometric pressure 29.191 in Hg

Temperature of barometer 75.5°F

Pressure Correction 0.122 in Hg

Pressure Corrected 29.069 in Hg

Standard Masses used to balance

$M_{pw} = M_{sw}$ = 253.7861 gm

True Mass of Pycnometer filled with distilled water 253.7881 gm

"Determined as shown in Appendix D"

Liquid level in Pycnometer Capillary Stem 6.2

Temperature of Pycnometer

"Determined by Platinum Resistance Thermometer" $31.30^{\circ}C$

Specific Volume of Distilled Water[A]

at $31.30^{\circ}C$ 1.0047469 ml/gm

The true mass of distilled water required to fill the pycnometer up to the division 6.2 in the capillary stem at $31.30^{\circ}C$ is calculated below

For the pycnometer filled with air:

$$M_{PE} = M_p + M_A \qquad \text{(A-4)}$$

where:

M_p = mass of pycnometer when evacuated

M_A = mass of air required to fill the pycnometer

For the pycnometer filled with distilled water:

$$M_{PF} = M_p + M_w \qquad \text{(A-5)}$$

where:

M_w = mass of distilled water required to fill the pycnometer.

[A] Chappuis, P., Bureau International des Poids et Mesures, Travaux et Memoires, 13, 1907.

Combining Equations (A-4) and (A-5) and solving for M_w one finds:

$$M_w = M_{PF} - M_{PE} + M_A \qquad \text{(A-6)}$$

With the exception of M_A, all the terms on the right hand side of Equation (A-6) are known. The term M_A is determined as follows:

$$M_A = \rho_A V_P \qquad \text{(A-7)}$$

where:

ρ_A = Density of Air, gm/ml

V_p = Volume of the Pycnometer, ml.

The density of air was calculated by making use of the equations developed by Barieau[3].

$$Z = 1 - (6.02 + 25.4y \pm 758y^2)10^{-4}p + (1.05 + 1.31y + 131y^2)\, 10^{-5}\, tP \qquad \text{(A-8)}$$

$$M = 28.968 - 10.952y \qquad \text{(A-9)}$$

$$\rho_A = \frac{PM}{RT} \qquad \text{(A-10)}$$

where:

Z = Compressibility Factor

y = Mole Fraction of Water Vapor in Air

P = Pressure, atm

t = Temperature, ^oC

T = Temperature, ^{o}K

M = Molecular Weight of Air

R = Gas Constant

It was assumed that the relative humidity was constant and equal to 50%. The assumption of constant relative humidity was not bad in view of the fact that the room was air conditioned. The mole fraction of water vapor, y, was calculated to be approximately 1.27×10^{-2}. By substituting the values of $y = 1.27 \times 10^{-2}$, P = 0.97215 atm. and $t = 21.39^{o}C$, into Equation (A-8), the compressibility factor Z was calculated to be 0.999596.

From Equation (A-9)

$$M = 28.968 - 10.952\ (1.27)\ 10^{-2}$$

$$= 28.829$$

From Equation (A-10)

$$\rho_A = \frac{(0.97215)\ (28.829)}{(82.054)\ (294.54)(0.999596)} \quad \ldots\ldots$$

$$= 1.16010 \times 10^{-3} \text{ gm/ml.}$$

Substituting this value of the density of air into Equation (A-7) assuming a 30 ml pycnometer, the mass of air, M_A is calculated:

$M_A = 1.16010\ (10^{-3})\ (30) = 0.034803$ grams

Therefore, from Equation (A-6):

$M_w = 253.7881 - 223.8379 + 0.0348$

$= 29.9850$ gm

The volume of the pycnomoter, V_p at 31.30°C is given by

$V_p = 29.9850\ (1.0047469) = 30.1273$ ml.

2. Calculation of the Volume of the Pycnometer at -165°C

The linear thermal expansion coefficient of fused quartz at -165°C is approximately -18×10^{-6} as shown in Table A-1. Then, from Equation (A-3) we have:

V_C at -165°C $= 30.1273\ (1\text{-}3 \times 18 \times 10^{-6})$

$= 30.1257$ ml.

3. Calculation of the Volume of the Nickel Stirrer

Weight of Nickel Stirrer as read from the analytical balance at 74.5°F	1.5952 gm
True Mass (Calculated as hown in Appendix D)	1.5952 gm
Density of Nickel[30]	8.90 gm/ml

Volume of Stirrer = $V_s = \frac{1.5952}{8.90} = 0.1792$ ml

The linear thermal expansion coefficient[2] at $-165^{\circ}C$ is 198×10^{-5}.

The change in volume of the stirrer, ΔV_s, is calculated by making use of Equation (A-1):

$$\Delta V_s = -0.1792\ (3)\ (198 \times 10^{-5})$$

$$= -0.0011 \text{ ml.}$$

4. Calculating of the Actual Pycnometer's Volume at $-165^{\circ}C$

The net volume of the pycnometer is the sum of the volume calculated in part 2 above and the absolute value of the change in the volume of the nickel stirrer.

$$V_{PC} = 30.1257 + 0.0011 = 30.1268 \text{ ml.}$$

Addition to Appendix A

THERMAL EXPANSION DATA OF FUSED QUARTZ

(GE TYPE 204)

After the completion of this thesis, we received some additional information from the National Bureau of Standards concerning the thermal expansion data of fused quartz (GE Type 204). This information may be of interest to other investigators. Therefore, it will be included as an "Addition to Appendix A".

It was previously arranged with the National Bureau of Standards to experimentally measure the thermal expansion data as a function of temperature for three different samples. These samples are described below.

Sample A: This sample was cut from the original tubing as received from General Electric Company.

Sample B: This sample was cut from the original tubing and then annealed at the laboratory of the School of Chemical Engineering and Materials Science at the University of Oklahoma.

The sample was annealed as follows:

1. The temperature of the oven was brought to 1180°C.

2. The sample was placed in the oven and kept for a period of two hours at 1180°C.

3. After two hours, the sample was cooled at a rate of 20°C per hour until the temperature reached 1000°C. Then the power of the oven was turned off and the sample was left in the furnace until the temperature dropped to approximately 65°C.

Sample C: This sample was originally subjected to a sequence of thermal conditions similar to those encountered in constructing the pycnometer. One end of the sample tube was sealed. The sample was then annealed exactly in the same manner as sample B.

Previously, the National Bureau of Standards sent the thermal expansion data for Samples A and B. The data for Sample B as shown in Table A-1, were used to correct for the volume of the pycnometer. Just very recently, the data for Sample C were also received. The complete data for the three different samples are presented in Table AA-1.

TABLE AA-1

THERMAL EXPANSION DATA OF THREE SAMPLES OF FUSED QUARTZ

(GE TYPE 204)

Temperature °K	Linear Thermal Expansion, $\frac{(L_T - L_{293})}{L_{293}} 10^6$		
	Sample A	Sample B	Sample C
320	+ 11.06	+ 11.47	+ 10.62
300	2.66	+ 2.87	+ 2.74
293	0	0	0
280	- 4.54	- 5.35	- 4.99
260	- 10.50	- 12.76	- 12.21
240	- 14.94	- 19.36	- 18.55
220	- 17.62	- 24.51	- 23.63
200	- 18.40	- 28.15	- 27.08
180	- 17.04	- 30.15	- 28.52
160	- 13.38	- 30.08	- 27.60
140	- 7.06	- 27.90	- 23.93
120	+ 2.20	- 22.69	- 17.14
100	+ 14.74	- 13.80	- 6.86
80	+ 30.74	+ 6.0	+ 7.28

The precision of each value was reported to be approximately $\pm$ 0.3 x 10^{-6}. The thermal expansion data for Sample B are also

listed in Table A-1.

As stated above, the data for Sample B were used to correct for the change in the volume of the pycnometer between room temperature and -165°C. It is interesting to examine the effect of using the thermal expansion data for Samples B and C. This is done as indicated below.

Define V_p = volume of the pycnometer at room temperature

V_{pc} = volume of the pycnometer at -165°C.

From Table AA-1:

$$\frac{L_{-165} - L_{293}}{L_{293}} = -18 \times 10^{-6} \quad \text{Sample B}$$

$$= -13 \times 10^{-6} \quad \text{Sample C}$$

Assume $V_p = 30.1273$ ml

Then by making use of Equation (A-3) we have:

$$V_{pc} = 30.1273\ (1-3\times18\times10^{-6}) = 30.1257 \text{ ml} \quad \text{(Sample B)}$$

$$V_{pc} = 30.1273\ (1-3\times13\times10^{-6}) = 30.1261 \text{ ml} \quad \text{(Sample C)}$$

The effect of this volume change on the density results is investigated as follows:

Consider the density of pure methane.

Mass of methane = 12.8798 gm

Therefore the density is calculated as:

$$\rho = \frac{12.8798}{30.1257} = 0.427535 \text{ gm/ml} \quad \text{(Sample B)}$$

$$= \frac{12.8798}{30.1261} = 0.427530 \text{ gm/ml} \quad \text{(Sample C)}$$

The difference in both density values is 5×10^{-6} gm/ml.

APPENDIX B

CALIBRATION OF THE VOLUMES OF THE WEIGHING BOMBS

The three weighing bombs which were used in this work were marked for identification purposes as Bomb No. 1, Bomb No. 3 and Bomb No. 4. Bombs No. 3 and 4 were exclusively used for weighing ethane and methane respectively. Bomb No. 1 was used for propane and for n-butane.

The external volume of each weighing bomb was calibrated as a function of pressure within the operating pressure range. This was achieved by 1) measuring the internal volume at room temperature and atmospheric pressure, 2) determining the effect of pressure on the volume, 3) calculating the volume of the metal in each bomb, and 4) calculating the total volume of each weighing bomb.

Measurement of the Internal Volume at Room Temperature and Atmospheric Pressure

The internal volume of each bomb was measured by direct differential weighing with distilled water. Each bomb was first evacuated to 0.002 mm. Hg. and then weighed on a 1 kilogram analytical balance at the Physical Chemistry

Laboratory at the University of Oklahoma. The bomb was then filled with distilled water and weighed using the same analytical balance. While filling each bomb with water, it was first completely immersed in a water bath with known temperature. The temperature of the water bath and the atmospheric pressure were read and recorded. The mass of the distilled water required to fill each bomb completely was taken as the difference between the second and the first weighing for the respective bombs. Because of the fact that the variations in room temperature were small (less than $2^{\circ}F$), the effect of air buoyancy was considered negligible. Then, the internal volume of each bomb was calculated by dividing the mass of the distilled water by its density at the corresponding temperature. The results are tabulated in Table B-1.

TABLE B-1

INTERNAL VOLUME OF THE WEIGHING BOMBS

AT ATMOSPHERIC PRESSURE

Bomb No.	Volume, cc
1	560.03
3	559.92
4	559.02

Determination of the Effect of Pressure on the Volume of the Bomb

The effect of pressure on the volume of each weighing bomb was experimentally determined using the apparatus presented in Figure 3, Chapter III.

The weighing bomb was placed in reservoir B and then was connected to both the vacuum system and to vessel A. Reservoir B was filled with water free from air bubbles until the liquid level reached a point somewhere in the lower portion of the capillary tube. Then the bomb was evacuated and filled with water until atmospheric conditions prevailed. The liquid level in the capillary tube was measured and recorded. A cathetometer was used to read the liquid level to the nearest 0.001 centimeter. By making use of a water pump, the pressure in the weighing bomb was raised and the corresponding rise in the capillary tube liquid level was measured and recorded. It should be pointed out that the weighing bomb could have been filled with any gas for pressure application, and that water was used mainly for safety precautions.

The change in the volume of the weighing bomb with increase in pressure caused an equal change in the volume of the water in vessel B. Because this vessel was free from leaks to the surrounding atmosphere, the change in the volume of

its water contents was calculated by knowing the change in the liquid level in the capillary tube. The experimental results are presented graphically in Figure B-1.

Calculation of the Volume of the Metal in Each Bomb

The volume of the metal of each bomb was determined by dividing the mass of the metal by the density of stainless steel. The mass of the metal of each weighing bomb was determined by evacuating the bomb and then weighing it. It should be pointed out that it was assumed that the metal of the bomb and that of the valve have the same density of 7.8 gm/cc. The calculated results are presented in Table B-2.

TABLE B-2

VOLUME OF THE METAL OF THE WEIGHING BOMBS AT ROOM TEMPERATURE

Bomb No.	Volume of Metal, cc
1	27.66
3	27.37
4	27.80

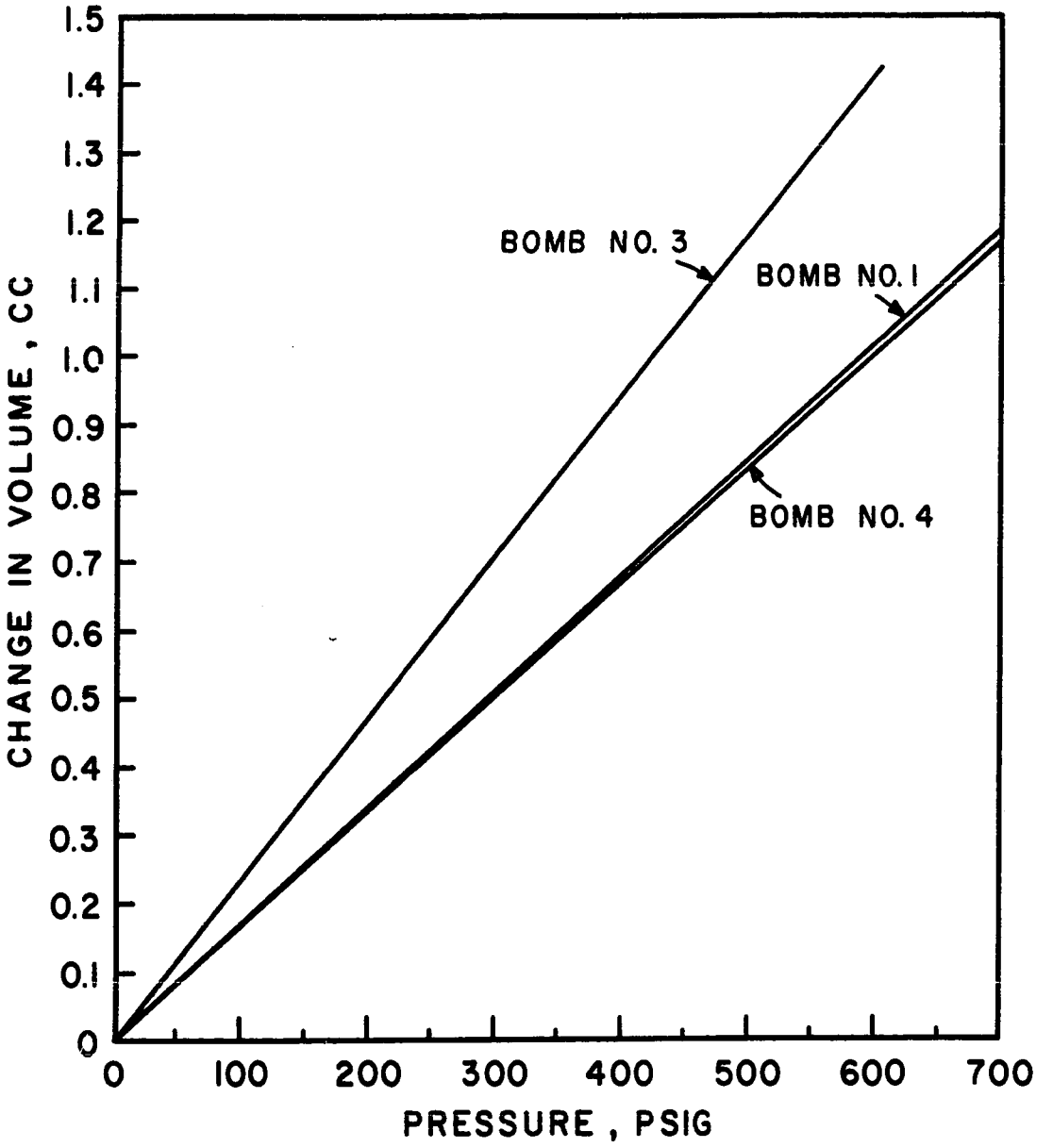

FIGURE B-1. CHANGE IN THE VOLUME OF THE WEIGHING BOMB AS A FUNCTION OF PRESSURE.

Calculation of the Total Volume of the Weighing Bombs

The volume of each weighing bomb at atmospheric pressure was calculated by adding the internal volume and the volume of the metal for each weighing bomb. The results are tabulated in Table B-3.

TABLE B-3

VOLUME OF THE WEIGHING BOMBS AT ATMOSPHERIC PRESSURE

Bomb No.	Volume, cc
1	587.69
3	587.72
4	586.39

The volume of any weighing bomb at any pressure, V_p, was determined by employing Equation B-1:

$$V_p = V_{atm.} + \Delta V \qquad \text{(B-1)}$$

where ΔV is the change in the volume with pressure. The change in volume, ΔV, is read directly from Figure B-1.

It is seen from Figure B-1 that the change in the volume of Bomb No. 3 is different from the change in the volumes of Bombs No. 1 and 4. This difference is attributed to the difference in the thermal history of the bombs.

The metal of Bomb No. 3 was originally annealed and then the metal sheets were hydroformed into hemispheres.

Bombs No. 1 and 4 after being constructed in the same way as Bomb No. 3, they were both heat-treated as follows:

1. The furnace was heated to 1750°F.
2. The bombs were placed in the oven at 1750°F for a period of 10 minutes.
3. Within one hour, the bombs were packed in dry ice for a period of 8 hours.
4. The bombs were then placed in an oven at 1100°F for a period of one hour.

APPENDIX C

TEMPERATURE MEASUREMENT

In this appendix, a detailed description of the calibrations and certifications of the instruments used in measuring the temperature is presented.

Platinum Resistance Thermometer

The temperature was measured by means of a Leeds and Northrup platinum resistance thermometer. It was calibrated by the National Bureau of Standards at the sulfur boiling point, the steam point, the ice point and the oxygen boiling point. The thermometer was calibrated to agree with the International Temperature scale to $\pm$ 0.01^{o}C between the freezing point of antimony and the oxygen boiling point.

The International Temperature Scale is defined in the temperature range 630.5^{o}C to -182.97^{o}C by a platinum resistance thermometer calibrated at the above mentioned four points. Two equations (C-1) and (C-2) are used to define this temperature scale. Above 0°C, the Callender Equation is used:

$$t\ (^{o}C) = \frac{R_t - R_0}{\alpha R_0} + \delta \left(\frac{t}{100} - 1\right) \frac{t}{100} \qquad (C\text{-}1)$$

Below 0°C, the Callender - Van Dusen Equation is used:

$$t\ (^{\circ}C) = \frac{R_t - R_0}{\alpha R_0} + \delta\left(\frac{t}{100} - 1\right)\frac{t}{100} + \beta\left(\frac{t}{100} - 1\right)\left(\frac{t}{100}\right)^3 \quad (C\text{-}2)$$

The constants in Equation (C-1) are determined from the calibrations at the sulfur boiling point, the steam point and the ice point. The constants in Equation (C-2) are determined by these three calibration points and the oxygen boiling point.

Certification of Thermometer

The constants which were substituted in Equations (C-1) and (C-2) for temperature interpolation throughout the experimental part of this work were reported by the National Bureau of Standards as follows:

Thermometer Serial Number 1628421

Test Number G36351

Completed January 28, 1966

α = 0.003926634

δ = 1.49222

β = 0.11007 (t below 0°C)

= 0 (t above 0°C)

R_0 = 25.5772 Abs. ohms.

Resistance Bridge

All resistance measurements in this work were made with a Leeds and Northrup G2 Mueller Bridge.

Equations (C-1) and (C-2) can be rearranged to show that any temperature in the above indicated range can be determined with only ratios of resistance. Equation (C-2) when arranged yields:

$$\frac{R_t}{R_0} = 1 + At + Bt^2 + C\,(t - 100)t^3 \qquad (C\text{-}3)$$

Rearrangement of Equation (C-1) yields:

$$\frac{R_t}{R_0} = 1 + At + Bt^2 \qquad (C\text{-}4)$$

where:

$$A = \left(1 + \frac{\delta}{100}\right)$$

$$B = -\alpha\,\delta/100^2$$

$$C = -\alpha\beta/100^4$$

Equations (C-3) and (C-4) show that as long as the resistance bridge used is self-consistent, the units of the resistance may be absolute ohms, international ohms, or any arbitrary unit, and if R_o is determined with the same resistance bridge.

The G-2 Mueller bridge used in this work was tested by the Leeds and Northrup Company in February 1963. A calibration certificate that accompanied the bridge gave the proper corrections to be used with the bridge readings in order to express the resistances in absolute ohms. These corrections were sufficient for determining a resistance or a change in resistance greater than 1 ohm to about 2 parts in 100,000. A check by A. L. Blancett* verified the values of these corrections and the self-consistency of the bridge.

Determination of the Ice Point

The platinum resistance thermometer used in this work was made consistent with the bridge by determining R_0 at the ice point. The value obtained in this work was 25.5775 ohms.

The ice point was determined in an ice bath which was prepared using distilled water and ice from a commercial ice machine. It should be pointed out that in accordance with

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*Blancett, A.L., "Volumetric Behavior of Helium-Argon Mixtures at High Pressure and Moderate Temperature", Ph.D. Thesis, University of Oklahoma, Norman, Oklahoma, 1966.

the findings reported by Canfield[7] machine ice was used instead of ice made from distilled water. Canfield[8] reported that the difference between the ice bath temperatures using both kinds of ice did not exceed 0.001°C.

APPENDIX D

MASS MEASUREMENT

A set of Class M mass standards, Serial No. 29876, were used in this work. This set was calibrated by the National Bureau of Standards, Washington, D.C. The following is a copy of their report of calibration:

NATIONAL BUREAU OF STANDARDS
REPORT OF CALIBRATION TEST NC. G 35659

ITEM: Set of Mass Standards 100G to 1MG
Mfr. Wm. Ainsworth and Sons Inc. Serial No. 29876
Stated Density 100 G to 1G 8.40 G per CM3 at 20c
500MG to 30MG 16.6 G per CM3 at 20c
20MG to 1MG 2.7 G per CM3 at 20c

The above items have the mass values shown with reference to the National Standard of Mass. See Attached Supplement for Limitations in use of apparent mass value and uncertainty from error in density

ITEM	NOMINAL	APP MASS CORR (MG)	TRUE MASS CORR (MG)	UNCERTAINTY (MG)	VOL AT 20°C (CM3)
100G	100.00	-0.258368	-0.273799	0.020334	11.90472913
50G	50.00	-0.038463	-0.046178	0.011286	5.95237541
30G	30.00	0.062144	0.057515	0.014392	3.57143542
20G	20.00	-0.141376	-0.144462	0.013478	2.38093516
10G	10.00	0.024222	0.022679	0.009522	1.19047888
5G	5.00	-0.037526	-0.038297	0.005060	0.59523353
3G	3.00	-0.015618	-0.016081	0.005383	0.35714094
2G	2.00	-0.014577	-0.014886	0.004884	0.23809347
1G	1.00	0.003671	0.003517	0.003392	0.11904804

ITEM	NOMINAL	APP MASS CORR (MG)	TRUE MASS CORR (MG)	UNCERTAINTY (MG)	VOL AT 20°C (CM3)
500 MG	500.00	-0.012487	-0.047850	0.001825	0.03011759
300 MG	300.00	-0.002097	-0.023315	0.002061	0.01807088
200 MG	200.00	-0.002007	-0.016153	0.001893	0.01204722
100 MG	100.00	0.000230	-0.006843	0.001323	0.00602368
50 MG	50.00	0.001244	-0.002293	0.000944	0.00301190
30 MG	30.00	0.000539	-0.001582	0.001836	0.00180713
20 MG	20.00	0.004004	0.010037	0.001787	0.00741112
10 MG	10.00	0.000750	0.003766	0.001286	0.00370509
5 MG	5.00	0.008573	0.010083	0.000931	0.00185558
3 MG	3.00	0.000201	0.001105	0.001833	0.00111151
2 MG	2.00	-0.001444	-0.000842	0.001785	0.00074042
1 MG	1.00	0.013713	0.014019	0.001286	0.00037556

The uncertainty figure is an expression of the overall uncertainty using three standard deviations as a limit to the effect of random errors of measurement, the magnitude of systematic errors from known sources being negligible.

Test Completed April 13, 1965
Washington, D.C. 20234

The Right-A-Weigh analytical balance used in this work was a single beam substitution balance. All the built-in weights in this balance were made from stainless steel. In the process of weighing, after placing the object to be weighed in the pan, enough stainless steel weights are removed from the beam until equilibrium is restored. Equilibrium is only achieved whenever the gravitational force caused by the counter weight on one end of the beam and the force caused by the remaining weights hanging on the other end of the beam and the object are equalized.

In any weighing process whenever high precision measurement of mass is required, it is necessary to either eliminate the effect of air buoyancy or to make proper correction for it. Elimination of this effect can be achieved only if the volumes of the two weights being compared are equal. Because such an equality in volume was not possible in this work, a proper correction was made.

In order to establish the proper correction for each individual weighing, the volumes of the objects being compared must be known. Because the balance was a single beam substitution balance, it was decided to determine the volumes of both sides of the beam together with the weights equipped with each side. The volume of the side with the counter weight was 34 ml. This volume was determined by Densmer[13]. He immersed the beam in water and measured directly the amount displaced. The volume of the other side of the beam was equal to the volumes of the stainless steel weights, the weight hanger bar assembly and the beam itself. These volumes were estimated to be 25.6 ml. 5 ml and 3.4 ml respectively. Addition of these three values gave a total of 34 ml which was equal to the volume of the other side of the beam. This result led to the conclusion that in order to calculate the effect of air buoyancy, the volume of the object being weighed should be compared with that of the stainless steel weights removed from

the beam during the weighing process.

In the process of determining the true mass of each gas condensed into the pycnometer, one must consider the two factors 1) the fact that the class M standards were made from materials different than stainless steel, and 2) the variation in air density between each two weighings.

1. Comparison of the Class M Standards with the Stainless Steel Weights

The weights indicated by the analytical balance in each weighing were compared with the set of class M Standards. Then, by knowing the true mass of each weights in the Class M Standards, the true mass of the weights in the balance was assumed to be equal to the total masses of the individual weights of the standards. In order to simplify the calculations involved, a buoyancy correction factor for the different materials of the standards and of stainless steel was determined. In other words, the standards were made equivalent to a set of stainless steel standards. The equation necessary to calculate this buoyancy correction factor is presented below[32]:

$$M_n = M_s \frac{\left(1 - \frac{\rho_A}{\rho_s}\right)}{1 - \frac{\rho_A}{\rho_n}} \qquad \text{(D-1)}$$

where:

M_s = Mass of the standards

M_n = Mass of the weight tested

ρ_s = Density of the standards

ρ_n = Density of the weight tested

ρ_A = Density of the air

Equation (D-1) was used to determine the buoyancy correction factors for the three different materials in the Class M standards as follows:

1.a. Standards 100 Gm to 1 Gm

$\rho_s = 8.4$ gm/cc

$\rho_n = 7.80$ gm/cc

$\rho_A = 1.16 \times 10^{-3}$ gm/cc

$$M_n = M_s \frac{1 - \frac{1.16 \times 10^{-3}}{8.4}}{1 - \frac{1.16 \times 10^{-3}}{7.80}}$$

$$= 1.00001\ M_s \qquad \text{(D-2)}$$

1.b. Standards 500 MG to 30 MG

$\rho_s = 16.6$ gm/cc

$\rho_n = 7.80$ gm/cc

$$\rho_A = 1.16 \times 10^{-3} \text{ gm/cc}$$

$$M_n = 1.000078\ M_s \qquad \text{(D-3)}$$

1.c. Standards 20 MG to 1 MG

$$\rho_s = 2.7 \text{ gm/cc}$$

$$\rho_n = 7.80 \text{ gm/cc}$$

$$\rho_A = 1.16 \times 10^{-3} \text{ gm/cc}$$

$$M_n = 0.999718\ M_s \qquad \text{(D-4)}$$

The use of the Equations (D-1), (D-2) and (D-3) is illustrated by considering the weighing of propane in run 2 of the ethane + propane system.

Balance reading	238.5350
Standards used to balance the above reading	138.5230
Sec. Standard	100

Standards (Class M)	True Mass of Standards grams	True Mass of S.S Weights	
100 gm	99.999726	100.000726	(D-2)
30	30.000058	30.000358	
5	4.999962	5.000012	
3	2.999984	3.000014	
500	0.499952	0.499991	(D-3)

20	0.020010	0.020004	(D-4)
3	0.003001	0.003000	
Sec. Standards		100.000726	
	Total	238.5249 grams	

2. The Effect of Variations in the Density of Air

The following equations[7] describe the buoyancy corrections arising from the change in both the density of air and the volume of the weighing bombs.

$$M_{BF} = \rho_{AF} V_{BF} + M_{SF} \left(1 - \frac{\rho_{AF}}{\rho_s}\right) \qquad \text{(D-5)}$$

$$M_{BE} = \rho_{AE} V_{BE} + M_{SE} \left(1 - \frac{\rho_{AF}}{\rho_s}\right) \qquad \text{(D-6)}$$

where:

M_{BF} = Mass of weighing bomb when full

M_{BE} = Mass of weighing bomb when empty

M_{SF} = Mass of standards required to balance the full bomb

M_{SE} = Mass of standards required to balance the empty bomb

ρ_{AF} = density of air when the full bomb was weighed

ρ_{AE} = density of air when the empty bomb was weighed

V_{BF} = Volume of the full bomb

V_{BE} = Volume of the empty bomb

ρ_s = density of standards

The mass of any gas charged from the weighing bomb, Mg is given by:

$$Mg = M_{BF} - M_{BE} \qquad \text{(D-7)}$$

Subtracting Equation (D-6) from (D-5) and substituting into Equation (D-7):

$$Mg = M_{SF}\left(1 - \frac{\rho_{AF}}{\rho_s}\right) - M_{SE}\left(1 - \frac{\rho_{AE}}{\rho_s}\right) + \rho_{AF}V_{BF} - \rho_{AE}V_{BE} \qquad \text{(D-8)}$$

The use of this equation is illustrated in Appendix F.

APPENDIX E1

ADDENDA AND CORRIGENDA

The word Derivitive as used in

Appendix E should be changed to "Derivative".

APPENDIX E

ERROR ANALYSIS

In this section, the limits of the absolute accuracy in the experimental results of the liquid density of the pure components and of the mixtures studied in this work are established. This is achieved by deriving a general expression which relates the total error in the density data to all the variables which contribute to this cause. This general expression is derived as indicated below.

The error in the experimental density results for any given liquid is caused by errors in measuring the variables involved in the liquid density determination. These variables are temperature, mass, volume, pressure and composition. Any error incurred in measuring any of these variables regardless of the accuracy in measuring the others, will cause an error in the density value. If each quantity is measured independently, then the density can be considered to be a function of each of these variables. Mathematically, this can be presented as shown in Equation (E-1):

$$\rho = \rho\,(t,M,V,P,X) \qquad \text{(E-1)}$$

where:

ρ = density of the liquid

t = temperature

M = Mass of the liquid

V = Volume of the liquid

P = Pressure in the system

X = composition

Differentiation of Equation (E-1) yields:

$$d\rho = \left(\frac{\delta\rho}{\delta t}\right) dt + \left(\frac{\delta\rho}{\delta M}\right) dM + \left(\frac{\delta\rho}{\delta V}\right) dV + \left(\frac{\delta\rho}{\delta P}\right) dP + \left(\frac{\delta\rho}{\delta X}\right) dX \quad \text{(E-2)}$$

The terms held constant in each partial derivitive in Equation (E-2) have been omitted for simplicity. It is understood that all variables are held constant in each partial differentiation except the one that the density is being differentiated with respect to. If the errors in the individual measurements are small, then it can be seen from Equation (E-2) that the total error in the experimental liquid density results, $\Delta\rho$, can be represented by Equation (E-3):

$$\Delta\rho = \left(\frac{\delta\rho}{\delta t}\right) \Delta t + \left(\frac{\delta\rho}{\delta M}\right) \Delta M + \left(\frac{\delta\rho}{\delta P}\right) \Delta P + \left(\frac{\delta\rho}{\delta V}\right) \Delta V + \left(\frac{\delta\rho}{\delta X}\right) \Delta X \quad \text{(E-3)}$$

where Δt, ΔM, ΔP, ΔV and ΔX are the errors in the individual

measurements of temperature, mass, pressure, volume and composition respectively.

Equation (E-3) is the general expression which was used to calculate the limits of the absolute accuracy of the experimental liquid density values of the different systems studied in this work. In order to apply this equation, all the terms on the right hand side were estimated as indicated below.

Estimation of the Partial Derivities

The methods used to calculate the different partial derivitives are presented first and then the resulting values are tabulated in Table E-1 for the pure components and Table E-2 for the mixtures.

1. The Partial Derivitive of the Density with Respect to Temperature

This quantity was estimated from knowledge of the liquid density values obtained from this work. As shown in Table 7, the density was presented as a function of temperature in accordance with Equation (2):

$$\rho = a + bt \qquad (2)$$

Differentiation of this equation yields:

$$\frac{d\rho}{dt} = b \qquad \text{(E-4)}$$

The values of b for each system was read directly from Table 7.

2. The Partial Derivitive of the Density with Respect to Mass

The density is defined by Equation (E-5):

$$\rho = \frac{M}{V} \qquad \text{(E-5)}$$

where:

ρ = density

M = mass

V = volume

Differentiation of Equation (E-5) with respect to mass yields:

$$\left(\frac{\delta\rho}{\delta M}\right)_{V,P,t,X} = \frac{1}{V} \qquad \text{(E-6)}$$

Because the same pycnometer was used in determining the liquid density of all the systems studied, it is clear from Equation (E-6) that the partial derivitive of the density with respect to mass is the same for all the systems.

For this work, the volume of the pycnometer was

approximately 30.13 ml. Therefore, from Equation (E-6):

$$\left(\frac{\delta\rho}{\delta M}\right)_{V,P,t,X} = \frac{1}{30.13} = 0.0332 \text{ gm/ml-gm}$$

3. The Partial Derivitive of the Density with Respect to Volume

Differentiation of Equation (E-5) with respect to volume yields:

$$\left(\frac{\delta\rho}{\delta V}\right)_{M,P,t,X} = -\frac{\rho}{V} \qquad \text{(E-7)}$$

From this equation and for a volume of 30.13 ml we have:

$$\left(\frac{\delta\rho}{\delta V}\right)_{M,P,t,X} = -0.0332\,\rho \qquad \text{(E-8)}$$

4. The Partial Derivitive of the Density with Respect to Pressure

Because this liquid is incompressible, the effect of a small change in pressure on the density is not expected to be significant. Therefore, the partial derivitive of the density with respect to pressure is assumed to be the same for all the systems. This quantity using the techniques

presented by Hougen and Watson[1] was estimated to be 3×10^{-5} gm/ml-in Hg.

5. The Partial Derivitive of the Density with Respect to Composition

The effect of impurities on the density of the pure components was assumed to be negligible. Therefore, the error in composition, ΔX, for the pure components was considered equal to zero.

In the case of mixtures, the partial derivitive with respect to composition was estimated as shown below.

For the three binary mixtures methane + ethane, methane + propane and ethane + propane, a functional relationship relating the density to the composition was established. This was achieved by means of least square curve fit using a digital computer. These relationships are as follows:

1. Methane + Ethane system:

$$\rho = 0.632269 - 0.1280\, X_{C1} - 0.0764\, X_{C1}^{2} \qquad \text{(E-9)}$$

$$\frac{d\rho}{dX} = -0.1280 - 0.1528\, X_{C1} \qquad \text{(E-10)}$$

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[1] Hougen, O.A. and Watson, K.M., "Chemical Process Principles", part II, John Wiley and Sons, Inc., New York, 1955, pp. 502-507.

2. Methane + Propane System:

$$\rho = 0.709780 - 0.1022X_{C1} - 0.1790X_{C1}^{2} \quad \text{(E-11)}$$

$$\frac{d\rho}{dX} = -0.1022 - 0.358X_{C1} \quad \text{(E-12)}$$

3. Ethane + Propane System:

$$\rho = 0.709780 - 0.0349X_{C2} - 0.0423X_{C2}^{2} \quad \text{(E-13)}$$

$$\frac{d\rho}{dX} = -0.0349 - 0.0846X_{C2} \quad \text{(E-14)}$$

For all other mixtures, the partial derivitive of the density with respect to composition was estimated by assuming linear relationship between the density and composition. For example, in the case of methane + n-butane mixture we have:

At $X_{C1} = 1.0$ $\rho = 0.4275$

At $X_{C1} = 0.884$ $\rho = 0.5061$

Therefore, $\frac{d\rho}{dX} = -\frac{0.5061 - 0.4275}{0.116} = -0.677$

Because the goal is to estimate the absolute accuracy in the experimental liquid density results, only the absolute values of the partial derivities will be tabulated in Tables

E-1 and E-2.

TABLE E-1

PARTIAL DERIVITIVES OF THE LIQUID DENSITY WITH RESPECT TO TEMPERATURE, MASS, VOLUME, AND PRESSURE FOR THE PURE COMPONENTS METHANE, ETHANE, AND PROPANE.

Component	$\frac{\delta\rho}{\delta t}$ (10^3) gm/ml-°C	$\frac{\delta\rho}{\delta M}$ (10^2) ml^{-1}	$\frac{\delta\rho}{\delta V}$ (10^2) gm/ml^2	$\frac{\delta\rho}{\delta P}$ gm/ml -in Hg
Methane	1.28	3.32	1.42	3×10^{-5}
Ethane	0.994	3.32	2.10	3×10^{-5}
Propane	0.973	3.32	2.36	3×10^{-5}

TABLE E-2

PARTIAL DERIVITIVES OF THE LIQUID DENSITY WITH RESPECT TO TEMPERATURE, MASS, VOLUME, PRESSURE AND COMPOSITION FOR THE MIXTURES STUDIED IN THIS WORK.

X_{C1} = Methane mole fraction, X_{C2} = Ethane mole fraction

$\frac{\delta\rho}{\delta t}$ = A, gm/ml -^{o}C; $\frac{\delta\rho}{\delta M}$ = B, 1/ml; $\frac{\delta\rho}{\delta V}$ = C, gm/ml^2;

$\frac{\delta\rho}{\delta P}$ = D, gm/ml -in Hg; $\frac{\delta\rho}{\delta X}$ = F, gm/ml

Mixture	X_{C1}	X_{C2}	A (10^3)	B (10^2)	C (10^2)	D	E (10^2)
CH_4+C_2H_6	0.1902		1.058	3.32	2.00	$3x10^{-5}$	15.7
	0.8668		1.323	3.32	1.54	$3x10^{-5}$	26.0
CH_4+C_3H_8	0.2575		0.937	3.32	2.21	$3x10^{-5}$	19.4
	0.8484		1.185	3.32	1.66	$3x10^{-5}$	40.5
C_2H_6+C_3H_8		0.2619	0.881	3.32	2.31	$3x10^{-5}$	5.7
		0.8087	0.979	3.32	2.18	$3x10^{-5}$	10.3
CH_4-n-C_4H_{10}	0.8843		1.205	3.32	1.68	$3x10^{-5}$	67.7
C_2H_6-n-C_4H_{10}		0.8833	0.954	3.32	2.18	$3x10^{-5}$	21.4
CH_4+C_2H_6+C_3H_8	0.3884	0.3216	1.025	3.32	2.01	$3x10^{-5}$	0.23
	0.7238	0.1668	1.184	3.32	1.73	$3x10^{-5}$	0.24

Estimation of the Errors in the Individual Measurements

1. Error in Temperature Measurement, ΔT

The accuracy of temperature measurement is well established as $\pm$ 0.01°C for a platinum resistance thermometer.

$$\Delta T = \pm 0.01^{\circ}C$$

2. Error in Measuring the Volume, ΔV

The error in measuring the volume is estimated to be $\pm$ 3 x 10^{-4} ml. This value accounts for 1) the uncertainties in the weighings required to determine the volume of the pycnometer at room temperature, 2) the effect of expansion or contraction of the pycnometer, and 3) the uncertainties in reading the liquid level in the capillary stem.

3. Error in Pressure Measurement, ΔP

The error in measuring the pressure by the Texas Instrument pressure gauge is estimated to be $\pm$ 0.005 in Hg.

4. Error in Mass Measurement, ΔM

The error in measuring the mass of the condensed gases is caused by the three sources, 1) uncertainties in weighing,

2) air buoyancy effect, and 3) error in determining the mass of the gases trapped in the transfer tubing between the pycnometer and the weighing bomb.

4.1 Uncertainties in Weighing:

The error due to uncertainty in weighing is equal to:

a)	Pure Components	$\Delta M = 0.0002$ gm	2 Weighings
b)	Binary Mixtures	$\Delta M = 0.0004$ gm	4 Weighings
c)	Ternary Mixtures	$\Delta M = 0.0006$ gm	6 Weighings

4.2 Air Buoyancy Effect:

As seen in Appendix D, the mass of the gas charged from the weighing bomb is given by Equation (D-8)

$$M_g = M_{sF}\left(1 - \frac{\rho_{AF}}{\rho_s}\right) - M_{sE}\left(1 - \frac{\rho_{AE}}{\rho_s}\right) + \rho_{AF}V_{BF} - \rho_{AE}V_{BE} \qquad \text{(D-8)}$$

But the volume of the standards is equal to $\frac{M_s}{\rho_s}$, therefore,

$$M_g = V_{SF}(\rho_s - \rho_{AF}) - V_{SE}(\rho_s - \rho_{AE}) + \rho_{AF}V_{BF} - \rho_{AE}V_{BE} \qquad \text{(E-15)}$$

Assume that V_{SF}, V_{SE}, and ρ_s are constant, then by differentiating Equation (E-15) and replacing the total derivitives by Δ_s we have

$$\Delta M_g = (V_{BF}-V_{SF})\ \Delta\rho_{AF}+(V_{SE}-V_{BE})\ \Delta\rho_{AE}+(\rho_{AF}-\rho_{AE})\ \Delta V_B \qquad \text{(E-16)}$$

In order to calculate ΔM_g, all the terms on the right hand side of the equation must be determined. The terms V_{BF}, V_{SF}, V_{BE}, V_{SE}, ρ_{AE} and ρ_{AF} were determined as shown in Appendix F. The term $\Delta\rho_{AF}$ and $\Delta\rho_{AE}$ are determined as described below.

The density of air is given by Equation (A-10):

$$\rho_A = \frac{PM}{RTZ} \qquad \text{(A-10)}$$

It is assumed that the molecular weight of air is constant. Then by differentiating Equation (A-10) and replacing the derivitives by Δs, one finds:

$$\Delta\rho_A = \frac{MP}{RTZ}\left(\frac{\Delta P}{P} - \frac{\Delta T}{T} - \frac{\Delta Z}{Z}\right) \qquad \text{(E-17)}$$

Assume

ΔP = 0.01 in Hg, ΔT = 0.01°C

ΔZ = 5×10^{-6} (Estimated by making use of Equation A-8)

P = 1 atm, T = 295°K Z = 0.999600

M = 28.829, R = 82.057

Substituting these values into Equation (E-17) and solving for the absolute value of $\Delta\rho_A$:

$$\Delta\rho_A = 2.45 \times 10^{-7} \text{ gm/ml}$$

The values of the terms on the right hand side of Equation (E-16) are:

$V_{BF} = 589$ cc $\quad V_{BE} = 588$ cc $\quad \Delta V_B = 0.1$ cc

$V_{SF} = 25$ cc $\quad V_{SE} = 23$ cc

$\rho_{AF} - \rho_{AF} = 1.2 \times 10^{-6}$ "Taken as an average value for the difference in the air densities for the different experimental runs".

From Equation (E-16) we have:

$$\Delta M_g = 2.8 \times 10^{-4} \text{ gram.}$$

Therefore, the error in the mass due to air buoyancy is:

a) For pure components $\Delta M_g = 2.8 \times 10^{-4}$ gm

b) For binary mixtures $\Delta M_g = 5.6 \times 10^{-4}$ gm

c) For ternary mixtures $\Delta M_g = 8.4 \times 10^{-4}$ gm

4.3 Error in Determining the Mass in the Transfer Tubing:

It is first necessary to determine the error in measuring the volume of the transfer tubing. Then by making use of the gas laws, the error in mass can be easily calculated. The error in measuring the volume of the transfer line is

determined as outlined below.

In order to measure the volume of the transfer tubing, the pycnometer and the pressure gauge were filled with air. The pressure was read directly from the pressure gauge. The temperature was read and recorded. Then, after isolating the pycnometer, the transfer line including the pressure gauge were evacuated to 0.002 mm Hg. The valves in the line were set at some known conditions. Then the air from the pycnometer was allowed to flow into the evacuated line. The final pressure and temperature were determined.

Let

V_T = Volume of transfer line including pressure gauge and the pycnometer

V_P = Volume of the pycnometer

P_i = Initial pressure before expansion

T_i = Initial temperature

P_f = Final pressure after expansion

T_f = Final temperature

n = Total number of gram-moles in pycnometer

For the initial condition using the ideal gas law:

$$P_i V_P = nRT_i \qquad \text{(E-18)}$$

For the final condition we have

$$P_f (V_T) = nRT_f \qquad \text{(E-19)}$$

Combining Equations (E-18) and (E-19) and solving for V_T one gets:

$$V_T = \frac{V_P P_i T_f}{P_f T_i} \qquad \text{(E-20)}$$

Differentiating this equation and replacing the derivitives by Δ_s we have:

$$\Delta V_T = \frac{V_p P_i T_f}{P_f T_i} \left(\frac{\Delta T_f}{T_f} + \frac{\Delta P_i}{P_i} + \frac{\Delta V_P}{V_P} - \frac{\Delta T_i}{T_i} - \frac{\Delta P_f}{P_f} \right) \qquad \text{(E-21)}$$

Assume

$$T_i = T_f = 295^{\circ}K \; ; \quad P_i = 730 \text{ mm Hg};$$

$$P_f = 335 \text{ mm Hg} \; ; \quad V_p = 30 \text{ cc} \; ; \; V_T = 66 \text{ cc}$$

$$\Delta T_i = \Delta T_f = 0.06^{\circ}C \; , \; \Delta P_i = \Delta P_f = 0.15 \text{ mm Hg}$$

$$\Delta V_P = 3 \times 10^{-4} \text{ cc}$$

Substituting these values into Equation (E-21) and considering the absolute values of the individual terms:

$$\Delta V_T = \frac{(30)\,(730)}{(335)} \left(\frac{0.06}{295} + \frac{0.15}{730} + \frac{0.0003}{30} + \frac{0.06}{295} + \frac{0.15}{335} \right)$$

$$= 0.07 \text{ cc}$$

The error in determining the volume of the transfer line ΔV is given by:

$$\Delta V = \Delta V_T - \Delta V_P \mp 0.07 \text{ cc}$$

The error in mass caused by this volume uncertainty is computed for the different systems by employing the ideal gas laws. From Equation (E-18)

$$n = \frac{PV}{RT} \qquad \text{(E-22)}$$

where n is the total number of gram-moles.

But - $$M = n \ (MW) \qquad \text{(E-23)}$$

where MW is the molecular weight.

Therefore, from Equations (E-22) and (E-23) we have:

$$M = \frac{PV \ (MW)}{RT} \qquad \text{(E-24)}$$

Assume $T = 295^{\circ}K$, $V = 0.07$ cc, $R = 82.057$. Substituting these values into Equation (E-24):

$$M = \frac{(0.07) \ P \ (MW)}{82.057 \ (295)(14.696)}$$

$$= 2.31 \times 10^{-7} \ P \ (MW) \qquad \text{(E-25)}$$

where P is in psia.

Equation (E-25) is used to calculate the error in measuring the mass of the gas trapped in the transfer line. The results obtained for the different systems are tabulated in Table E-3.

TABLE E-3

ERROR IN THE MEASUREMENT OF MASS DUE TO THE UNCERTAINTY IN DETERMINING THE MASS OF THE GAS TRAPPED IN THE TRANSFER TUBING.

System	GAS TRAPPED IN THE TRANSFER TUBING	
	ΔM_g, gm	Mole Fraction of Light Component
Methane	0.00004	
Ethane	0.00001	
Propane	0.00001	
Methane + Ethane	0.00002	0.1901
	.00004	0.8668
Methane + Propane	0.00002	0.2575
	.00004	0.8484
Ethane + Propane	.00001	0.2619
	0.00001	0.8087
Methane + n-Butane	.00004	0.8843
Ethane + n-Butane	.00002	0.8833
Methane + Ethane + Propane	0.00002	0.3884
	0.00003	0.7238

The total error in the measurement of mass is now calculated as the sum of the errors caused by the weighing process, the air buoyancy effect, and the uncertainty in measuring the mass of the trapped gas in the transfer tubing. The final results are tabulated in Table E-4.

TABLE E-4

Total Error in the Measurement of the Mass, ΔM_T

System	ΔM_T (10^4), gm	Mole Fraction of Light Component
Methane	5.2	
Ethane	4.8	
Propane	4.8	
Methane + Ethane	9.8	0.1901
	10.0	0.8668
Methane + Propane	9.8	0.2575
	10.0	0.8484
Ethane + Propane	9.7	0.2619
	9.7	0.8087
Methane + n-Butane	10.0	0.8843
Ethane + n-Butane	9.8	0.8833
Methane + Ethane + Propane	14.4	0.3884
	14.4	0.7238

5. Error in Composition Measurement

The composition of component i in a mixture is defined

by Equation (E-26):

$$X_i = \frac{n_i}{n_T} \qquad \text{(E-26)}$$

where:

X_i = mole fraction of component i

n_i = total number of moles of component i

n_T = total number of moles in the mixture

Differentiating Equation (E-26) and replacing the derivities by Δ_s:

$$\Delta X_i = \frac{n_T \Delta n_i - n_i \Delta n_t}{n_T^2} \qquad \text{(E-27)}$$

From Equations (E-26) and (E-27) we have:

$$\Delta X_i = \frac{1}{n_T} (\Delta n_i - X_i \Delta n_T) \qquad \text{(E-28)}$$

Substituting the values $\Delta n_i = \frac{\Delta M_i}{(MW)_i}$, and $\Delta n_T = \frac{\Delta M_T}{(MW)_M}$:

$$\Delta X_i = \frac{1}{n_T} \left(\frac{\Delta M_i}{(MW)_i} - X_i \left(\frac{\Delta M_T}{(MW)_M}\right)\right) \qquad \text{(E-29)}$$

where:

$(MW)_i$ = molecular weight of component i

$(MW)_M$ = molecular weight of the mixture

Equation (E-29) is used to calculate the total error in the composition. All the terms on the right hand side of the equation are known. ΔM_i and ΔM_T are tabulated in Table E-4. n_i, n_T and $(MW)_M$ are calculated from the known masses of the different components in each mixture. It should be pointed out that only the maximum possible error was calculated. In other words, the negative sign on the right hand side of Equation (E-29) was replaced by a positive sign. The final calculated results are listed in Table E-5.

TABLE E-5

ERROR IN COMPOSITION OF MIXTURES, ΔX

X_{C1} = Methane Mole Fraction; X_{C2} = Ethane Mole Fraction

Mixture	X_{C1}	X_{C2}	Error in Composition of Light Component, $\Delta X(10^5)$
Methane + Ethane	0.1901		5.9
	0.8668		10.0
Methane + Propane	0.2575		7.2
	0.8484		10.0
Ethane + Propane		0.2619	4.2
		0.8087	6.6
Methane + n-Butane	0.8843		10.0
Ethane + n-Butane		0.8833	7.1
Methane + Ethane + Propane	0.3884	0.3216	8.2
	0.7238	0.1668	10.1

Calculation of the Limits of the Absolute Accuracy of the Liquid Density Results

The absolute accuracy of the experimental results were calculated by making use of Equation (E-3). For the binary mixtures methane + ethane, methane + propane and ethane + propane, the accuracy was calculated at two experimental data points for each mixture. The first data point corresponded to the mixture with the lowest mole fraction of the light component. The second data point corresponded to the mixture with the highest mole fraction of the same light component. The values of the accuracy obtained at these two data points established the limits of the accuracy for each mixture. The final calculated results were listed in Table E-6.

TABLE E-6

CALCULATED ACCURACY OF THE EXPERIMENTAL LIQUID DENSITY RESULTS

X_{C1} = Methane Mole Fraction; X_{C2} = Ethane Mole Fraction

System	X_{C1}	X_{C2}	Accuracy (10^5)
Methane			3.4
Ethane			3.2
Propane			3.3
Methane + Ethane	0.1901		5.8
	0.8668		7.7
Methane + Propane	0.2575		6.3
	0.8484		9.1
Ethane + Propane		0.2619	5.0
		0.8087	5.5
Methane + n-Butane	0.8843		11.8
Ethane + n-Butane		0.8833	6.4
Methane + Ethane + Propane	0.3884	0.3216	8.3
	0.7238	0.1668	9.1

APPENDIX F

SAMPLE CALCULATION

In calculating the density values, all the experimental data were processed using an IBM digital computer. In this appendix, a complete sample calculation for a binary mixture (methane + ethane), Run No. 2, is presented.

The density of a substance is defined as the mass per unit volume of the substance. Mathematically, this definition can be stated as:

$$\rho = \frac{M}{V} \qquad \text{(F-1)}$$

It is clear from Equation (F-1), that a sample calculation requires the determination of the mass and the volume.

Determination of the Mass of the Condensed Gases

The total mass of the condensed gases of both components is equal to the mass of gases charged from the weighing bombs less the mass trapped in the transfer tubing between the weighing bomb and the pycnometer.

1. Determination of the Total Mass Charged from the Weighing Bombs

The mass of each gas charged from its weighing bomb is calculated by means of Equation (D-8).

$$Mg = M_{sf}\left(1 - \frac{\rho_{AF}}{\rho_s}\right) - M_{SE}\left(1 - \frac{\rho_{AE}}{\rho_s}\right) + \rho_{AF} V_{BF} - \rho_{AE} V_{BE} \qquad (D\text{-}8)$$

The required data to calculate the mass of methane and that of ethane charged from bombs No. 4 and boms No. 3 respectively in Run No. 2 of the methane + ethane system are as follows:

	Full Bombs' Data	
	Methane	Ethane
Measured Pressure	340 psi.	465 psi.
Mass (Balance Reading)	221.5823 gm.	248.1023 gm.
Temperature of the Balance while Weighing	71.5°F	70.8°F
Differential Thermometer (inside the pressure barricade)	4.35°C	4.13°C
Barometric Pressure	29.080 in Hg.	29.114
Temperature of Barometer	72°F	72°F
Standards Compared with the Mass Indicated by the Balance:		
Class M Standards	121.5703 gm.	148.0903 gm.
Sec. Standards	100 gm.	100 gm.

Empty Bombs' Data

	Methane	Ethane
Calculated Pressure	210 psi.	195 psi.
Mass (Balance Reading)	217.7830 gm.	234.4646
Temperature of the Balance while Weighing	71°F	70.0°F
Differential Thermometer (inside the pressure barricade)	4.23°C	4.08°C
Barometric Pressure	29.012 in Hg.	29.080
Temperature of Barometer	72°F	72°F

Standards Compared with the Mass Indicated by the Balance:

Class M Standards	117.7710 gm.	134.4526 gm.
Sec. Standards	100 gm.	100 gm.

The pressure of the gas in the weighing bomb at the end of each run was either calculated or measured by the pressure gauge. Calculation of the pressure was accomplished by a trial and error method using the equation

$$P = \frac{ZnRT}{V} \qquad \text{(F-2)}$$

where:

P = pressure in the weighing bomb, atm.

n = gm-moles of the gas in the bomb

Z = compressibility factor of the gas

R = gas constant

T = temperature of the gas, ^{o}K

V = volume of the gas, cc
"internal volume of the bomb"

The number of gram-moles of the gas in the bomb was determined from knowledge of the weight of the empty bomb and the weight of the bomb charged with the gas. The volume was equal to the predetermined internal volume of the bomb. The temperature was measured in the pressure barricade. This meant that all the terms on the right hand side of Equation (F-2) with the exception of Z were known. Then the pressure was calculated by trial and error using the compressibility factor charts for the different gases studied in this work.

These data are used to evaluate all the terms on the right hand side of Equation (D-8) as shown below.

Calculation of the Mass of Methane

M_{SF} = 221.5718 (calculated as shown in Appendix D)

M_{SE} = 217.7726 (calculated as shown in Appendix D)

ρ_{AF} at 71.5°F = 1.15303×10^{-3} gm/cc

ρ_{AE} at 71°F = 1.15109×10^{-3} gm/cc

Determined by making use of Equations (A-8), (A-9) and (A-10) as shown in Appendix A.

ρ_s = 7.80 gm/cc "All standards were made equivalent to a set of stainless steel standards as shown in Appendix D."

ΔV_{BF} (340 psi) = 0.55 cc From Figure B-1

ΔV_{BE} (210 psi) = 0.34 cc From Figure B-1

It is interesting at this point to examine the effect of thermal expansion on the change in the volume of the weighing bomb. The cubical expansion coefficient is approximately three times as large as the linear expansion coefficient. Therefore, the change in the volume of the weighing bomb is given in terms of the linear expansion coefficient by the equation

$$V - V_o = 3 V_o \alpha_s (T-T_o) \qquad (F-3)$$

where:

V = volume of the bomb at temperature T

V_o = volume of the bomb at temperature T_o

α_s = linear thermal expansion coefficient of stainless steel

The literature value[A] of α_s is given as 5×10^{-6} in/in-^oF. Then for a temperature change of 0.5^oF, the change in the volume of the bomb is calculated from Equation (F-3) as:

$$V - V_o = 3\,(590)(5 \times 10^{-6})(.5) = 0.0044 \text{ cc}$$

Therefore, the volume of the full bomb V_{BF} and the volume of the empty bomb V_{BE} are calculated as follows:

V_{BF} = 586.39 + 0.55 = 586.94 cc (see Appendix B)

V_{BE} = 586.39 + 0.34 = 586.73 cc

From Equation (D-8), the mass of methane, M_{gl} is given by:

$$M_{gl} = 221.5718 \left(1 - \frac{1.75303 \times 10^{-3}}{7.80}\right) - 217.7726\left(1 - \frac{1.15109 \times 10^{-3}}{7.80}\right)$$

$$+ 586.94\,(1.15303 \times 10^{-3}) - 586.73\,(1.15109 \times 10^{-3})$$

$$= 221.5718 \times 0.999852 - 217.7726 \times 0.999852 + 0.67676 - 0.67538$$

A. Armco Product Bulletin, PH 15-7 Mo Stainless Steel, Armco Steel Corporation.

$= 221.53901 - 217.74037 + 0.67676 - 0.67538$

$= 3.80002$ gm.

Calculation of the Mass of Ethane

$M_{SF} = 248.0923$ (calculated as shown in Appendix D)

$M_{SE} = 234.4545$ (calculated as shown in Appendix D)

$\rho_{AF} = 1.15584 \times 10^{-3}$ gm/cc (Determined by making use of Equations

$\rho_{AE} = 1.15461 \times 10^{-3}$ gm/cc (A-8), (A-9) and (A-10) as shown in Appendix A

$\rho_{S} = 7.80$ gm/cc "All standards were made equivalent to a set of stainless steel standards".

ΔV_{BF} (465 psi) = 1.10 cc From Figure B-1

ΔV_{BE} (195 psi) = 0.46 cc From Figure B-1

$V_{BF} = 587.72 + 1.1 = 588.82$ cc (See Appendix B)

$V_{BE} = 587.72 + 0.46 = 588.18$ cc (See Appendix B)

From Equation (D-8) the mass of ethane, M_{g2}, is given by:

$$M_{g2} = 248.0922 \left(1 - \frac{1.15584 \times 10^{-3}}{7.80}\right) - 234.4545 \left(1 - \frac{1.15461 \times 10^{-3}}{7.80}\right)$$

$$+ 588.82 \left(1.15584 \times 10^{-3}\right) - 588.18 \left(1.15461 \times 10^{-3}\right)$$

$= 13.63724$ gm.

Determination of the Amount Trapped in the Transfer Tubing

Calculations are carried out for Run No. 2 of the binary system (methane + ethane). The density will be calculated for the liquid level of the mixture at 8.8 divisions on the pycnometer capillary stem.

It is appropriate at this time to review the condensation process for the binary mixture methane + ethane. First, the ethane was condensed. The transfer line was then evacuated and the methane was condensed. After sufficient amount of methane was charged to the pycnometer, the temperature of the system was lowered approximately 15°C. The mixture was thoroughly mixed to achieve homogeneity.

Considering this condensation process, the data needed to calculate the amounts trapped in the transfer tubing are presented below.

	Condensation Process	
	Ethane	Methane
Pressure in Transfer Tubing	.035°	9.200°
Room Temperature	70.0°F	70.8°F
Molecular Weight	30.068	16.042
Volume of Transfer Tubing	36.306 cc	36.606 cc

Calculation of the Amount of Methane

In order to calculate the amount of methane in the transfer tubing, the composition of the gas in the line must be determined. The composition is determined by assuming this mixture to behave as an ideal solution. This assumption leads to the relationship:

$$y_i = \frac{\alpha \ x_i}{1 + (\alpha-1) \ x_i} \qquad \text{(F-4)}$$

where:

y_i = mole fraction of component i in the vapor

x_i = mole fraction of component i in the liquid

α = relative volatility

For methane + ethane system, $\alpha = 800$

$$x = \frac{3.800/16.042}{\frac{3.800}{16.042} + \frac{13.6373}{30.068}} = 0.342$$

From Equation (F-2)

$$y = \frac{800 \ (0.342)}{1+799 \ (0.342)} = 0.9976$$

The molecular weight of the mixture, $(MW)_m$, in the line is calculated as

$$(MW)_m = 0.9976(16.042) + 0.0024(30.068) = 16.076$$

The number of gram-moles in the line was calculated by employing the ideal gas law

$$n = \frac{PV}{RT} \qquad (F\text{-}5)$$

All the terms on the right hand side of the equation must be determined. This was accomplished as follows:

$P = 9.200^{\circ} = 4.597$ psi (measured by T.I. pressure gauge)

The volume and the temperature in the transfer line are as follows:

1. The main portion of the transfer line up to the value near the pycnometer, excluding the Buordon tube volume

   $V = 36.106$ cc , $T = 70.8^{\circ}F = 294.71^{\circ}K$

2. The volume of the Buordon tube in the pressure gauge

   $V = 0.5$ cc , $T = 120^{\circ}F = 322.04^{\circ}K$

3. The volume of the capillary stem of the pycnometer inside the cryostat

   $V = 0.06$ cc , $T = 200^{\circ}K$ "the temperature mass was assumed equal to the average value between the operating temperature, $-165^{\circ}C$, and room temperature, $21^{\circ}C$

Substituting these values into Equation (F-5):

$$n = \frac{4.597}{14.696(82.057} \left(\left(\frac{36.100}{294.71} \right) + \frac{0.5}{322.04} + \frac{0.06}{200} \right)$$

$$= 0.00381 \ (0.1225 + 0.00015 + 0.0003)$$

$$= 4.73 \times 10^{-4} \text{ gm-moles}$$

Let n_1 = number of gram-moles of methane

n_2 = number of gram-moles of ethane

Then:

$$n_1 = 4.73 \ (10^{-4}) \ (0.9976) = 4.718 \times 10^{-4} \text{ gm-moles}$$

$$n_2 = 0.011 \times 10^{-4} \text{ gm-moles}$$

Now, let M_1 = mass of methane in the line

M_2 = mass of ethane in the line

Then:

$$M_1 = 4.718 \times 10^{-4} \ (16.042) = 0.00755 \text{ gm}$$

$$M_2 = 0.011 \times 10^{-4} \ (30.068) = 0.00003 \text{ gm}$$

Calculation of the Amount of Ethane Trapped during the Condensation Process

Pure Ethane

Equation (F-3) is used to calculate the number of gm-moles of ethane.

$P = 0.035^{\circ} = 0.0175$ psia Texas Instrument Calibration

$T = 70^{\circ}F = 294.26^{\circ}K$

$V = 36.306$ cc (It is clear that the effect of temperature difference in the Buordon tube is negligible)

From Equation (F-3)

$$n = \frac{(0.0175)\ (36.306)}{(14.696)(82.057)(294.26)} \text{ gm-mols}$$

The mass of ethane is therefore given by:

$$M = n\ (30.068) = 5.4 \times 10^{-5} \text{ gm}$$

From the above calculated values, the total mass of ethane, n_{2T}, which was not condensed was:

$$n_{2T} = 3 \times 10^{-5} + 5.4 \times 10^{-5} = 8.4 \times 10^{-5} \text{ gm}$$

From the above calculations, the mass of condensed methane, M_{C1} and the mass of condensed ethane, M_{C2} are:

$$M_{C1} = 3.80002 - 0.00755 = 3.79247 = 3.7925 \text{ gm}$$

$$M_{C2} = 13.63724 - 0.00008 = 13.63716 = 13.6372 \text{ gm}$$

Determination of the Volume of the Condensed Gases

The volume of the condensed gases is equal to the volume of the pycnometer at the division 8.8 on the graduated capillary stem. From Table A-2, page A-10, by linear interpolation the volume of the pycnometer is 30.1289 ml.

Calculation of the Liquid Density of the Mixture

The liquid density of the mixture is calculated by making use of Equation (F-1).

$$M = M_{C1} + M_{C2} = 3.7925 + 13.6372 = 17.4297 \text{ gm}$$

$$V = 30.1289$$

$$\rho = \frac{17.4297}{30.1289} = 0.578504 \text{ gm/ml}$$

The composition corresponding to the calculated density value is computed from the known masses of the components as shown below.

$$\text{Gm - moles Methane} = N_{C1} = \frac{3.7925}{16.042} = 0.23641$$

$$\text{Gm - moles Ethane} = N_{C2} = \frac{13.6372}{30.068} = 0.45354$$

Total number of gm-moles = 0.23641 + 0.45354 = 0.68995

$$\text{The Methane Mole Fraction} = X_{C1} = \frac{0.23641}{0.68995} = 0.34265$$

The temperature corresponding to the calculated density value is determined from the platinum resistance thermometer reading.

For the liquid level 8.8 , $R_T = 8.1811$ ohms

$T = -165.345^{\circ}C$

Similar calculations using an IBM 1410 digital computer was made to determine the density at different liquid levels and consequently at different temperatures. The final results are presented in Table F-1.

TABLE F-1

LIQUID DENSITY OF METHANE + ETHANE MIXTURE (RUN NO. 2)

Methane Mole Fraction X_{C1}	Temperature $^{\circ}C$	Liquid Density gm/ml
0.34264	- 165.345	0.578504
	- 165.172	0.578305
	- 164.997	0.578120
	- 164.796	0.577896
	- 164.567	0.577643

Calculation of the Liquid Density at -165.0°C

In order to determine the liquid density at -165.0°C, the least square method was used to fit the data presented in Table F-1. The data were found to fit Equation (F-6).

$$\rho = 0.39612611 - 0.0001103\ t \qquad \text{(F-6)}$$

where t is in °C.

The maximum and minimum deviations between the smoothed data obtained from Equation (F-4) and the date in Table F-1 are 5.4×10^{-6} and 1.3×10^{-7} gm/ml respectively.

The liquid density at -165°C was computed as:

$$\rho\ -165^{\circ}C = 0.39612611 - 0.0001103\ (-165.0)$$

$$= 0.578121 \text{ gm/ml}$$

Calculation of the Excess Volume Data at -165.0°C

The excess volume is calculated by means of Equation (F-7):

$$V^{E}_{T,P} = V_m - (X_{C1}\ V_{C1}^{\circ} + X_{C2}\ V_{C2}^{\circ}) \qquad \text{(F-7)}$$

where:

V^{E} = Excess volume, ml/gm-mol

V_m = Molar volume of the mixture at T and P, ml/gm-mol

V_{C1} = Molar volume of methane at T and P, ml/gm-mol

V_{C2} = Molar volume of ethane at T and P, ml/gm-mol

X_{C1} = Mole fraction of methane

X_{C2} = Mole fraction of ethane

$X_{C1} = 0.34264$

$X_{C2} = 0.65736$

$$V_{C1}^{o} = \frac{16.042}{0.427535} = 37.5221 \text{ ml/gm-mol}$$

$$V_{C2}^{o} = \frac{30.068}{0.632269} = 47.5557 \text{ ml/gm-mol}$$

$$V_m = \frac{0.34264(16.042) + 0.65736\ (30.068)}{0.578121} = 43.6967 \text{ ml/gm-mol}$$

$$V^E = 43.6967 - (0.34264 \times 37.5221 + 0.65736 \times 47.5557)$$

$$= -0.4211 \text{ ml/gm-mol}$$

In calculating the excess volume value, it was assumed that the effect of pressure was negligible. The validity of this assumption was verified as follows:

Consider the binary mixture methane + ethane with the composition

$X_{C1} = 0.86677$

$X_{C2} = 0.13323$

The quantity $\frac{\partial \rho}{\partial P}$ was estimated using the method described by Hougan and Watson(A).

$$\frac{\partial \rho}{\partial P} = 6 \times 10^{-5} \text{ gm/ml-psi for the mixture}$$

$$= 5.5 \times 10^{-5} \text{ gm/ml-psi for ethane}$$

The vapor pressure of methane at -165.0°C is approximately 11 psia.

The pressure of the mixture at -165.0°C is 9.4 psia

The pressure of ethane at -165.0°C is extremely small

Consider the calculation of the excess volume at the methane vapor pressure -

$P_{methane} - P_{mixture} = 1.6$ psia

$P_{methane} - P_{ethane} = 11$ psia

Density of Methane = 0.427535 gm/ml (-165.0°C, 11 psia)

Density of the Mixture = 0.465048 gm/ml (-165.0°C, 9.4 psia)

Density of ethane = 0.632269 gm/ml (-165.0, .01 psia)

Density of the mixture at -165.0°C and 11 psia is estimated:

A. Hougan, O.A., and Watson, K.M., "Chemical Process Principles", Part 2, John Wiley and Sons, Inc., New York, 1955, pp. 502-507.

$$\rho_m = 0.465048 + 1.6\ (6)\ (10^{-5}) = 0.465144 \text{ gm/ml}$$

Density of ethane at -165.0°C and 11 psi is estimated:

$$\rho_{C2} = 0.632269 + 11\ (5.5)\ 10^{-5} = 0.632874 \text{ gm/ml}$$

Molecular weight of the mixture = $(MW)_m$ = 17.91

The molar volume of the mixture = V_m = $\dfrac{17.91}{0.465144}$
at -165°C and 11 psia.

= 38.5042 ml/gm-mol

The molar volume of ethane = V_{C2} = $\dfrac{30.068}{0.632874}$
at -165.0°C and 11 psia.

= 47.5102 ml/gm-mol

The molar volume of methane = V_{C1} = 37.5221 ml/gm-mol
at -165.0°C and 11 psia.

$$V^E = 38.5042 - 37.5221 \times 0.86677 + 47.5102\ (0.13323)$$

$$= 38.5042 - 38,8528 = -\ \underline{0.3486} \text{ ml/gm-mol}$$

The excess volume value calculated (neglecting the effect of pressure as shown in Table 8) is -0.3450 ml/gm-mol.