DETERMINATION OF PARTIAL VOLUMES
AT INFINITE DILUTION VIA
THE INJECTION METHOD

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PREFACE

A new method, the Injection Method, was developed which permitted partial volumes to be evaluated directly at the infinitely dilute state without an extrapolation of experimental data. Equipment was designed, constructed, and operated within the framework of this method to obtain these partial volumes. Partial volumes of ethane at infinite dilution in methane were experimentally determined to test the method and to permit limits of accuracy to be assigned. This data will be employed to test theoretical models. The pressure range of 160 to 2,000 psia at 100°F was studied.

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CHAPTER I

INTRODUCTION

Purpose of Study

The state of infinite dilution is intrinsically of interest because it represents an important limiting condition in the study of mixtures. Theoretical models based on molecular interactions are most easily formulated at this state, for here a solute molecule is only affected by solvent molecules. Empirically, given the thermodynamic properties of the pure components and the corresponding thermodynamic properties of these components at infinite dilution, equations describing the thermodynamic properties of these mixtures might assume the form of an interpolating equation using concentration as a parameter. These properties should also be useful in connection with the development of an equation of state for mixtures, since such an equation must correctly describe the partial properties at infinite dilution. Finally, mixed second virial coefficients may be calculated at this terminal concentration using experimentally obtained partial volumes.

Investigations made at the state of infinite dilution are few and have been confined solely to organic liquids (1). Since this study was only concerned with gases, it represents research into a heretofore unexplored area.

The primary purposes of this study were to build an apparatus for the determination of the partial volumes of a gaseous solute at infinite dilution in a gaseous solvent and to develop the associated operating techniques. The method that was employed is new and is called the Injection Method. Partial volumes were obtained which pertain directly to the infinitely dilute state. No extrapolation of experimental data was required.

Partial molar volumes for ethane at infinite dilution in methane were determined at a temperature of 100° F in the pressure range of 160 to 2,000 psia.

The Injection Method

This method is based on the experimental measurement of quantities related to the partial volume. For a binary the partial volume of the infinitely dilute component is given by:

$$\bar{v}_1 = \lim_{n_1 \to 0} \left(\frac{\partial V}{\partial n_1}\right)_{T,P,n_2} \qquad (1)$$

The right hand side of equation (1) may be rigorously transformed into:

$$\lim_{n_1 \to 0} \left[\left(\frac{\partial V}{\partial n_1}\right)_{T,P,n_2} = - \frac{(\partial P/\partial n_1)_{T,V,n_2}}{(\partial P/\partial V)_{T,n_1,n_2}} \right] \qquad (2)$$

Equation (2) is further converted by a similar transformation to:

$$\lim_{n_1 \to 0} \left[\left(\frac{\partial V}{\partial n_1}\right)_{T,P,n_2} = v_2 \, \frac{(\partial P/\partial n_1)_{T,V,n_2}}{(\partial P/\partial n_2)_{T,V,n_1}} \right] \qquad (3)$$

Substitution of equation (3) into equation (1) yields the working equation, viz.:

$$\bar{v}_1 = \lim_{n_1 \to 0} \left[v_2 \frac{(\partial P/\partial n_1)_{T,V,n_2}}{(\partial P/\partial n_2)_{T,V,n_1}} \right] \tag{4}$$

The partial derivatives in equation (4) were experimentally evaluated by use of the following approximation:

$$\lim_{n_1 \to 0} \left(\frac{\partial P}{\partial n_1}\right)_{T,V,n_2} = \left(\frac{\Delta P}{n_1}\right)_{T,V,n_2} \tag{5}$$

Experimentally, a small amount of the solute was injected into the solvent and the associated increase in pressure measured. These changes in pressure were plotted versus the number of moles injected into the mixture. A line was drawn through the origin and these data points. The slope of this line is numerically equal to $\partial P/\partial n_1$. To be mathematically rigorous, however, the value of this partial derivative should have been evaluated at the point where n_1 is zero. The curve was experimentally found to be linear for concentrations less than 5%. Thus the slope calculated in this range was identical to the value of the slope at n_1 equals zero. Therefore no extrapolation of experimental data was necessary to evaluate $\partial P/\partial n_1$ at infinite dilution.

The denominator of equation (4) was obtained by following the same experimental procedure as was used for the binary, except that methane was used as the injected gas and the solvent. Values of v_2

were obtained by interpolating volumetric data on methane reported by Douslin (2).

Multiplying the quotient of the experimentally obtained quantities with the numerically obtained specific volume in accordance with equation (4) yielded the desired partial volume at infinite dilution. This value applied to the constant temperature of the experiment and to the initial pressure of the solvent. From these experimentally obtained quantities, the partial compressibility factor may be calculated according to:

$$\bar{Z}_1 = P\bar{v}_1/RT \qquad (6)$$

CHAPTER II

EQUIPMENT

Design Requirements

The equipment was designed to permit evaluation of $(\partial P/\partial n_i)_{T,V,n_j}$ and to satisfy its mathematical requirements, i.e., the change in pressure associated with increasing the number of moles had to be measured at constant temperature and volume.

Maintaining isothermal conditions required the construction of a thermostat large enough to house the high pressure bombs and their immediate connections and also to provide ample working space. This thermostat was required to maintain the temperature to roughly 0.05°F in order that the error in $(\partial P/\partial n_i)$ caused by fluctuations in temperature did not exceed 1% at the 2,000 psia pressure level.

In accordance with the mathematics, isochoric conditions had to be observed. Although there was a change in volume during the injection phase, the increase in pressure was not measured until the volume of the mixture was restored to its original value. Thus, the requirement for isochoric conditions was satisfied.

Determination of the moles of solute and solvent present in their bombs was accomplished indirectly by measuring related quantities. Such a method required the accurate measurement of the volume of the main bomb and of the burette bomb.

Finally, the equipment had to be exceedingly leak-tight because small pressure changes had to be accurately measured at high absolute pressure levels.

Function of Equipment

A schematic of the experimental apparatus that was built to satisfy these design requirements is shown in Figure 1. The function of this equipment may be illustrated by considering the experimental procedure that was followed: the respective pressures of the solvent and the solute in the thermostated main bomb and ethane burette were alternately measured by respective use of the high and low pressure gauges. The solvent at a high pressure was then released from the main bomb into the adjacent ethane burette, which contained the solute at a relatively lower pressure. This expanded mixture was then compressed by pumping mercury into the burette via the mercury screw pump until the volume of the mixture was restored to the solvent's original volume. An electrical contact was incorporated to determine the top level of the mercury. Such a procedure thereby satisfied the mathematical requirement of isochoric conditions, even though the volume was changed during the injection phase. The pressure increase was measured by use of the differential pressure transducer. The capacitor bomb served to maintain a constant reference pressure on the back-side of the transducer. During each run the temperature and moles of solvent were invariant. In subsequent injections, which followed a similar procedure, the solute concentration was increased and the associated pressure change measured by the transducer.

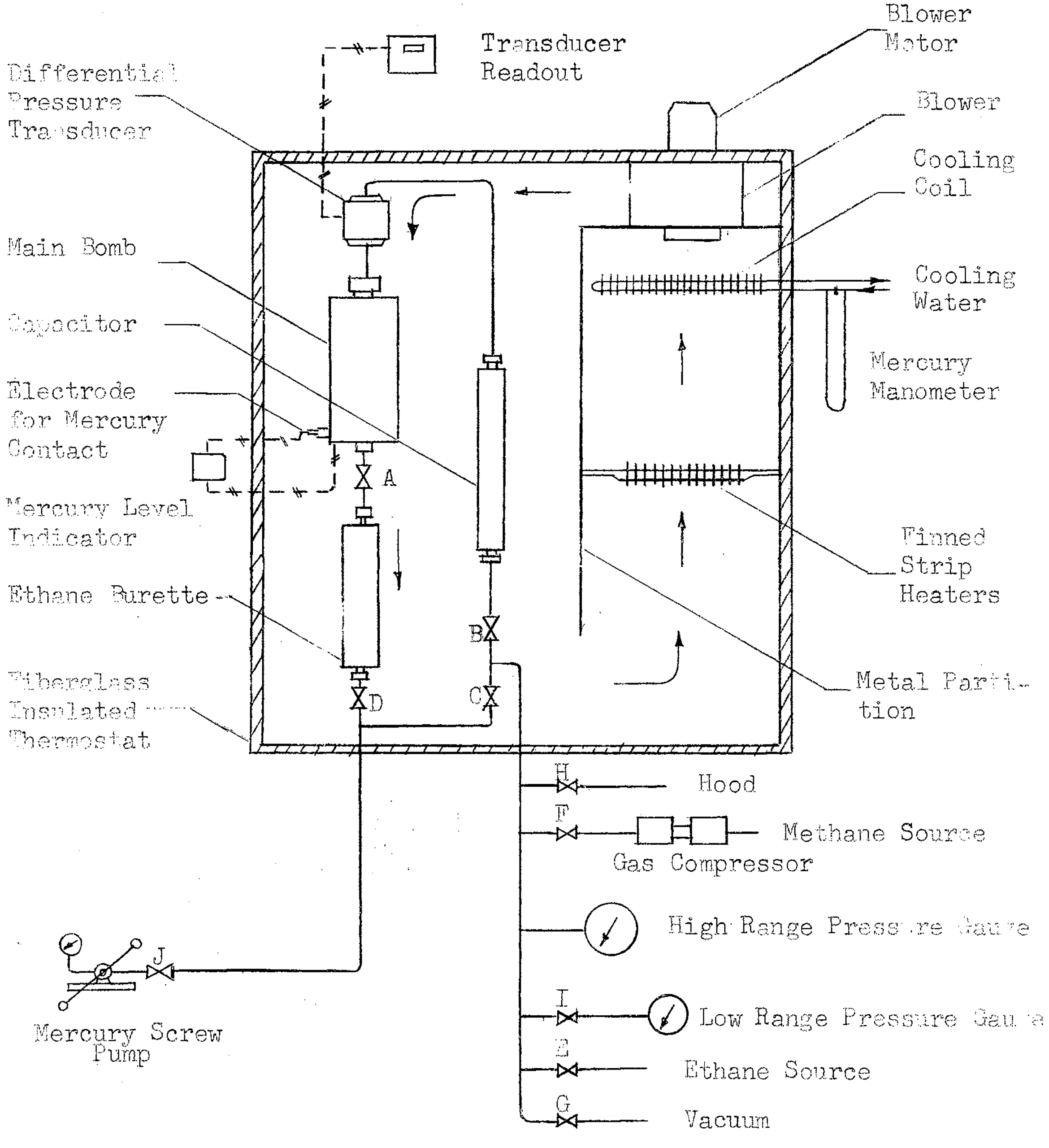

Figure 1. Equipment for Measurement of Partial Volume at Infinite Dilution

The moles of solute and solvent present in their respective bombs before an injection were calculated according to:

$$n_1 = V_1/v_1 \tag{7}$$

and

$$n_2 = V_2/v_2 \tag{8}$$

The values of V_1 and V_2 are accurately known from calibration. Values for the specific volumes, v_1 and v_2, were obtained by interpolation of volumetric properties as given in the literature (3).

Description of Individual Units

Thermostat

The thermostat design permitted maximum usage of the air blower capacity. Both the intake and the discharge of the blower were unimpaired and represented open volumes. Such a design permitted the full rated blower circulation of 225 cubic feet per minute to be realized. The air passed over three finned electrical heaters, a cooling coil and then into the blower suction. It then discharged into the section which contained the bombs. This circulation pattern utilized the blower as a mixing device and thereby produced a constant temperature air discharge. The blower motor is located exterior to the thermostat, directly above the blower. Such location prevented the heat given off by the motor from disrupting the constant temperature conditions of the thermostat. The motor was secured to the frame through high frequency vibration pads, and this minimized the transmission of motor vibrations into the equipment frame. A shaft extender, which rotated in a bearing plate, connected the motor and the blower armature.

A stroboscopic light was employed after the motor was mounted to assure that the motor armature shaft and shaft extender rotated through the same center line. The mounting screws of the motor were adjusted until maximum rpm was attained as indicated by the strobescopic light. A general decrease in the noise level was also observed.

A heat sink was provided by a cooling coil secured from an old gas compressor. Cold tap water served as the cooling medium. The water flow rate was measured by a mercury manometer located on the inlet side. Location of the manometer on this side assured that it received water at a constant temperature. A small globe valve acted as an adjustable pressure drop device between the manometer taps. A valve was used, rather than an orifice, because the range of flow rates was too great to be adequately covered by a single orifice plate. Because of the simple design of the heat sink, control of the temperature at ambient temperatures and below was not as good as it was at 100°F and higher. This was one of the factors in the choice of 100°F as the lowest of operating temperatures.

Three 250-watt finned strip heaters provided the source of heat. They were located on a horizontal plane 13 inches below and parallel to the cooling coil. The two outside heaters were wired in parallel and were controlled by the 7.5 ampere thermostat heater powerstat. Having wired them in parallel, the same voltage was applied to both, thus assuring that equal heat dissipation was obtained from both of them. The center heater was connected directly to a Fisher Model 22 Proportional Temperature Controller, which added heat as was necessary to maintain isothermal conditions. This controller employed a thermistor probe located directly in front of the air blower discharge.

A 20-gauge sheet metal box of 18-inch depth, 45-inch height, and 30-inch width constituted the walls of the thermostat. The metal partition was also made of 20-gauge sheet metal and supported the blower, cooling coil and heaters. Its primary function was to divide the thermostat into two volumes, thus defining the air circulation pattern. Insulation was provided by surrounding the metal box with a 2-inch thick layer of fiberglass insulation and a one-half inch layer of plywood which supported and housed the thermostat.

Finally, access to the thermostat was gained via a hinged door on which was mounted four inches of fiberglass insulation, followed by a layer of heavy duty aluminum foil. The foil acted as a cover for the insulation and prevented the air from shredding it.

Experiments have demonstrated that this thermostat maintained the temperature to $\pm$ 0.04°F.

Thermocouples

Two copper-constantan thermocouples were employed to measure the temperature. Both were calibrated by comparing the emf they developed to a National Bureau of Standards total immersion mercury thermometer calibrated to 0.01°F. The emf developed by each thermocouple was measured by a Leeds and Northrup Millivolt Potentiometer (Catalog number 8686). This potentiometer permitted measurement of the temperature to 0.04°F. The electrical leads from the two thermocouples passed to the thermocouple selector switch, which in turn was connected to the potentiometer. By use of this switch, each one of the thermocouples could alternately be connected to the potentiometer. The wiring circuit was designed so that the only junction of dissimilar thermocouple metals was at the thermocouple tips. Such a system of wiring prevented emfs developed at wiring connection points from entering the circuit.

The probe thermocouple was located in front of the blower discharge, whereas the main bomb thermocouple was inserted into a 4-inch deep hole drilled into the main bomb's shell and parallel to its center line. A distilled water ice bath was used to provide a constant reference junction temperature for both thermocouples. Table I contains calibration data for the two thermocouples.

Differential Pressure Transducer

The function of the transducer was to measure the increase in the pressure of the main bomb caused by the introduction of the solute into the solvent. A constant reference pressure was maintained by the capacitor bomb on the back side of the transducer. This differential pressure was converted by the transducer into an electrical output which was measured by the Leeds and Northrup Millivolt Potentiometer. The instrument (Consolidated Electrodynamics Corporation, Type 4-351-0005, serial no. 2518,200 psi differential) is self-compensating for temperature change in the range from -65°F to 250°F. Complete specifications for the transducer are given in Appendix A.

A Budenburg Dead Weight Gauge (serial no. 2167) was used to calibrate the transducer in the pressure range from 0 to 2,000 psig at a temperature of 100°F. The results of this calibration are tabulated in Table II. The output voltage was found to be linearly related to the applied differential pressure at any given pressure throughout the 2,000 psig line pressure range. Figure 2 is a graph of this relation

TABLE I

CALIBRATION DATA FOR THERMOCOUPLES

Temperature, °C	Probe, mv.	Main Bomb, mv.
41.08	1.650	1.654
59.98	2.448	2.464
60.06	2.463	2.469
79.82	3.335	3.347
80.22	3.356	3.363
100.14	4.277	4.287

TABLE II

DATA AND RESULTS OF CALIBRATION OF DIFFERENTIAL PRESSURE TRANSDUCER

Initial Pressure, psig	Differential Pressure psid	Transducer emf output, mv	Sensitivity, psid/ mv	Average Sensitivity, psid/ mv
0.00	14.26	2.935	4.859	4.859
511.69	83.95	17.306	4.851	4.851 ±.003
	84.71	17.470	4.849	
	152.64	31.447	4.854	
1041.83	97.69	20.187	4.839	4.844 ±.004
	98.98	20.457	4.838	
	112.75	23.242	4.851	
	168.17	34.701	4.846	
	182.22	37.612	4.845	
1508.46	81.89	17.006	4.815	4.822 ±.006
	95.06	19.725	4.819	
	118.94	24.666	4.822	
	167.53	34.688	4.830	
1835.57	17.60	3.636	4.842	4.843 ±.001
	34.43	7.108	4.844	
	45.49	9.388	4.845	
	93.95	19.405	4.842	
	155.49	32.101	4.844	

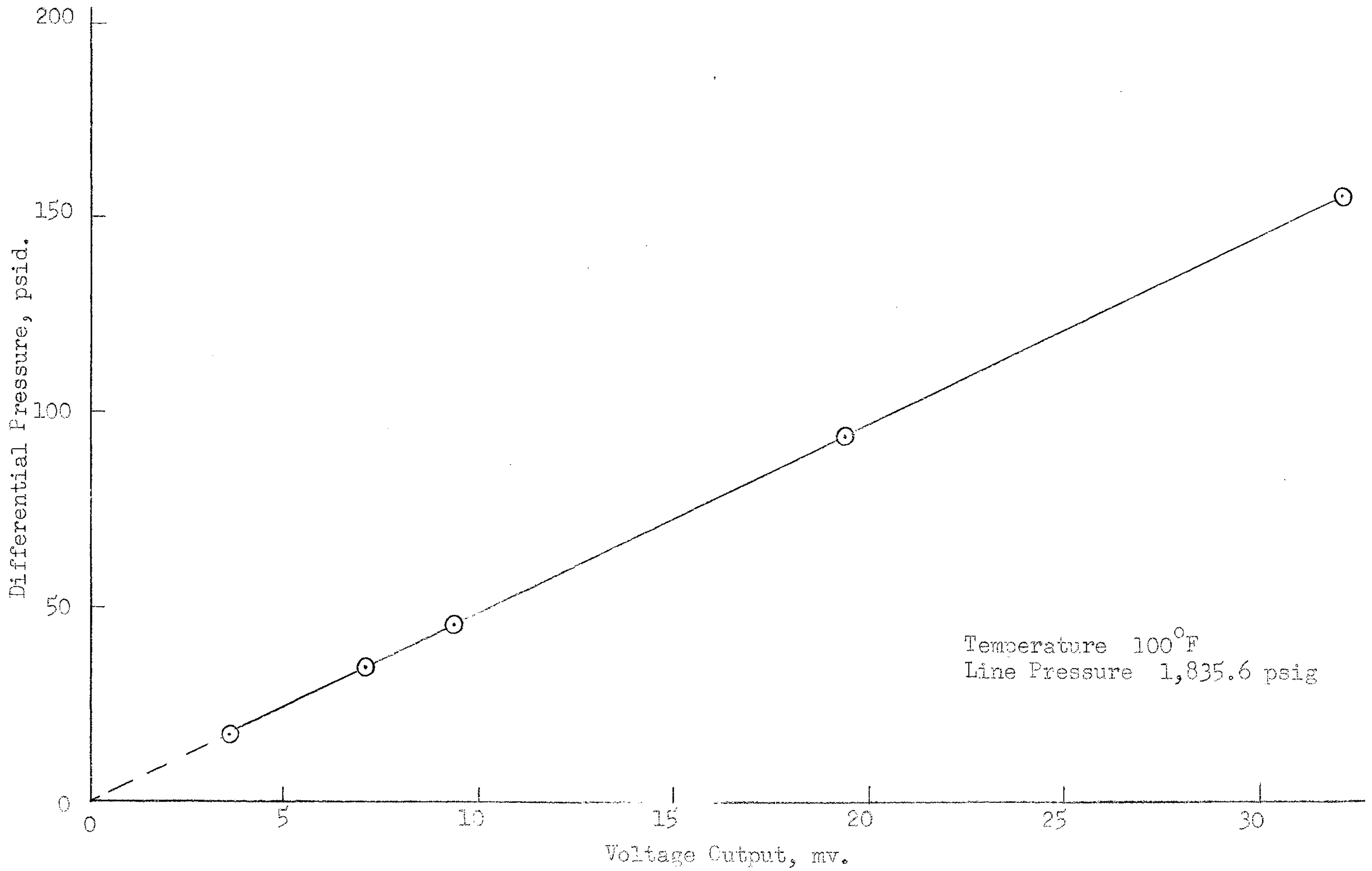

Figure 2. Calibration Curve Demonstrating Linearity of Transducer

at 1,836 psig. The slope of this line represents the value of the transducer's sensitivity (psid/emf). It was found to vary slightly with the line pressure. Figure 3 shows the relation of the sensitivity to the line pressure.

The zero point and sensitivity of the transducer would have changed if the input voltage to the transducer was not held exactly at the specified 10 volts. In order accurately to measure the input voltage, a resistor circuit was employed. A wiring schematic of this resistor circuit and the transducer circuit is shown in Figure 4. Use of this resistor circuit allowed the applied voltage to be measured to ±0.01 mv. This tolerance lies well within the required ±0.1v limit. Unfortunately, the resistor circuit added a small current to the transducer circuit which caused the zero point of the transducer to shift. This difficulty was eliminated by opening the resistor circuit single throw switch. This switch was closed only during the operation of adjusting the input voltage.

The transducer was rated for an overpressure of 2,000 psi on its "Hi" side and 400 psi on its "Lo" side. During a run, when valve A was opened, the methane rushed into the ethane burette, thereby decreasing the pressure in the main bomb about 600 psi. Since the capacitor maintained a constant back pressure, the transducer experienced a differential pressure of 600 psid. This pressure differential, however, was less than 2,000 psi and therefore no damage was incurred by the transducer. The "Hi" side of the transducer was located on the capacitor side.

If for any reason these over-pressure limits are exceeded, permanent damage to the transducer will result.

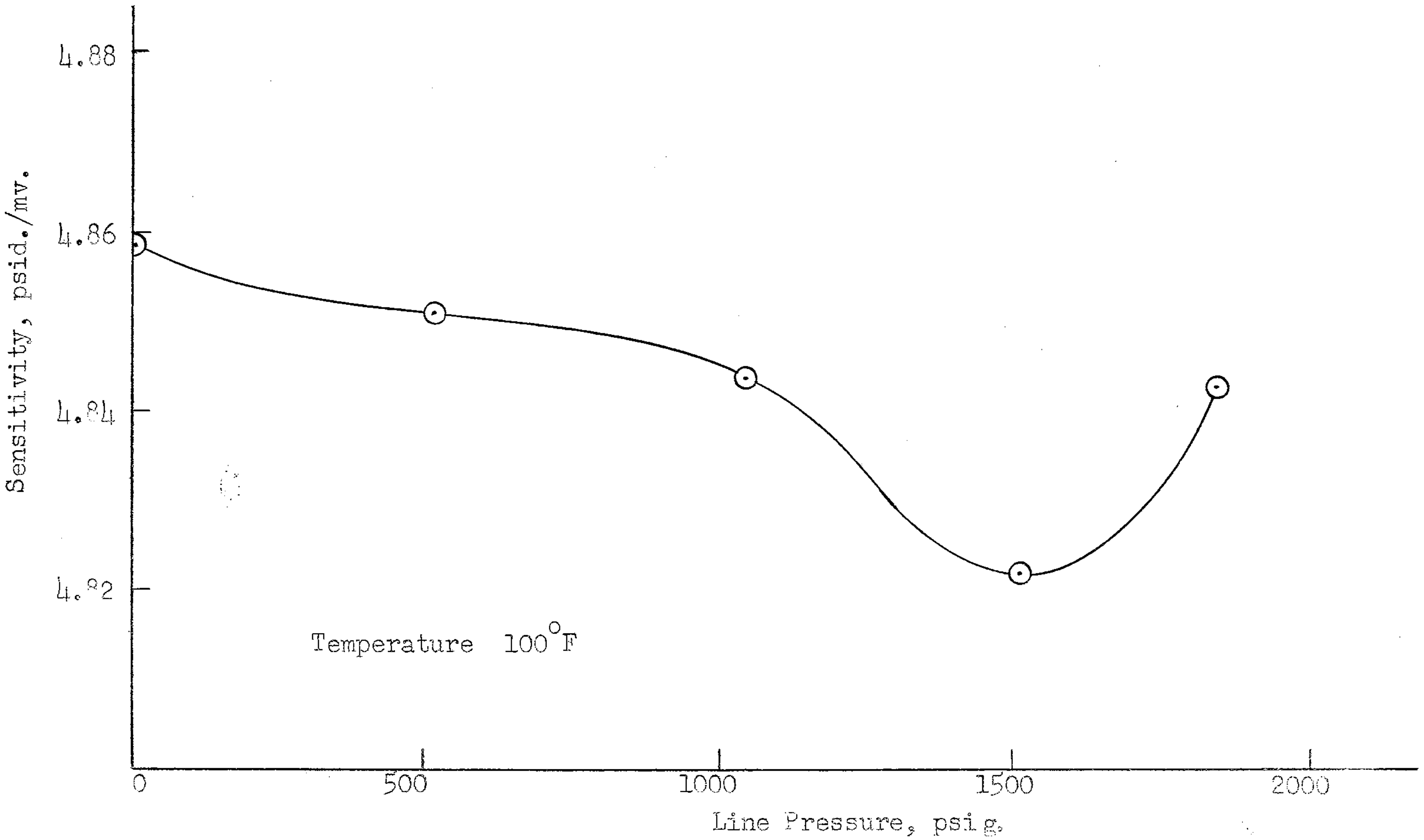

Figure 3. Calibration Curve for Sensitivity of Pressure Transducer

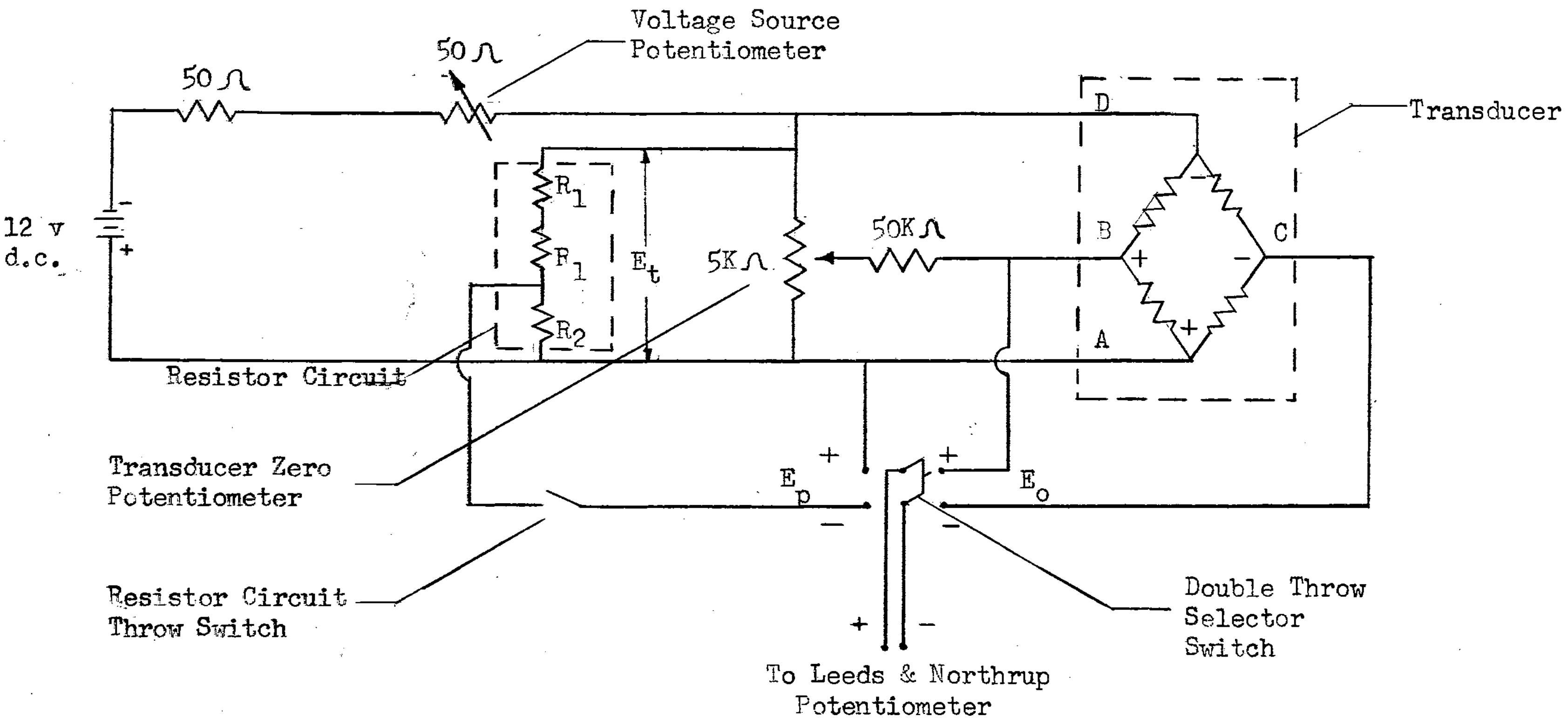

Figure 4. Wiring Schematic for Differential Pressure Transducer

Mercury Screw Pump

The mercury screw pump (Ruska Instrument Corporation, Cat. no. 2426.1-M288, Serial no. 12668) was used as a means to drive the mercury up into the burette bomb. The cylinder piston was driven by the manual turning of the pump handle. Thirty-two rotations of the handle were required to drive the piston through the 10 cc volume chamber. Thus, only a small volume of mercury was pumped into the burette with each rotation of the handle. Such a condition provided good control over the height of the mercury column when it was being pumped into the tubing connecting the main bomb and burette bomb. This reduced the possibility of inadvertently pumping mercury past the electrical contact into the main bomb.

A pressure of 6,000 psi was the maximum attainable in this pump. A 0-5,000 psig pressure gauge and mercury reservoir were mounted on its side.

Mercury Electrical Contact

The function of this contact was to permit the establishment of an accurate fixed upper level for the mercury when it was pumped into the main bomb. When the mercury contacted the electrode, it completed an electrical circuit, thus causing an electric light bulb to light. Once this level was attained, the volume of the main bomb was fixed and could be reproduced with every pumping. A constantan wire, housed in a Conax brand packing gland, served as the electrode. The wire was bent to form a tip which extended about 1/8th inch into the bottom tubing of the main bomb. It was positioned here because inside the bottom tubing the change in height of the mercury column was great with a small rotation of the mercury screw pump handle. This allowed good control over the height of the mercury column. Also, location of the contact close to the bottom of the main bomb reduced the dead volume inherently present in this tubing. The positioning of this contact is shown in Figure 5.

High Pressure Bombs

Three bombs were required in the construction of the equipment. All of them were located inside the thermostat and were secured to two 0.080 inch thick vertical steel angles. The bombs have a rated maximum pressure of 10,000 psi.

The purpose of the capacitor bomb (Autoclave Engineers, "MD Test Tube Reactor", Cat. no. 10-12) was to maintain a constant reference pressure for the transducer. It has a volume of about 25 ml.

The ethane burette bomb (Autoclave Engineers, "MD Test Tube Reactor", Cat. no. 10-8) was used to contain the ethane before an injection. Its volume was sized so that a one mole per cent mixture would be obtained by the introduction of a sample of ethane at 300 psig into a sample of methane at 5,000 psig. The inside ends of the top and bottom covers for this bomb were rounded so that the mercury would not trap any gas at the top during the compression phase and so that all the mercury would leave the bomb when the level was collapsed.

The volume of the burette bomb was determined by direct weighing. Measurement was made of the mass of mercury necessary to completely fill this volume. From this mass, the burette volume was readily calculated from density values of mercury applicable at the temperature of calibration (4). The following calibration procedure was

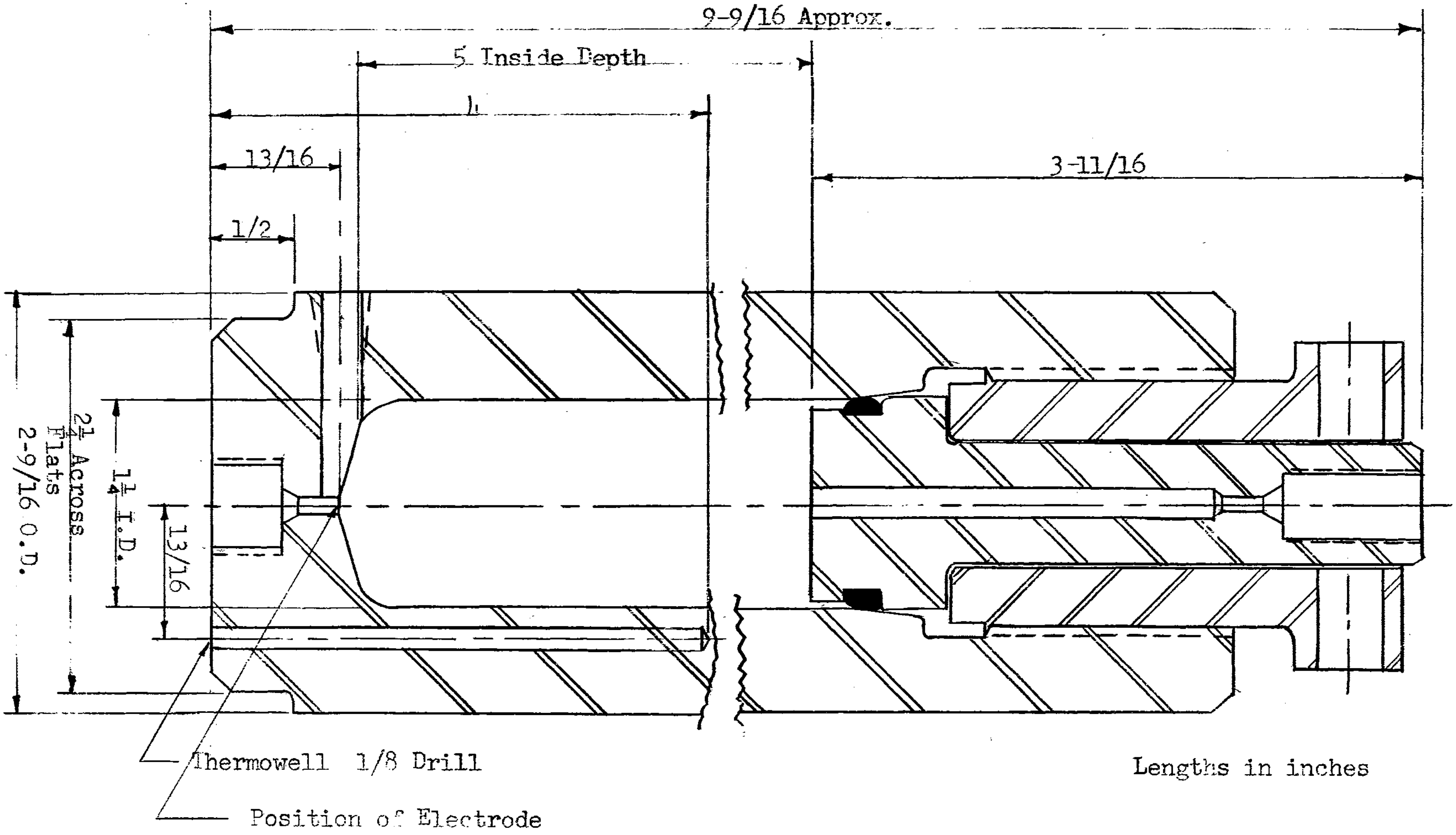

Figure 5. Construction of Main Bomb

employed: a vacuum provided with a mercury trap was applied to the top valve of the burette system. Mercury was then slowly sucked up through the bottom valve until it flowed into the trap. During filling, the bomb and valves were tapped. Before weighing the filled bomb, the valves were pounded with a hammer to dislodge any mercury trapped in the stem gland packing. Several runs were made. The results of these runs are tabulated in Table III. The volume was found to be 21.590 ml. The system was cleaned after each run by passing ethyl ether through it. Before installation in the thermostat, the bomb was cleaned with soap solution, cleaning solution, distilled water, and finally ethyl ether.

The main bomb (Autoclave Engineers, "O Ring Reactor", Cat. no. OM-100) served as a container for the gas mixture. A groove in the inside bottom surface of the bomb was a consequence of locating the mercury electrode near the bottom. This groove would trap any mercury which would be inadvertently pumped into the bomb past the electrode. It was experimentally found that by offsetting the bomb by 6° from the center-line, any such excess mercury would flow out through the bottom opening. This bomb has been tested to 4,000 psia and 120°F without leaks.

Because of the thick steel walls, temperature fluctuations in the thermostat of 0.04°F were reduced so that the temperature of the sample in the main bomb was held to within 0.02°F. This bomb was cleaned with hot soapy water, distilled water, and finally ethyl ether before installation in the thermostat. Figure 5 contains a drawing of its construction.

TABLE III

DATA AND RESULTS OF CALIBRATION OF VOLUME OF ETHANE BURETTE

Run	Temp. °C	Mass Burette in Vaco, gms	Mass Burette + Hg in Vaco, gms	Mass of Hg, gms	Density Hg, gm/ml	Volume Burette ml
1	25.7	1469.45	1761.66	292.21	13.532	21.593
2	25.7	1469.05	1761.01	291.96	13.532	21.576
3	25.7	1468.97	1761.98	293.01	13.532	21.653
4	26.4	1469.05	1760.48	291.43	13.531	21.538
5	26.4	1468.97	1761.28	292.31	13.531	21.603
6	26.4	1469.00	1760.56	291.56	13.531	21.548
7	24.0	1468.97	1761.18	292.21	13.536	21.588
8	27.8	1468.97	1761.31	292.34	13.537	21.596
9	27.8	1468.97	1761.56	292.59	13.537	21.614

A different technique was required for the determination of the volume of the main bomb. Two factors prevented an application of the previous technique. First, it was not desirable to bring mercury into contact with the transducer's diaphragm. Secondly, it would be difficult to know when the volume of the bomb had been exactly filled with mercury. The technique employed for calibration of the volume is an application of the method used in a Burnett Apparatus (5). This method provides for the determination of the ratio of the main bomb to that of the burette bomb by the successive isothermal expansion of a gas from the main bomb into the ethane burette. Such a procedure is described by the following equation:

$$P_r/P_{r+1} = N + (N-1)\frac{B}{RT}P_r \qquad (9)$$

From the definition of N we have:

$$V_2' = V_1/(N-1) \qquad (10)$$

In accordance with equation (9), a plot of P_r/P_{r+1} versus P_r at constant temperature yields a linear curve having an intercept equal to N. This curve is linear because in the derivation of equation (9) the terms containing the third and higher virial coefficients are assumed negligible. Since this is true for helium at 200 psia and 100°F, it was chosen as the experimental gas. All measurements were made at 100°F and pressures below 200 psia.

The following experimental procedure was followed. Isothermal conditions were established in the thermostat with the temperature of operation being 100°F. Valves A, B, C, D, and G were opened. Valves E, F, H and I were closed. The vacuum pump was started and the system evacuated. Valve G was closed after a ten-minute pause. The transducer was then zeroed.

Since helium was used as the sample gas, a MP cylinder of it replaced the methane MP cylinder in the line leading to the equipment. The pressure regulator on the helium cylinder was set to deliver the gas at a 200 psig pressure. Valve F was opened, thus allowing this gas to enter the main bomb, ethane burette and the pressure capacitor. Valves F and A were closed. Valve H was opened, thus releasing the 200 psig pressure helium to the hood. This valve was closed, and valve G opened. The tubing system, capacitor and burette were thereby evacuated. After thermal equilibrium had been obtained, a transducer reading was recorded. Since the capacitor was evacuated, the transducer measured the absolute pressure in the main bomb. Valve D was closed, thereby sealing off the ethane burette.

Valve A was opened, allowing the helium to rush into the evacuated burette. The emf output of the transducer was measured, once pressure and thermal equilibrium had been established. Valve A was closed. Valve D was opened slowly, thus allowing the pressure of the gas in the burette to decrease gradually, finally becoming a vacuum. Valve D was then closed.

Subsequent expansions, following an identical procedure as described above, were performed with the transducer emf output being measured after each expansion. About five expansions were performed for each run, six runs being made. These data were fitted to a least squares computer program, which calculated the slope and intercept of the straight line defined in equation (9). Table IV contains a tabu-

TABLE IV

DATA FOR CALIBRATION OF THE VOLUME OF THE MAIN BOMB

Sample Gas: Helium

Temperature: $100.00 \pm .02^{\circ}$F

Run	P_r, psia	P_r/P_{r+1}
3	180.61	1.2015
	150.32	1.2013
	125.12	1.2012
	104.17	1.2020
	86.66	1.2022
	72.08	1.2047
	59.84	1.2046
	49.67	1.2068
4	185.40	1.2013
	156.29	1.2011
	128.49	1.2015
	106.95	1.2023
	88.95	1.2030
	73.95	1.2054
	61.35	1.2057
	50.88	1.2085
5	183.83	1.2013
	153.03	1.2007
	127.46	1.2011
	106.11	1.2025
	88.25	1.2028
	73.37	1.2040
	60.93	1.2077
	50.46	1.2039

TABLE IV (Continued)

Run	P_r, psia	P_r/P_{r+1}
6	171.13	1.1995
	142.67	1.1969
	119.20	1.1979
	99.51	1.1983
	83.03	1.1946
	69.51	1.1959
	58.13	1.1971
	48.56	1.1889
	40.84	1.2076
	33.82	1.1992
7	139.43	1.1985
	116.33	1.1949
	97.36	1.1981
	81.27	1.1974
	67.86	1.1942
	56.83	1.1995
	47.37	1.1992
	39.51	1.1955
10	167.26	1.1983
	139.57	1.1962
	116.68	1.1985
	97.36	1.1968
	81.35	1.1979
	67.91	1.1985

lation of the experimental data pertaining to this calibration. Figure 6 contains a plot of the data of Table IV. A value of 1.2014 for N was obtained. Using this value of N, the value of V_2' calculated from equation (10) was found to be 107.2 ml.

During injection runs, however, a mercury slug existed in the tubing between the electrode and the closed valve A. The volume of this tubing was ascertained by a determination of the mass of mercury necessary to fill it. A medicine dropper was weighed before and after filling the tube, which was installed in the equipment. Access to the tube was gained through the top of the main bomb. This difference in mass, divided by the density of mercury, represented the volume of the tube. The tube volume was found to be 0.904ml. Subtracting the tube volume from the volume defined in equation (10) yielded the value for the volume of the main bomb, viz., 106.3 ml.

Pressure Gauges

A Heise brand bourdon tube pressure gauge (No. 41215) was employed for measurements of system pressures up to 5,000 psig. The gauge was wall mounted to the control panel via high frequency vibration pads, thereby completely isolating it from blower motor vibrations. The inlet to the gauge was attached to the feed line manifold.

To zero the gauge, a vacuum was drawn and the dial adjustment knob manipulated until the zero mark lined up with the pointer. Safety glass and blowout protection were provided as safety features. The gauge was calibrated with the Budenburg Dead Weight Gauge which is accurate to 0.05%.

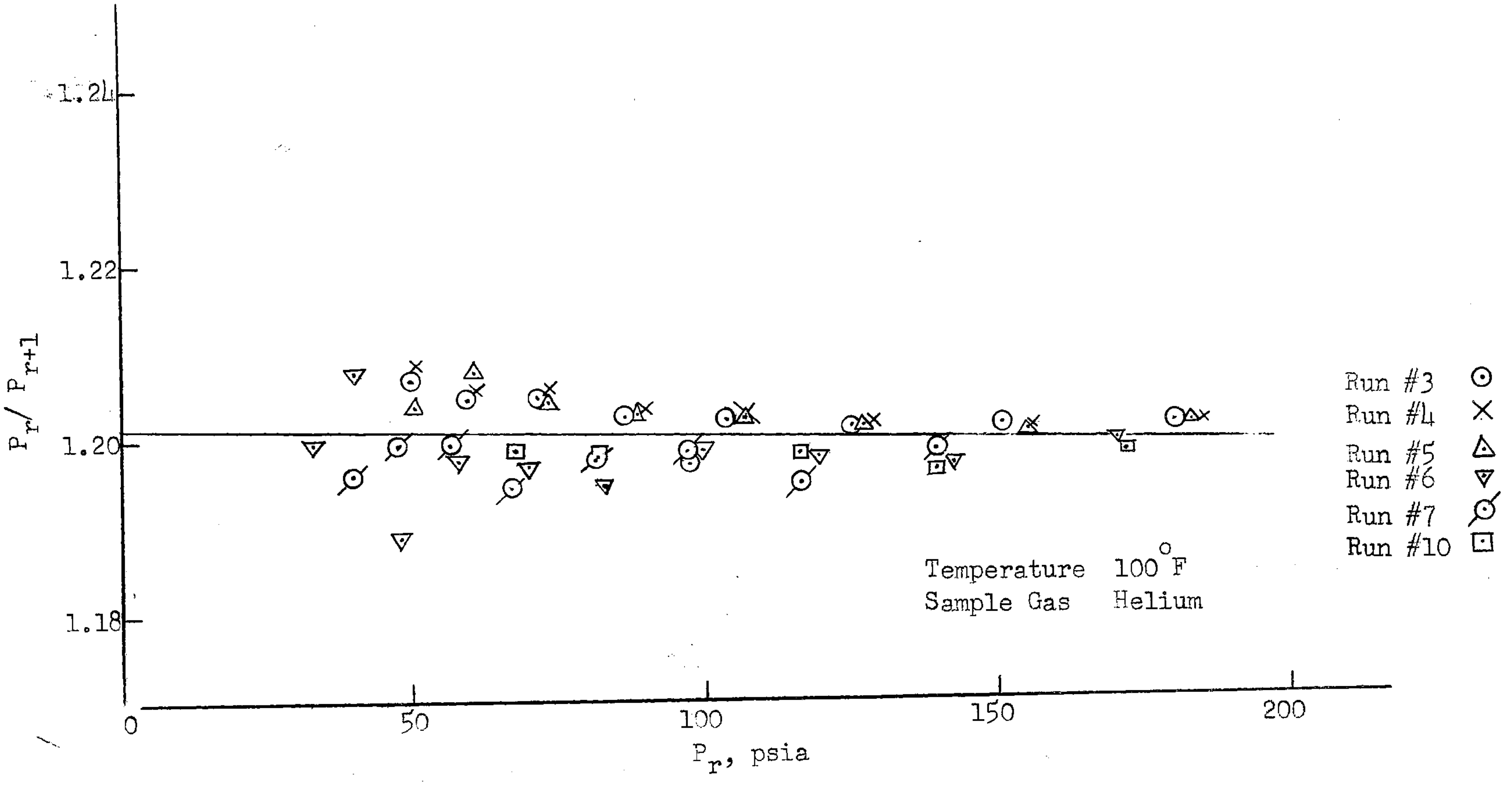

Figure 6. Results from Calibration of Main Bomb Volume

The low range pressure gauge was used to measure solute pressures up to 60 psig. This gauge was also calibrated by use of a dead weight gauge. Figures 7 and 8 present plots of the corrections in pressure to be applied to the respective readings of the gauges.

Leak Testing

The requirement of measuring small differential pressures at high absolute pressures placed a great emphasis on the necessity of having leak-tight equipment. A high majority of the leaks was discovered by pressurizing the equipment to 4,000 psia and then brushing bubble solution onto all the joints. If bubbles appeared, then the joint was tightened or the tubing rotated until the seal was perfect. All these corrective operations were performed only after the removal of the high system pressure.

A portable mass spectrometer set to detect helium was incorporated as a means of detecting very small leaks. To begin the operation, all the joints were covered with pieces of polyethylene, thus forming air-tight pockets which would trap any helium which might be leaking from the joint. The system was pressurized to 4,000 psia, with helium and the bombs heated to 120°F. A sniffer prober attached to the mass spectrometer was then inserted into the polyethylene pockets. If helium were present due to a leak, the spectrometer would immediately indicate a rise in helium concentration. This procedure facilitated the detection and elimination of two very small leaks.

As a test for leak-tightness, the system was pressurized to 2,000 psia and the main bomb and capacitor sealed off from the re-

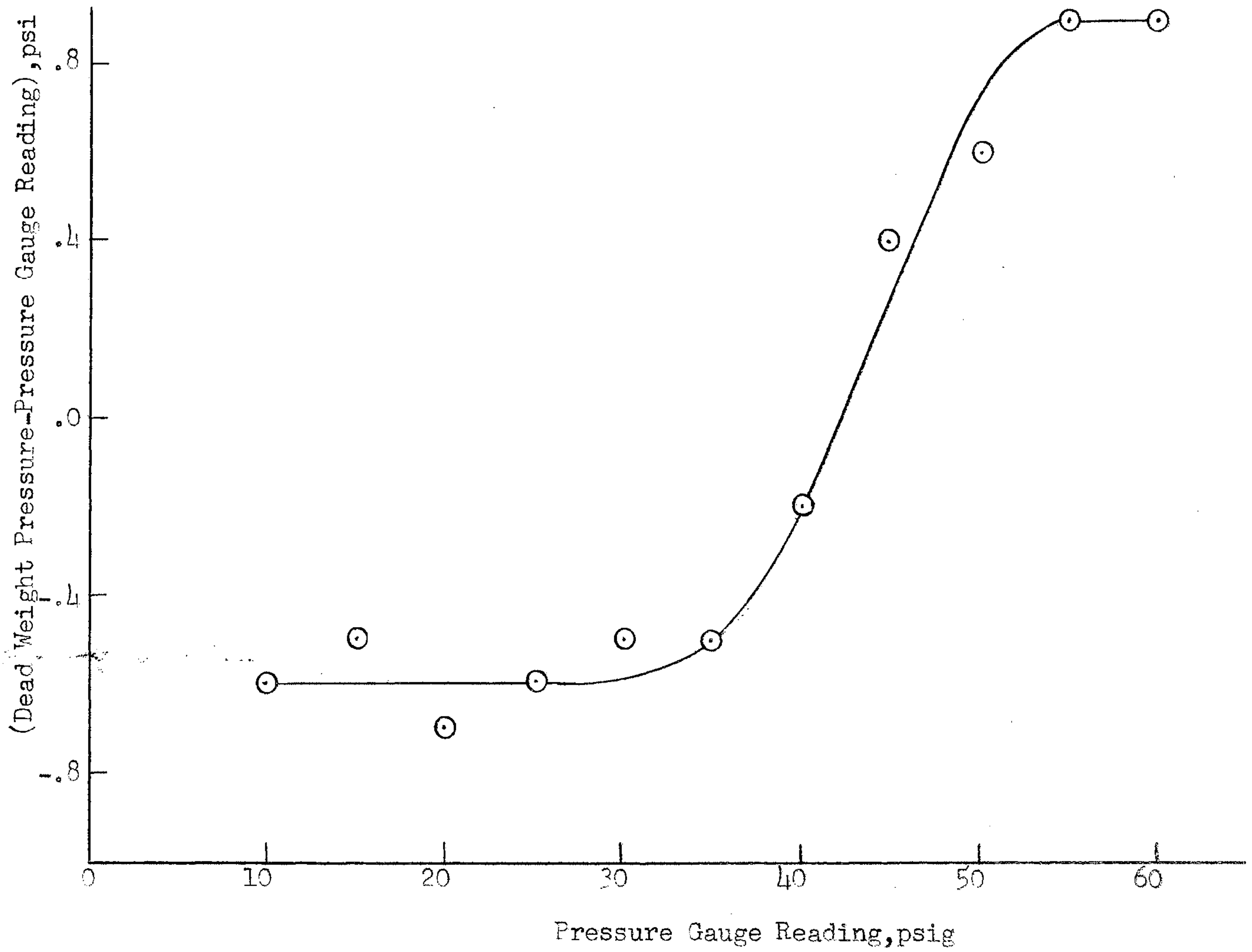

Figure 7. Correction Curve for Low Range Pressure Gauge

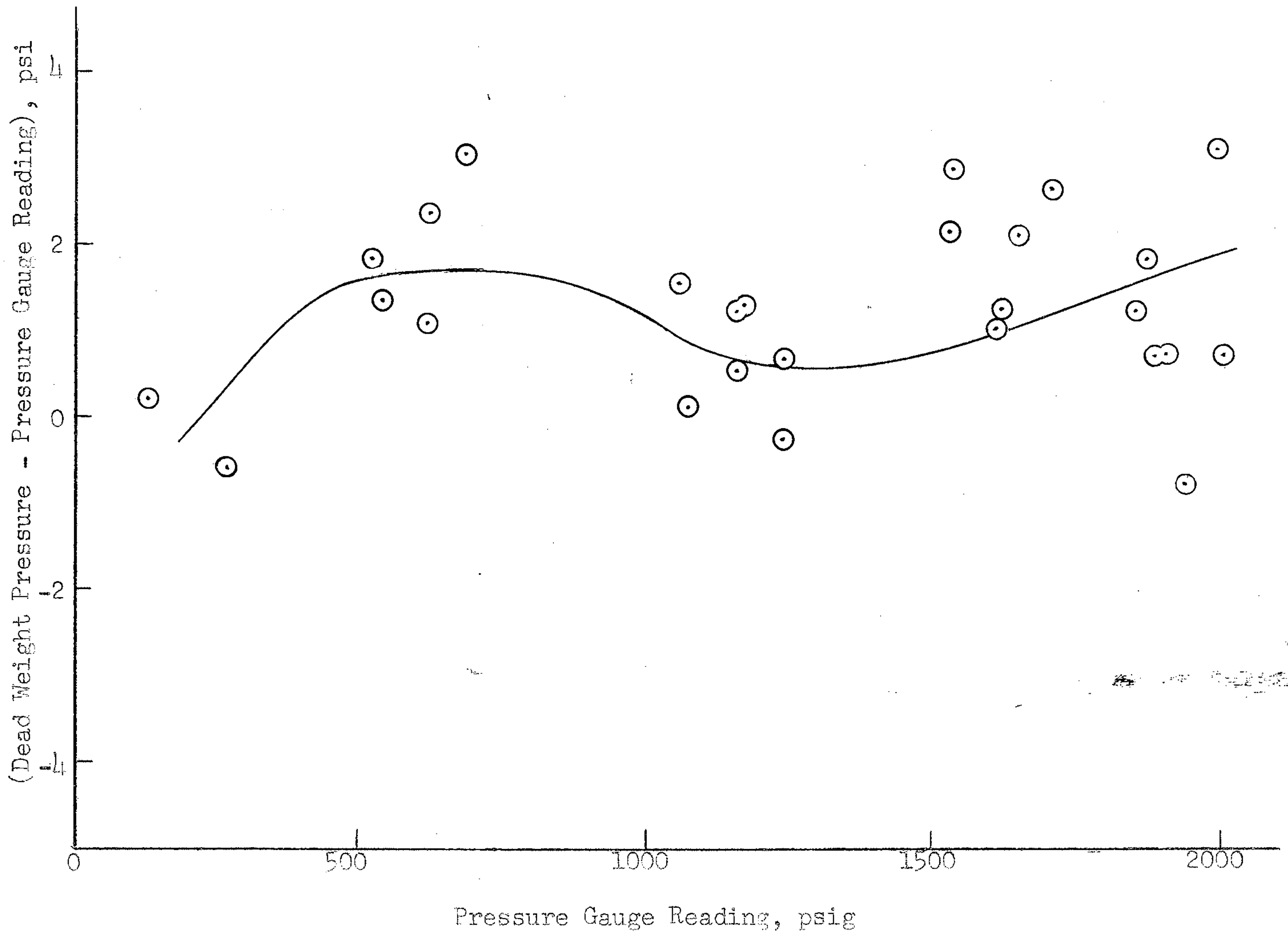

Figure 8. Correction Curve for High Range Pressure Gauge

maining connections. After a two-hour period, there was no change in the transducer readout. Since the transducer is sensitive to a hundredth of a psi pressure change, this test sufficed as a rigorous proof for the leak-tightness of the equipment.

CHAPTER III

EXPERIMENTAL PROCEDURE

Operation of Individual Units

Differential Pressure Transducer

Before any transducer readings may be taken, the supply voltage to the transducer must be set at 10.00 volts. To accomplish this, the following steps are to be followed:

1. The battery switch is turned on, thereby applying about 10 volts to the transducer.
2. The double pole of the selector switch is thrown to the resistor circuit side, and the double pole of the thermocouple selector switch is placed in the middle position between its two contacts.
3. The single throw resistor circuit switch is closed. These three steps apply the resistor circuit voltage to the Leeds and Northrup Potentiometer terminals.
4. A reading of 49.751 mv is now set on this potentiometer's scale.
5. The voltage source potentiometer knob (located on the pressure transducer readout panel) is adjusted until the Leeds and Northrup Potentiometer is balanced. 10.000 volts are now being applied to the transducer.

This adjustment of supply voltage should be performed before each transducer reading is taken.

Prior to its use to measure differential pressures, the transducer must be zeroed. The following steps describe the procedure necessary to do this:

1. Valves A, B, C and D are opened. This applies the same pressure to both sides of the transducer.
2. The double pole arm of the selector switch is thrown to the pressure transducer side, and the single throw resistor circuit switch is opened.
3. The transducer is now zeroed by rotating the transducer zero potentiometer knob (located on the pressure transducer readout panel) until the transducer output is balanced by the Leeds and Northrup Potentiometer reading set on its dials. Any convenient Leeds and Northrup Potentiometer reading may be chosen.

Since the transducer experiences a zero and sensitivity shift with temperature, the transducer should not be zeroed until after the equilibrium temperature has been reached.

Once a differential pressure has been applied, the transducer will have an emf output greater than that initially balanced by the Leeds and Northrup Potentiometer. This new emf output, and all such outputs, are measured by this potentiometer. The difference between these two emfs is directly proportional to the applied differential pressure, thereby providing an experimental measurement of this pressure difference.

When the Lo side of the transducer experiences the greatest pressure, a positive emf is generated, and the circuit as presently wired will permit immediate measurement of the emf output. Since the transducer is bi-directional, it will measure a differential pressure applied to either side. When the Hi side of the transducer experiences the greatest pressure, however, a negative emf is generated. If the two wires leading to the terminals of the transducer side of the selector switch are reversed, the Leeds and Northrup Potentiometer will measure the negative emf as if it were positive.

Thermostat

There are two independent sources of heat in the thermostat, viz., two manually controlled finned strip heaters, and a single finned strip heater. A Fisher Proportional Temperature Controller controls the single strip heater. The amount of heat given off by the two strip heaters is controlled by adjustment of the 7.5 ampere manual thermostat heater powerstat. A heat sink is provided by cold tap water which passes through a finned cooling coil.

To attain the desired bath temperature, the heat supplied by the heaters must be balanced against the heat removed by the cooling coil. In the first stages of adjustment, the temperature controller is not incorporated. It was experimentally found that the best temperature control was obtained when a substantial cooling water rate was employed. For all the 100°F runs, 0.15 gpm was chosen as the flow rate. A mercury manometer is used to indicate the water flow rate. The cooling water manometer valve is adjusted so that 20" of water head is developed. Corrective adjustments are then made on the tap water supply valve as necessary to maintain this differential pressure. With an 85-volts setting on the manual powerstat, the bath temperature was experimentally found to be held to within 2°F of 100°F without use of the temperature controller.

The temperature controller is now employed. Settings are made on the fine and coarse temperature control knobs so that the voltmeter needle on the temperature controller oscillates about some voltage between 0 and 80 volts. This voltmeter measures the voltage being supplied to the single finned strip heater. To determine the proper settings of the temperature controller knobs, a Thermo-Electric Free Potentiometer (Type 3589-R), accurate to 0.1 microvolt, was employed. Use of this high accuracy potentiometer permitted measurement of the temperature to 0.004°F. For the 100°F level of operation, coarse and fine settings of E and 5.278, respectively, are required. The gain knob is set at the highest value possible, which will still permit oscillation of the voltmeter needle about some voltage. A setting of 4.6 was employed. The reduction of the manual powerstat knob setting to 75 volts completes the adjustments necessary to establish isothermal bath conditions at 100°F. The bath temperature was found to fluctuate about the 100°F level with a maximum deviation of only 0.04°F.

Mercury Screw Pump

Before the screw pump may be used, the height of the mercury level must be fixed in the feed tube leading to the bottom of the thermostat. To accomplish this, valves C, D and H are opened, thus exposing the mercury in the reservoir and in the tubing to ambient pressure. Valves K and J are opened.

Then the screw pump chamber is completely filled with mercury by rotating the handle counter-clockwise until the piston reaches the back of the chamber. Valve K is now closed, preparing the pump for use. The above procedure is repeated after every injection.

During the course of an injection, it is necessary twice to refill the pump chamber. At the point where the piston has been completely driven into the chamber, there is usually a substantial pressure present in the pump. To remove this pressure, valve J is closed, and the piston is withdrawn until the pressure drops to 0 psig. Valve K is opened. Withdrawal of the piston by the counter-clockwise turning of the pump handle causes the mercury to flow from the reservoir into the chamber, thereby filling it. When the piston withdrawal is complete, valve K is closed and a pressure developed in the chamber equal to the feed line pressure before valve J is opened. During the period when the mercury level is collapsed out of the bombs, the emptying of the pump chamber follows a similar procedure as above, only in reverse. During this withdrawal period, the pump occasionally will vibrate due to friction between the piston and the chamber wall. Rotating the pump handle in the clockwise direction for a half turn usually eliminates this problem.

Diaphragm Gas Compressor

The compressor is employed to increase the solvent pressure from 200 psig up to a maximum of 10,000 psig. For this study, the compressor was never used at pressures greater than 5,250 psig. Compressed air is used as the motive force in driving the compressor. It is supplied to the compressor, at a maximum pressure of 175 psig, via a 3/4" pipe line. A pressure regulator mounted on the compressed air feed line prevents more than 100 psig pressure air from being delivered to the compressor. At no time should the compressed air delivered to the compressor exceed 100 psig in pressure.

A knockout drum is mounted on the compressed air line before the compressor inlet and serves to prevent condensed water from entering the compressor. This drum is provided with a valve located near its bottom to permit drainage of accumulated water.

The operation of the compressor is straight-forward. First, the pressure regulator of the solvent gas is set to deliver gas to the compressor inlet at 200 psig pressure. Valve L is then opened, thus exposing the compressor to the 100 psig air. The compressor will then compress the solvent up to a maximum of 10,000 psig. To stop the compressor at the desired pressure, valve L is closed. Leaving the compressor exposed to the 200 psig pressure solvent gas will not cause it any damage.

Experimental Procedure

1. The thermostat is allowed to come to thermal equilibrium at the desired temperature of operation. Usually two hours are required.
2. Valves D, C and H are opened. The mercury screw pump is entirely filled with mercury. The handle is turned clockwise, as valve J is simultaneously opened. After a few turns, valve K is opened. The mercury level is now located about 9" from the bottom of the thermostat. Valve K is closed, thereby sealing off the mercury reservoir.

3. All the valves, except E, F, H, K, L and I, are opened. The vacuum pump is then started and allowed to run for about ten minutes. The Heise gauge is zeroed.

4. Valve G is closed and the vacuum pump turned off. Hereafter, step 3 will be repeated any time the system is evacuated. Normal evacuation time is about 10 minutes.

5. The pressure regulator on the methane cylinder is set to deliver 200 psig pressure gas to the diaphragm compressor.

6. Valve F is opened, thus filling the system with methane at a pressure of 175 psia.

7. The diaphragm compressor is started by opening valve L to a setting so that air at 100 psig is delivered to the compressor. This pressure is read from the gauge mounted on the compressor. The compressor is permitted to run until the desired pressure in the main bomb is reached, as indicated by the Heise gauge.

8. Valves L and then F are closed. Valve M, on the solvent pressure regulator, is closed.

9. When thermal equilibrium of the gas in the bomb system is obtained, as evidenced by an invariant Heise gauge reading, valves A and B are closed, thereby sealing off the main bomb and capacitor. Usually 30 minutes are required to reach equilibrium.

10. The pressure of the main bomb, as indicated on the Heise gauge, is recorded.

11. The transducer is zeroed. A reading is taken five minutes later. If this reading is different from the zero point, then thermal equilibrium was not attained. Open valves A and B, and wait 15

minutes more. Repeat steps 9 through 11 until an invariant zero point is attained.

12. Valve F is opened. Valve H is slowly opened until the system pressure reaches 15 psia.
13. Valve G is opened, the vacuum pump turned on, thereby evacuating both the exposed tubing system and the burette. Valve G is closed and the vacuum pump turned off. The Heise gauge should read zero.
14. Valve C is closed. The screw pump is now incorporated to fill the burette with mercury. About 90 rotations are necessary to make electrical contact at low pressures. Eighty to 85 rotations are necessary to make contact at high pressures.
15. Once the mercury column has reached the closed valve A, the pressure, as seen on the screw pump pressure gauge, will develop very rapidly. (If it does not, then the burette was not properly evacuated, and steps 13 and 14 must be repeated). The handle is then backed off by a one-half rotation. The zero point of the transducer is checked. It should be invariant.
16. Valve A is opened slightly and the mercury column <u>very carefully</u> driven to make electrical contact with the electrode. Contact is established when the main bomb light lights up. Because the valve is almost closed, the mercury must squeeze by the valve stem, thus forcing any gas trapped inside the valve to be displaced into the main bomb.
17. The screw pump handle and the handle of valve A must be simultaneously manipulated so that with valve A completely closed,

the mercury column is just barely touching the bottom tip of the electrode. If this precaution is not observed, the tip of the stem of valve A will displace the mercury upwards past the tip of the electrode. A mercury slug is now located between the electrode and the closed valve A.

18. A transducer reading is taken, once equilibrium has been attained. At low pressures a steady state reading requires about five minutes; at high pressures, about thirty minutes are required.

19. Since this reading is the basis for all ΔP values, extreme care must be given in order that this value may be reproduced in subsequent pumpings up. To accomplish this, valve A is opened and the screw handle rotated counter-clockwise for 15 rotations. The handle is now rotated clockwise until electrical contact is made. Step 17 is repeated.

20. Two thousand psig is developed in the screw pump. The handle is then rotated 180° counter-clockwise. This decrease in pressure is a measure of how much gas is trapped below the closed valve A. This pressure drop is recorded next to the transducer reading of step 18. Steps 19 and 20 are repeated until identical transducer readings are obtained.

21. The mercury column is now slowly collapsed out of the burette by rotating the screw handle counter-clockwise. Two emptyings of the pump chamber are required. By counting turns it is possible to know when the mercury column has returned to its original level.

22. Valve H is opened, valve D closed, and then valve C opened. This procedure causes the mercury slug, located in the tubing leg between valves C and D, to flow down. Valve D is opened. Valve H is closed and the burette evacuated via the vacuum pump.
23. The solute is introduced into the burette by first setting the desired pressure on the pressure regulator located on the solute sample bomb, and then opening valve E.
24. A rinsing technique is employed to remove any trace quantities of methane that might have remained in the burette. The burette is filled with the solute gas to about a 100 psig pressure. Valve H is opened, thus passing the gas to the hood. The system is evacuated. This technique is repeated three times before the burette is filled for an injection.
25. The pressure of the solute in the burette is recorded, as indicated on the Heise gauge. If the sample pressure is less than 60 psig, then valve I is opened and the pressure read from the low pressure gauge. Readings should not be taken until after thermal equilibrium has been attained.
26. Valve D is closed. Valve H is opened until all the solute pressure is expended. Valve I is closed, if it was opened. The tubing system is evacuated via the vacuum pump.
27. Valve C is closed.
28. The screw pump is now incorporated to drive a mercury column to below valves D and C.
29. A pressure about 200 psi greater than the burette pressure is developed in the screw pump. Valve D is opened. The screw pump

is now used to introduce about 10 cc of mercury into the burette. This may be estimated by displacing one cylinder full of mercury from its 10 cc chamber.

30. A check is made on the transducer's reading. It should be invariant.

31. Valve A is slowly opened, thus allowing the methane to rush into the burette. It will be noted that the main bomb light will be extinguished as the mercury slug between the electrode and valve A is driven into the burette.

32. The mercury screw pump is now employed very carefully to drive the mercury level up to the bottom of the main bomb, thereby re-establishing electrical contact with the electrode and lighting the main bomb light bulb.

33. Steps 17 to 22 are repeated. During a run, the main bomb and probe thermocouples should indicate the same temperature. Readings should not be taken until they do.

34. Another aliquot sample of ethane is prepared by opening valve D, thus filling the burette with ethane. Introducing ethane into the main bomb mixture employs the same procedure as introducing it into the pure methane initially present in the main bomb. Steps 23 to 33 are repeated for each injection. Usually three injections are required for a run.

35. Once all the injections have been completed, it is necessary to remove the mercury slug from between the electrode and valve A. The mercury column is pumped to below valve A, the valve opened, and then the column collapsed by the counter-clockwise turning

of the handle for ten slow revolutions. Valve A is closed.

36. The mercury column is collapsed to below the thermostat.

37. Valve D is closed. A pressure is developed in the tubing system 50 psi greater than the pressure reading on the screw pump gauge.

38. Valve C is opened, thereby causing the mercury slug in the tubing leg to flow down. Valve D is opened. Step 2 is repeated.

39. To empty the bombs, a pressure is developed in the feed manifold via the gas compressor equal to the initial pressure in the main bomb. Valves A and B are opened. The emptying procedure is completed by opening valve H and releasing all the gas to the hood.

CHAPTER IV

RESULTS AND DISCUSSION

Three independent quantities are required for the calculation of the partial volume, viz., the two pressure derivative terms, $\partial P/\partial n_1$ and $\partial P/\partial n_2$, and the specific volume term, v_2. The first two terms are evaluated experimentally. The volume term is calculated from the BWR equation (6). This Chapter is divided into three separate sections giving treatment to each of the above quantities.

Pressure Derivatives, $\partial P/\partial n$

The pressure derivatives express the rate of change of the pressure of the system due to injection of material at isothermal and isochoric conditions. Figures 9 and 10 show the increases in methane pressure due to respective injections of ethane and methane into methane. The initial methane pressure is used as a parameter. An examination of the curves generated shows that excellent consistency of data has been obtained, i.e., each set of data points defines a straight line which passes through the origin. This result experimentally justifies the approximation expressed in equation (5). The slope of these lines yields $\partial P/\partial n$ values pertaining to the value of the pressure parameter. Tables V and VI, respectively, present tabulations of the calculated values of $\partial P/\partial n$ for ethane and methane

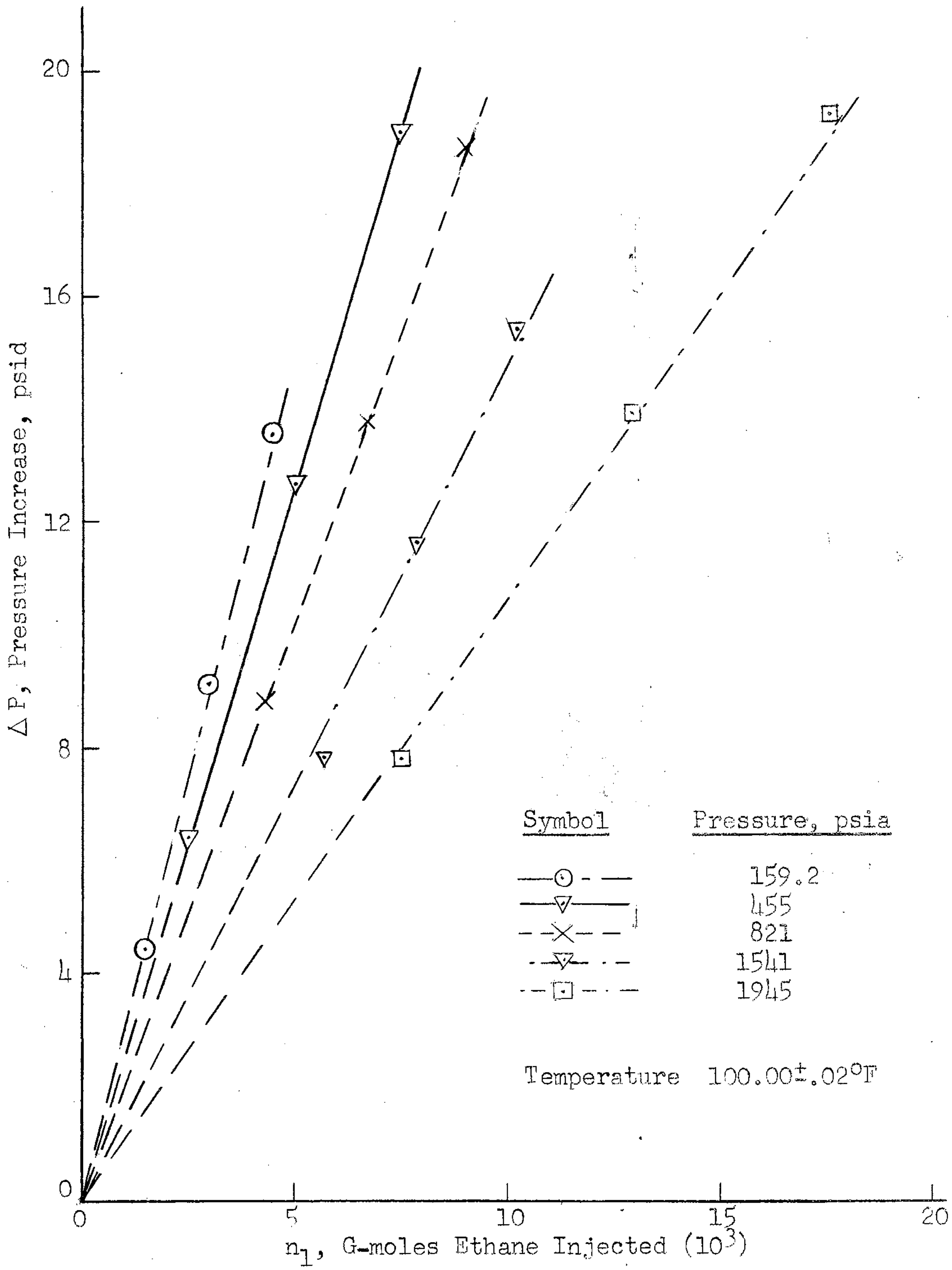

Figure 9. Ethane Injected Into Methane

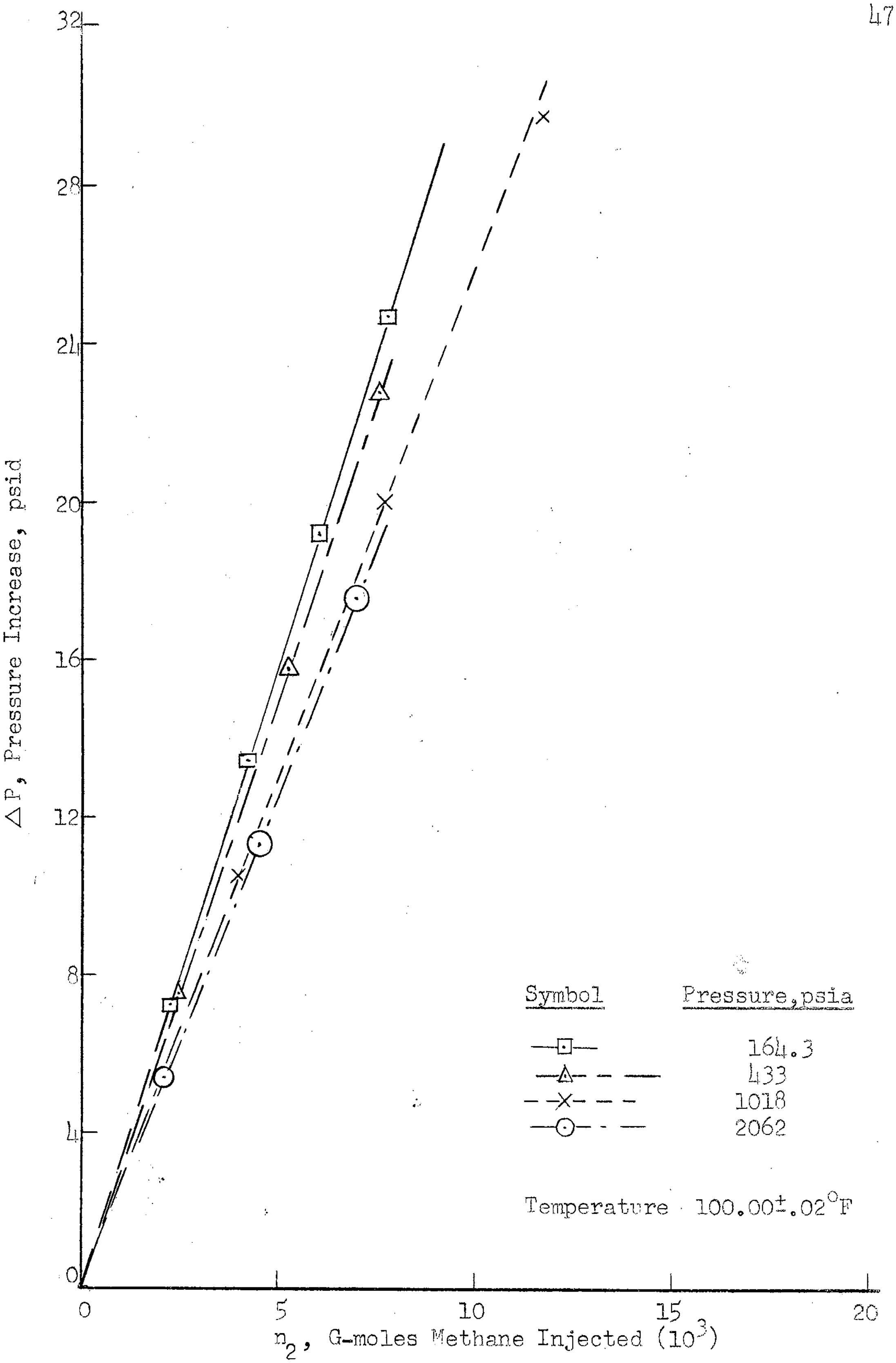

Figure 10. Methane Injected Into Methane

TABLE V

INJECTION OF ETHANE INTO METHANE
EXPERIMENTAL RESULTS
AT 100.00±.02°F

Run	Initial Methane Pressure psia	ΔP, psid	n_1, G-moles Injected(10^3)	$\frac{\Delta P}{n_1}$, $\frac{\text{psid}}{\text{mole}}$	Ave. Value $\frac{\partial P}{\partial n_1}$, $\frac{\text{psid}}{\text{mole}}$
21	159.2	4.500	1.47	3060	3060
		9.175	2.98	3080	
		13.568	4.46	3040	
25	1036	4.431	2.17	2040	2040
		8.702	4.26	2040	
		12.842	6.31	2040	
26	1541	7.894	5.66	1400	1460
		11.719	7.90	1480	
		15.481	10.27	1510	
28	1945	7.861	7.56	1040	1070
		13.924	12.98	1070	
		19.318	17.65	1100	
34	821	8.842	4.36	2030	2060
		13.882	6.71	2070	
		18.703	9.01	2080	
50	455	6.425	2.49	2580	2550
		12.729	5.01	2540	
		18.916	7.51	2520	
51	307	5.469	1.93	2830	2820
		11.123	3.93	2830	
		16.519	5.87	2810	

TABLE VI

INJECTION OF METHANE INTO METHANE
EXPERIMENTAL RESULTS
AT 100.00±.02°F

Run	Initial Methane Pressure, psia	△P,psid	n_2,G-moles Injected(10^3)	$\frac{\Delta P}{n_2}$, $\frac{\text{psid}}{\text{mole}}$	Ave. Value $\frac{\partial P}{\partial n_2}$, $\frac{\text{psid}}{\text{mole}}$
16	1018	5.420	2.11	2570	2530
		11.334	4.47	2540	
		17.442	7.00	2490	
36	433	7.523	2.50	3010	2990
		15.666	5.28	2970	
		22.786	7.60	3000	
37	1117	6.588	2.51	2620	2640
		14.057	5.31	2650	
		20.233	7.68	2640	
40	164.3	7.360	2.32	3170	3180
		13.482	4.23	3190	
		19.216	6.05	3180	
		24.770	7.81	3170	
41	2062	10.586	4.01	2640	2570
		20.002	7.74	2580	
		29.763	11.76	2530	
		39.315	15.66	2510	
42	1631	7.833	3.09	2540	2530
		15.334	6.07	2530	
		23.075	9.12	2530	
43	601	7.214	2.56	2820	2830
		13.516	4.77	2830	
		21.268	7.52	2830	
44	406	5.929	2.04	2910	2950
		12.411	4.14	3000	
		18.121	6.23	2910	
		23.832	8.00	2980	

TABLE VI (Continued)

Run	Initial Methane Pressure, psia	ΔP, psid	n_2, G-moles Injected(10^3)	$\frac{\Delta P,\text{psid}}{n_2\ \text{mole}}$	Ave. Value $\frac{\partial P,\text{psid}}{\partial n_2\ \text{mole}}$
45	830	5.778	2.18	2650	2670
		11.464	4.28	2680	
46	531	6.533	2.24	2920	2900
		12.557	4.39	2860	
		19.599	6.70	2930	
47	714	6.508	2.37	2750	2730
		12.361	4.57	2710	

versus pressure obtained from this ΔP versus n data.

Appendix B presents equations for $\partial P/\partial n_1$ and $\partial P/\partial n_2$ derived from the BWR equation. Table VII presents the quantities calculated from this equation which are required in the calculation of the partial volume and compressibility factor. Appendix C contains the IBM 1620 digital computer program which was used to perform the calculations.

Experimentally obtained values of $\partial P/\partial n$ and values calculated from the BWR equation of state are graphically presented in Figure 11 for comparison.

This figure shows that there is general agreement between the shapes of the experimental curves and the BWR curves. However, it will be noted that the experimental curve lies about 15% below the BWR curve. These discrepancies may be attributed to errors in the equation of state and the error in the measurement of ΔP caused by gas trapped inside the valve near the stem tip. Although the equation of state is fairly accurate in its description of pure components, it does not show a similar accuracy in its ability to describe mixtures. Any such inaccuracies are compounded by the method of calculation, i.e., the equation is first differentiated and then evaluated at the state of infinite dilution. This limiting condition places the greatest stress on the combining laws used for the calculation of constants in the equation. This last argument applies only to the $\partial P/\partial n_1$ curve which employed combining laws. The $\partial P/\partial n_2$ curve, however, was expected to be in better agreement with the corresponding experimental curve, for it describes a property of pure methane. The discrepancy between these curves may be due to the inability adequately to compensate for

TABLE VII

VALUES OBTAINED FROM THE BWR EQUATION OF STATE AT 100°F

Pressure, psia	$\frac{\partial P}{\partial n_1}, \frac{psid}{mole}$	$\frac{\partial P}{\partial n_2}, \frac{psid}{mole}$	v_2, l/mole	$\bar{v}_1$, l/mole	$\bar{Z}_1$
100	3340	3420	3.70	3.62	.968
200	3230	3380	1.84	1.75	.936
400	2950	3260	.901	.815	.871
600	2680	3130	.589	.504	.808
800	2450	3040	.433	.350	.746
1000	2230	2950	.341	.258	.688
1200	2040	2870	.279	.198	.634
1400	1890	2840	.236	.157	.587
1600	1760	2800	.204	.128	.547
1800	1680	2800	.179	.108	.517
2000	1640	2820	.160	.0930	.496

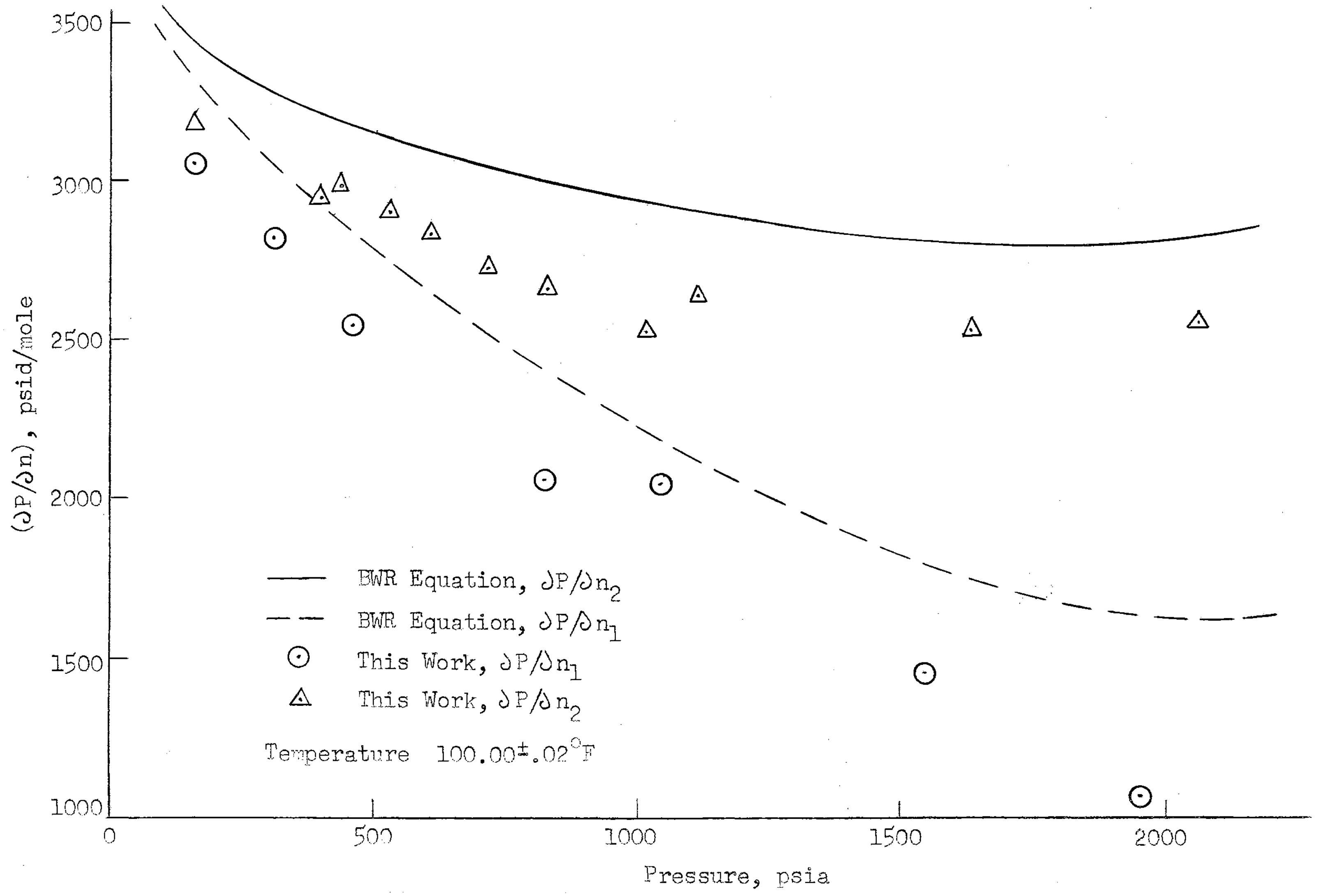

Figure 11. Comparison of Experimental Results to BWR Equation of State Values

the error caused by the trapped gas. A plot of ΔP_c versus pressure in Figure 16 shows that the scattering of points about the mean is roughly 10%. Such a difference could account for the discrepancy between the experimental and equation of state curves.

Specific Volume of Solvent

Figure 12 is a graph of the density of methane at 100°F versus pressure. This graph was obtained by the interpolation of specific volume data for methane as reported by Douslin. In his paper he listed specific volumes as parameters characterizing tabulated pressures at fixed isotherms. Deviations between the calculated pressures and the experimentally obtained pressures are tabulated. Unfortunately, experimental results are reported at temperatures of 30°C (86°F) and 50°C (122°F). Thus, it was necessary to use the BWR equation to calculate pressures at 37.78°C (100°F) pertaining to given values of the specific volumes. These calculated pressures were corrected to agree with experimentally obtained pressures by use of values of the tabulated pressure deviations interpolated to 100°F.

Partial Volume of Solute

For a given experimentally obtained value of $\partial P/\partial n_1$, values for $\partial P/\partial n_2$ and v_2, corresponding to the same pressure, were obtained from their respective curves in Figures 11 and 12. Substitution of these values into equation (4) permitted values for $\bar{v}_1$ to be calculated. Finally, values for $\bar{Z}_1$ were calculated by use of equation (6). Table VIII is a tabulation of these calculated results.

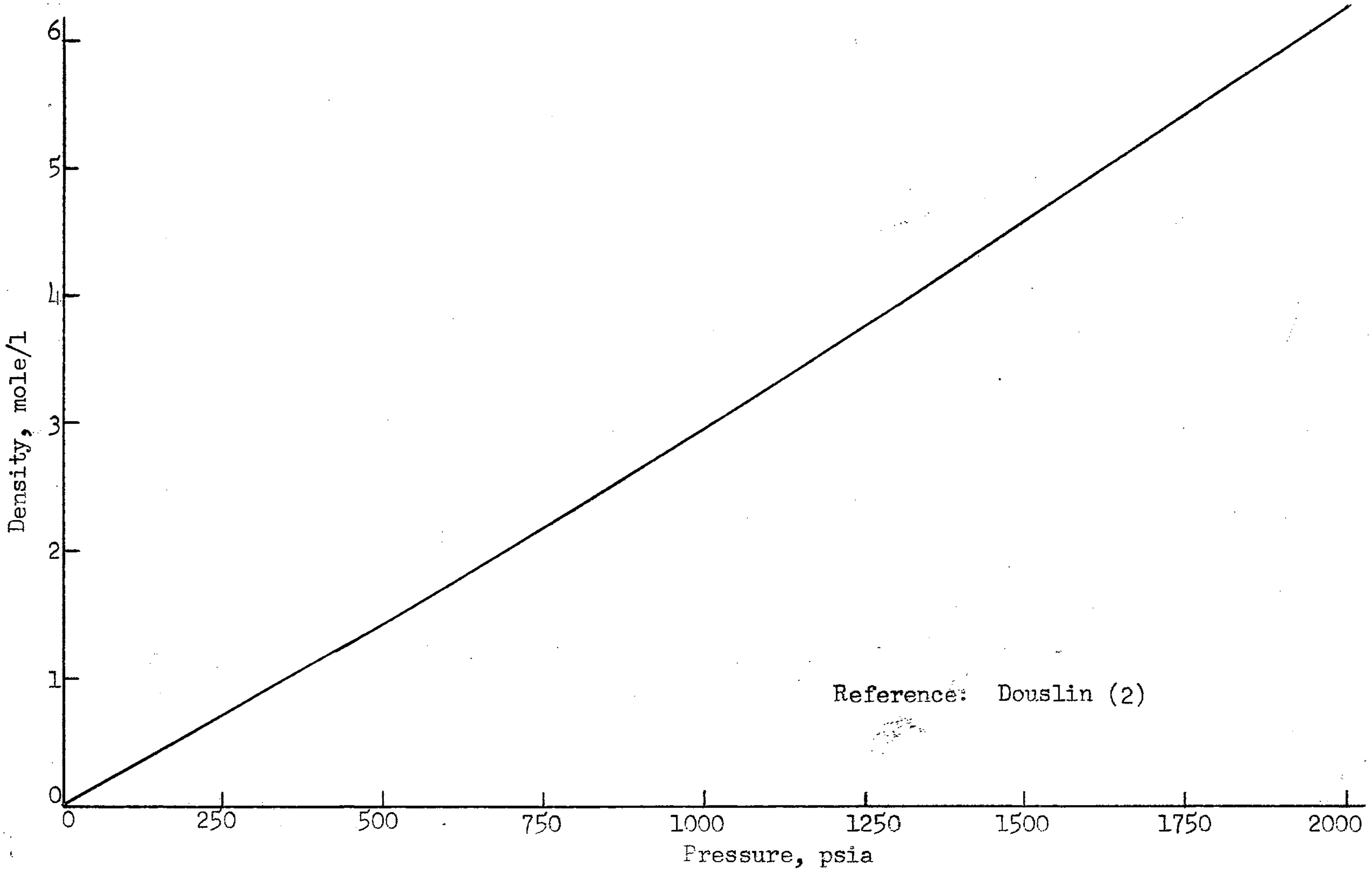

Figure 12. Density of Methane Versus Pressure at 100°F

TABLE VIII

PARTIAL VOLUMES AND COMPRESSIBILITY FACTORS OF ETHANE AT INFINITE DILUTION IN METHANE AT 100.00±.02°F

Pressure, psia	$\frac{\partial P}{\partial n_1}$, psid/mole	$\frac{\partial P}{\partial n_2}$, psid/mole	v_2, l/mole	$\bar{v}_1$, l/mole	$\bar{Z}_1$
159.2	3060	3180	2.312	2.23	.945
1036	2040	2580	.3269	.258	.715
1541	1460	2530	.2118	.122	.503
1945	1070	2660	.1647	.0665	.344
821	2060	2670	.4209	.324	.710
455	2550	2960	.7862	.677	.821
307	2820	3070	1.199	1.10	.902
1018	1900	2530	.3333	.251	.678
433	2590	2990	.8271	.716	.827
1117	1810	2640	.3013	.206	.615
164.3	3060	3180	2.2401	2.15	.943
2062	980	2570	.1548	.0614	.338
1631	1360	2530	.1992	.107	.466
601	2310	2830	.5869	.479	.768
406	2650	2950	.8850	.795	.861
830	2060	2670	.4163	.321	.711
531	2430	2900	.6689	.560	.793
714	2160	2730	.4892	.388	.737

In Figure 13, values of $\bar{v}_1$ are plotted versus pressure. Although there existed a large discrepancy between the experimental and BWR values for $\partial P/\partial n_1$ and $\partial P/\partial n_2$, these differences apparently cancel when the quotient of these partial derivatives is formed in the calculation of $\bar{v}_1$. Two references are provided for comparison, viz., the BWR equation and results based on literature values. The work involved in this latter reference was performed by Jee (7) and incorporated volumetric properties of ethane in the ethane-methane binary, as reported by Sage and Lacey. These references, however, are acceptable only as guideposts in defining the true values of $\bar{v}_1$. This conclusion is based on several observations. First, there is very poor agreement between the two references. Causes for inaccuracies in the BWR equation have already been discussed. The results obtained by Jee show considerable scattering of data points for the other isotherms and systems he investigated. This scattering was probably caused by extrapolation of data having an insufficient accuracy. Thus, his final results are not acceptable as being definitive.

Figure 14 is a plot of the values of $\bar{v}_1$ corrected for the trapped gas error versus values of $\bar{v}_1$ with the trapped gas error present. The average difference between corresponding values is small, thus showing that the method of calculation has a marked effect in canceling this error. The values of $\bar{v}_1$ are seen to have a greater accuracy than the values for $\partial P/\partial n$ when comparisons to the BWR and Jee's results are considered.

Figure 15 presents a plot of $\bar{Z}_1$ versus pressure. It is included in order to provide a complete presentation of the experimental re-

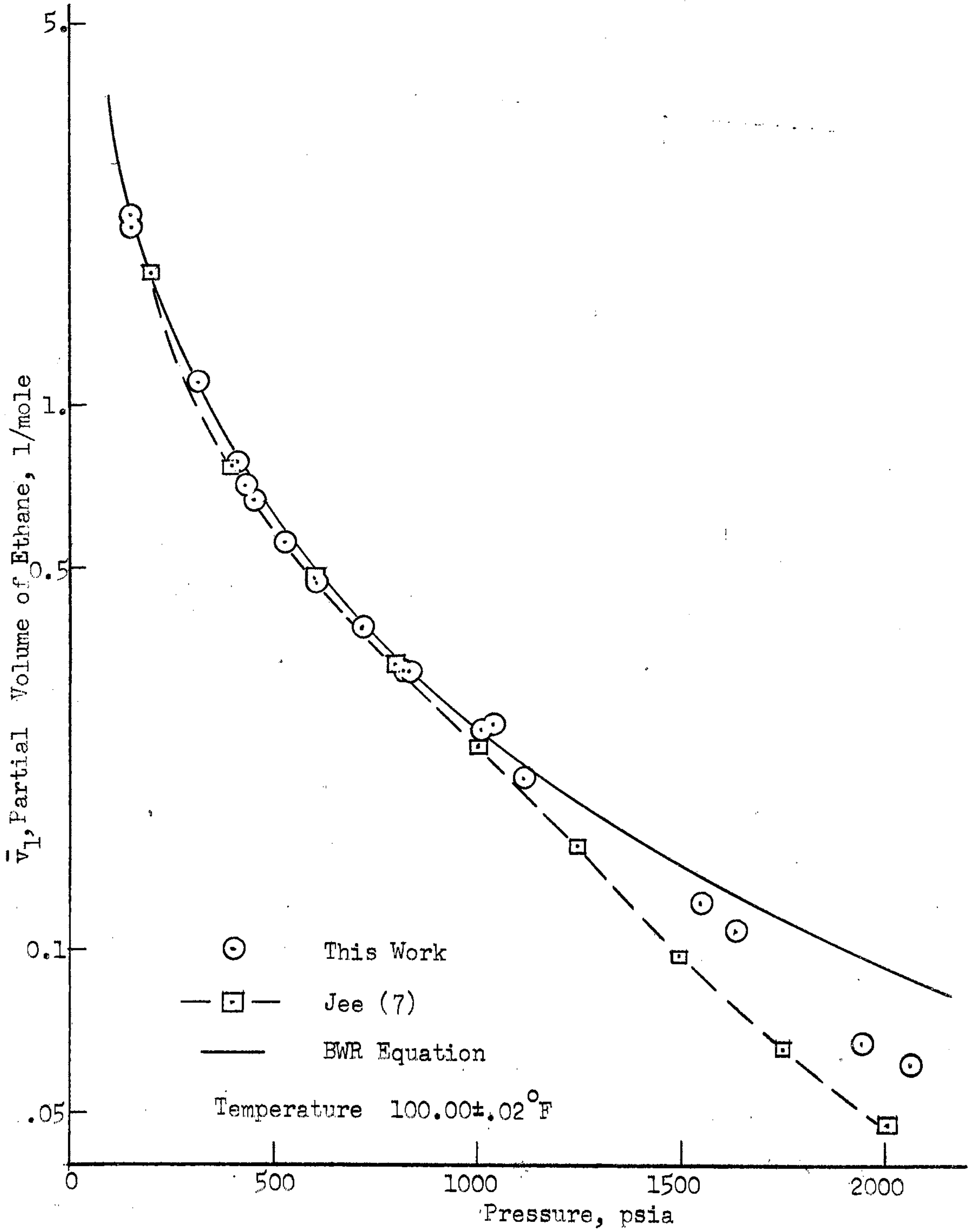

Figure 13. Partial Volumes of Ethane at Infinite Dilution in Methane at 100°F

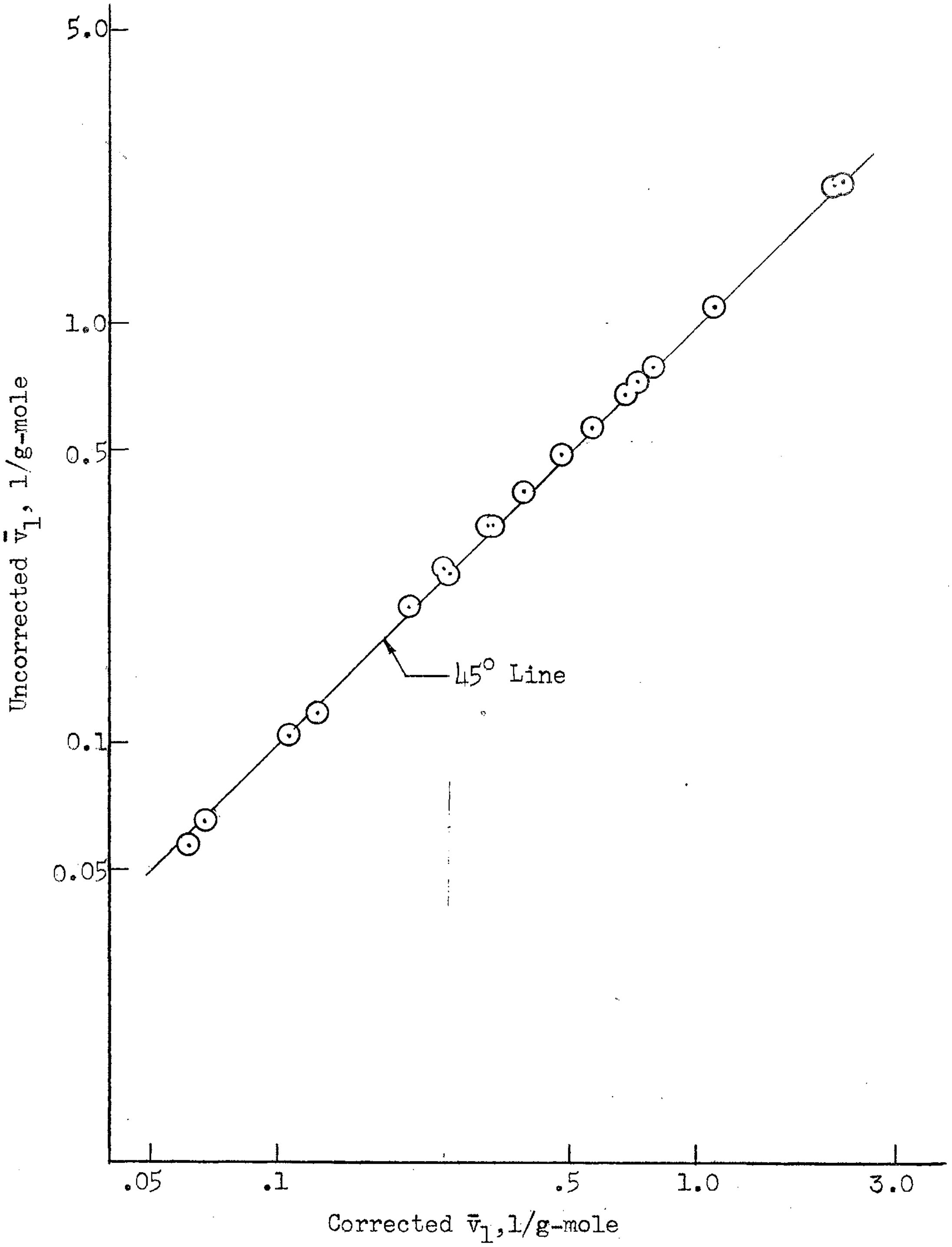

Figure 14. Effect of Trapped Gas Error on Partial Volumes

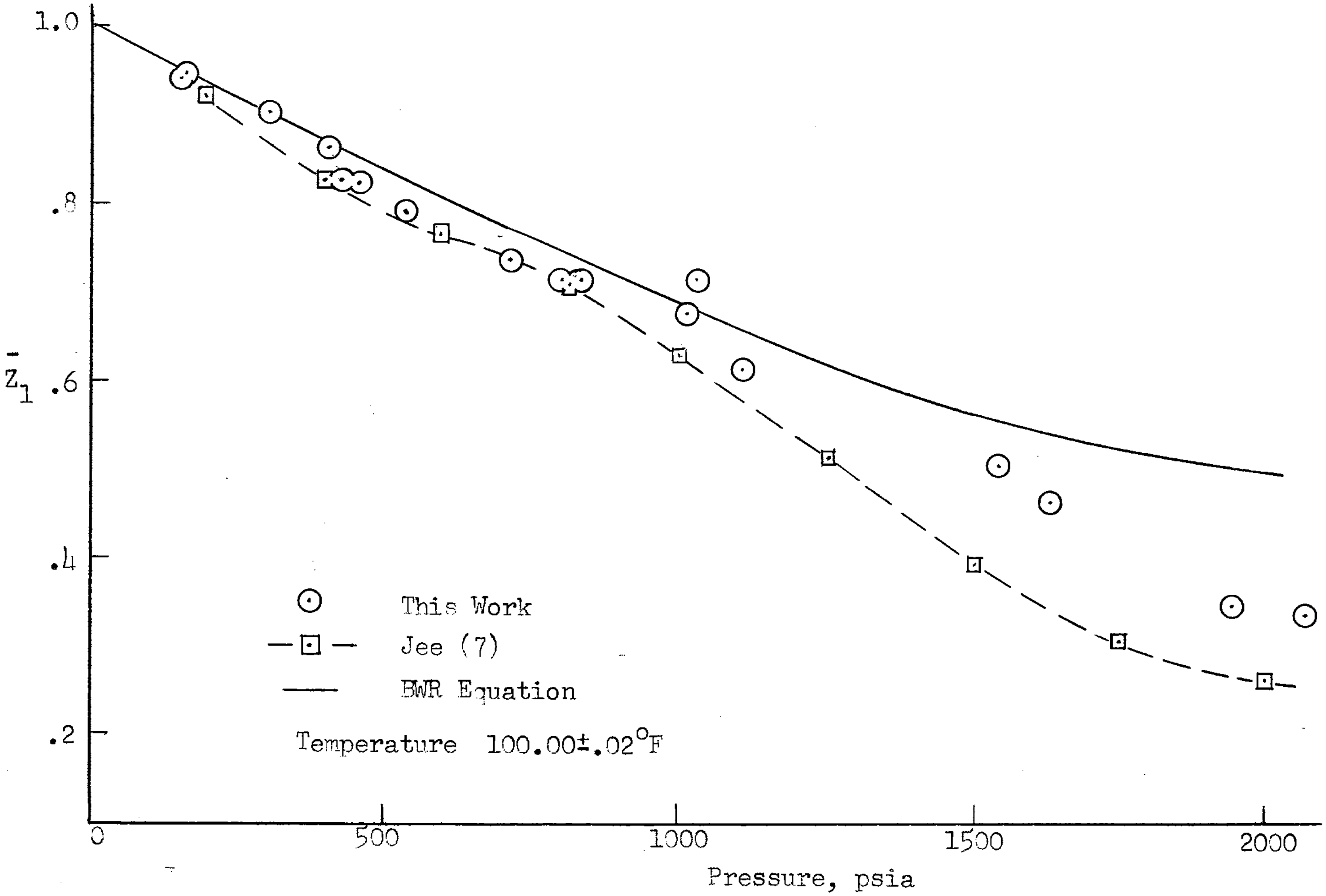

Figure 15. Ethane at Infinite Dilution in Methane

sults. The data points tend to follow the results obtained by Jee, more so than the BWR curve. Both the Jee points and the experimental data points demonstrate a point of inflection near the 600 psia pressure range. The BWR also shows this, but only to a slight degree. It is interesting to note that this point of inflection occurs near the critical pressure of ethane (710 psia).

CHAPTER V

ERROR ANALYSIS

An error analysis is presented to establish limits of accuracy for the calculated partial quantities and to point out the major sources of errors present in this experiment. The method employed for the calculation of errors is that developed by Beers (8). It describes the effect of independent and correlated errors on the dependent variable according to the equation:

$$\epsilon_y^2 = \sum_{i=1}^{m} \left(\frac{\partial y}{\partial x} \epsilon_{x_i} \right)^2 \qquad (11)$$

where the correlating equation is given by:

$$y = y(x_1, x_2, \cdots, x_m)$$

All sources of error in this experiment are assumed to be independent. The correlating equation used to calculate the effect on $\bar{v}_1$ due to experimental errors is:

$$\bar{V}_1 = V_2 \cdot \frac{(\partial P/\partial n_1)_{T,V,n_2}}{(\partial P/\partial n_2)_{T,V,n_1}} \qquad (4)$$

An application of Beers' method to equation (4) yields:

$$\epsilon_{\bar{V}_1}^2 = \left[\frac{\partial \bar{V}_1}{\partial(\partial P/\partial n_1)} \right]^2 \epsilon_{\partial P/\partial n_1}^2 + \left[\frac{\partial \bar{V}_1}{\partial(\partial P/\partial n_2)} \right]^2 \epsilon_{\partial P/\partial n_2}^2$$

$$+ \left[\frac{\partial \bar{V}_1}{\partial V_2} \right]^2 \epsilon_{V_2}^2$$

Proper substitution of the differentiated quantities of equation (4) into equation (12) yields:

$$\epsilon_{\bar{V}_1}^2 = \bar{V}_1^2 \left[\left(\frac{\epsilon_{\partial P/\partial n_1}}{\partial P/\partial n_1} \right)^2 + \left(\frac{\epsilon_{\partial P/\partial n_2}}{\partial P/\partial n_2} \right)^2 + \left(\frac{\epsilon_{V_2}}{V_2} \right)^2 \right] \qquad (13)$$

Estimation of the error terms in the right-hand side of equation (13) will be presented in outline form. A summary of this outline is presented in Table IX. The following discussion employs the same format as that of Table IX.

I. Error in $(\partial P/\partial n_1)$ and $(\partial P/\partial n_2)$

The evaluation of $(\partial P/\partial n_1)$ is based on the approximation set forth in equation (5), viz.:

$$\lim_{n_1 \to 0} (\partial P/\partial n_1) = \Delta P/n_1 \qquad (14)$$

A. Error in n_1 and n_2

Values for n_1 and n_2 were experimentally obtained from measurements of the pressure of the respective gas in the ethane burette. The volume of the burette was known from calibration and the temperature fixed at 100°F for all runs. Specific volumes for the gases were obtained from the literature. In order to estimate the error in the values of n_1 and n_2, the following equation is used:

$$PV = ZnRT \qquad (15)$$

Consider first the error present in the values for n_1. Equation (15) may be solved for n_1 to yield:

$$n_1 = PV_1/Z_1RT \qquad (16)$$

Manipulation of equation (16) in accordance with equation (11) yields:

TABLE IX

SOURCES OF EXPERIMENTAL ERROR

- I. Error in $(\partial P/\partial n_1)$ and $(\partial P/\partial n_2)$
  - A. Error in n_1
  - B. Error in ΔP for a single injection
    - 1. Transducer
      - a. K varies with line pressure
      - b. K varies with differential pressure
      - c. Input voltage
      - d. Zero and sensitivity shift
    - 2. Potentiometer
      - a. Readings
      - b. Accuracy
    - 3. Non-mechanical errors
      - a. Temperature fluctuations
      - b. Non-mixing of the solute and solvent
      - c. Reproducibility of main bomb volume
      - d. Gas trapped in valve A
  - C. Error in $\partial P/\partial n_1$ and $\partial P/\partial n_2$
- II. Error in v_2

$$\epsilon_{n_1}^2 = n_1^2 \left[\left(\frac{\epsilon_P}{P}\right)^2 + \left(\frac{\epsilon_{V_1}}{V_1}\right)^2 + \left(\frac{\epsilon_Z}{Z}\right)^2 + \left(\frac{\epsilon_T}{T}\right)^2 \right] \tag{17}$$

Typical values for the variables in equation (17) are:

$P=45$ psia
$V_1=21.590$ ml
$T=560^{\circ}R$

The value for ϵ_P is equated to the sum of the error in reading the low range pressure gauge (.1 psi) and the error possible from calibration of this gauge (.1 psi). Thus $\epsilon_P=0.2$ psi. The error in the temperature, ϵ_T, is due to fluctuations in the burette temperature ($0.03^{\circ}F$) and error in calibration of the probe thermocouple ($0.04^{\circ}F$). Thus $\epsilon_T = 0.07^{\circ}F$. The error in the volume, ϵ_{V_1}, is due to inaccuracies in the calibration (0.024ml) and a change in the volume due to possible mercury and grease contamination of the burette's wall (estimated as 0.05ml). The calibration error (0.024ml) represents the value of the standard deviation from the mean of the volume (21.590 ml). Thus ϵ_{V_1} = 0.074 ml. The accuracy of the literature values used is reflected in the accuracy of Z_1. Sage and Lacey estimate the accuracy of their work to be 0.1%. Thus $\epsilon_Z = 0.001Z$. Substitution of these quantities into equation (17) yields:

$$\epsilon_{n_1} = 0.0047n_1$$

Since the experimental determination of the values for n_1 and n_2 employs the same method, and values of Z_2 are known to 0.03% from Douslin's work, then it is safe to assign a similar error to n_2, viz.:

$$\epsilon_{n_2}=0.0047n_2$$

B. Error in ΔP for a single injection

1. Transducer Errors

To complete the error analysis of $\partial P/\partial n$, considerations must also be given to the errors present in ΔP. The relationship between the transducer's output and the differential pressure applied across it may be expressed as:

$$\Delta P = K\Delta \text{emf} \qquad (18)$$

The relationship of the transducer sensitivity, K, to the line pressure and the differential pressure was obtained by calibration. There are two sources of error in the K value:

a. The value of K is dependent on the line pressure.

b. At a given line pressure, the transducer is not linear in the 0 to 200 psid differential range.

The first source of error does not have any effect on the calculation of $\bar{v}_1$. This fact becomes apparent when equations (14) and (18) are substituted into equation (4), thus yielding:

$$\bar{V}_1 = \lim_{n_1 \to 0} \left[V_2 \frac{(K\Delta \text{emf})_1/n_1}{(K\Delta \text{emf})_2/n_2} \right]$$

or

$$\bar{v}_1 = \lim_{n_1 \to 0} \left[v_2 \frac{(\Delta\,\mathrm{emf})_1 / n_1}{(\Delta\,\mathrm{emf})_2 / n_2} \right] \qquad (19)$$

Equation (19) shows that $\bar{v}_1$ is independent of the variation of K with line pressure. The second source of error in K creates a small error in calculation of the differential pressures. Calibration of the transducer showed that the average deviation of K due to non-linearity over the 200 psid differential pressure range at line pressures up to 2,000 psia is only 0.003 psi/mv. Thus $\epsilon_K = 0.003$ psi/mv.

Other inaccuracies in the transducer which could lead to error in the ΔP term are:

c. Deviation of the input voltage from the specified 10.0 volts.

d. Zero and sensitivity shifts due to temperature change.

The input voltage was measured by use of the resistor circuit. Figure 4 contains a wiring schematic of the resistor circuit. The resistance of the eight feet of 18 gauge connecting wire is assumed to be zero. From Ohm's Law we have:

$$i = E_t/(R_1+R_1+R_2) \qquad (20)$$

Experimentally, the following magnitudes were used:

$E_t = 10$ v

$\Sigma R_1 = 2,000$ ohms

$R_2 = 10$ ohms

Substitution of these quantities into equation (20) yields:

$$i = 0.0049751 \text{ amps}$$

Since $$E_p = i\,\Sigma R_2 \qquad (21)$$

then $$E_p = 49.751 \text{ mv.}$$

Substitution of equation (20) into equation (11) will yield after algebraic manipulations:

$$\epsilon_i^2 = i^2 \left[\left(\frac{\epsilon_t}{E_t}\right)^2 + \left(\frac{\epsilon_{\Sigma R_1}}{\Sigma R_1}\right)^2 + \left(\frac{\epsilon_{R_2}}{R_2}\right)^2 \right] \qquad (22)$$

From the manufacturer's specifications on the resistors we have:

$$\epsilon_{\Sigma R_1} = .01\%\,\Sigma R_1$$

$$\epsilon_{R_2} = .005\%\,R_2$$

For this calculation $\epsilon_t = 0$. Substitution of these quantities into equation (22) yields:

$$\epsilon_i = .0001\,i$$

From equations (11) and (21) it may be shown that:

$$\epsilon_{E_p}^2 = E_p^2 \left[\left(\frac{\epsilon_i}{i}\right)^2 + \left(\frac{\epsilon_{R_2}}{R_2}\right)^2 \right] \qquad (23)$$

Substitution of the appropriate quantities into equation (23) yields:

$$\epsilon_{E_p} = 0.01\text{mv.}$$

Thus the input voltage may be accurately fixed to within 0.00001v. Since the manufacture specifications for the transducer only require the input voltage to be accurate to within 0.1v, the error due to an inaccuracy in the input voltage is negligible.

The transducer is rated for a thermal zero shift of -0.006%FR/$^{\circ}$F and a thermal sensitivity shift of -0.001%FR/$^{\circ}$F. Experimentally, the transducer was not zeroed until thermal equilibrium has been attained in the thermostat. Thus, bath temperature fluctuations of 0.04°F were not great enough to cause a significant error in transducer readings due to thermal zero and sensitivity shifts.

2. Potentiometer Errors

Measurement of the Δemf term in equation (18) was experimentally accomplished by a Leeds and Northrup potentiometer accurate to 0.001 mv. The potentiometer was found to be so sensitive to the transducer output voltage that a change of 0.001 mv in the potentiometer setting caused its null galvanometer to deflect. Assuming the potentiometer to be 100% accurate, the only source of error in the Δemf term is due to inaccuracies in reading the dials. Such reasoning places the value of $\epsilon_{\Delta emf}$ at 0.002mv.

3. Non-mechanical Errors

Non-mechanical sources of error which also influence the accuracy of ΔP are:

a. Bath temperature fluctuations
b. Non-mixing of the solute and solvent
c. Reproducibility of main bomb volume
d. Gas trapped in valve A

The error due to bath temperature fluctuations may be roughly estimated from a difference equation of the ideal gas law, viz.:

$$\frac{\Delta P}{\Delta T} = \frac{P}{T}$$

or

$$\epsilon_{\Delta P, T} = \frac{P}{T}\Delta T \qquad (24)$$

From experimental measurement, ΔT may be assigned the value of 0.02°F in the main bomb. The temperature of operations is 560°F. Substitution of these quantities into equation (24) yields:

$$\epsilon_{\Delta P, T} = 3.57 \times 10^{-5} P \qquad (25)$$

Errors in ΔP due to non-mixing of the solute and the solvent were reduced to a negligible magnitude by the experimental procedure of pumping the mercury up and down in the burette (thereby mixing the gases), and the long period of time allowed for diffusion of the gases in the bomb. No experimental measurements were taken until invariant transducer emf readings were observed.

The error in ΔP caused by a change in volume of the main bomb due to inaccuracies of the mercury column in making exact electrical contact with the electrode are assumed to be negligible. This assumption is based on the precautions described in step 17 of the experimental procedure.

An estimate of the error in ΔP, due to the gas trapped in valve A, may be obtained from the experimental data.

Following steps 18 to 20 in the experimental procedure yielded a set of Δemf readings for each injection. In the first pumping up, no gas was trapped in the valve because the burette had been evacuated, and the initial emf reading therefore represented an emf value without the error due to the trapped gas. Subsequent pumpings up, in accordance with steps 19 and 20, yielded decreasing values of emf which finally assumed a fixed value. At this point the dead volume of the valve had been filled with trapped gas. The difference in emfs between the initial emf and the fixed value of the decreased emf provided a measure of the error in ΔP due to the trapped gas. Table X contains a tabulation of this ΔP versus main bomb pressure data. Figure 16 is a graph of these data. The standard deviation of these points from the mean provides an estimate for ϵ_{tg} viz., .053 psi.

These four major sources of error may be combined to yield an estimate of the error in the ΔP term of equation (14). The working equation is:

$$\epsilon_{\Delta P}^2 = \left(\frac{\partial \Delta P}{\partial K}\epsilon_K\right)^2 + \left(\frac{\partial \Delta P}{\partial \Delta emf}\epsilon_{\Delta emf}\right)^2 + \left(\epsilon_{\Delta P,T}\right)^2 + \left(\epsilon_{tg}\right)^2$$

Substitution of equation (25) and the differentiated equation (14) into the above equation yields:

$$\epsilon_{\Delta P}^2 = \left(\frac{\Delta P}{K}\epsilon_K\right)^2 + \left(K\epsilon_{\Delta emf}\right)^2 + \left(3.57\times10^{-5}P\right)^2 + \left(\epsilon_{tg}\right)^2 \qquad (26)$$

TABLE X

CORRECTIVE VALUES FOR ΔP TO ACCOUNT FOR TRAPPED GAS

P, psia	Δemf_{error}, mv	ΔP_c, psid
165	.010	.049
304	.027	.131
451	.071	.344
527	.060	.291
596	.077	.374
708	.128	.621
824	.136	.660
995	.163	.790
1001	.132	.640
1620	.239	1.16

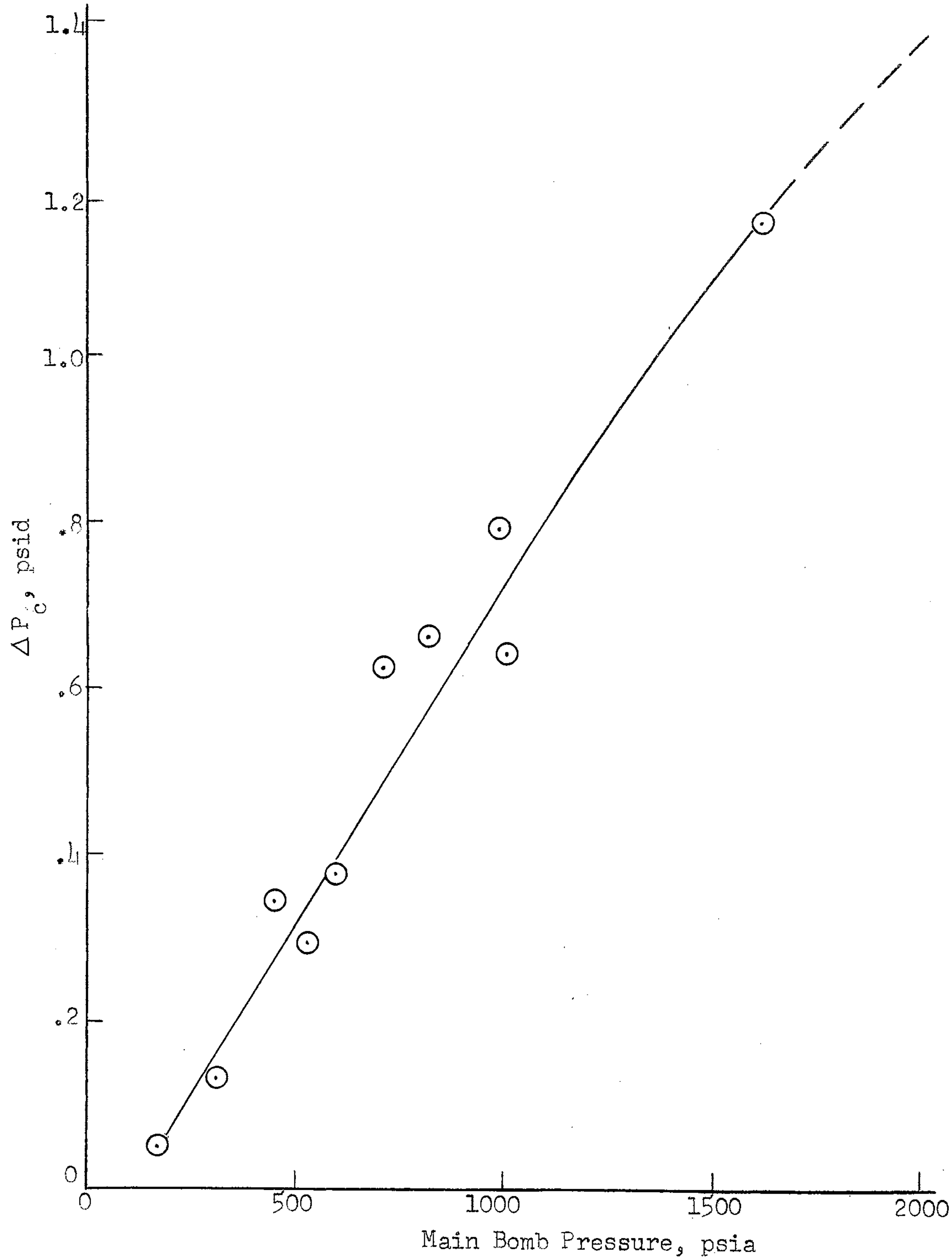

Figure 16. Corrective Terms for ΔP

Typical values for the unassigned quantities in equation (26) are:

$$\Delta P = 6 \text{ psid}$$

$$K = 4.85 \text{ psi/mv}$$

Substitution of these quantities into equation (26) yields:

$$\epsilon^2_{\Delta P} = .00284 + (3.6\text{x}10^{-5}P)^2$$

For $P = 200$ psia $\quad\quad \epsilon_{\Delta P} = .054$ psi

For $P = 2,000$ psia $\quad\quad \epsilon_{\Delta P} = .090$ psi

C. Error in $\partial P/\partial n_1$ and $\partial P/\partial n_2$

Usually three injections per run were made, thus yielding three ΔP versus n data points. The value of $\partial P/\partial n$ was taken as the arithmetic average of these points and was calculated according to:

$$\frac{\partial P}{\partial n} = \frac{1}{3}\left(\frac{\Delta P'}{n'} + \frac{\Delta P''}{n''} + \frac{\Delta P'''}{n'''}\right) \qquad (27)$$

An application of equation (11) to equation (27) with subsequent substitutions of equation (27) yields:

$$\epsilon^2_{\partial P/\partial n} = \frac{1}{9}\left[\left(\frac{\epsilon_{\Delta P'}}{n'}\right)^2 + \left(\frac{\epsilon_{\Delta P''}}{n''}\right)^2 + \left(\frac{\epsilon_{\Delta P'''}}{n'''}\right)^2 + \left(\frac{\Delta P'}{n'^2}\epsilon_{n'}\right)^2 + \left(\frac{\Delta P''}{n''^2}\epsilon_{n''}\right)^2 + \left(\frac{\Delta P'''}{n'''^2}\epsilon_{n'''}\right)^2\right] \qquad (28)$$

The following values were obtained from Run 21:

$\Delta P' = 4.50$ psid $\quad\quad n' = 1.47\text{x}10^{-3}$ g-moles

$\Delta P'' = 9.18$ psid $\quad\quad n'' = 2.98\text{x}10^{-3}$ g-moles

$\Delta P''' = 13.57$ psid $\quad\quad n''' = 4.46\text{x}10^{-3}$ g-moles

The associated error terms are:

$\epsilon_{\Delta P'} = .054$ psi $\qquad \epsilon_{n'} = .0047n'$

$\epsilon_{\Delta P''} = .108$ psi $\qquad \epsilon_{n''} = .0094n''$

$\epsilon_{\Delta P'''} = .162$ psi $\qquad \epsilon_{n'''} = .0141n'''$

Substitution of these values into equation (28) yields:

$$\epsilon_{\partial P/\partial n_1} = 27.6 \text{ psi/g-mole at } 159.2 \text{ psia}$$

A value at the highest pressure may be obtained from Run 28, viz.:

$$\epsilon_{\partial P/\partial n_1} = 11.2 \text{ psi/g-mole at } 1945 \text{ psia}$$

Similar considerations applied to $\partial P/\partial n_2$ yield for Runs 40 and 41 respectively:

$$\epsilon_{\partial P/\partial n_2} = 23.6 \text{ psi/g-mole at } 164.3 \text{ psia}$$

$$\epsilon_{\partial P/\partial n_2} = 19.9 \text{ psi/g-mole at } 2062 \text{ psia}$$

II. Error in v_2

The error in v_2 is easily ascertained by comparison of the values computed by the BWR equation to the values experimentally obtained by Douslin. He estimates the error in his specific volume data to range from 0.03% at the lowest temperature and pressure (32°F, 240 psia) to 0.2% at the highest temperature and pressure (662°F, 4570 psia). Thus, it seems conservative to assign an average accuracy of 0.1% to values used in the 100°F, 160 to 2,000 psia range. The maximum deviation between values of v_2 calculated from the BWR and Douslin's experimental results is 0.03%. Thus, the per cent error in the v_2 value may be fixed at 0.13%. Hence:

$$\epsilon_{v_2} = .0013v_2$$

In order to calculate the effect of inaccuracies in experimental readings on the value of v_2, the following relationship is used:

$$v_2 = v'_2 \left(\frac{P'}{P}\right) \left(\frac{T}{T'}\right) \qquad (29)$$

The unprimed quantities refer to experimentally measured quantities, whereas the primed quantities refer to values pertaining to Douslin's work.

All the error in measurement of the temperature and pressure in Douslin's work is assumed to be zero. The v'_2 term is considered to contain all the error. Thus:

$$\epsilon_T = .02^\circ F$$

$$\epsilon_P = 2 \text{ psia}$$

Substitution of equation (29) into equation (11) yields:

$$\epsilon_{v_2}^2 = v_2^2 \left[\left(\frac{\epsilon_{v'_2}}{v'_2}\right)^2 + \left(\frac{\epsilon_P}{P}\right)^2 + \left(\frac{\epsilon_T}{T}\right)^2 \right] \qquad (30)$$

Substituting numerical values into equation (30) yields:

$$\epsilon_{v_2}^2 = v_2^{\,2}\left[1.7\text{x}10^{-6} + (2/P)^2\right] \qquad (31)$$

For P = 200 psia $\qquad \epsilon_{v_2} = .010\ v_2$

For P = 2000 psia $\qquad \epsilon_{v_2} = .0016 v_2$

III. Error in $\bar{v}_1$

The above work in parts I and II has assigned estimates to the error quantities in equation (13). Substitution of these values into equation (13) yields:

$$\epsilon_{\bar{v}_1} = 0.015\ \bar{v}_1 \text{ l/g-mole at 200 psia}$$

$$\epsilon_{\bar{v}_1} = 0.013\ \bar{v}_1 \text{ l/g-mole at 2,000 psia}$$

Thus, the error in the measurement of partial volumes is about 1.4%.

IV. Error in $\bar{Z}_1$

An estimate for the error present in the calculation of $\bar{Z}_1$ may be obtained by substituting equation (6) into equation (11), thereby obtaining:

$$\epsilon_{\bar{Z}_1}^2 = \bar{Z}_1^2 \left[\left(\frac{\epsilon_P}{P} \right)^2 + \left(\frac{\epsilon_{\bar{V}_1}}{\bar{V}_1} \right)^2 + \left(\frac{\epsilon_T}{T} \right)^2 \right] \tag{32}$$

The error in the gas constant is assumed to be zero. Estimates of the values for the error quantities in equation (32) have been previously fixed at:

$\epsilon_P = 2$ psi

$\epsilon_T = 0.02^\circ F$

$\epsilon_{\bar{V}_1} = 0.015\ \bar{v}_1$ l/g-mole at 200 psi

$\epsilon_{\bar{V}_1} = 0.013\ \bar{v}_1$ l/g-mole at 2,000 psi

Substitution of these values into equation (32) yields:

$\epsilon_{\bar{Z}_1} = 0.018\ \bar{Z}_1$ at 200 psi

$\epsilon_{\bar{Z}_1} = 0.013\ \bar{Z}_1$ at 2,000 psi

CHAPTER VI

RECOMMENDATIONS

The major source of error in the determination of the partial volume was due to the gas trapped in valve A. A reliable solution to this problem would be to replace valve A and possibly valve D with ball valves. Because of the construction of this type of valve, it would not be possible for any gas to be trapped inside.

Presuming the above problem to be eliminated, a second difficulty might be encountered, viz., a slug of mercury might remain in the tubing between valve A and the ethane burette when the mercury column is collapsed after a gas injection. This problem was not encountered in this work because the trapped gas should have forced all the mercury down from valve A, when the mercury was being withdrawn. The elimination of this mercury slug might be easily accomplished by the installation of a vibrator onto valve A. Just before the mercury column was to be collapsed, the vibrator would be activated, thereby causing all the mercury in this tube to fall out during the withdrawal phase.

The second largest source of error was due to the inability very accurately to measure the pressure of the solute in the ethane burette. A pressure gauge accurate to 0.01 psi would eliminate this bottleneck.

A stabilizing of the cooling water flow rate might give better temperature control. In this work, the source of the cooling water was a direct connection to a tap water valve. A more constant source would be provided by use of a water pump, which would be supplied from a large volume container.

Finally, if a vacuum pump with a larger capacity were employed, the evacuations could be performed more rapidly and with a greater efficiency.

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APPENDIX A

DIFFERENTIAL PRESSURE TRANSDUCER SPECIFICATIONS

Manufacturer: Consolidated Electrodynamic Corporation

Type: 4-351-0005

Pressure Range: ±200 psid

Serial No.: 2518

Test Temperature: +75°F

Compensated Temperature Range: -65°F to +250°F

Sensitivity: ±40.28 mv

Combined Non-linearity and Hysteresis: ±0.06% FR

Zero Shift: -0.006% FR/°F

Sensitivity Shift: -0.001% FR/°F

Input Resistance: 444 ohms across terminals +A and -D

Output Resistance: 351 ohms across terminals +B and -C

Rated Excitation: 10.0 vdc

APPENDIX B

DERIVATIONS FROM THE BWR EQUATION OF STATE

Evaluation of $\bar{v}_1$ via equation (4) required the partial differentiation of the BWR equation with respect to the number of moles. An expression of the equation is given by:

$$P = RT\rho + (B_0RT - A_0 - C_0/T^2)\rho^2 + (bRT - a)\rho^3 + a\alpha\rho^6 + c\rho^3\frac{(1+\gamma\rho^2)}{T^2}e^{-\gamma\rho^2} \qquad (33)$$

where the combining rules for the constants are given in the referenced paper (6).

Differentiation of equation (33) with respect to n_1 holding T, V and n_2 constant yields:

$$\begin{aligned} n_2\left(\frac{\partial P}{\partial n_1}\right)_{T,V,n_2} = {} & RT\rho_2 + (B_{0_1} + B_{0_2})RT\rho_2^2 - 2\sqrt{A_{0_1}A_{0_2}}\,\rho_2^2 \\ & - 2\sqrt{C_{0_1}C_{0_2}}\,\rho_2^2/T^2 - 3\rho_2^3(a_1a_2^2)^{1/3} \\ & + 3(a_1a_2^2)^{1/3}\alpha_2\rho_2^6 + 3a_2(\alpha_1\alpha_2^2)^{1/3}\rho_2^6 \\ & + \rho_2^3 e^{-\gamma_2\rho_2^2}\left[3c_1^{1/3}c_2^{2/3}(1+\gamma_2\rho_2^2) - \right. \\ & \left. 2c_2\rho_2^4\gamma_2\sqrt{\gamma_1\gamma_2}\right]/T^2 + 3\rho_2^3RT(b_1b_2^2)^{1/3} \end{aligned} \qquad (34)$$

In the computer program employed to calculate $\bar{v}_1$, the constants of species one were equated to the constants of species two. Such a process caused the right-hand side of equation (34) to equal $n_2 \cdot (\partial P/\partial n_2)_{T,V,n_1}$. The quotient of these partials, multiplied by the value of v_2 (also calculated by the BWR), yielded the desired value of $\bar{v}_1$. Table B-1 tabulates the values of the constants employed. The methane constants were obtained from Douslin's work. The ethane constants were obtained from a monograph on API Research Project 37 (9).

TABLE B-1

BWR EQUATION PARAMETERS USED IN EQUATIONS (33) AND (34)

Coefficient	Methane	Ethane
B_o $(ft^3/lb\ mole)$	.728158	.237507
A_o $(psi)(cu.ft)^2/lb\ mole^2$	6782.0481	7001.40
C_o $(psi)(^oR)^2(cu.ft)^2/lb\ mole^2(10^{-6})$	388.900	3334.26
b $(cu.ft)^2/lb\ mole^2$	.64655049	3.43107
a $(psi)(cu.ft)^3/lb\ mole^3$	2627.880	26547.9
c $(psi)(^oR)^2(cu.ft)^3/lb\ mole^3(10^{-6})$	701.92373	6476.86
α $(cu.ft)^3/lb\ mole^3$	1.3559120	.742830
γ $(cu.ft)^2/lb\ mole^2$	2.6936076	2.5000

APPENDIX C

COMPUTER PROGRAM TO CALCULATE PARTIAL VOLUMES FROM THE BWR EQUATION

```
      DIMENSION G(10),A(5)
    1 FORMAT(F10.0,F10.0,F10.0,E15.0)
   23 FORMAT(F8.1,F8.1,E11.4,E12.5,E12.5,F8.4,F7.4)
   88 FORMAT(1HZ)
  114 FORMAT(F10.0,F10.0,F10.0,F10.0,F10.0,F10.0)
      R=10.73147
   46 READ 1,AO2,BO2,A2,CO2
      READ 1,B2,ALP2,GAM2,C2
   44 READ 1,AO3,BO3,A3,CO3
      READ 1,B3,ALP3,GAM3,C3
      READ 114,G(1),G(2),G(3),G(4),G(5),G(6)
      DO 2 L=1,6
      BO1=BO3
      AO1=AO3
      A1=A3
      CO1=CO3
      B1=B3
      ALP1=ALP3
      GAM1=GAM3
      C1=C3
      T=560.
      P=G(L)
      Z2=2.
      Z1=.5
      DO 5 NC=1,100
      ZM=(Z1+Z2)/2.
      D=P/(ZM*R*T)
      PT1=1.+(BO2-AO2/(R*T)-CO2/(T**3*R))*D+(B2-A2/(R*T))*D*D
      PT2=C2*D*D*(1.+GAM2*D*D)*EXP(-GAM2*D*D)/(R*T*T*T)
      ZC=PT1+PT2+A2*ALP2*(D**5)/(R*T)
      IF(ABS(ZM-ZC)-.0001) 6,6,7
    7 IF(ZC-ZM) 8,6,9
    9 Z1=ZM
      GO TO 5
    8 Z2=ZM
    5 CONTINUE
      PUNCH 88
      GO TO 2
    6 DO 10 M=1,2
      X=R*T*D+(BO1+BO2)*R*T*D*D-2.*D*D*SQRT(AO1*AO2)
      X=X-2.*D*D*SQRT(CO1*CO2)/(T*T)+3.*D*D*R*T*((B1*B2*B2)**.3333)*D
      X=X-3.*D*D*D*((A1*A2*A2)**.333)+3.*ALP2*((A1*A2*A2)**.333)*(D**6)
      X=X+3.*A2*((ALP1*ALP2*ALP2)**.333)*(D**6)
      U=SQRT(GAM1*GAM2)
      U1=3.*(1.+GAM2*D*D)*((C1*C2*C2)**.3333)
      U2=U1-2.*C2*GAM2*(D**4)*U
      X=X+U2*D*D*D*EXP(-GAM2*D*D)/(T*T)
      A(M)=X
      AO1=AO2
      BO1=BO2
      CO1=CO2
      A1=A2
      B1=B2
      ALP1=ALP2
      GAM1=GAM2
   10 C1=C2
      V=ZM*R*T/P
      VBAR=V*(A(1))/(A(2))
      TP=T-460.
      ZBAR=P*VBAR/(R*T)
      PUNCH 23,TP,P,A(1),A(2),VBAR,V,ZBAR
    2 CONTINUE
      IF(SENSE SWITCH 1) 46,45
   45 CONTINUE
      END
```

APPENDIX D

CALIBRATION OF STANDARD RESISTORS

TABLE D-1

CALIBRATION OF STANDARD RESISTORS

Nominal Size, ohms	Symbol	Leeds and Northrup Cat. Number	Serial No.	Resistance ohms	Accuracy %
10.0	R_2	4025-B	1609309	10.0000	.005
1000.0	R_1	4035-B	1611766	999.99	.005
1000.0	R_1	4035-B	1611768	1000.02	.005

APPENDIX E

SAMPLE CALCULATIONS

The following calculations are typical of those required to determine the partial volume and compressibility factor at infinite dilution. The data of Run 51 is employed. This run considered ethane injected into methane at 307 psia and 100°F. The raw experimental data obtained in this run is given in Table E-I.

The transducer output voltages represent the values obtained after several pumpings up and down of the mercury were performed in accordance with steps 19 and 20 of the experimental procedure.

The required calculation scheme is presented systematically.

1. Calculation of P:

The corrected pressure in the main bomb, before the injection and with the mercury slug present between the electrode and valve A, is taken to be a measure of the pure solvent pressure. To calculate this value, the following steps are required:

From Figure 8, the correction to be applied to a Heise gauge reading of 304 psia is +1 psia. Thus, the corrected pressure is 305 psia.

The introduction of mercury into the tubing between the electrode and valve A causes an increase in the main bomb's

TABLE E-I

RAW EXPERIMENTAL DATA OF RUN 51

Main bomb pressure = 304 psia

Zero point of transducer = 1.300 mv

Transducer output with mercury slug in tube = 1.729 mv

Injection	Pressure of Ethane in Burette, psig	Transducer Output after Injection, mv
1	18.7	2.820
2	20.1	3.949
3	19.0	5.023

pressure. This pressure increase is measured by the transducer according to equation (18). From Figure 3, K = 4.854 psi /mv at 305 psia. Substitution of this value of K and the experimental data into equation (18) yields:

$$\Delta P = 4.854\ (1.729-1.300)\ \text{psid}$$

or

$$\Delta P = 2.08\ \text{psid}$$

Since the pure solvent pressure is the sum of the Heise gauge correction and the above increase in pressure, the final calculated value for P is 307 psia.

2. Calculation of n_1:

The pressure gauge reading for the ethane in the burette (18.7 psig) is corrected via the calibration curve in Figure 7. For a gauge reading of 18.7 psig, the correction to be added is -.6 psi. Thus, the corrected ethane pressure is 18.1 psig.

Table E-II contains the specific volume data on ethane as reported by Sage and Lacey. Figure 17 incorporated this data to present the relation of the g-moles of ethane present in the 21.590 ml volume burette at 100°F to the corrected reading of the low range pressure gauge. At 32.8 psia (18.1 psig):

$$n'_1 = 0.00193\ \text{g-moles}$$

Values of n_1 for successive injections are similarly calculated. The total moles of ethane injected is the sum of the moles introduced in each injection. Thus

$$n''_1 = .00393\ \text{g-moles}$$

and

$$n'''_1 = .00587\ \text{g-moles}$$

TABLE E-II

VOLUMETRIC PROPERTIES OF ETHANE AT 100°F AS REPORTED BY SAGE AND LACEY (3)

Pressure, psia	Specific Volume, ft^3/lb	G-moles Ethane in Burette (10^3)
14.696	13.485	.8528
20	9.888	1.1630
40	4.899	2.3474
60	3.237	3.5526
100	1.9057	6.0344
150	1.2393	9.2793

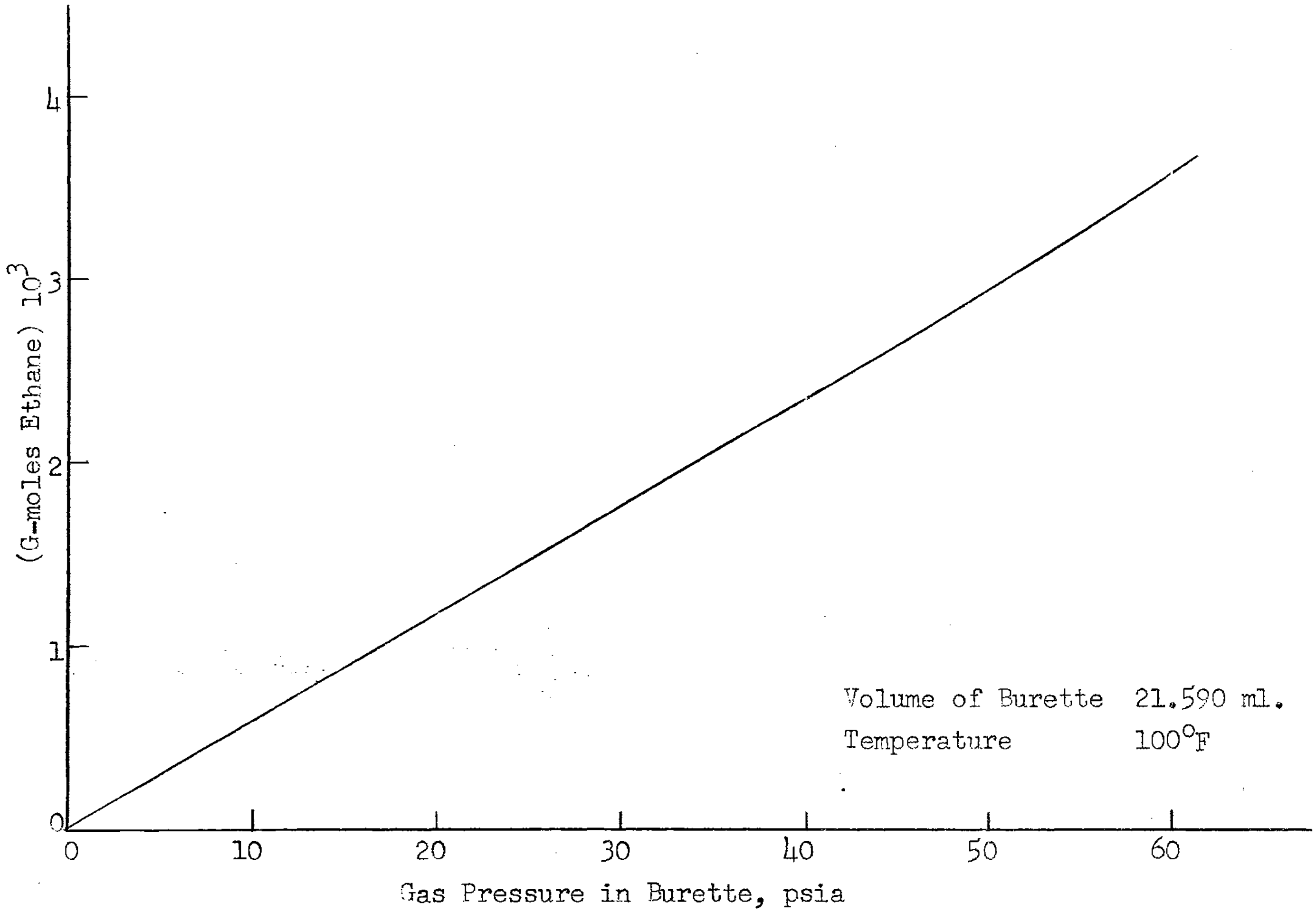

Figure 17. Graph to Determine G-moles of Ethane in Burette

3. Calculation of ΔP:

The experimental data of the first injection is substituted into equation (18) to yield:

$$\Delta P = 4.854\ (2.820 - 1.729)\ \text{psid.}$$

or

$$\Delta P = 5.294\ \text{psid.}$$

This value of ΔP must be corrected for the trapped gas error. From Figure 16, the corrective term for ΔP at 307 psia is 0.174 psid. Thus, the corrected value for ΔP is:

$$\Delta P' = 5.469\ \text{psid}$$

The corrected pressure increase for the second injection is:

$$\Delta P'' = 4.854\ (3.949 - 1.729) + 2\ (.174)$$

or

$$\Delta P'' = 11.123\ \text{psid.}$$

Similar considerations applied to the calculation of ΔP for the third injection yield:

$$\Delta P''' = 16.519\ \text{psid}$$

4. Calculation of $\partial P/\partial n_1$:

The value of $\partial P/\partial n_1$ is calculated according to equation (5). The average value of $\partial P/\partial n_1$ is taken to be the arithmetic sum of the three points, viz.:

$$\frac{\partial P}{\partial n_1} = \frac{1}{3}\sum_{i=1}^{3}\left(\frac{\Delta P}{n_1}\right)^{(i)}$$

Substitution of the calculated values into the above equation yields:

$$\left(\frac{\partial P}{\delta n_1}\right)_{T,V,n_2} = 2,820\ \text{psid/g-mole at 307 psia}$$

5. Calculation of $\bar{v}_1$:

From the curves of Figures 11 and 12, the following values are obtained at 307 psia:

$$\frac{\partial P}{\partial n_2} = 3070 \text{ psid/g-mole}$$

$$\rho_2 = 0.8340 \text{ g-mole/l}$$

Since $v_2 = 1/\rho_2$ then:

$$v_2 = 1.199 \text{ l/g-mole}$$

Substitution of these quantities into equation (4) yields:

$$\bar{v}_1 = 0.902 \text{ l/g-mole}$$

6. Calculation of $\bar{Z}_1$:

Substitution of the appropriate quantities into equation (6) yields:

$$\bar{Z}_1 = 0.902$$

NOMENCLATURE

B = second viral coefficient, l/g-mole

E_o = output voltage from transducer, mv

E_p = output voltage from resistor circuit, mv

E_t = input voltage to transducer, volts

e = base of natural logarithm

i = current in resistor circuit, amperes

K = sensitivity of transducer, psi/mv

N = $(V_1 + V_2') / V_2'$

n_1 = g-moles of ethane

n_2 = g-moles of methane

n_1', n_1'', n_1''' = g-moles of solute injected in first, second and third injections, respectively

P = pressure, psia

P_r = pressure in main bomb after r^{th} expansion of gas, psia

R = gas constant, .0820544 l atm/°K g-mole

R_1 = 1,000 ohm resistor in resistor circuit

R_2 = 10 ohm resistor in resistor circuit

T = absolute temperature

$\bar{v}_1$ = partial volume of ethane at infinite dilution, l/g-mole

V_1 = volume of ethane burette, ml

V_2 = volume of main bomb, ml

V_2' = volume of the main bomb plus the volume of mercury (in contact with the electrode) which fills the tubing between the main bomb and valve A, ml

v_2 = specific volume of methane, l/g-mole

$\bar{Z}_1$ = partial compressibility factor of ethane at infinite dilution

Greek Letters

Δemf = change in transducer output due to a difference in pressure applied across the transducer, mv

ΔP = increase in pressure, psid

ΔP_c = corrective term added to ΔP to compensate for trapped gas error

$\Delta P', \Delta P'', \Delta P'''$ = pressure increases in main bomb due to first, second and third injections, respectively

ϵ_1 = error associated with 1th quantity

ϵ_{tg} = error in ΔP due to trapped gas

Σ = summing operator

ρ = density, g-moles/l

Ω = ohm

Abbreviations

BWR = Benedict-Webb-Rubin

gpm = gallons per minute

Hg = mercury

l = liter

psid = pounds per square inch difference

rpm = revolutions per minute

VITA

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