AN EXPERIMENTAL INVESTIGATION OF
PVT PROPERTIES, AT LOW PRESSURES
USING A MODIFIED BOYLE'S LAW
APPARATUS

By

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PREFACE

PVT data for benzene and methanol have been obtained experimentally at low pressures using a modified Boyle's law apparatus. The results obtained, for the most part, did not agree with the literature values. An attempt has been made to investigate the probable errors which were involved.

I am indebted to Dr. F. A. L. Dullien for his guidance in the initial phases of this work and to Professor Wayne C. Edmister for his counseling during the latter part of this study. The aid of the entire staff and graduate students of the School of Chemical Engineering is appreciated. Special thanks is also due Eugene McCroskey for his help in the construction of the apparatus.

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TABLE OF CONTENTS

LIST OF FIGURES

Figure Page

LIST OF TABLES

CHAPTER I

INTRODUCTION

The volumetric properties of vapors have long been of interest. These properties are important in many of the processes in which the chemical engineer is interested such as absorption, distillation, adsorption and other unit operations.

Several equations have been used to calculate the volumetric behavior of gases and vapors. These include the Benedict-Webb-Rubin, the Beattie-Bridgeman, Redlich-Kwong, and others. None of these equations was derived theoretically. Because of this, it is difficult to determine the constants of these equations when mixtures are considered. The virial equation of state has theoretical significance in that the virial coefficients are related to the interactions of molecules. The second virial coefficient accounts for two body interactions and the third virial coefficient accounts for three body interactions.

The virial equation of state can be written in two different forms:

The Leiden form

$$PV = RT(1 + B/V + C/V^2 + \ldots) \qquad (1)$$

The Berlin form

$$PV = RT + B'P + C'P^2 + \dots \qquad (2)$$

where B is equal to B' and C' equals $(C - B^2)/RT$.

A large amount of work has been done during the last 25 years to determine experimentally the second virial coefficients of vapors at low pressures. At these pressures (below one atmosphere) the virial equation of state can be terminated after the second term. The second virial coefficients of many pure compounds have been found. The behavior of the second virial coefficients for binary mixtures of non-polar compounds has also been characterized to a large extent. Some work has been done on binary mixtures containing a polar and a non-polar component or two polar components. However, more work is required before the behavior of the second virial coefficients of these mixtures is completely characterized.

This study was initiated with two goals. These were (1) to construct an apparatus suitable for obtaining PVT properties at low pressures and (2) to obtain experimentally second virial coefficients of binary mixtures containing a polar and a non-polar component (benzene-methanol and benzene-ethanol). In the preliminary work to check the second virial coefficients of the pure compounds some unforeseen difficulties were encountered. Due to these difficulties, the experimental investigation made in this study did not progress to the point of considering mixtures.

With this introduction, the major goals of this study can now be stated:

1. A brief review of the various types of apparatus which have been used to obtain PVT properties at low pressures.
2. To design and construct a low pressure PVT apparatus.
3. Discussion of the results obtained in the preliminary study on the pure components (benzene and methanol) with an analysis of the various sources of error including adsorption which were the probable cause of the deviation of the results obtained in this study from those in the literature.

CHAPTER II

LITERATURE SURVEY

The literature survey made in this work consists of two parts. The first part is a general review of the various apparatus which have been used to determine second virial coefficients at low pressure. In the second part, a discussion is presented on two of the ways in which second virial coefficients have been theoretically interpreted.

Experimental Methods

The two methods most used in the low pressure determination of experimental second virial coefficients are those using the so-called Boyle's law apparatus and the differential method. A third method has been used with binary mixtures in which the second virial coefficient is determined from the pressure change on mixing. Still another method which is used to determine second virial coefficients is that used by Burnett (6). Since this method has not been used in low pressure work, it will not be discussed here.

One of the first investigators to use the Boyle's law apparatus for the determination of second virial coefficients was Lambert (2). His apparatus consisted of a glass U-tube with one leg closed, a mercury inlet at the bottom and a vacuum source connected to the other leg. The sample was introduced into the closed leg and was then compressed in stages with mercury at constant temperature. With a vacuum being pulled on the other leg, the pressure could be measured by the difference in the mercury heights in the two legs of the U-tube. The volume was obtained from a previous calibration of the closed leg of the U-tube. From a series of pressure-volume readings, the second virial coefficient was determined by the slope of the line obtained by plotting PV (pressure-volume product) versus P (pressure). This apparatus was originally used to obtain the second virial coefficients of pure substances. When the use of this apparatus was extended to binary mixtures, the mixture was made up in an auxiliary apparatus where known amounts of each component were vacuum distilled into a mixing chamber and then a sample of this mixture was introduced into the Boyle's law apparatus and data were taken for calculating the second virial coefficient. Carter (7) used a modification of the Boyle's law apparatus in which the two components of the mixture were first used as pure compounds in separate U-tubes. These pure samples were then mixed and the PVT properties of a sample of this mixture were obtained in one of the U-tubes.

The apparatus used in this work is of a similar design and is discussed in detail later.

Cottrell and Hamilton (9) have used another variation of this method. Their apparatus consisted of four calibrated volumes into which the sample was consecutively expanded. The pressure was measured between each expansion giving a series of pressures and volumes from which second virial coefficients were obtained.

Similar types of apparatus have been used by a number of other investigators (10, 13). The main advantage of the Boyle's law apparatus is its relative simplicity. The accuracy in this type of apparatus is dependent upon the accuracy of the volume calibration and the accuracy in the subsequent measurement of the pressure and volume.

The differential method was first used by Whytlaw-Gray (1) and later by one of his associates, Bottomley (4). A similar type of apparatus was used by Hamann and Pearse (16). With this type of apparatus, the PVT properties of a vapor are found with reference to a gas whose PVT properties are well known. Nitrogen is usually used as the reference gas. In Bottomley's work, the vapor sample being tested and the reference gas were always held at the same pressure in separate bulbs over mercury. A quantity of mercury was removed from the sample bulb after which mercury was removed from the reference gas bulb until the pressures were again equal. The respective changes in volume were obtained by weighing the amount of mercury which was removed from each bulb. In this way, he obtained a series of ratios of the sample volume to the reference gas volume. With these ratios, he could obtain the second virial coefficient of the vapor being tested. Hamann and Pearse compressed the sample and the reference gas in three interconnected volumes which were of equal volumes for each gas. The difference in the pressure of the sample and the reference gas was then measured while the sample and reference gas are occupying the same volume. The data of the above investigators were obtained at constant temperature.

This type of apparatus was used to eliminate the errors of measuring the pressure and volume at each point of a PVT run. The accuracy in Bottomley's apparatus is dependent upon the setting of the manometer points (these indicate when the sample and the reference gas are at the same pressure), the calibration of the dead space and connecting tubes of the bulbs, and the error present in weighing the mercury which was withdrawn from the bulbs at each point of a pressure-volume run. With this type of apparatus the mixtures must be made up in an auxiliary apparatus before they can be injected into the sample bulb and a PVT run made.

The third method was first used by Knobler, Beenakker and Knaap (20) at liquid oxygen temperatures for binary mixtures. This method consists of having the two components of the mixture at the same temperature and pressure, mixing them, and then measuring the pressure change on mixing and from this the second virial coefficient of the mixture was calculated. This method was not seriously considered in this work since this method had been used only for rather ideal mixtures and the problems which may be encountered in more non-ideal mixtures at ordinary temperatures were unknown.

Since 1950, much attention has been given to revising the apparatus used for the experimental determination of second virial coefficients at low pressure in order to eliminate or at least minimize the effects of adsorption. The most important step in this direction has been to eliminate the exposure of the vapor sample and the mercury used for compressing the sample to stopcock grease. Therefore, in all the apparatus used in low pressure PVT work today, stopcocks have been replaced by metal valves or, in some cases, other types of special valves (3). The cleaning of the apparatus also affects the amount of adsorption.

Theoretical Interpretation of the Second Virial Coefficients of Vapors

There are essentially two methods which have been used to interpret the second virial coefficients of vapors. One of these is based upon the Berthelot equation of state and the second is concerned with the Stockmayer potential.

The second virial coefficients of non-polar vapors follow the principle of corresponding states. The Berthelot equation has been found to represent a uniform relation between the second virial coefficient and the reduced temperature, T/T_c, between reduced temperatures of 0.6 and 1.0 (12, 15). This relation is given by the following equation:

$$B = (9/128)(RT_c/P_c)(1 - 6T_c^2/T^2) \qquad (3)$$

where B is the second virial coefficient, R is the universal gas constant, T_c is the critical temperature, T is the absolute temperature, and P_c is the critical pressure.

The second virial coefficient of a mixture can be expressed as:

$$B_m = x^2 B_{11} + 2x(1-x)B_{12} + (1-x)^2 B_{22}$$

where B_m is the second virial coefficient of the mixture, x is the mole fraction of substance 1, $(1-x)$ is the mole fraction of substance 2, B_{11} and B_{22} are the second virial coefficients of pure component 1 and 2 respectively, and B_{12} accounts for the interaction between component 1 and 2.

The Berthelot equation of state has been extended with success to mixtures of non-polar vapors using the following mixing rules (12, 15):

$$(V_{12}^c)^{1/3} = 1/2\,(V_{11}^c)^{1/3} + 1/2\,(V_{22}^c)^{1/3} \qquad (5)$$

$$\text{and} \quad T^c_{12} = (T^c_{11}T^c_{22})^{1/2} \tag{6}$$

where V^c_{12} is the critical volume of the mixture, V^c_{11} and V^c_{22} are the critical volumes of components 1 and 2 respectively, T^c_{12} is the critical temperature of the mixture, and T^c_{11} and T^c_{22} are the critical temperatures of components 1 and 2 respectively.

With the success of the above use of the Berthelot equation on binary mixtures of non-polar compounds, experiment seems to verify that the Berthelot equation of state accounts for all forces acting between molecules except the dipole-dipole forces. These are forces between the dipoles of polar compounds which must be considered when calculating second virial coefficients of polar compounds. The difference between the observed second virial coefficient and that calculated by the Berthelot equation is ascribed to these forces, which are assumed to be due to a small amount of dimerization and may be treated by the law of mass action. This general approach was first used by Lambert (21). The observed second virial coefficient can then be represented by:

$$B = B_B + B_d \tag{7}$$

where B is the observed second virial coefficient, B_B is that calculated from the Berthelot equation, and B_d is expressed by the following equation:

$$B_d = -RT/K_p \tag{8}$$

where K_p is the dissociation constant.

This equation can be used when the dipoles of a polar substance are not at the center of the molecule so that for certain mutual orientations, the dipoles can approach each other more closely causing an association. This can be represented by an equilibrium constant where the energy term could be the representative of the depth of the potential well and the entropy could represent the restrictions placed on the mutual orientations.

Equations 7 and 8 can then be used with Equation 4 for mixtures of a non-polar component and a polar component assuming no association between the non-polar molecules in the following way:

$$B_m = x^2 B_{11} + 2x(1 - x)B_{12} + (1 - x)^2 (B_{22} - RT/K_p) \qquad (9)$$

where B_{11} and B_{22} are the second virial coefficients of the two pure components calculated from the Berthelot equation of state. This type of reasoning can also be extended to binary mixtures of two polar components by considering association between like and unlike molecules.

The method used by Stockmayer is a rigorous treatment of the second virial coefficient of a gas composed of spherical molecules. It assumes that these molecules are attracted according to the sixth power of their separation distance and repelled according to the s power and in addition have a dipole at their centers. The expression for B is given by statistical mechanics:

$$B = (N/R)\int_0^\infty\int_0^\pi\int_0^\pi\int_0^{2\pi}(1 - e^{-E/RT})r^2 \sin\theta_1 \sin\theta_2 dr\, d\theta_1 d\theta_2 d\varphi \qquad (10)$$

where N is the number of moles and in general E is a function of r, the distance of separation, of θ_1 and θ_2, the angles made by the dipoles with the line joining their centers, and of φ, the angle between the planes which pass through the line of centers and contain the two axes. For non-polar molecules, E is assumed so little dependent on orientation that an average value may be taken and the integration is performed for only one coordinate, the distance of separation. For polar molecules with dipole interactions, E is given by the following:

$$E = (4\varepsilon)\left\{(d/r)^s - (d/r)^6 - t\sqrt{2}(d/r)^3\right\} \qquad (11)$$

where ε is the maximum energy of interaction in the absence of dipole forces, d is the collison diameter and t is called the reduced dipole energy and is given by:

$$t = 8^{-1/2}(u^2/\varepsilon d^3) \qquad (12)$$

where u is the dipole moment.

Stockmayer first worked with s equal to infinity (hard core molecules) and s equal to 24 (24). He then used this potential to represent the virial coefficients of ammonia and water at high temperatures. Hirschfelder, McClure, and Weeks repeated Stockmayer's calculations using s equal to 12 (19). Rowlinson (23) extended this work to other gases at lower temperatures. He found good agreement with experimental values and compared the values calculated using the Stockmayer potential to those calculated using an equilibrium constant to account for dipole associations. He then justified the use of the equilibrium constant to account for dipole effects on the second virial coefficients.

CHAPTER III

APPARATUS DESCRIPTION

As previously mentioned, the apparatus used in this work was a modified Boyle's law apparatus used by Carter (7). The unique feature of this apparatus was that it had two U-tubes, one for each component, with a mixing chamber connected to the sample side of each U-tube. In this way, the amounts of the two pure substances could accurately be determined by making a pressure-volume run on each in their respective U-tube. These samples could then be mixed in the mixing chamber and a pressure-volume run made with a part of this mixture in one of the U-tubes.

The reference letters in the following discussion refer to the sketch of the apparatus in Figure 1. The sample legs (A) of the two U-tubes were constructed of precision bore pyrex tubing. They are approximately 18 inches long and one had a diameter of 3/4 inches and the other a diameter of 1/2 inch. These different diameters were used to give different surface to volume ratios which might be used to detect adsorption. The vacuum legs (B) up to the location of the sample inlets (D) were standard pyrex tubing, 19 millimeter with the 3/4 inch sample leg

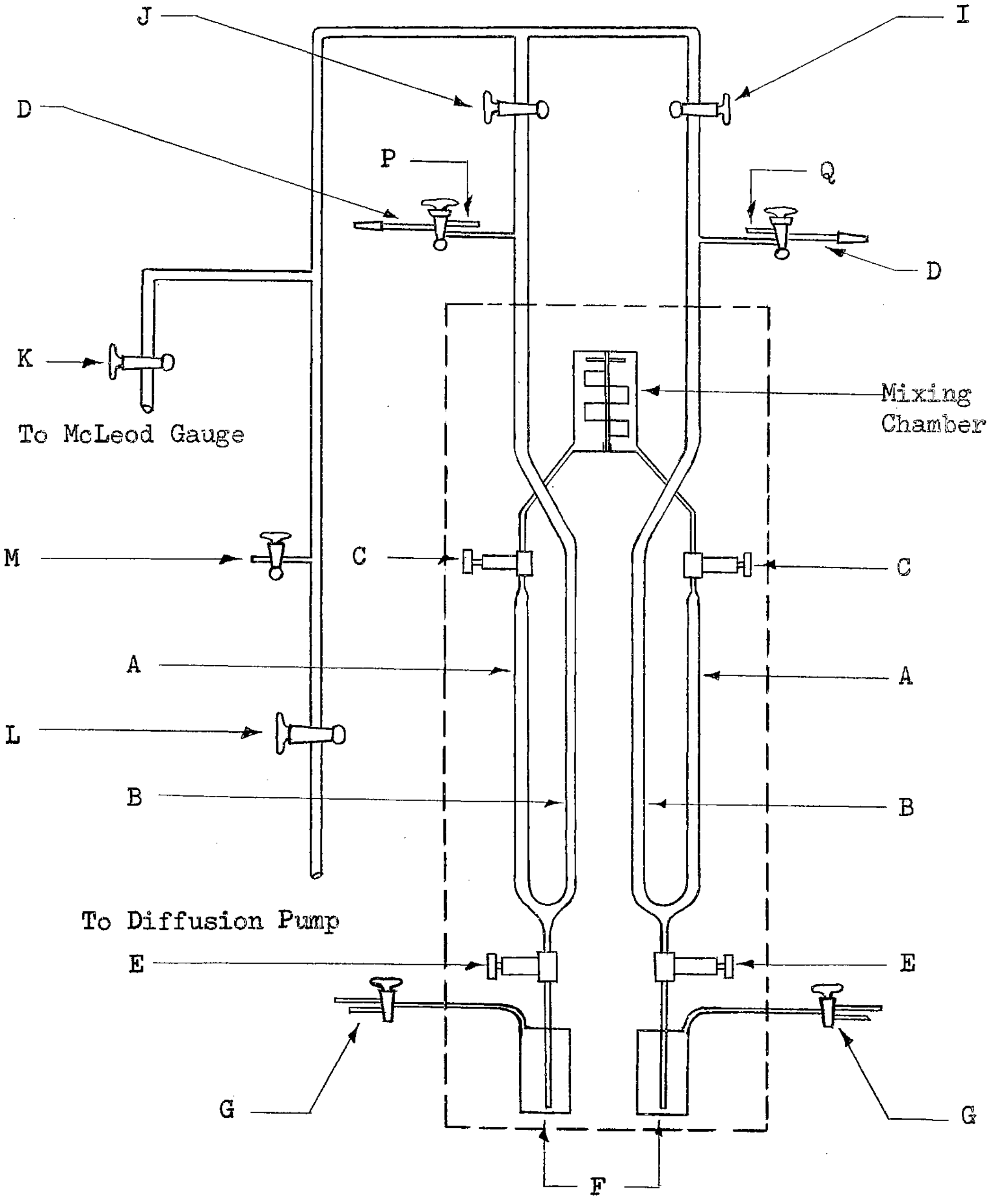

Figure 1. Sketch of Apparatus

and 14 millimeter with the 1/2 inch sample leg. The glass tubing leading to the McLeod gauge and to the diffusion pump was standard 14 millimeter pyrex tubing.

A Hoke bellows type valve model M440 (C) was at the top of each sample leg. These valves were used instead of stopcocks to avoid contaminating the samples with stopcock grease. The valves were constructed of monel with teflon seats and were connected to the glass by kovar to glass seals and stainless steel fittings. Monel, stainless steel and kovar are all resistant to mercury. A cylindrical mixing chamber with a volume of approximately 250 milliliters was connected to the valves on the sample legs by 8 millimeter pyrex tubing as described above. This mixing chamber contained a glass paddle stirrer which included two glass enclosed iron rods. This stirrer could be rotated by rotating a magnet around the outside of the mixing chamber. The stainless steel fittings were covered on the outside by a vacuum wax to seal any minute leaks.

The sample inlets (D) were constructed of 8 millimeter pyrex tubing, a 3-way mercury sealed high vacuum stopcock and a tapered joint to which the sample tubes could be connected. I, J, K, and L were high vacuum 6 millimeter bore glass stopcocks and M was a 2 millimeter bore high vacuum stopcock.

At the bottom of each U-tube was another bellows valve (E) leading to a mercury reservoir (F). These valves were connected to the glass in the manner previously described. The mercury reservoirs had a volume of approximately 500 milliliters. Air pressure or a vacuum could be exerted on the mercury through the two 3-way stopcocks (G).

The vacuum in the U-tubes was measured by a Cenco model 94151 McLeod gauge. This gauge was used extensively in the leak testing and also for checking the pressure on the vacuum side of the U-tubes while making a run. The vacuum was maintained on the U-tubes by a Welch Duo-seal two stage vacuum pump connected to an oil diffusion pump. A single stage Welch Duo-seal vacuum pump was used as a secondary vacuum source for use with the mercury reservoirs at the bottom of the U-tubes.

The U-tubes and mercury reservoirs were contained in a temperature-controlled air bath. This bath had the inside dimensions of 50 inches high, 16 inches wide and 12 inches deep. The bath was made of sheet metal. Insulation for the bath consisted of 2 inches of glass wool. A 1/8 inch plywood cover was used to hold the insulation in place. The back of the box was removable. A 42 inch by 16 inch double 3/8 inch plate glass window was in the front of the bath. The two plates were separated by one inch of dead air space for insulation. A 140 cubic feet per minute Harco-Fasco type blower was placed in the upper left rear corner of the bath. This blower pulled air from within the box over three 250 watt strip heaters and a cooling coil located in the upper rear of the bath. The heaters and cooling coil were enclosed in a sheet metal case punctured with holes through which the air from within the bath could be pulled. This blower then distributed the air down a 4 inch by 4 inch duct located down the rear left corner of the bath. The heat output of one of the heaters was regulated by a 7.5 ampere Variac which was held constant. The heat output of the other two heaters was regulated by a 7.5 ampere Variac which was controlled by a Fisher model 44 temperature controller. This controller had a thermistor probe which was placed directly under the exhaust of the blower mentioned above. Another blower of the same type as above was placed in the lower right corner of the bath to give additional circulation.

The U-tubes and the bellows valves were mounted inside the bath on a 1/2 inch thick transite board. Transite blocks were used for additional support to fasten the glass tubes to the board. An angle iron frame with aluminum rods was used as a mounting rack for the sample inlets and the glass tubing leading to the vacuum pump and the McLeod gauge. Extensions were placed on the bellows valves so they could be adjusted from outside the bath. Tygon tubing was used to connect the lower bellows valves to the mercury reservoirs. The initial lighting for the apparatus consisted of a 48 inch dual overhead fluorescent light.

During operation, the mercury heights inside of the U-tubes were measured by a Gaertner precision cathetometer.

This cathetometer could be read directly to 0.005 centimeters and a reading could be estimated to 0.003 centimeters.

The cathetometer and thermostated temperature bath rested on a two foot high wooden bench beneath which the vacuum pumps were placed. The McLeod gauge stood on the floor directly beside the thermostated bath. A photograph of the apparatus is presented in Figure 2.

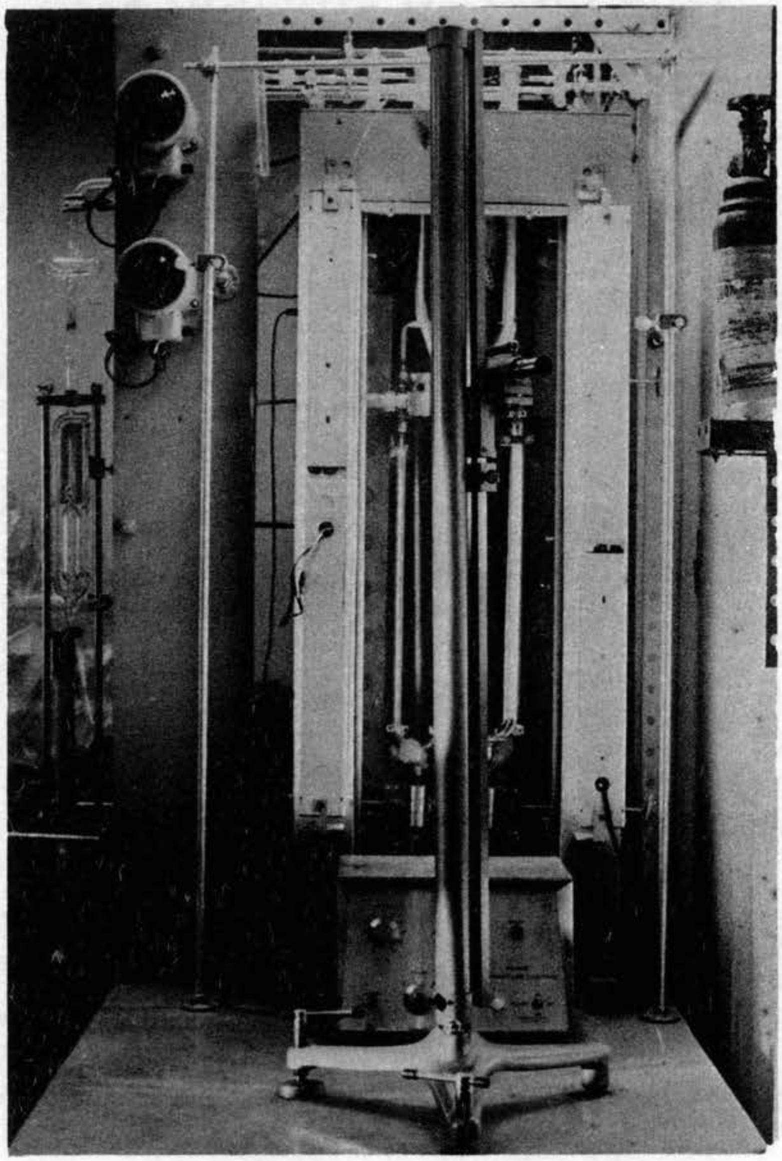

Figure 2. Photograph of Apparatus.

CHAPTER IV

EXPERIMENTAL PROCEDURE

Temperature Controller Setting

As mentioned previously, a Fisher model 44 temperature controller was used to control the temperature of the bath. This controller used a thermistor probe as a sensing element. The voltage drop across the thermistor was balanced by a bridge in the internal circuit. If the bridge was unbalanced on the low temperature side, a relay turned the controlled-heaters on. When the bridge was balanced again, the controlled-heaters were turned off. This controller had only on-off control. The bridge had three resistances which could be set to give the desired control point. These were labeled "range", "coarse", and "fine".

The blowers and the constant heater were turned on with a Variac setting of from 20 to 40 if the desired temperature was 60°C or below and at 90 if the desired temperature was 80°C or above. The controller with maximum dial settings was now turned on with a Variac setting of 100 to 140. The water in the cooling coil was turned on as an additional heat sink.

After the temperature of the bath had risen to within

2 degrees of the desired control point, the reading of the "range" dial was lowered until the relay shut off and this dial was then turned to the next higher position. Next, the "coarse" dial reading was lowered until the relay again shuts off and it likewise was turned to the next higher dial reading. The "fine" dial was now adjusted until the desired control temperature was reached. The Variacs were now adjusted so that the on-time of the controlled heater was approximately equal to the off-time and these times were as short as possible. This was a trial and error procedure. The dial readings were then recorded. Any time in the future when this temperature was again desired, the recorded controller settings for this temperature could be used with possibly minor adjustments in the "fine" dial reading.

A Beckmann thermometer was used to check the temperature variation at 60°C and at 80°C. It was found that the variation within the bath was ±0.02°C. The temperature did have a tendency to drift over long periods of time due to temperature changes in the room which would change the resistances of the resistors in the bridge circuit of the controller which in turn would change the control point. This drift could be eliminated when a run was being made.

Sample Preparation

Research grade (99.98 mol %) benzene and spectrograde methyl alcohol were used in this work. These samples were not purified further. However, they were kept over Drierite which would adsorb any moisture which might have been present.

The sample tubes were cylindrical glass tubes from which the samples could be introduced into the U-tubes. An arm at the top included a high vacuum stopcock and a ground glass joint which could be connected to the sample inlets on the apparatus.

The sample was drawn into the sample tube by first pulling a vacuum on the tubes and then pulling the sample into the tube with this vacuum. The sample was frozen and a vacuum pulled on it. It was then allowed to melt, and refrozen under vacuum. This was done several times to assure that the sample was adequately degassed. Degassing was accomplished while the sample tube is connected to the apparatus. The coolant used for freezing the sample (acetone-dry ice or liquid nitrogen) was placed in a dewar flask which could be raised around the sample tube. After degassing, the sample was ready to be used.

Leak Testing

A Tesla coil was used to detect leaks in the glass part of the apparatus. The system was assumed to be sufficiently free of leaks if (1) a vacuum could be pulled below 0.1 microns mercury pressure on the U-tubes and (2) the rise in pressure under static conditions over a period of 8 hours or more was not more than 10 to 20 microns mercury pressure.

Volume Calibration of Sample Legs

As previously mentioned, the sample legs of the U-tubes were constructed of precision bore pyrex tubing. The tolerance on this tubing was ±0.0002 inches. The volume of sample in the leg could be determined from the height of the mercury in the leg and the diameter except that at the top of each sample leg was a bellows valve, a stainless steel tubing fitting, a kovar seal and a tapering of the tubing so that it could be connected to the glass of the kovar seal. This volume must be found by calibration.

A reference point was chosen at the top of the sample leg as a distinct line which could be read with the cathetometer. The distance from this reference point to a point located sufficiently far down the U-tube to assure that the tubing was precision bore at this point was called the calibration height. The volume above this imaginary line was called the calibration volume. This is illustrated in Figure 3.

The calibration volume was found by making a pressure-volume run using argon at 320°K. The second virial coefficient of argon at this temperature had previously been found to be zero (18).

The volume of a sample for any given mercury height in the sample leg could then be found by adding the calibration volume to the volume contained in the precision

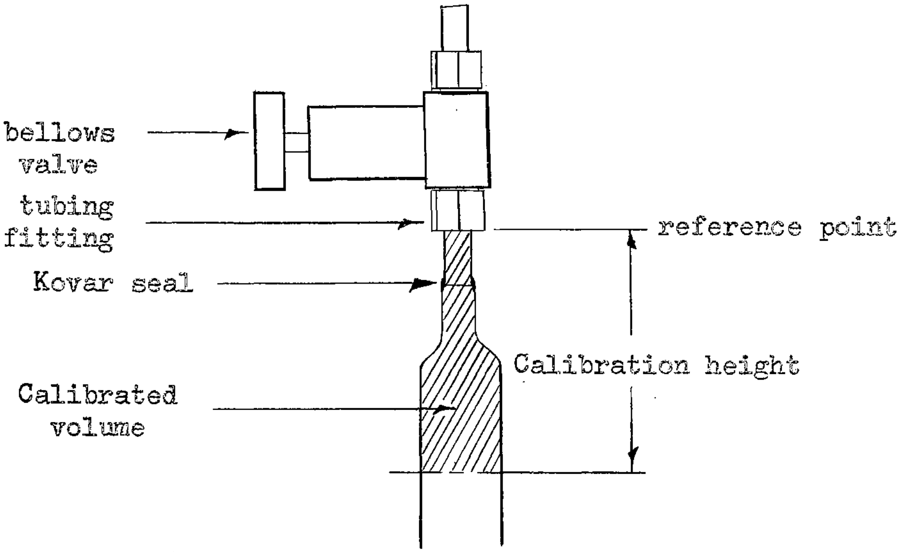

Figure 3. Illustration of Calibrated Volume

bore part of the sample leg. This is illustrated in the calculation procedure found in Appendix A. When a run was being made, the mercury used for the compression of the sample was never allowed to rise into the calibrated volume section of the sample leg.

Operation of Apparatus

To begin a run a vacuum is first pulled on the U-tube using the primary vacuum pump with stopcocks L, K, I, and D open and stopcocks J and M and valves C and E closed. The diffusion pump is turned on when the pressure is below 100 microns mercury pressure. Upon initial startup, the system was evacuated for 6 to 8 hours before a series of runs was started. By regulating valve E mercury from the mercury reservoir is allowed to rise to just above valve E. The mercury used here was tripled distilled. If during operation, the mercury became contaminated, it was filtered and redistilled. Stopcock D is now opened and the stopcock on the sample tube is closed. After the desired temperature is attained and the controller is controlling about this temperature, stopcock I is closed. The stopcock on the sample tube is now opened allowing the sample to vaporize into the U-tube. After opening this stopcock for approximately one minute, it is closed and the vapor sample is in the U-tube ready to be used.

Valve E is now opened allowing mercury to rise into the U-tube to a height of about 6 to 8 inches. Stopcock I is now opened and the vacuum side of the U-tube is evacuated. After the pressure on the vacuum side of the U-tube is below 5 microns mercury pressure and the sample has reached thermal equilibrium (15 to 20 minutes), the two mercury heights in the U-tube are read using the cathetometer and recorded. Before using, the cathetometer is leveled by following the procedure described by the manufacturer (14). Each reading is repeated twice and if the two readings differ by more than 0.05 millimeters, a third reading is made. The room temperature is recorded to correct the calibrated bar of the cathetometer for temperature expansion. The reference point at the top of the sample leg is also read with the cathetometer and recorded along with the bath temperature. The reference point is checked once for each run to correct for any change in the position of the cathetometer during the leveling procedure before each run.

Valve E is again opened allowing more mercury to rise in the U-tube, approximately 10 centimeters above its previous height in the vacuum leg. After an 8 to 10 minute waiting period, allowing for thermal equilibrium to be reached, the mercury heights are again read with the cathetometer and recorded. This procedure is repeated 8 to 10 times for a run from the lowest pressure possible (determined by the sample size) to the highest pressure (determined by the length of the vacuum leg or the saturation pressure of the sample which must never be approached).

Air at approximately 10 psig is used through stopcock G to force the mercury into the U-tube. After obtaining the desired number of readings, the mercury is withdrawn to the point of the initial reading. Stopcock I is now closed and some sample is allowed to vaporize from the sample tube to the vacuum leg of the U-tube to equalize the pressure in the two legs. The mercury is then withdrawn to just above valve E. A vacuum from the secondary vacuum pump through valve G is used to pull the mercury out of the U-tube. Stopcock I is again opened and after the apparatus is completely evacuated, it is ready for the next sample.

The procedure used in the volume calibration with argon is the same as mentioned above except in the method of injecting the sample into the U-tube. The argon cylinder was connected with tubing to P or Q, the open arms of the 3-way stopcocks on the sample inlets. After allowing sufficient argon to flow through the lines to assure that all the air was carried away, argon under 6 psig pressure was introduced into the sample tubes by use of the 3-way stopcock on the sample inlet. The argon was then allowed to expand from the sample tube into the system. This procedure was used so that an excess amount of argon would not be introduced into the U-tube.

Cleaning of the Apparatus

Since the apparatus was permanently installed, cleaning created a slight problem. First, the mercury reservoirs were disconnected; then, the portion of the apparatus between the sample inlet and valve C could be cleaned. A solution of ethyl alcohol-sodium hydroxide was used to remove any stopcock grease which may have found its way into the U-tube. After rinsing this out with water, a solution of sulfuric and chromic acid was used to clean the U-tubes. After rinsing again with water, the U-tubes were rinsed with methanol. After the preliminary drying by evaporation, the U-tubes were dried under vacuum and degassed using a natural gas-air flame on the outside of the glass.

CHAPTER V

DISCUSSION OF RESULTS

Over the period during which the experimental results were obtained, some changes in the apparatus were made with the main purpose being to improve the results. These changes will be discussed before the results are discussed.

The first experimental difficulty encountered was the measuring of the mercury meniscus using the cathetometer. The background of the meniscus and the lighting were found to be very important in determining the clarity of the meniscus in the scope of the cathetometer. The best background contrast which was found was completely black with a narrow white stripe directly behind the mercury column. The reflection from the mercury surface caused by the lighting was also troublesome. A series of light bulbs placed inside the thermostated bath was found to be unsatisfactory because they upset the temperature control and still caused some unwanted reflection. An acceptable lighting arrangement was finally obtained by placing a 36 inch fluorescent light on each side of the front window.

After various changes in the experimental technique (which will be discussed later) up to Run 92, the experimental results obtained except for a few cases were still unsatisfactory. At this point, the 3/4 inch U-tube was revised in that the valve at the top of the sample leg was removed. A sketch of this revised apparatus is shown in Figure 4. The reason for removing this was to check if the valve or teflon seat were the cause of the erratic results obtained. The results obtained with this revised apparatus will be discussed later.

During the course of the experimental work, glass breakage created a problem at times. Breakage of the bellows in the bellow valves leading to the mercury reservoirs was also a problem. In the final revision of the apparatus, these valves were replaced by Hydromatics series 715 stainless steel ball valves. These valves worked very well as replacements for the bellows valves.

A summary of all the results obtained in this work for the second virial coefficients of benzene and methanol appear in Table I and Table II, respectively. As one can see upon examination of these tables, a very small number of the determined second virial coefficients agree satisfactorily with the literature values. The literature values are listed at the beginning of these tables. The runs for each compound are listed in the sequence in which they were made except for several runs in which the data were totally inconsistent and impossible to analyze. The run numbers are in the sequential order in which all the runs were made.

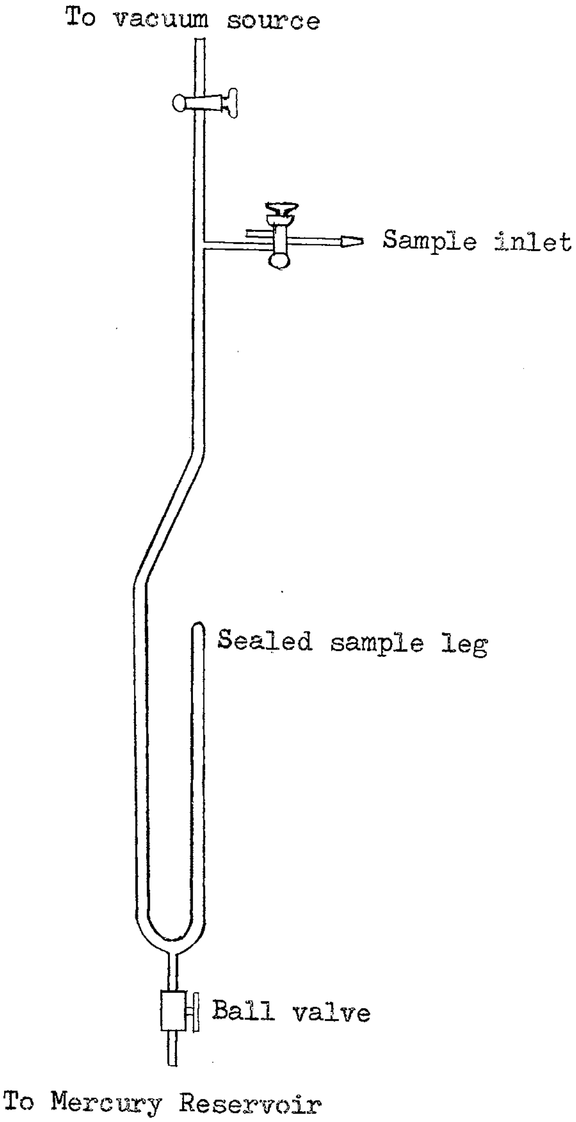

Figure 4. Revised Sketch of One U-Tube of the Apparatus

TABLE I

TABULATION OF EXPERIMENTAL RESULTS AND COMPARISON WITH LITERATURE VALUES FOR BENZENE

Run Number	Temperature (°C)	Second Virial Coefficient, ml/mole	Difference from literature value
	60.00	-1100	Ref (21)
	80.00	- 950	"
	100.00	- 850	"
21	60.03	-3056	-1956
22	60.03	-2124	-1024
23	60.03	-2624	-1524
24	60.03	-2160	-1060
25	60.05	-3267	-2167
26	60.05	-1238	- 138
27	60.05	-1201	- 101
28	60.05	-1021	78
29	60.08	-1789	- 689
30	60.07	- 933	167
31	59.99	-1485	- 385
32	60.00	-1842	- 742
33	59.97	-1589	- 489
34	60.04	-1795	- 695
35	60.03	-1523	- 423
37	60.01	-1746	- 646
42	59.97	-1534	- 434
81	79.94	-1607	- 657
82	79.94	-1469	- 519
87	79.98	-1685	- 735
88	79.99	-1728	- 778
89	80.01	-1617	- 667
90	79.92	-1445	- 495
91	100.15	-1117	- 272
92	80.08	-1580	- 630
98	60.06	-1246	- 146
99	60.05	-1356	- 256
104	60.05	-1137	- 37
105	60.06	-1151	- 51

TABLE II

TABULATION OF EXPERIMENTAL RESULTS AND COMPARISON WITH LITERATURE VALUES FOR METHANOL

Run Number	Temperature (°C)	Second Virial Coefficient, ml/mole	Difference from literature value
	60.00	-1220	Ref (21)
	80.00	- 980	"
38	60.05	-1268	- 48
39	59.99	-1226	- 6
40	60.00	-1373	- 153
41	60.05	-1416	- 194
52	59.79	-1531	- 311
53	59.99	-1529	- 309
54	59.87	-1398	- 178
55	60.16	-1467	- 247
56	60.08	-1429	- 209
57	59.98	-1429	- 209
59	59.97	-3081	-1861
60	59.98	-3023	-1803
61	60.00	-2867	-1647
62	59.97	-2644	-1424
68	60.28	-2719	-1499
69	79.92	-1106	- 126
70	60.08	-2531	-1311
71	79.92	- 980	--
72	79.92	-1058	- 78
73	80.02	-1037	- 57
74	59.97	-2298	-1078
75	59.97	-2106	- 886
76	59.98	-1993	- 773
83	80.02	-1414	- 464
84	79.94	-1443	- 493
85	80.02	-1105	- 125
86	80.00	-1101	- 121
100	60.05	-1320	- 100
101	60.01	-1292	- 72
102	60.00	-1317	- 97
103	60.00	-1218	2

The first phase of the experimental work consisted of calibrating the volumes of the U-tubes as previously indicated. The results of these runs are tabulated in Appendix B. The value of the calibration volume is 9.00 ml for the 3/4 inch U-tube (used in Runs 21-28), 9.471 ml for the 1/2 inch U-tube (used in Runs 29-92) and 21.643 ml for the revised 3/4 inch U-tube (used in Runs 98-105). The effect of an error in the calibration volume on the determined second virial coefficient is discussed in Appendix C.

The second phase of the experimental work is to reproduce the literature values of the second virial coefficients for the pure compounds. The first attempt at this was made with benzene in the 3/4 inch U-tube at 60°C. The results of Runs 21-25 were very unsatisfactory and differed from the literature values by -1000 to -2000 ml/mole. The behavior of the data of these runs is similar to that of Runs 87-92 and will be discussed when the latter runs are considered. After Run 25, the apparatus was cleaned and Runs 26-28 were made. The improvement in the results over those of the previous runs is quite apparent. However, at the time when these runs were originally analyzed, the results of these runs were thought to be worse than they actually are (see Appendix B) so the experimentation proceeded as will be described. The behavior of the data of these runs is illustrated by Figure 5 which shows the relationship between PV and P for Run 28. The scatter of the data in these runs was rather large, but

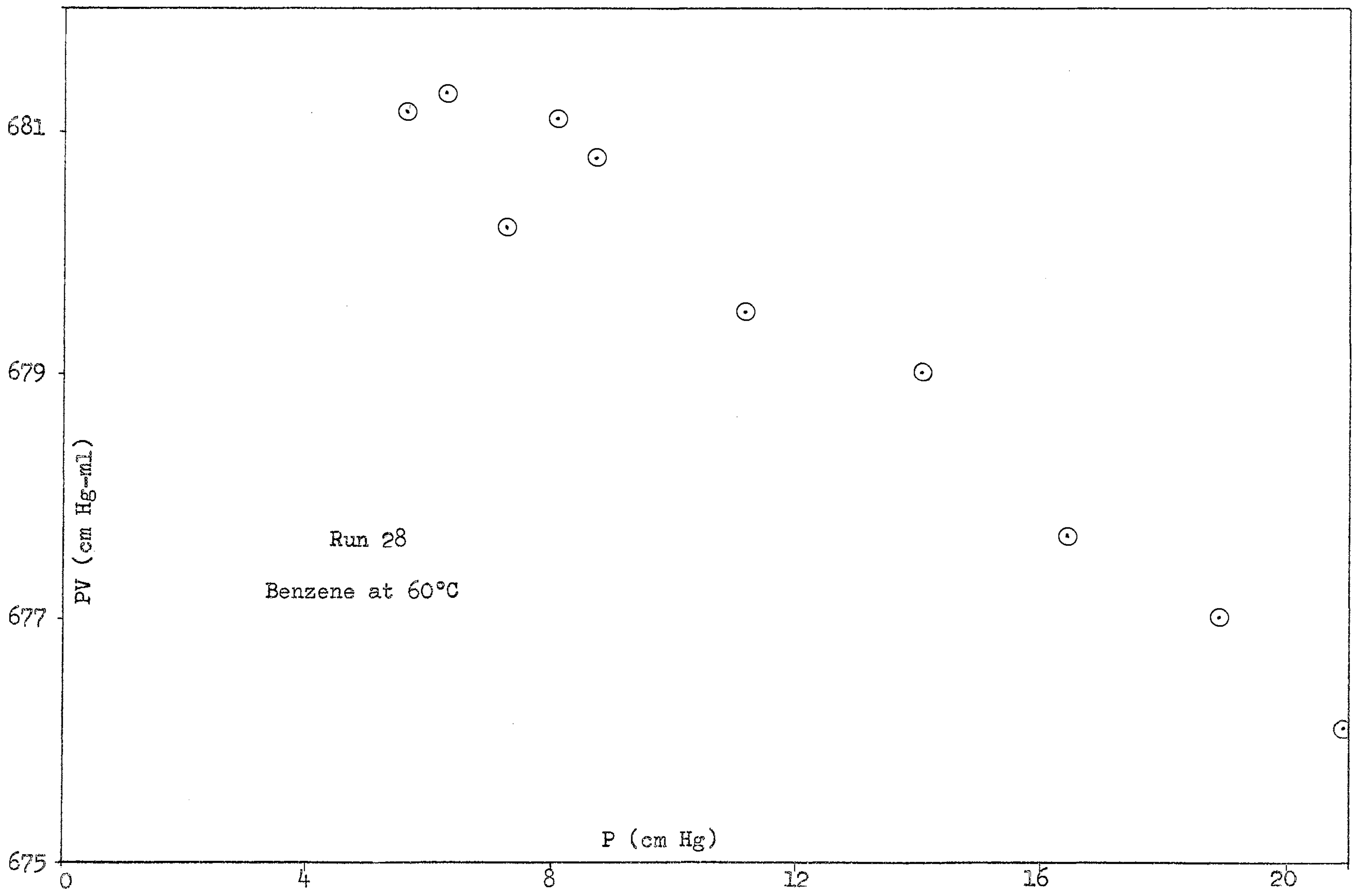

Figure 5. Relationship Between PV and P for Run 28

the curvature noted in later runs does not exist. It is believed by the author that if more care were taken in runs which behaved as these acceptable results could be obtained.

Runs with benzene at 60°C in the 1/2 inch U-tube are included in the next attempt to obtain acceptable results. The results of these runs with the exception of Run 30 differed from the literature value by -400 to -800 ml/mole. These results are considered further when adsorption is later discussed. The unusual behavior of Run 30 is difficult to explain. It could be explained by a unique combination of the probable errors involved, a leak which is very unlikely, or some error in the experimental technique which was not apparent at the time of the run.

Being unsuccessful in obtaining acceptable results for benzene, Runs 38-41 were made with methanol at 60°C in the 1/2 inch U-tube. Runs 38 and 39 gave good results but no success was made in the attempt to reproduce these results with Runs 40 and 41. Adsorption by some contaminating material introduced between Run 39 and Run 40 is probably responsible for the behavior noted. The general behavior of these runs is illustrated by Figure 6. Here, a distinct concave curvature towards the pressure axis is noted which will later be shown to be due to adsorption. This curvature exists for the experimental data from each of these runs. Run 42 was made with benzene to see if any improvement could be made over Runs 29-37. As shown by

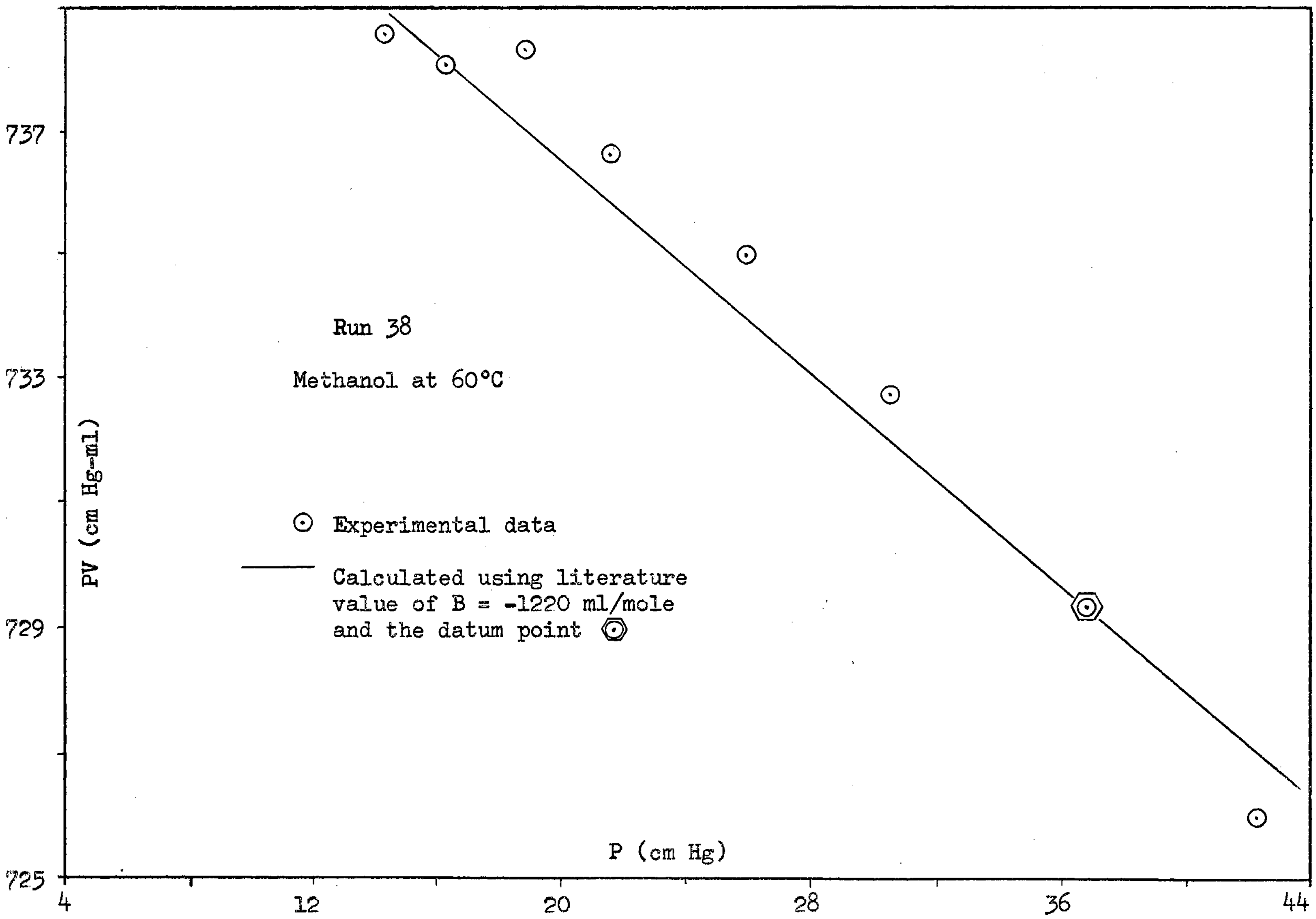

Figure 6. Relationship Between PV and P for Run 38

the result of this run, there was no such improvement.

In Runs 52, 53, 55, 56, 57, 59, 60, 61, and 62 data were obtained with a compression and an expansion of the sample or with multiple compressions or expansions of the sample. The behavior of the data obtained from these runs is illustrated in Figure 7. It is interesting to note here that the PV product at a given pressure obtained from expansions or compressions after the initial compression are always less than the PV product calculated from the data of the initial compression. This indicates that a part of the sample disappears through adsorption with increasing pressure and does not totally reappear when the pressure is again lowered. This may be partially explained by the fact that as the pressure increases the adsorbing surface (the glass of the U-tube) is being covered by mercury. Any material which was on the surface before it was covered would then be trapped by the mercury against the wall. Upon contact of the adsorbed material with the mercury, the mercury has an excellent opportunity to adsorb this material and after the pressure is again reduced, a part of the originally adsorbed material may still be held by the mercury.

Between Runs 57 and 59, the apparatus was cleaned in the manner previously mentioned. This had a very marked affect upon the determined second virial coefficient. It can be seen from Table II (page 34) that the values found for B from Runs 52-57 differed consistently from the

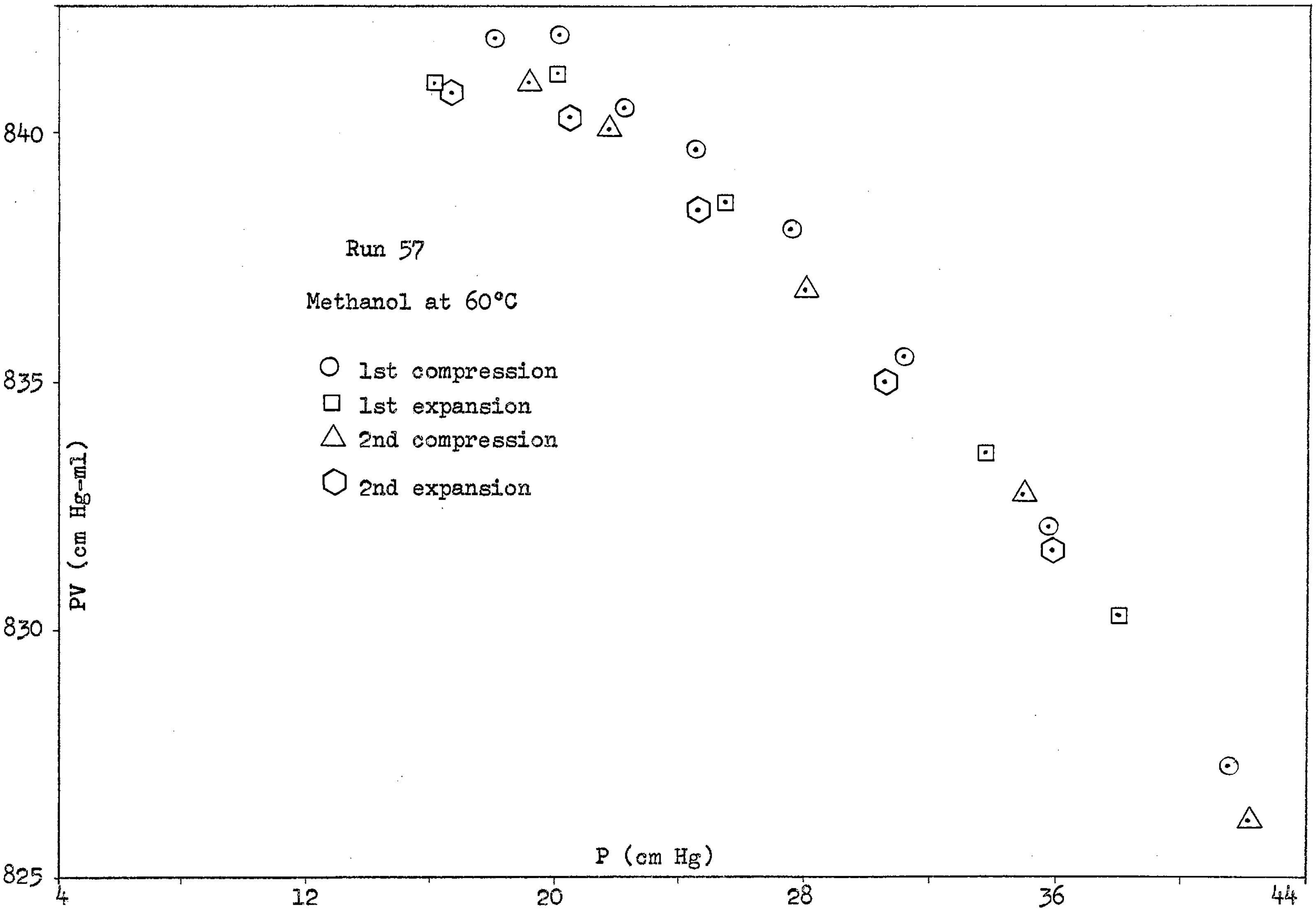

Figure 7. Relationship Between PV and P for Run 57

accepted value by -200 to -300 ml/mole whereas those obtained from Runs 59-62 differed by -1500 to -1800 ml/mole. This large deviation can probably be explained only in that some impurity or contaminant was introduced in cleaning. This was probably due to incomplete rinsing of the apparatus. The surface may also have become more selective to adsorption upon cleaning but, due to the size of the difference noted in the calculated second virial coefficients, this is rather improbable.

The data from Runs 63-67 were so inconsistent that the results were of no value whatsoever and are, therefore, omitted here. The apparatus was cleaned several times during this series of runs and was finally thoroughly cleaned before the next series of runs was made.

The next series of runs (68-76) was made with methanol at 60°C and 80°C. It is seen in the tabulated results of Table II (page 34) that acceptable results were obtained for the runs at 80°C. The data of Runs 69, 72, and 73 have a slight concave curvature towards the pressure axis when the PV product is plotted versus P as shown in Figure 8 for Run 69. This curvature does not exist in Run 71 as seen in Figure 9. Runs 68, 70, 74, 75, and 76 were made at 60°C and the results of these runs are not good. The behavior of these runs is illustrated by Figures 10 and 11 where the experimental data of Runs 70 and 74 are compared with data calculated using the accepted value of B. Since no changes were made in the equipment or

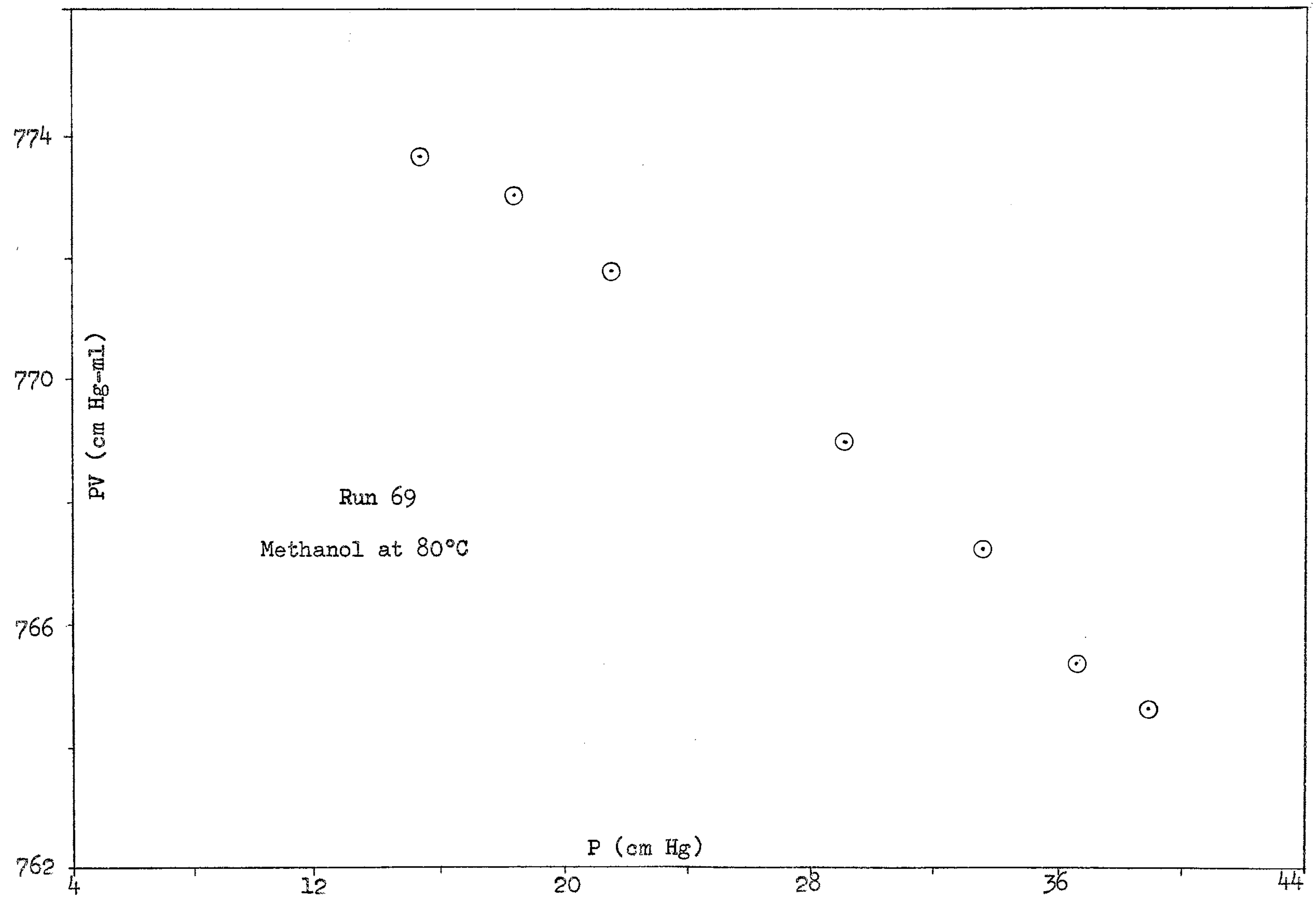

Figure 8. Relationship Between PV and P for Run 69

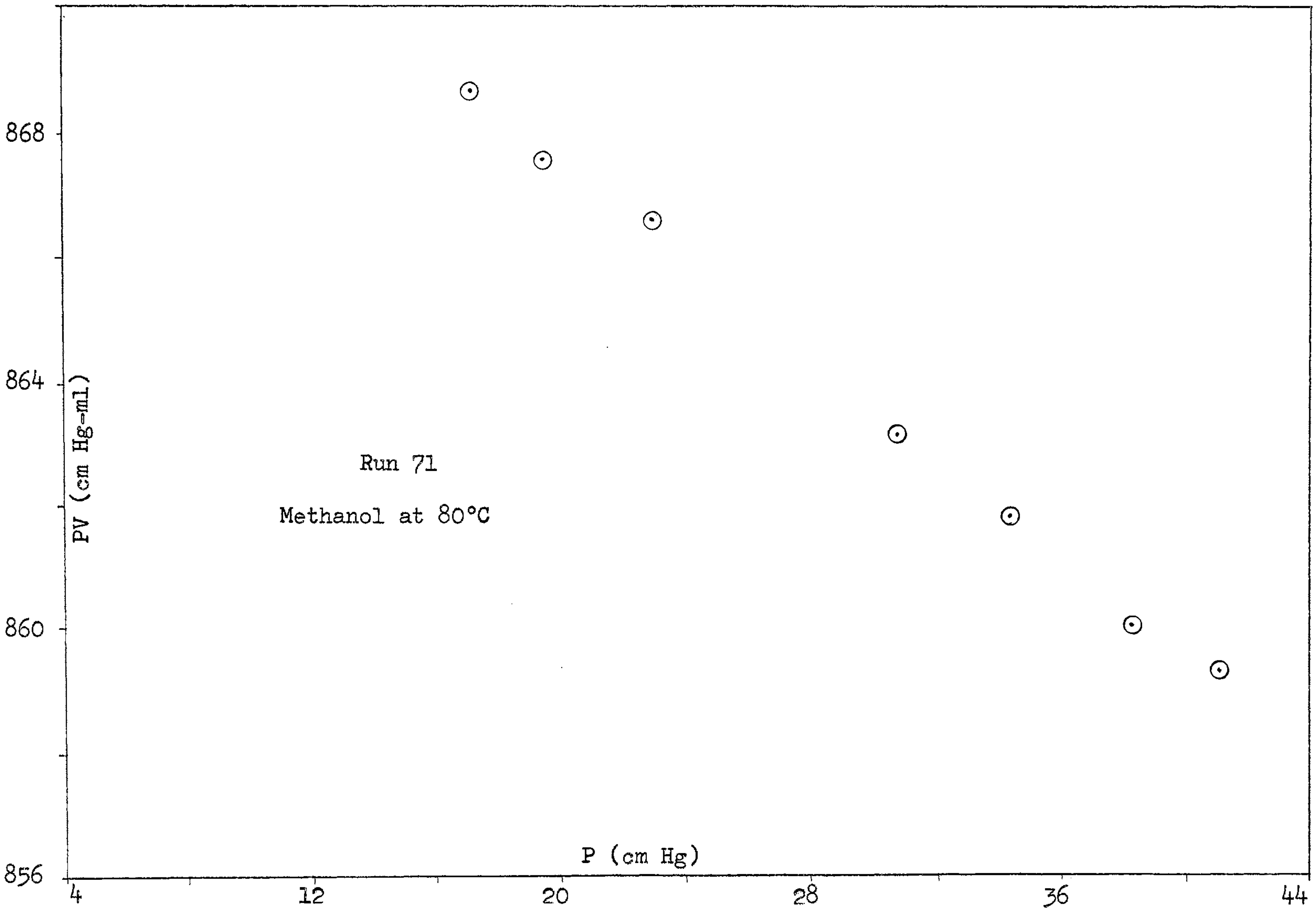

Figure 9. Relationship Between PV and P for Run 71

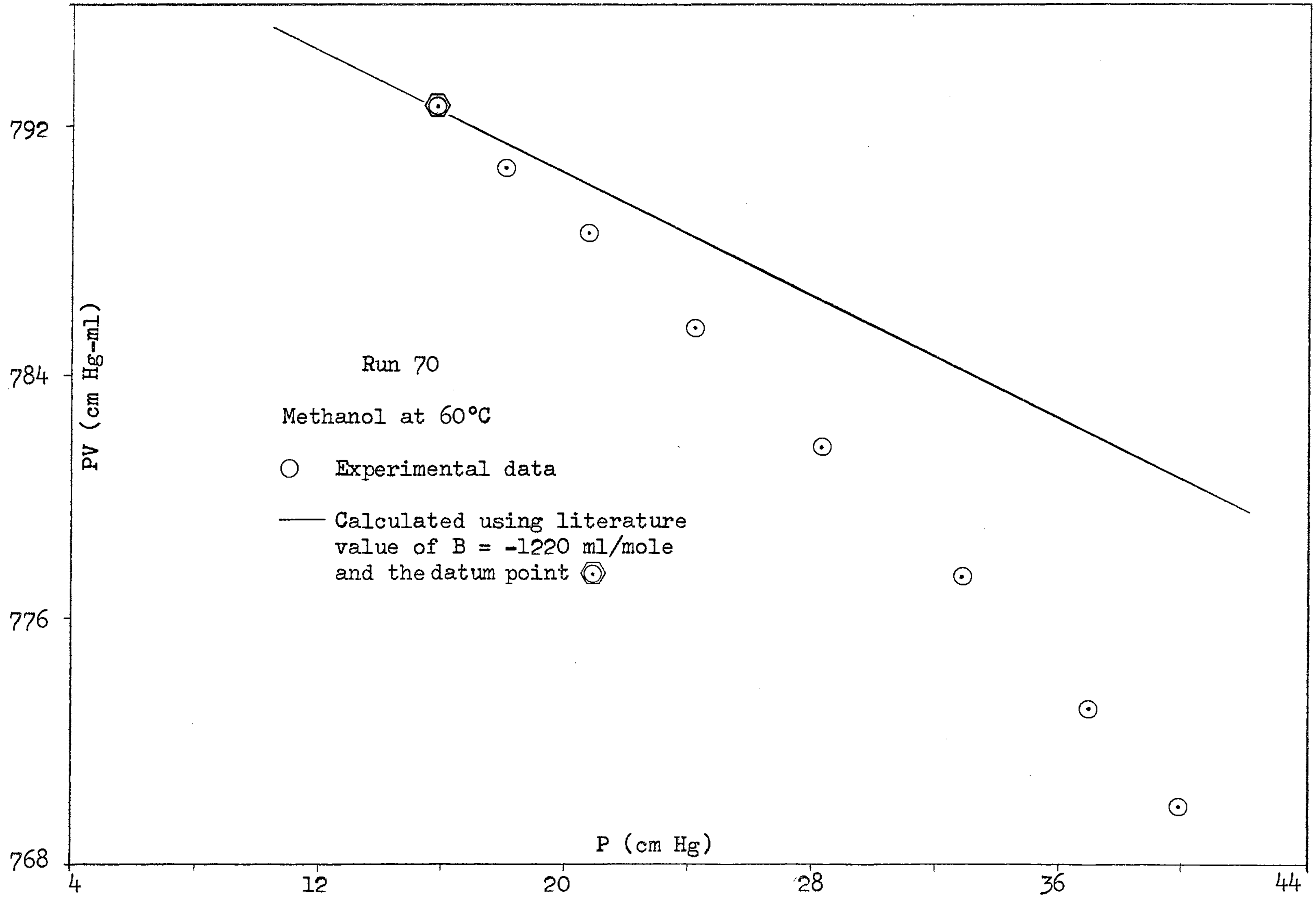

Figure 10. Relationship Between PV and P for Run 70

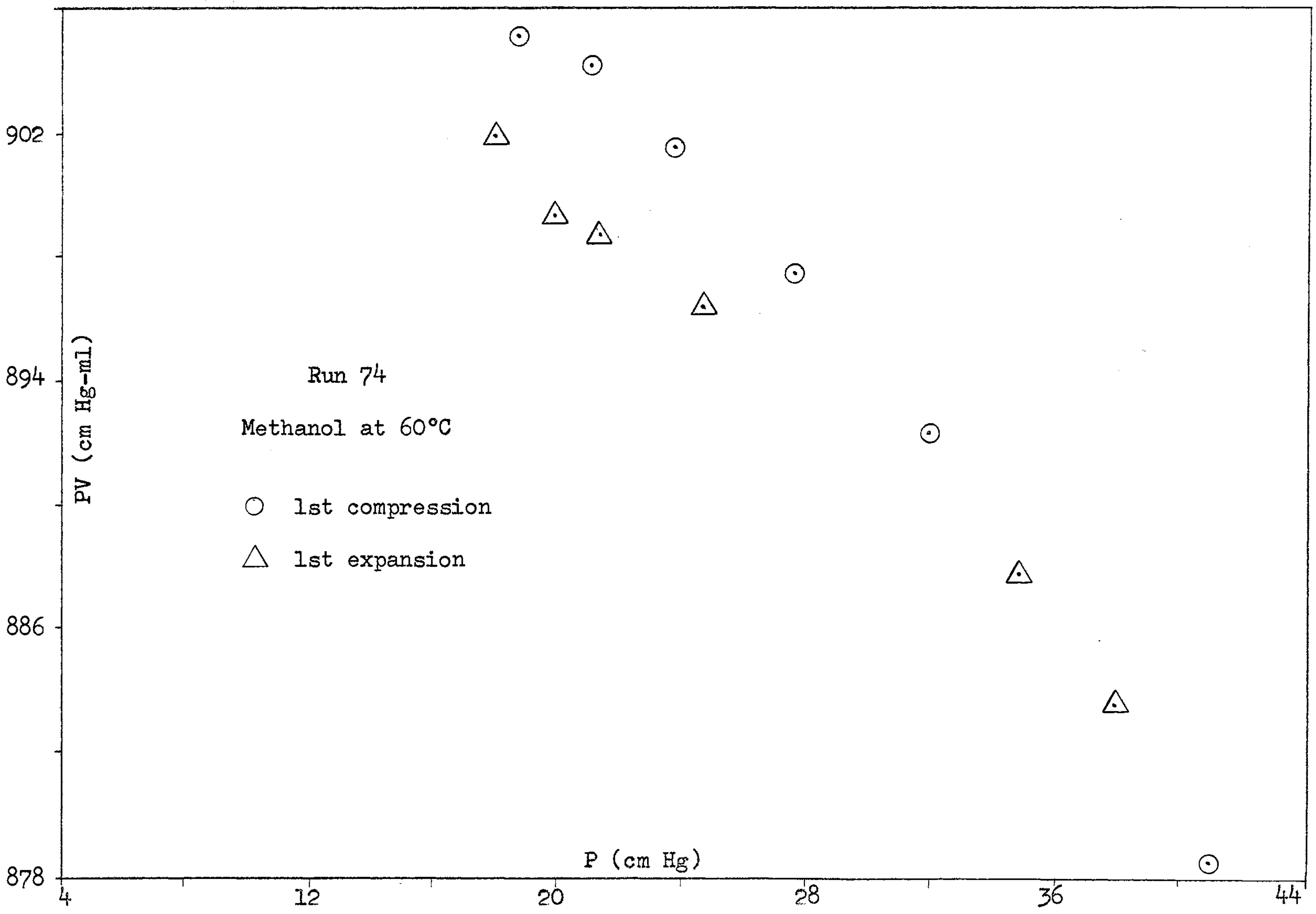

Figure 11. Relationship Between PV and P for Run 74

procedure, the large difference seen in the results obtained at 60°C and 80°C can only be explained by adsorption on the glass and mercury surface and, since the difference is so marked, there is also the possibility that some impurity was present which would readily adsorb the methanol at 60°C and have little or no effect at 80°C. Further evidence that a part of the sample was removed by adsorption is illustrated by Figure 11. This is similar to the behavior noted in Figure 7 (page 40), although more pronounced and can be explained in the same manner.

In Runs 81, 82, 87-90, and 92 an attempt was made to obtain results for benzene at 80°C. The second virial coefficients obtained from these runs differed from the acceptable results by -400 to -800 ml/mole. A concave curvature towards the pressure axis is apparent in the data of these runs. This is illustrated in Figure 12. The general behavior of this run is also illustrated with a comparison with data calculated from the literature value of the second virial coefficient. This behavior will be discussed later when adsorption is considered. Run 91 was made with benzene at 100°C. There is a slight improvement in the resulting second virial coefficient but it is not an acceptable value. This improvement is probably due to a lessening effect of adsorption at this higher temperature.

Runs 83-86 were made with methanol at 80°C. The results of Runs 83 and 84 gave results similar to those of

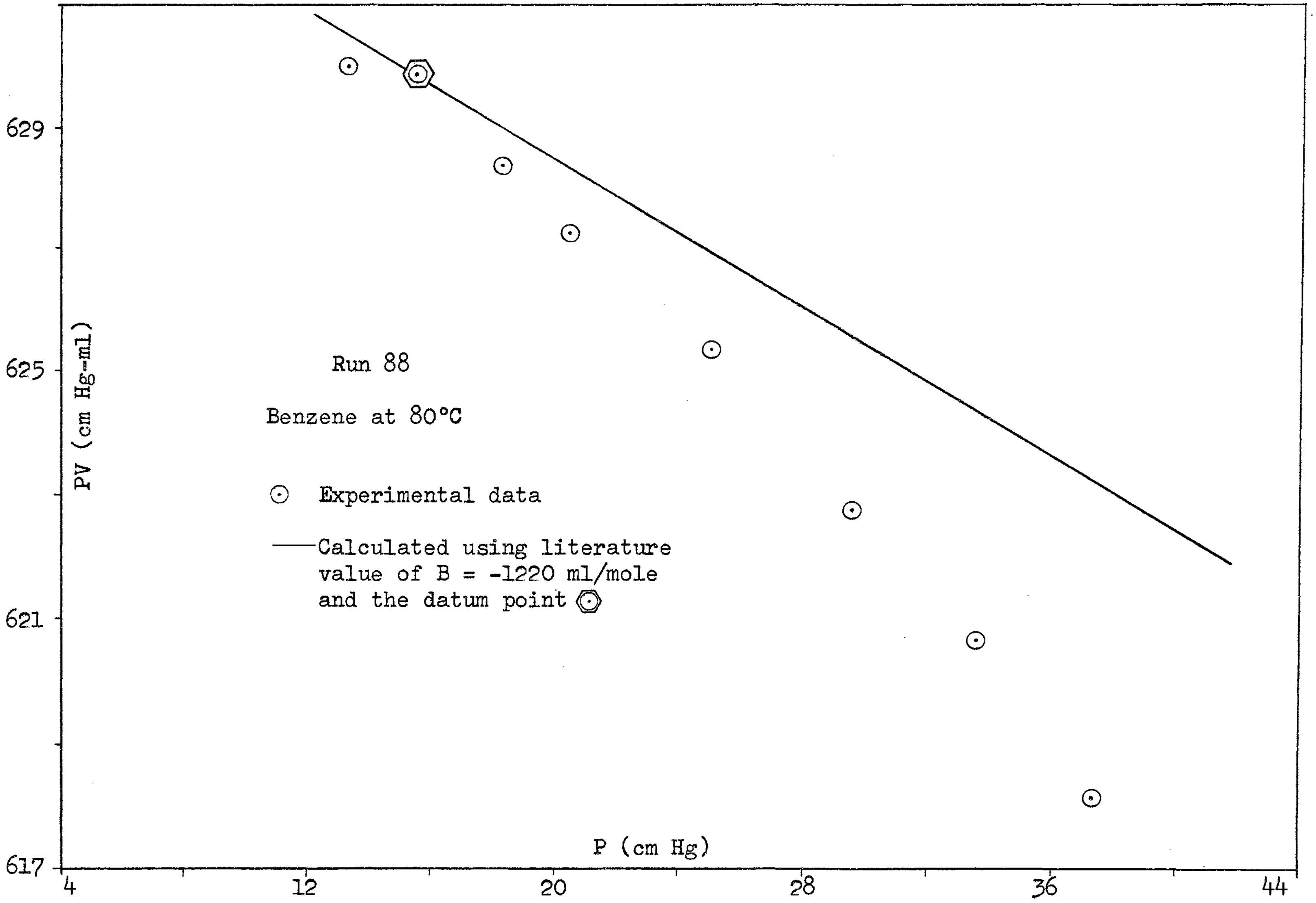

Figure 12. Relationship Between PV and P for Run 88

Runs 81 and 82 with benzene. The improvement in Runs 85 and 86 is quite apparent, although no changes were made in the experimental technique. Runs 87-92 were made immediately after Run 86 with the behavior illustrated by Figure 12. This behavior could be explained by the fact that an impurity was introduced into the U-tube when benzene was used in Runs 81 and 82; during Runs 83 and 84 with methanol, this impurity was in some way removed allowing for the improvement noted in Runs 85 and 86, and was again introduced with benzene in Runs 87-92.

At this point in the experimental investigation, the 3/4 inch U-tube was revised as discussed previously. After calibration with argon, Runs 98, 99, 104, and 105 were made with benzene and Runs 100-103 with methanol at 60°C. There is significant improvement in the results of these runs on the average over any of those previously considered. It is impossible to state whether the noted improvement is due to the revision which was made since the apparatus was thoroughly cleaned before these runs. It is seen that the results obtained for benzene from Runs 104 and 105 are better than those from Runs 98 and 99. It is believed that a large part of the deviation between the resulting second virial coefficients and the literature values is due to the sizable standard error which was present in the calibration volume used in these calculations. This standard error could cause an error in the determined second virial coefficient of -100 to -180 ml/mole. This is shown in the analysis in Appendix C. The general behavior of the data of these runs is illustrated in Figures 13 and 14 where a comparison with the literature values is also made. A slight concave curvature towards the pressure axis is noted in the data of these runs.

The results of the various series of runs made in this study are compared with each other by plotting PV/NRT versus P. This has been done for benzene at 60°C, benzene at 80°C, methanol at 60°C and methanol at 80°C in Figures 15, 16, 17, and 18, respectively. The runs chosen for these comparisons are all characteristic of the behavior of all the runs in the series to which it belongs.

The above figures again show a concave curvature of the data towards the pressure axis in most cases. These figures also show the marked deviation of some of the data from that calculated from the literature values of the second virial coefficients. The general behavior noted in these figures can be explained in the same manner as the PV versus P behavior of the data.

As this discussion has proceeded at various times, adsorption has been mentioned as the probable main source of error. The curvature which is noted in the results of a large number of the runs has been attributed to adsorption (8). This discussion is mainly qualitative due to lack of data on the adsorption of benzene and methanol by glass and mercury surfaces. Adsorption by an impurity which was in some way introduced into the U-tubes is also

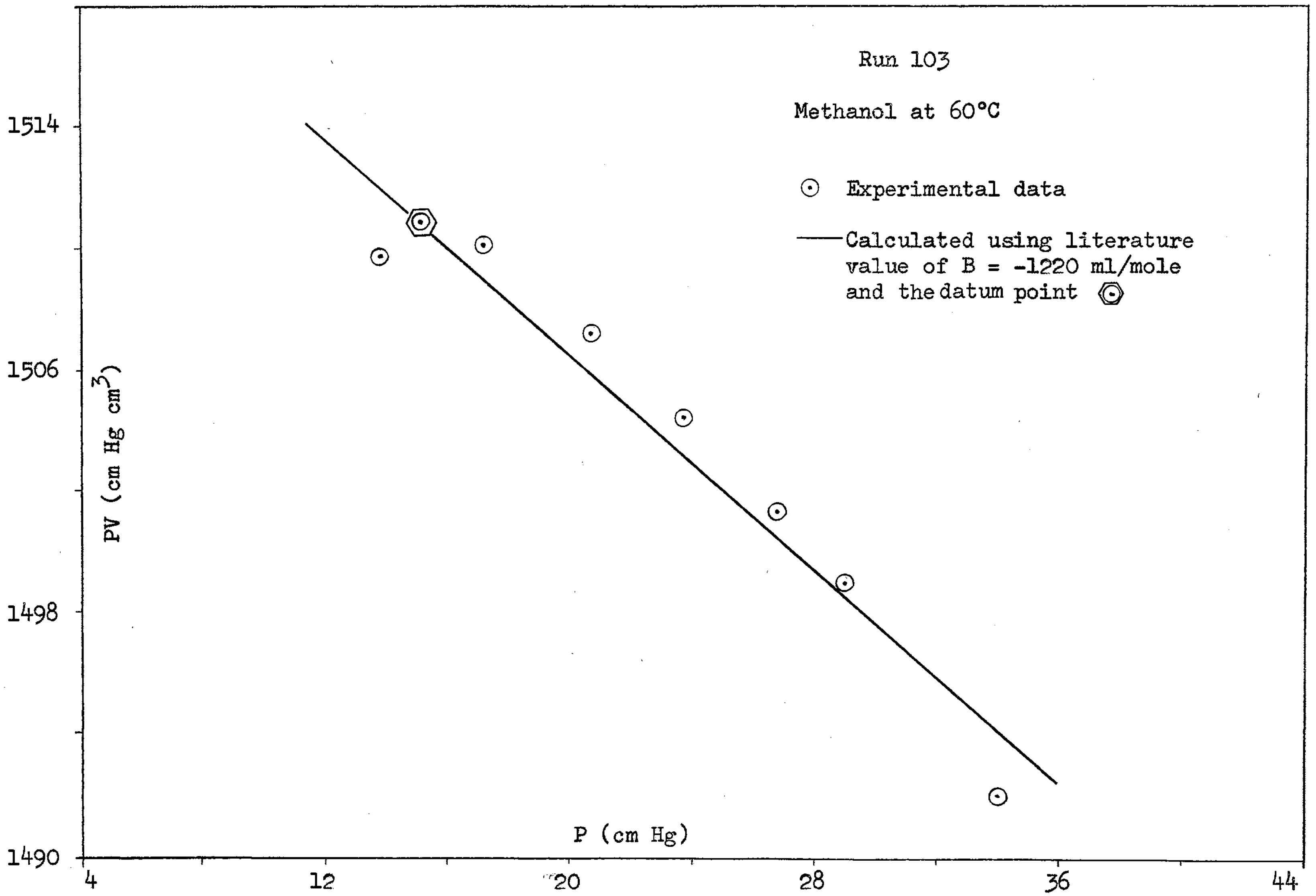

Figure 13. Relationship Between PV and P for Run 103

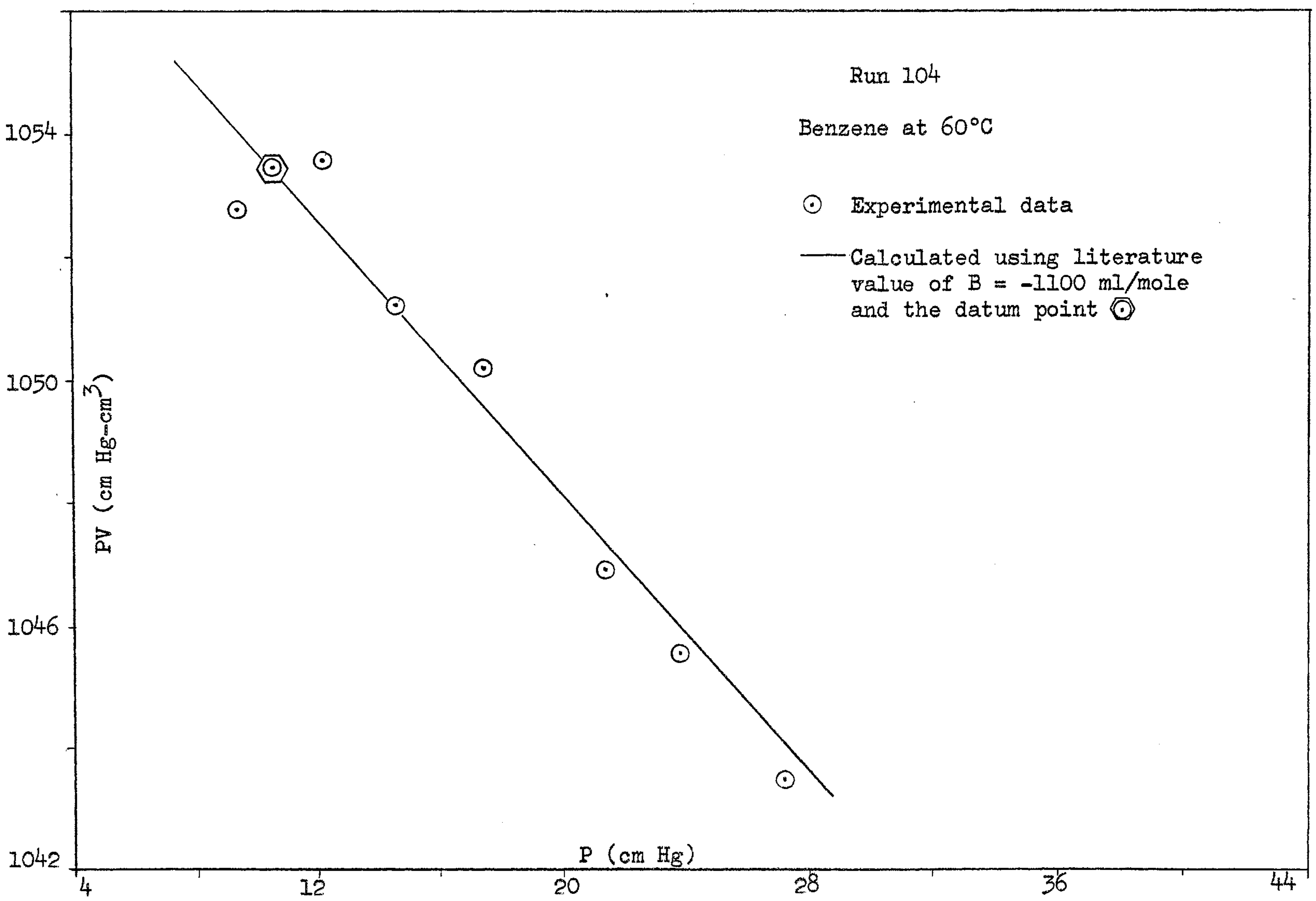

Figure 14. Relationship Between PV and P for Run 104

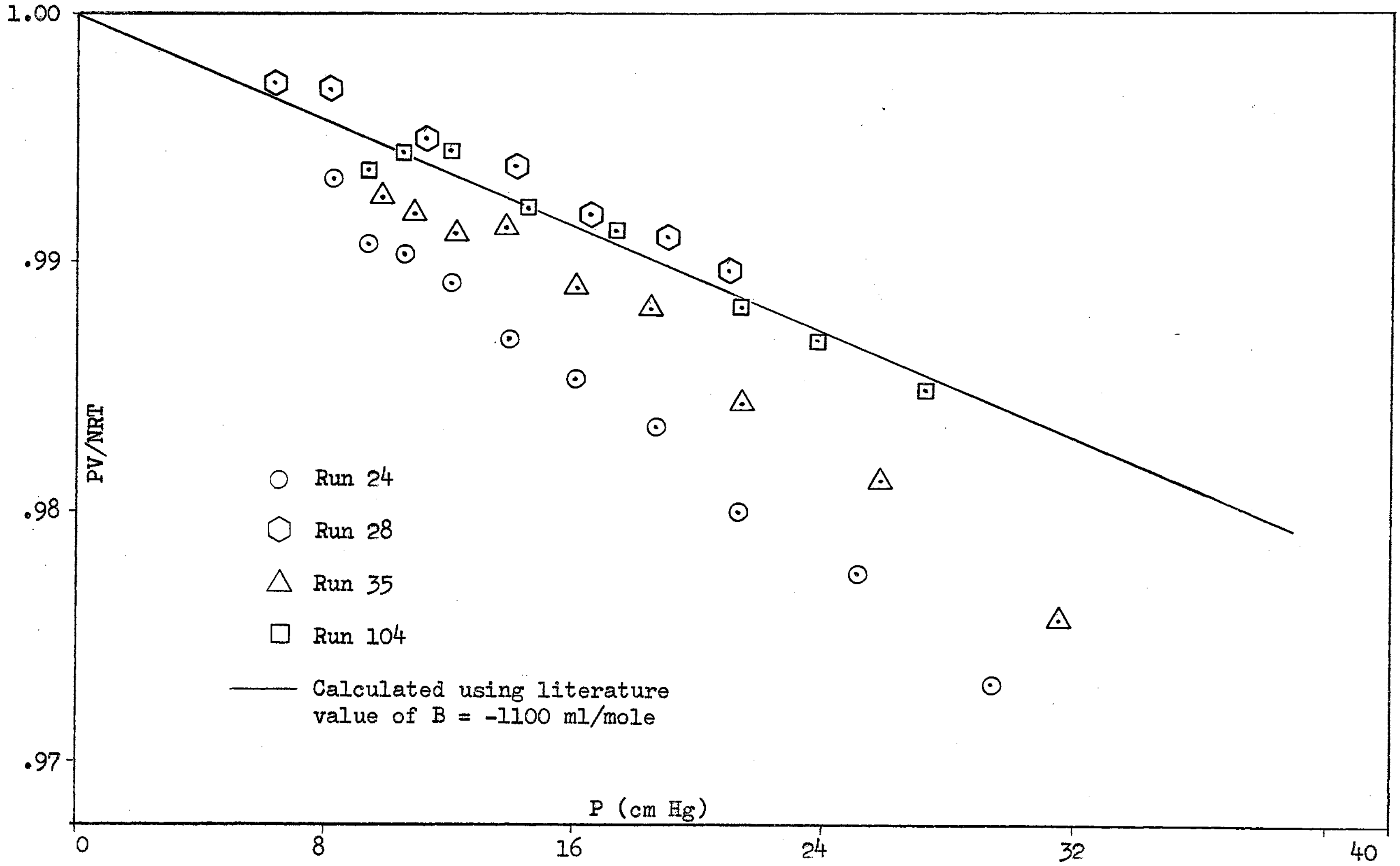

Figure 15. Comparison of Data for Benzene at 60°C

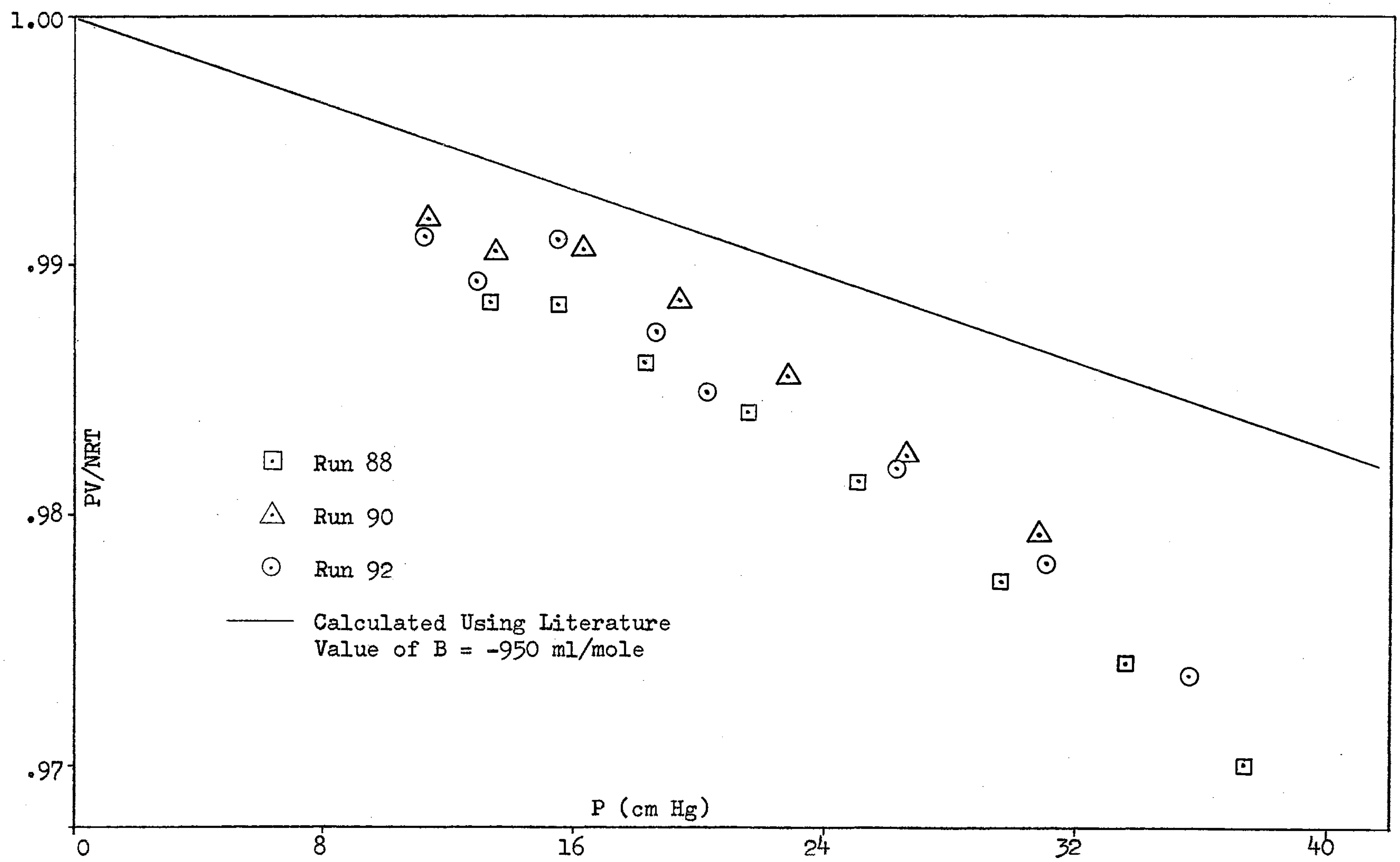

Figure 16. Comparison of Data for Benzene at 80°C

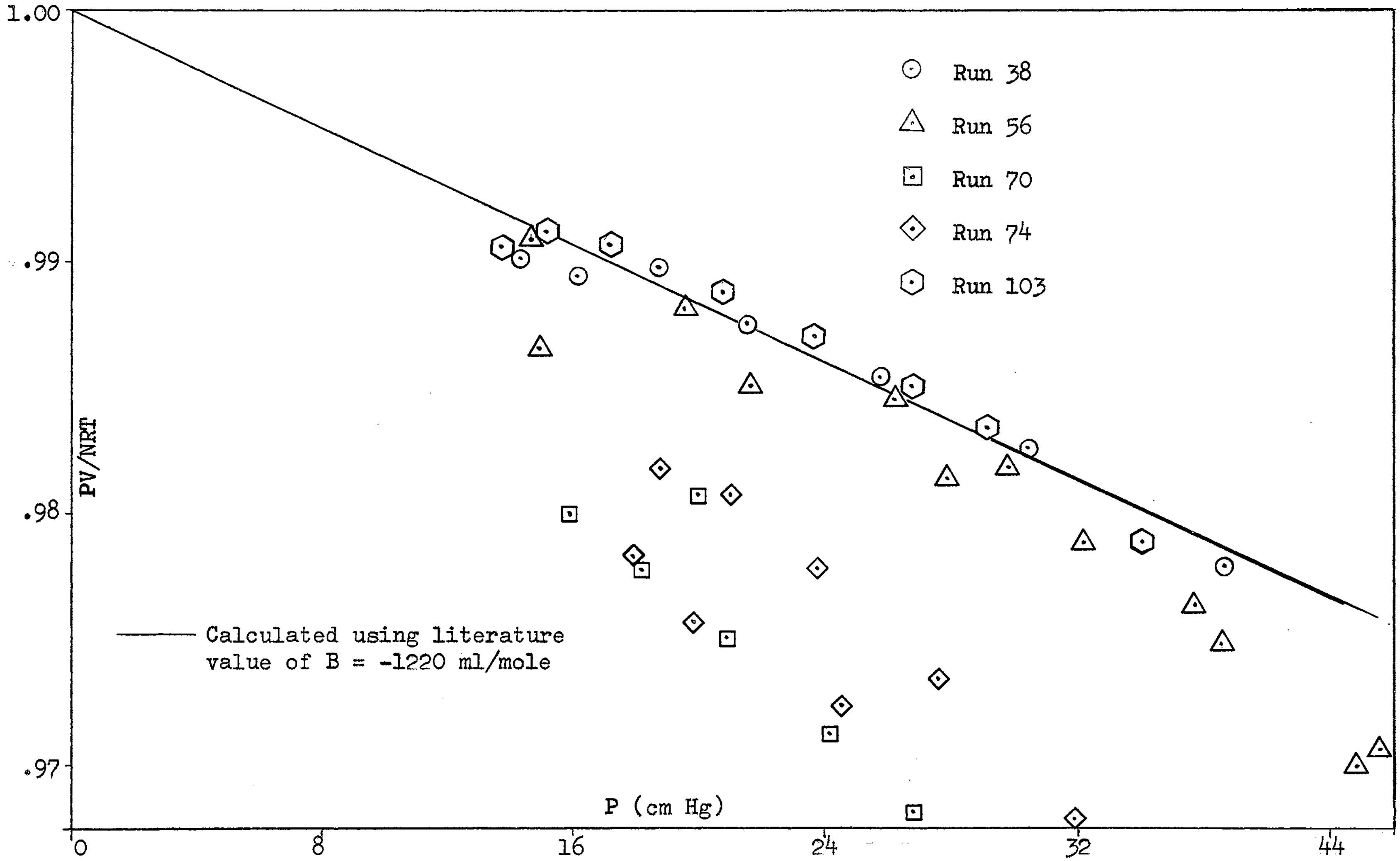

Figure 17. Comparison of Data for Methanol at 60°C

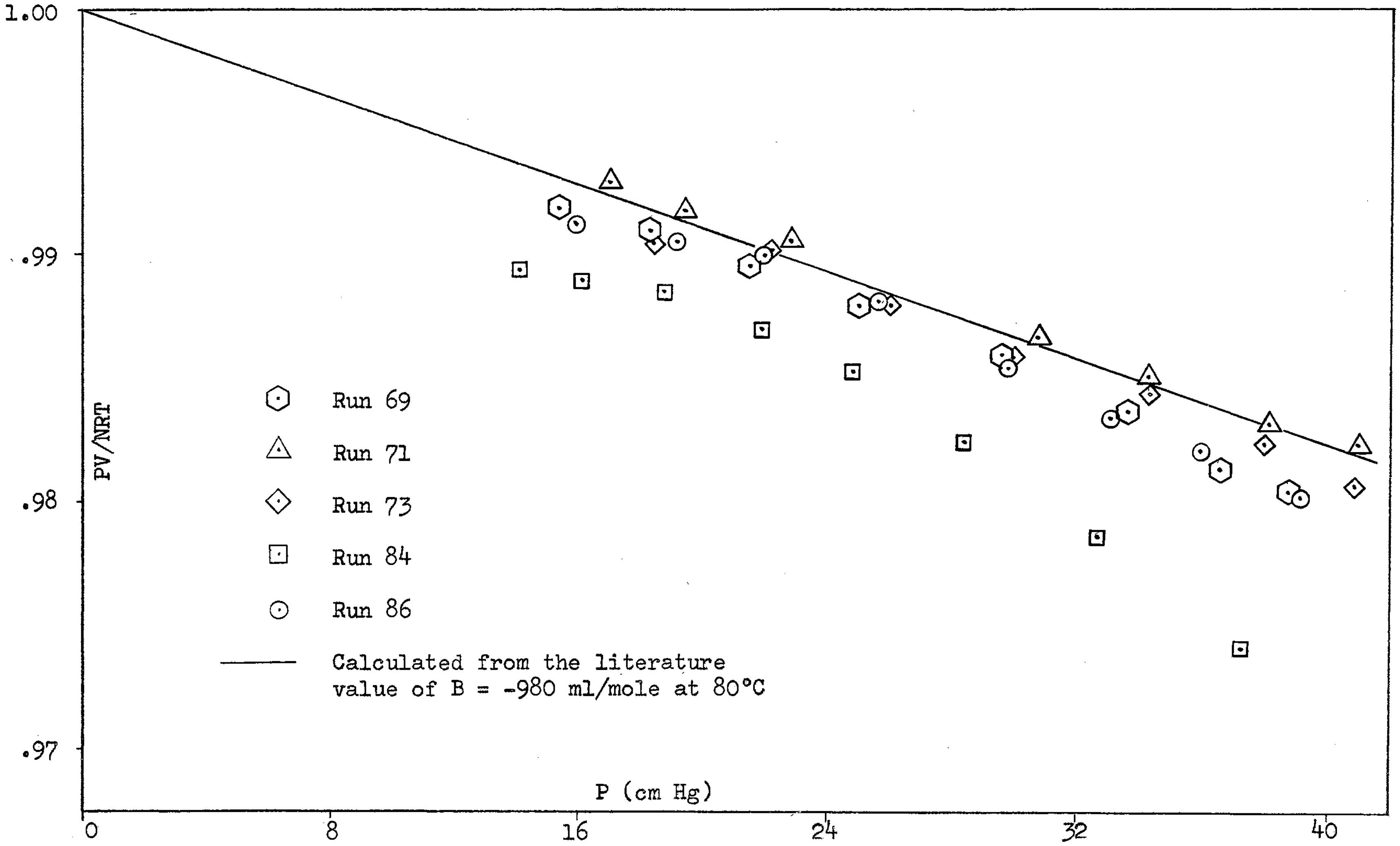

Figure 18. Comparison of Data for Methanol at 80°C

postulated. A majority of the resulting second virial coefficients are thought to be in error due to this reason. The adsorption is probably due to the contamination of the glass and mercury by stopcock grease. This stopcock grease more than likely found its way into the U-tubes by way of the stopcocks on the sample inlets. As the sample was introduced through these stopcocks, small amounts of stopcock grease were carried into the U-tubes. Some of the contamination is also thought to be due to incomplete rinsing after the U-tubes were washed.

Bottomley (5) has done some work on the adsorption of benzene by pyrex glass. The results of his work were obtained at lower pressures than those used in this work, but these results are used as a qualitative comparison with some of the calculations discussed in Appendix D. He also stated qualitatively that the adsorption increased many fold: (1) when the system used was contaminated with traces of stopcock grease and (2) when pressures above 70 per cent of the saturation pressure were used. Seventy per cent of the saturation pressures of benzene and methanol are 28 and 42 cm Hg, respectively, at 60°C. This was not important at 80°C since pressures equal to 70 per cent of the saturation pressures were never approached at this temperature. Even at 60°C, the data which were at a slightly higher pressure than 70 per cent of the saturation pressure behaved no differently than those directly below this pressure.

In the runs where the resulting second virial coefficients agree reasonably well with the literature values, the concave curvature towards the pressure axis is still apparent in most cases. Figures 5 (page 36) and 8 (page 42) are examples of this. All that can be stated about these runs is that the conditions are such that the adsorption was much less than in the other cases.

It is noted that the experimental PV products have a tendency to curve away from those calculated from the literature value of the second virial coefficient at both pressure extremes. At high pressures, the amount of material adsorbed is expected to increase, thereby causing the curvature as noted. At low pressures, the deviation is due to the increase in surface area exposed to the sample which has a tendency to over compensate the effect of the decreasing pressure.

Some calculations are made in Appendix D to illustrate the amount of the sample adsorbed. This was done for three different series of runs. This analysis of adsorption at least illustrates that for a given series of runs the behavior of each run of the series is very similar. These calculations also show that the amounts of sample assumed to have been adsorbed are not unreasonable.

The author believes that adsorption by the glass and mercury surfaces or by a contaminating material is the main reason why acceptable results (deviating from the literature values by ±100 ml/mole) were not obtained in this study. This is verified to a large extent by the discussion of the errors in Appendixes C and D.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

This study reported in this thesis included (a) a review of the types of apparatus used for low pressure determination of second virial coefficients, (b) a description of the apparatus used and the experimental procedure followed, and (c) a discussion of the results obtained with the probable sources of error.

The main points realized by this study may be summarized as:

1. The results obtained from experiment for the second virial coefficients of methanol and benzene were not acceptable when compared with literature values in all but a very few instances.
2. In all runs in which the results were not acceptable, the mercury and glass surfaces are postulated to have been contaminated by some foreign material which can be examined only qualitatively from the results obtained.
3. In the few runs in which acceptable results were obtained, there was still adsorption by

the glass or mercury which caused a concave curvature towards the pressure axis when the PV product is plotted versus the pressure.

4. In working with the type of apparatus used in this study, contamination of the mercury and glass surfaces is one of the most important factors which must be eliminated if acceptable results are to be obtained.
5. Upon evaluation of the probable errors involved other than adsorption, it is seen that the accuracy with which the calibration volume is determined and the sample size as related to the calibration volume have the largest effect on the second virial coefficient.

From information gained in this study, the following recommendations concerning future work may be made:

1. Be extremely careful in keeping the glass and mercury surfaces free from contamination.
2. Determine the calibration volumes with as much accuracy as possible.
3. When extending this work to binary mixtures, consider other methods for making up the mixtures so that no valve would be required at the top of the sample legs.

SELECTED BIBLIOGRAPHY

1. Addingley, C. G., and R. Whytlaw-Gray. "An Accurate Method for Comparing the Compressibilities of Gases Below Atmospheric Pressure," Trans. Fara. Soc., 24, 378 (1928).

2. Alexander, E. A., and J. D. Lambert. "The Second Virial Coefficient of Acetaldehyde," Trans. Fara. Soc., 37, 421 (1941).

3. Bottomley, G. A. "A Valve for Grease-Free Manipulation of Mercury," J. Sci. Instrument, 34, 369 (1957).

4. Bottomley, G. A., D. S. Massie, and R. Whytlaw-Gray. "A Comparison of the Compressibilities of Some Gases With That of Nitrogen at Pressures Below One Atmosphere," Proc. Roy. Soc., A, 200, 201-18 (1949).

5. Bottomley, G. A., and C. G. Reeves. "The Adsorption of Vapours on Pyrex Glass and Its Influence in the Measurement of Virial Coefficients," Trans. Fara. Soc., 53, 1455 (1957).

6. Burnett, E. S. "Compressibility Determination Without Volume Measurements," J. Applied Mechanics, 58, A136 (1936).

7. Carter, W. B. "Second Virial Coefficients of the Acetonitrile-Acetaldehyde System," M. S. Thesis, Univ. Calif., Berkeley, California (1959).

8. Casado, F. L., D. S. Massie, and R. Whytlaw-Gray. "Molecular Weight and Limiting Density of Propane," J. Chem. Soc. (London), 1746 (1949).

9. Cottrell, T. L., and R. A. Hamilton. "Second Virial Coefficients of Gases and Mixtures. I. CO_2 + He Mixtures," Trans. Fara. Soc., 52, 156-60 (1956).

10. Cox, J. D., and R. J. L. Andon. "Second Virial Coefficient of Pyridine and Benzene and Some Methyl Homologs Between 135 and 165°C," Trans. Fara. Soc., 54, 1622-9 (1958).

11. Dalton, B. J. "Calculation of the Standard Error by Least Squares' Methods," Information Circular, United States Department of the Interior, Bureau of Mines (unpublished April, 1963).

12. Fox, J. H. P., and J. D. Lambert. "The Second Virial Coefficients of Mixed Organic Vapours," Proc. Roy. Soc., A, 210, 557 (1951).

13. Francis, P. G., and M. L. McGlashan. "Second Virial Coefficients of Vapor Mixtures," Trans. Fara. Soc., 51, 593-9 (1955).

14. Gaertner Scientific Corp. Instructions for the use of Gaertner M907 and M908 Cathetometers, File No. 701C, October, 1950 (Chicago).

15. Guggenheim, E. A., and M. L. McGlashan. "Corresponding States in Mixtures of Slightly Imperfect Gases," Proc. Roy. Soc., A, 206, 448 (1951).

16. Hamann, S. D., and J. F. Pearse. "The Second Virial Coefficients of Some Organic Molecules," Trans. Fara. Soc., 48, 101 (1952).

17. Handbook of Chemistry and Physics, 40th Edition. Chemical Rubber Publishing Company, 1958-1959.

18. Hirschfelder, J. O., C. R. Curtiss, and R. B. Bird. Molecular Theory of Gases and Liquids. New York: John Wiley and Sons, Inc., 1954.

19. Hirschfelder, J. O., F. T. McClure, and J. F. Weeks. "Second Virial Coefficients and Forces Between Complex Molecules," J. Chem. Physics, 10, 201 (1942).

20. Knobler, C. M., J. J. M. Beenakker, and H. F. P. Knaap. "Second Virial Coefficient of Gaseous Mixtures at 90°K," Physica, 25, 909-16 (1959).

21. Lambert, J. D., G. A. H. Roberts, J. S. Rowlinson, and V. J. Wilkinson. "The Second Virial Coefficients of Organic Vapors," Proc. Roy. Soc., A, 196, 113 (1949).

22. Mantell, C. L. Adsorption. New York and London: McGraw-Hill Book Company, Inc., 1945, p. 25.

23. Rowlinson, J. S. "The Second Virial Coefficients of Polar Gases," *Trans. Fara. Soc.*, 45, 974 (1949).

24. Stockmayer, W. H. "Second Virial Coefficients of Polar Gases," *J. Chem. Physics*, 9, 398, 863 (1941).

APPENDIX A

DATA ANALYSIS

The following discussion is an illustration of the calculational procedure used to determine the second virial coefficient from the experimental data. The data used here is from Run 38, a run using methanol.

EXPERIMENTAL DATA

Radius of precision bore tube = R = 0.25 inches
Calibration volume . . . . = Calv = 9.471 cm^3
Calibration height . . . . = Calh = 8.000 cm
Room Temperature . . . . . . = t = 28.2°C
Reference point cathetometer reading = Refp = 56.096 cm
56.090 cm
56.094 cm

T(°C) Bath temperature	R_n(cm) Cathetometer reading of Hg height in vacuum leg		S_n(cm) Cathetometer reading of Hg height in sample leg		
60.08	84.736	84.736	42.015	42.005	42.006
60.08	76.916	76.914	39.860	39.860	
60.08	67.310	67.308	36.555	36.551	36.553
60.08	59.085	59.085	33.040	33.044	33.046
60.08	50.150	50.148	28.463	28.460	
60.08	43.312	43.310	24.405	24.402	
60.08	35.782	35.782	19.464	19.466	
60.08	29.268	29.270	14.805	14.810	14.805

Taking the arithmetic average of cathetometer readings:

$R_{n,avg}$	$S_{n,avg}$	$R_{n,avg}$	$S_{n,avg}$
84.736	42.009	50.149	28.461
76.915	39.860	43.311	24.403
67.309	36.553	35.782	19.465
59.085	33.043	29.269	14.807

$(\text{Refp})_{\text{avg}} = 56.093$ $\qquad T_{\text{avg}} = 60.08°\text{C}$

Temperature correction from NBS calibration = 0.03°C

$T_{\text{corrected}} = 60.05°\text{C}$

Partial pressure of mercury at 60°C = 0.0025 mm Hg (17).

The pressure and volume are now calculated from the following equations:

$$P_n = (R_n - S_n)(E)(F) - \text{PPHG} \qquad \text{(A-1)}$$

$$V_n = \text{Calv}(G) + (\text{Refp} - \text{Calh} - S_n)(A)(G)(F) \qquad \text{(A-2)}$$

and

$$E = 1/(1 + 0.18169 \times 10^{-3}T + 0.2951 \times 10^{-8}T^2 + .11456 \times 10^{-9}T^3) \qquad \text{(A-3)}$$

$$F = 1 - 0.000011(t - 20) \qquad \text{(A-4)}$$

$$G = (1 + 32.5 \times 10^{-7}(T - 46.84))^2 \qquad \text{(A-5)}$$

$$A = (2.5400)^2 \pi R^2 \qquad \text{(A-6)}$$

where

R_n - is the cathetometer reading of the height of the mercury in the vacuum leg for the $n^{\underline{th}}$ reading (cm)

S_n - is the cathetometer reading of the height of the mercury in the sample leg for the $n^{\underline{th}}$ reading (cm)

P_n - the pressure for the $n^{\underline{th}}$ reading (cm Hg)

V_n - the volume for the $n^{\underline{th}}$ reading (cm^3)

Calv - the calibration volume (cm^3)

Calh - the calibration height (cm)

Refp - the reference point reading of the cathetometer (cm)

T - - the bath temperature (°C)

t - - the room temperature (°C)

R - - the radius of the sample leg (inches)

n - - the number of different readings per run

E - - the pressure correction allowing for the cubical expansion of the mercury with temperature

F - - the correction for the linear expansion of the cathetometer scale with temperature

G - - the correction term for the thermal expansion of pyrex

A - - the cross-sectional area of the U-tube (cm^2)

PPHG - the partial pressure of mercury at bath temperature.

After calculating the pressures and volumes with the preceding equations, a least mean square straight line is found for the equation:

$$P_n V_n = NR_o T + NBP \tag{A-7}$$

where

N - is the number of moles (g-moles)

R_o - is the universal gas constant ($cm\ Hg\text{-}cm^3$)/g-mole-°K)

B - is the second virial coefficient (ml/mole) by use of the following equations:

$$\text{Slope, } NB = \frac{\Sigma(P_n)^2 V_n - \Sigma P_n V_n \Sigma P_n/n}{\Sigma(P_n)^2 - (\Sigma P_n)^2/n} \qquad \text{(A-8)}$$

$$\text{Intercept, } NR_oT = (\Sigma P_n V_n)/n - NB(\Sigma P_n)/n \qquad \text{(A-9)}$$

$$N = NR_oT/R_oT \qquad \text{(A-10)}$$

$$\text{and} \quad B = NB/N \ . \qquad \text{(A-11)}$$

A program for the IBM 1620 digital computer was written incorporating these equations to do these calculations. The results for Run 38 are tabulated below.

P_n	V_n	P_nV_n
42.260	17.179	725.98
36.650	19.901	729.37
30.419	24.090	732.81
25.756	28.537	735.00
21.450	34.341	736.61
18.700	39.481	738.30
16.137	45.737	738.06
14.302	51.637	738.53

NR_oT = 746.04

N = 0.0003590

NB = -0.45518

B = -1268

The data taken with a calibration run is the same as that shown for Run 38. However, this data is analyzed in a slightly different manner. Since argon was used in the calibration and the second virial coefficient of argon is zero at 320° K, the data is fitted to the following equation:

$$PV + P(\text{Calv}) = NR_oT \qquad \text{(A-12)}$$

where P is determined by Equation (A-1) and V is the volume as calculated by Equation (A-2) with the calibration volume set equal to zero. A calibration height (Calh) of 8.000 cm is used for all the runs made in this work.

When the above equation is fitted to the experimental data, the slope of the line is the calibration volume. This is given by the following equation:

$$\text{Slope, Calv} = \frac{\Sigma P_n^2 V_n - \Sigma P_n V_n \Sigma P_n / n}{\Sigma (P_n)^2 - (\Sigma P_n)^2 / n} . \qquad \text{(A-13)}$$

The results of these calculations are tabulated in Table III, Appendix B.

APPENDIX B

CALIBRATION VOLUMES

The calibration volumes are determined from the data as indicated in Appendix A. The results of the calibration runs for the 3/4 inch diameter U-tube, the 1/2 inch diameter U-tube and the revised 3/4 inch U-tube are tabulated in Table III.

The average value for the calibration volume of the 3/4 inch U-tube is found to be 9.051 ± 0.096 ml. If the values obtained from Runs 7-10 and 17 are omitted, this value is 9.087 ± 0.028 ml. The improvement obtained in the standard error and the fact that the omitted values all deviate from this average value by more than four times the standard error is used as sufficient reason to neglect these values. The second virial coefficients calculated for Runs 26-28 are -855, -896 and -757 ml/mole respectively when this value is used as the calibration volume. Since these values are all below the literature value, a quantitative explanation should be made for this behavior. The only errors which could cause deviation in this direction of this magnitude are either a leak or a sizable error in the calibration volume. Since the author is certain that there were no leaks in the apparatus, it

TABLE III

CALIBRATION VOLUMES

1/2 inch U-tube

Run	Calibration volume (ml)
1	9.552
2	9.600
3	9.485
4	9.504
5	9.471
6	9.466
43	9.483
45	9.473
46	9.471
47	9.429
48	9.442
49	9.451
50	9.470

3/4 inch U-tube

Run	Calibration volume (ml)
7	8.899
8	8.961
9	8.930
10	8.902
11	9.045
12	9.065
13	9.074
14	9.048
15	9.144
16	9.089
17	9.231
18	9.080
19	9.128
20	9.111

Revised 3/4 inch U-tube

Run	Calibration volume (ml)
96	21.784
97	21.710
106	21.646
107	21.508
112	21.656
113	21.558

	Average value of calibration volume (ml)	Standard Error (ml)
1/2 inch U-tube		
-all runs included	9.484	0.046
-less runs 1, 2, and 47	9.472	0.017
3/4 inch U-tube		
-all runs included	9.051	0.096
-less runs 7-10 and 17	9.087	0.028
Revised 3/4 inch U-tube		
-all runs included	21.643	0.090

is assumed that this behavior is caused by an error in the calibration volume. For this reason, the calibration volume used for Runs 21-28 is chosen as 9.000 ml.

The average value for the calibration volume of the 1/2 inch U-tube is 9.484 ± 0.046 ml. If the results of Runs 1, 2, and 47 are omitted, the average value becomes 9.472 ± 0.017 ml. Here again sufficient reason is obtained for dropping these values from the improvement in the value for the standard error and the fact that Runs 1 and 2 differ from this average value by more than four times the standard error and Run 47 differs from the average value by more than two times the standard error. Another reason for omitting the results of Runs 1 and 2 is that they were the first runs made on the equipment so the possibility that they are in error is greater. Thus, the value of 9.472 ± 0.017 ml was used as the calibration volume for Runs 29-92.

The average value for the calibration volume of the revised 3/4 inch U-tube is 21.643 ± 0.090 ml. This value was used for Runs 98-105 even though there is a relatively large standard error present in using this value.

APPENDIX C

ERROR ANALYSIS

Expected error in PV product obtained from 1/2 inch diameter U-tube assuming 0.003 cm error in each cathetometer reading and .017 ml error in the calibration volume for the 1/2 inch U-tube.

Expected error in the Pressure

2 - cathetometer readings -- error is ± 0.006 cm

Pressure = P ± 0.006 cm Hg = P ± 0.6/P%

Expected error in volume

Error in the calibration volume

From analysis of data for calibration volume

Calv = 9.472 ± 0.017 ml

Error in cross-sectional area of the U-tube

From the tolerance on the precision bore tubing

$$D = 0.5 \pm 0.0002 \text{ inches}$$

$$= 0.5 \pm 0.04\%$$

$$A = (2.5400)^2 \pi (0.25)^2 \pm 0.08\%$$

$$= 1.26677 \pm 0.08\% \text{ cm}^2$$

Error in volume excluding the calibration volume

Define h as: h = Refp - Calh - Sn (cm)

2 - cathetometer readings in the measurement of h

$$h = h \pm 0.6/h\%$$

$$\text{Volume} = A \times h$$

$$= 1.26677\,h \pm (0.08 + 0.6/h)\%\ \text{cm}^3$$

Total volume with expected error

$$\begin{array}{r} 9.472 \pm 0.017 \\ +\ 1.26677h \pm 1.26677h(0.0008 - 0.006/h) \\ \hline = 1.26677h + 9.472 \pm (.017 + .001013h - .0076) \end{array}$$

or

$$V = 1.26677h + 9.472 \pm \frac{(2.46\ +\ 0.1013h)}{(1.26677h + 9.472)}\%$$

The error in the PV product, σ, is now

$$\sigma = \pm[.6/P + (2.46 + .1013h)/(1.26677h + 9.472)]\% .$$

An example is presented below in which the expected error in the PV product is calculated by the above equation for Run 38.

at $P = 42.260$ cm Hg

$$PV = 725.98 \pm 1.36$$

at $P = 25.756$ cm Hg

$$PV = 735.00 \pm 1.24$$

at $P = 14.302$ cm Hg

$$PV = 738.53 \pm 1.13 .$$

The arithmetic average of the absolute values of the deviations of the PV products from the fitted line for this run is found to be 0.61. This same arithmetic average averaged over all of the runs made was found to be

0.66. Therefore, the actual results obtained give better results than is expected from the previous expected error analysis even though the arithmetic average was increased for a majority of the runs due to the curvature which has been previously noted. However, it should be noted that an error in the calibration volume is not included in the arithmetic average deviation considered above.

The effect of the deviation of the PV products from the straight line fitted to the data on the determined second virial coefficients is considered in the next section.

Statistical Analysis of Standard Error in B

This analysis does not consider the accuracy of the calculated second virial coefficients with respect to literature values. However, it is a good estimate of the standard error of B which could be expected from the scatter of the experimental data about the least mean square fitted straight line. The magnitude of the deviation of the data scattered about the fitted line in this work is larger than if the tendency of curvature was not present. The results of this analysis are presented in Table IV. These results actually indicate that the scatter inherent in the cathetometer readings was not large and results dependent upon just this scatter would be very acceptable.

It should be mentioned that these standard errors do not include the effect of an error in the calibration

TABLE IV

STANDARD ERROR IN SECOND VIRIAL COEFFICIENT FROM STATISTICAL ANALYSIS

Run Number	Second Virial Coefficient (ml/mole)	Standard Error (ml/mole)
105	-1151	31
104	-1137	11
103	-1219	59
102	-1317	45
101	-1292	66
100	-1320	18
99	-1356	25
98	-1246	16
92	-1580	36
91	-1117	33
90	-1445	35
89	-1618	39
88	-1728	37
87	-1685	45
86	-1101	37
85	-1105	38
84	-1443	61
83	-1414	46
82	-1469	65
81	-1607	45

The average standard error of the above runs is 39.1.

volume. Such error causes a change of the slope of the data on a PV versus P plot but it would not affect the scatter of the experimental data about the fitted line.

Since a least mean square fit is used with Equation (A-7), the following equations are used in the analysis (11):

The standard error in the PV values

$$S_{pv} = \left\{\frac{n\Sigma(P_nV_n)^2 - \Sigma[(P_nV_n)]^2}{n(n-2)}\right\}^{1/2} \qquad (C\text{-}1)$$

The standard error in the intercept

$$S_A = S_{pv}\left\{\frac{\Sigma P^2_n}{n\Sigma P^2_n - (\Sigma P_n)^2}\right\}^{1/2} \qquad (C\text{-}2)$$

The standard error in the slope

$$S_B = S_{pv}\left\{\frac{n}{n\Sigma P^2_n - (\Sigma P_n)^2}\right\}^{1/2} \qquad (C\text{-}3)$$

The estimated error in the temperature

$$S_T = 0.03°C \qquad (C\text{-}4)$$

Now, since in the calculation of B, one has

$$B = \frac{\text{slope (NB)}}{\text{Intercept }(NR_oT)/R_oT} \qquad (C\text{-}5)$$

the percentage error in B will be equal to the sum of the percentage errors in the slope, the intercept and the temperature. The percentage error in B is then given by the following equation:

$$\% \text{ error in } B = (S_A/NR_oT + S_B/NB + S_T/T)100 \ . \qquad \text{(C-6)}$$

The standard error in B is now equal to the percentage error in B multiplied times the value of B.

Error in the Second Virial Coefficient Due to an Error in Calibration Volume

The error in the calculated second virial coefficient is a linear function of the error in the calibration volume. For example, if the error in the virial coefficient was 30 ml/mole caused by an error of 0.01 ml in the calibration volume, then if the error in the calibration volume was 0.02 ml the error in the virial coefficient would be 60 ml/mole. Likewise, if the error in the calibration was -0.01 ml, the error in the calculated virial coefficient would be -30 ml/mole.

The error in the calculated virial coefficient due to an error in the calibration volume is also a function of the number of moles of sample used. Figures 19, 20, and 21 show this relationship. The data used in these figures were obtained by varying the calibration volume by a known increment and using the digital computer program previously mentioned, calculating the corresponding change in the virial coefficient. These figures show that as the number of moles decreases the error involved in the calculated second virial coefficient increases very rapidly for a

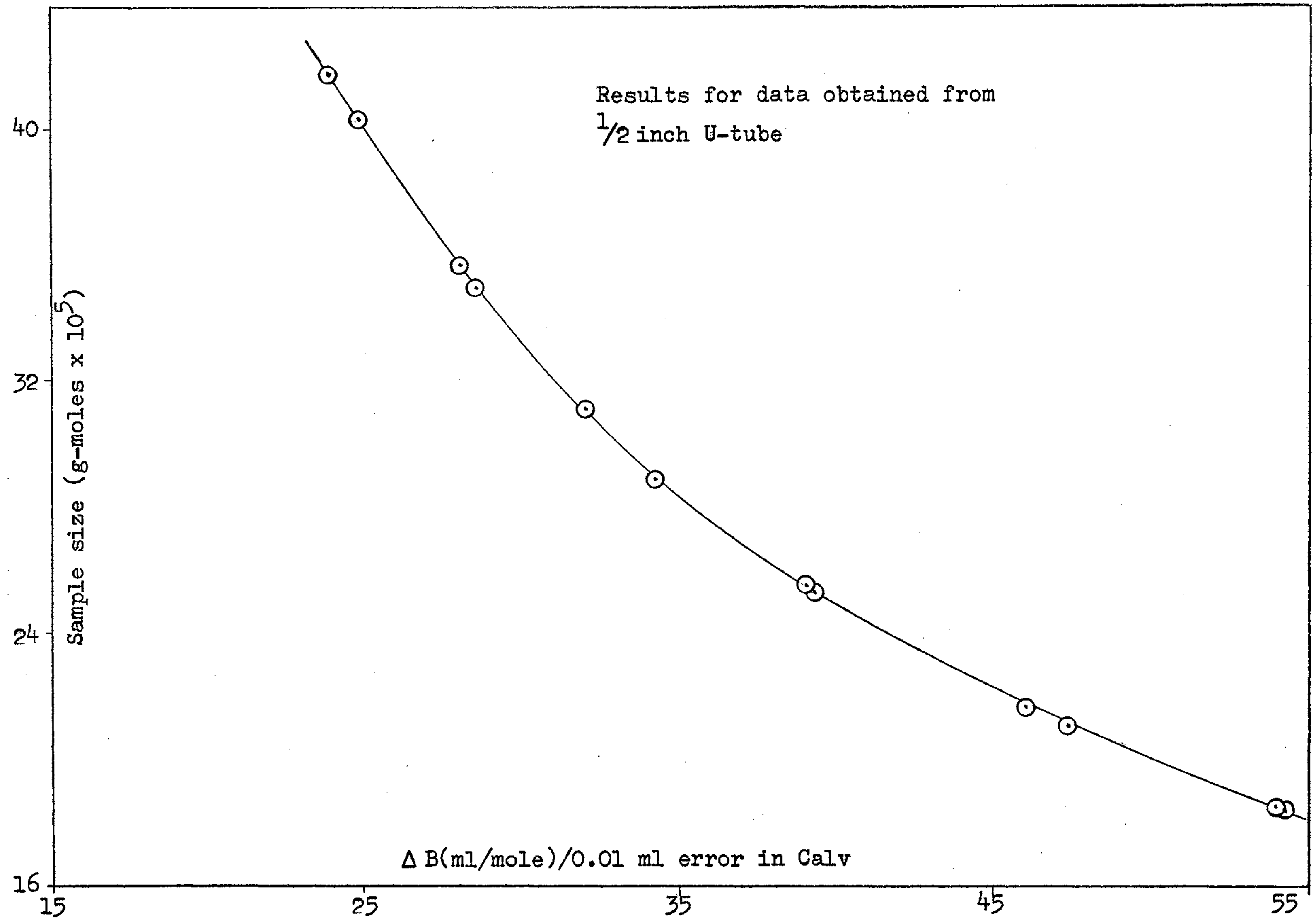

Figure 19. Relationship Between Moles of Sample and the Error in B Due to Error in the Calibration Volume

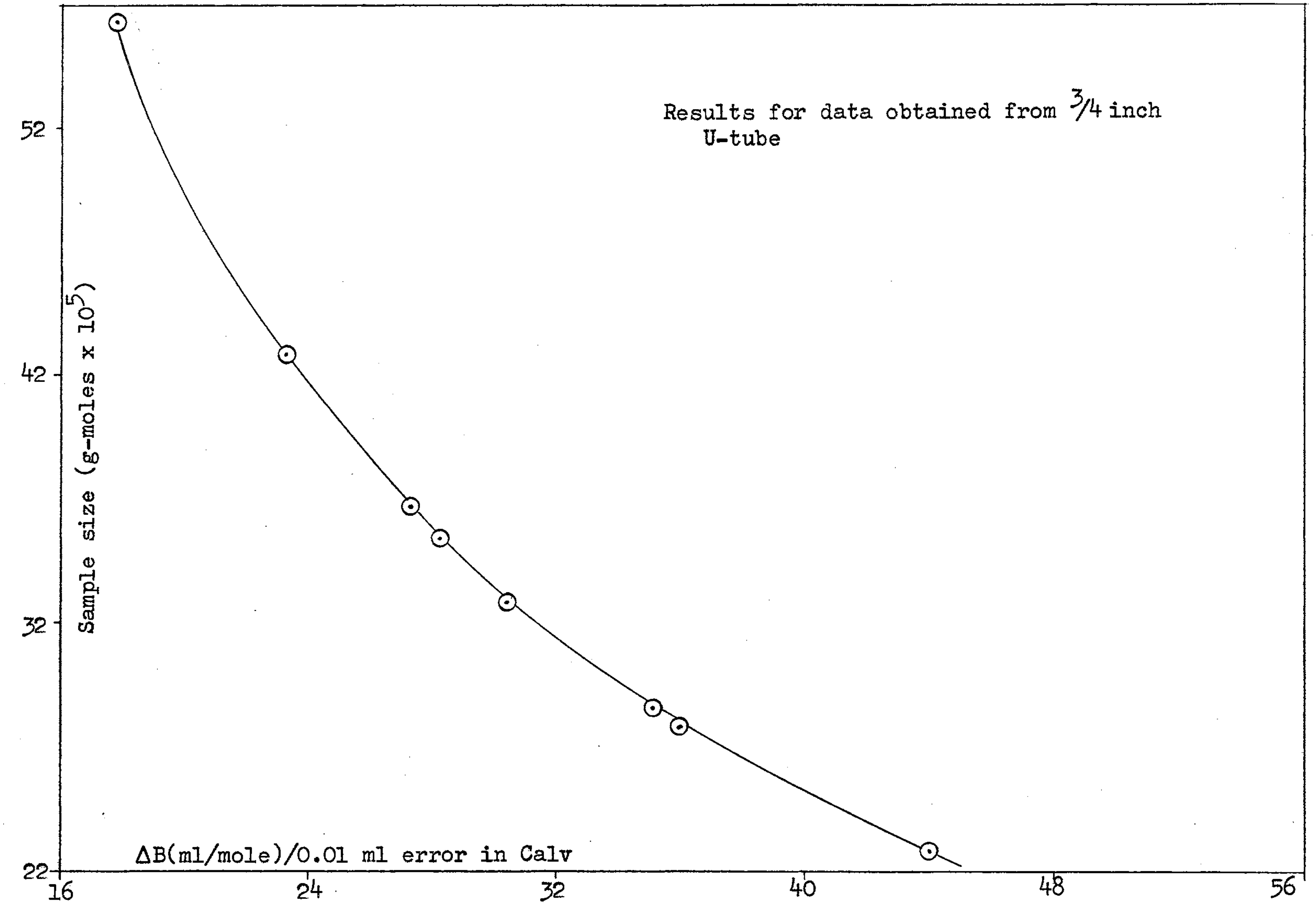

Figure 20. Relationship Between Moles of Sample and the Error in B Due to Error in the Calibration Volume

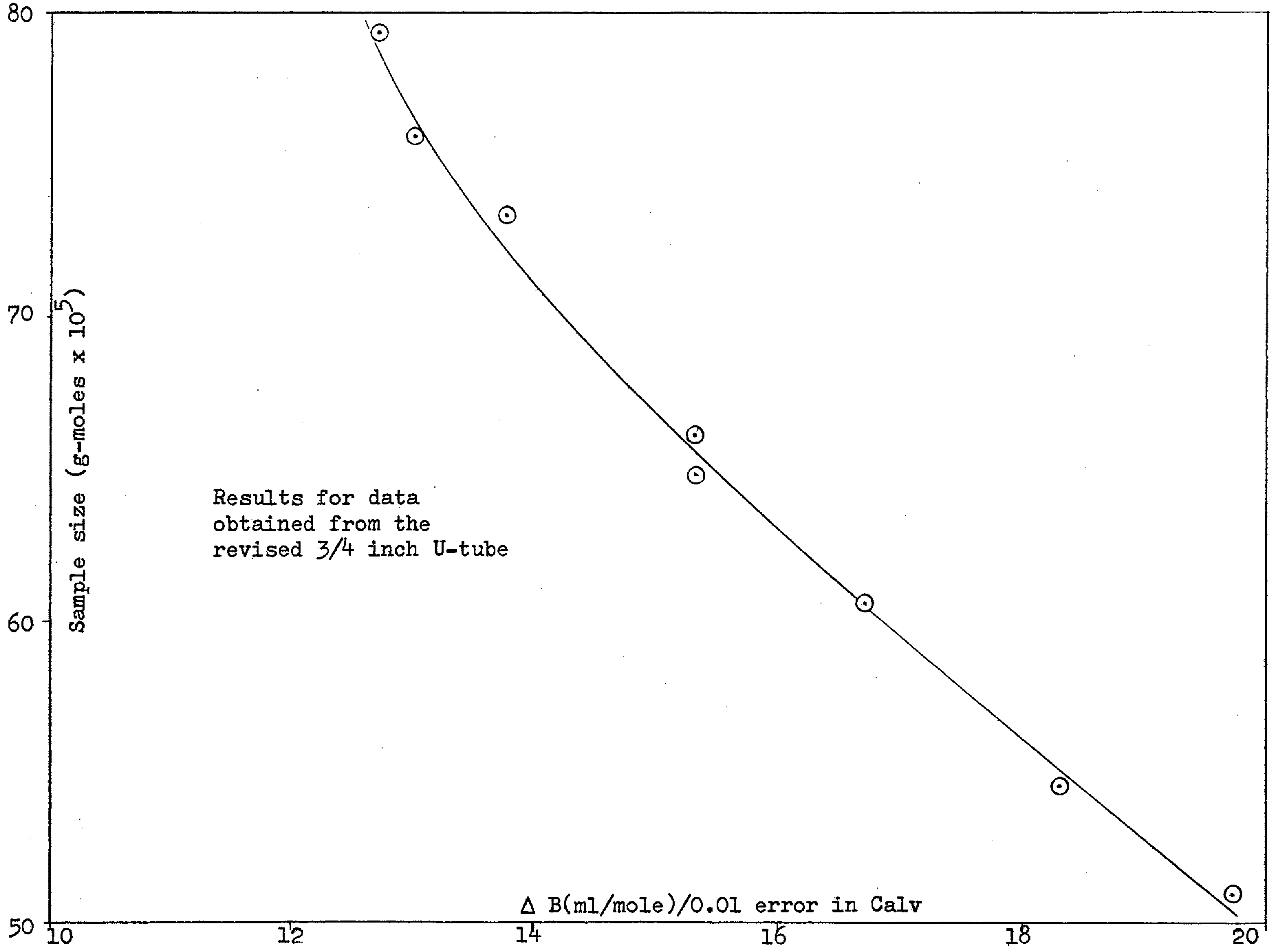

Figure 21. Relationship Between Moles of Sample and the Error in B Due to Error in the Calibration Volume

given error in the calibration volume. This can be qualitatively used to partially explain why the results for methanol on the average were better than those for methanol. The amount of benzene used in a run was always less than the amount of methanol used in a corresponding run.

From this analysis and the standard errors involved in the calibration volumes, the error in the second virial coefficient resulting from the calibration volume is 41 to 92 ml/mole for the 1/2 inch U-tube, 100 to 225 ml/mole for the 3/4 inch U-tube assuming a standard error of 0.05 ml, and 100 to 180 ml/mole for the revised 3/4 inch U-tube.

APPENDIX D

SOME ADSORPTION CALCULATIONS

Adsorption is considered here for three different series of runs. For two of these, the same method of analysis is used and in the third a slightly different analysis is used. The first method is used on Runs 31-37 and Runs 87-90. Here, an experimental PV value at approximately the same pressure for each run in a series is used with the literature value of the second virial coefficient to calculate the PV products which would give acceptable results. The difference between the experimentally determined values and those calculated, ΔPV, is proportional to the number of moles adsorbed, N. If this ΔPV is divided by the volume, $\Delta P/V$, a quantity proportional to the moles adsorbed per unit area is obtained. The relationship between $\Delta PV/V$ and the pressure is illustrated in Figures 22 and 23. If the quantity $\Delta PV/V$ is divided by R_oT and multiplied by the volume to area ratio the resulting quantity is the number of moles adsorbed per unit area. A summary of these calculated values is presented in Table V. The volume to area ratio used for this calculation was 0.643 which is only an approximate value. A quantitative comparison is made with some data from the literature at

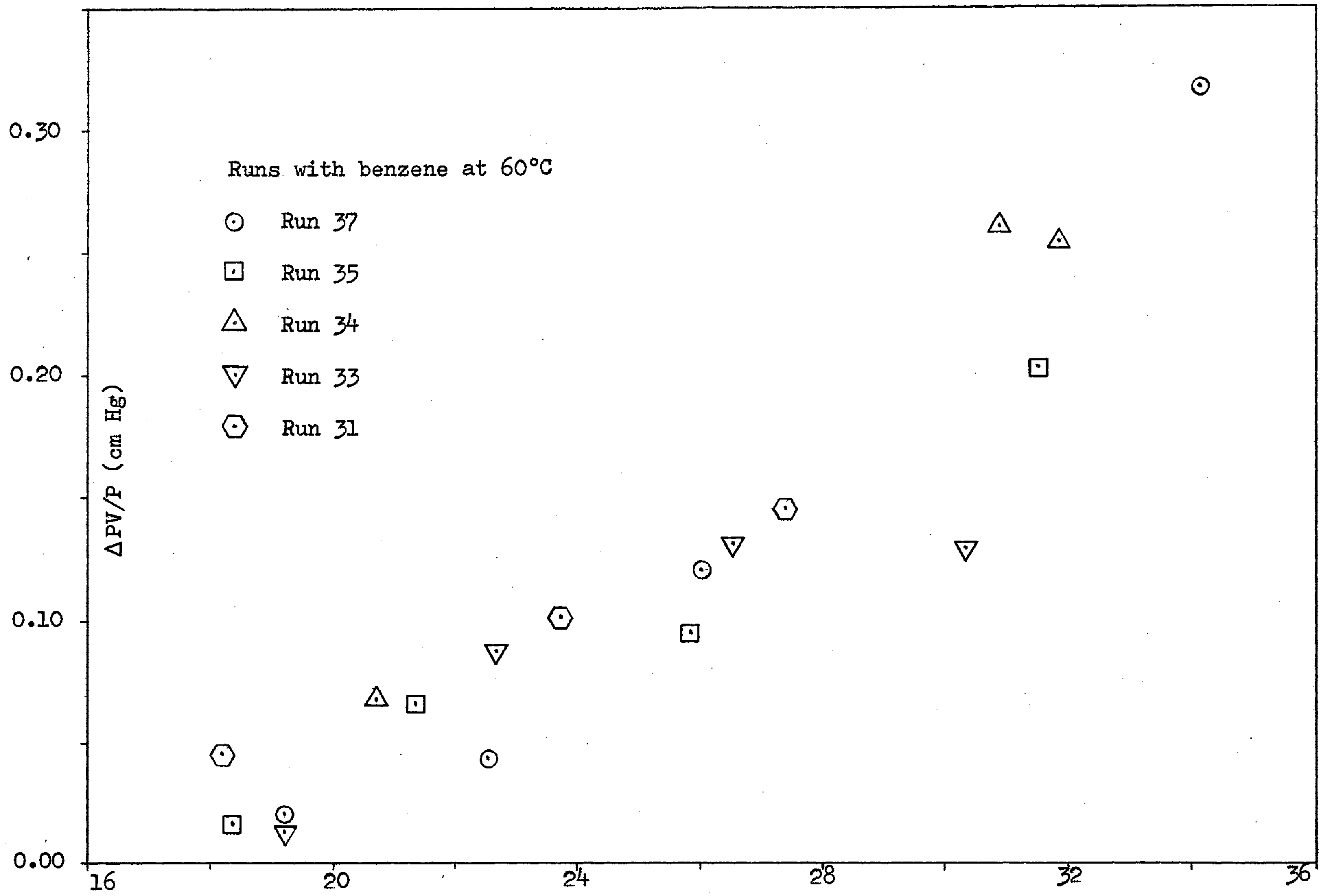

Figure 22. Deviation of Experimental Values of PV From Those Calculated Using the Literature Value of B as a Function of P

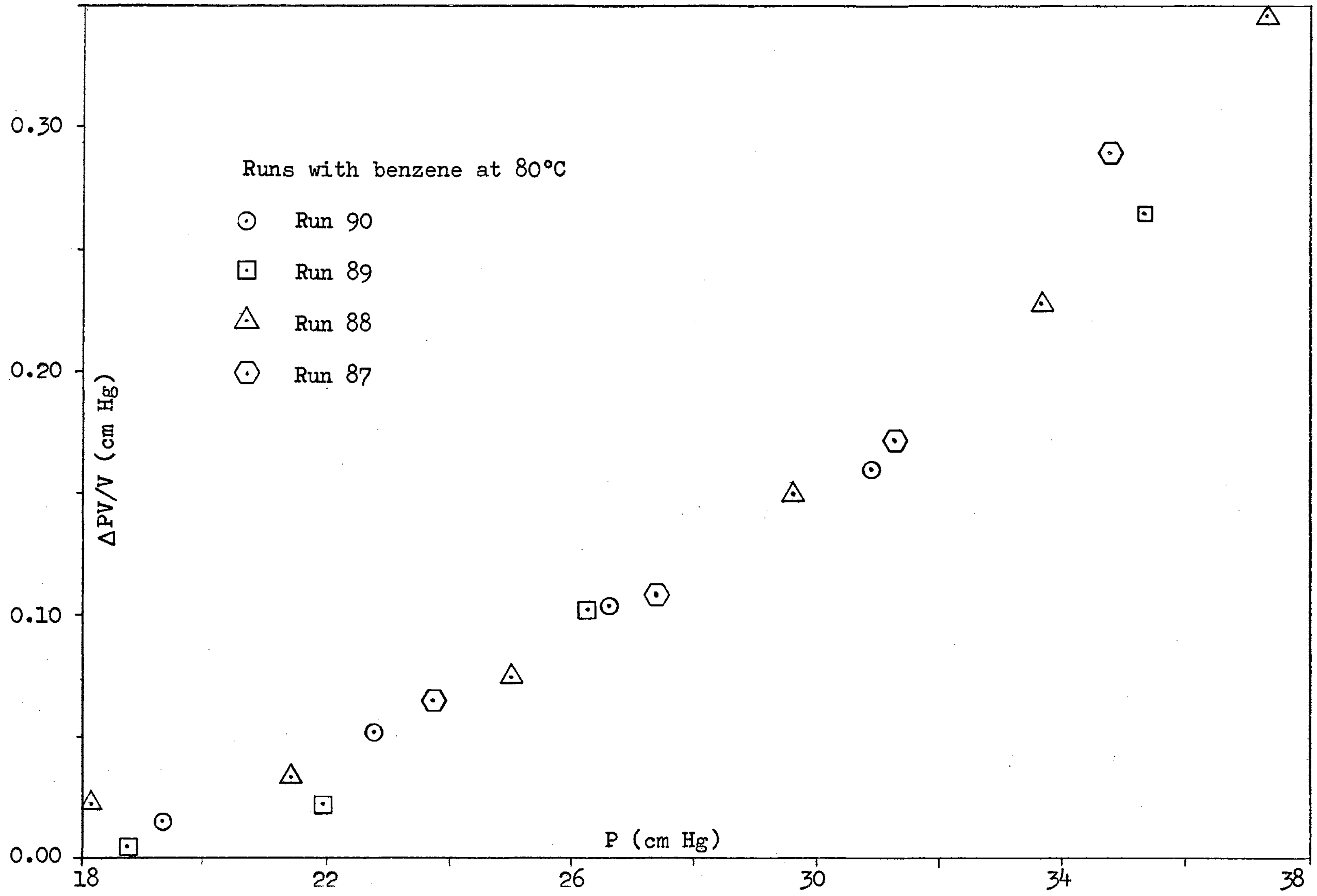

Figure 23. Deviation of Experimental Values of PV From Those Calculated Using the Literature Value of B as a Function of P

TABLE V

RESULTS OF ADSORPTION CALCULATIONS

Pressure (cm Hg)	$\Delta N/A$ (g-moles/10^{10}cm^2)			
	Methanol	Benzene		
	60°C	Literature* 35°C	60°C	80°C
2.0		2.5		
3.5		3.0		
6.0		3.2		
8.0		3.2		
18.0				21.0
20.0			112	
23.252	1.24			
24.0				137.0
26.0			267	
28.864	51.3			
30.0				315.0
32.0			588	
36.0				631.0
38.913	360			

*See reference 5.

35°C. The values obtained from the above calculations are from 6 to 200 times as large as the literature values cited. This is partially due to the large increase in the pressure and probably mainly due to the presence of a contaminating material in the apparatus used in this work. The temperature difference would tend to decrease the amount of material adsorbed. This comparison at least qualitatively shows that the values obtained in these calculations are at least reasonable.

Another qualitative estimate can be made to show that the values obtained above are reasonable. If when the amount of adsorbed material equals 631 g-moles/10^{10}cm^2 a mono-layer of adsorbed material is postulated over the entire surface, molecules with molecular dimensions on the order of 10^{-7} cm would be required assuming the molecules to be square. Since this number is many times the molecular dimensions of benzene or methanol, there would still be many vacant sites available and the mono-layer would not cover the entire surface.

In the second method of analysis, an equation similar to the Freundlich adsorption equation was used (22).

$$\Delta PV = W V P^x$$

where ΔPV is the change in the PV product due to adsorption (cm Hg-ml), V is the volume (proportional to the area)(ml), P is the pressure (cm Hg) and W and x are constants. W also contains the proportionality constant relating the surface area to the volume.

This equation is incorporated into the calculation of the PV product. The constants W and x are determined such as to minimize the standard estimate of the error in the least mean square fit of the straight line relationship between PV and P. By minimizing the standard estimate of the error, the curvature is essentially removed from the data.

The above procedure was followed for Run 54 using the digital computer. The results are illustrated on Figure 24. The values obtained for W and x are 6.18×10^{-12} and 6.553 respectively. The number of moles adsorbed calculated by the above equation with these constants are tabulated in Table V (page 85). It is noticed that the number of moles adsorbed at the lower pressures by use of this equation is very small. Improvement in the data obtained with this correction as shown in Figure 24 is quite good.

This adsorption correction equation is then used to correct the results of Runs 53, 55, 56, and 57 which are runs made in the same series as Run 54. Since some of these runs had multiple compressions and expansions made on the sample, only the data from the first compressions are used. The improvements in the calculated second virial coefficients are given in Table VI. Although the values of the second virial coefficients calculated using this correction are slightly over corrected, the results are much closer to the literature values and the deviations

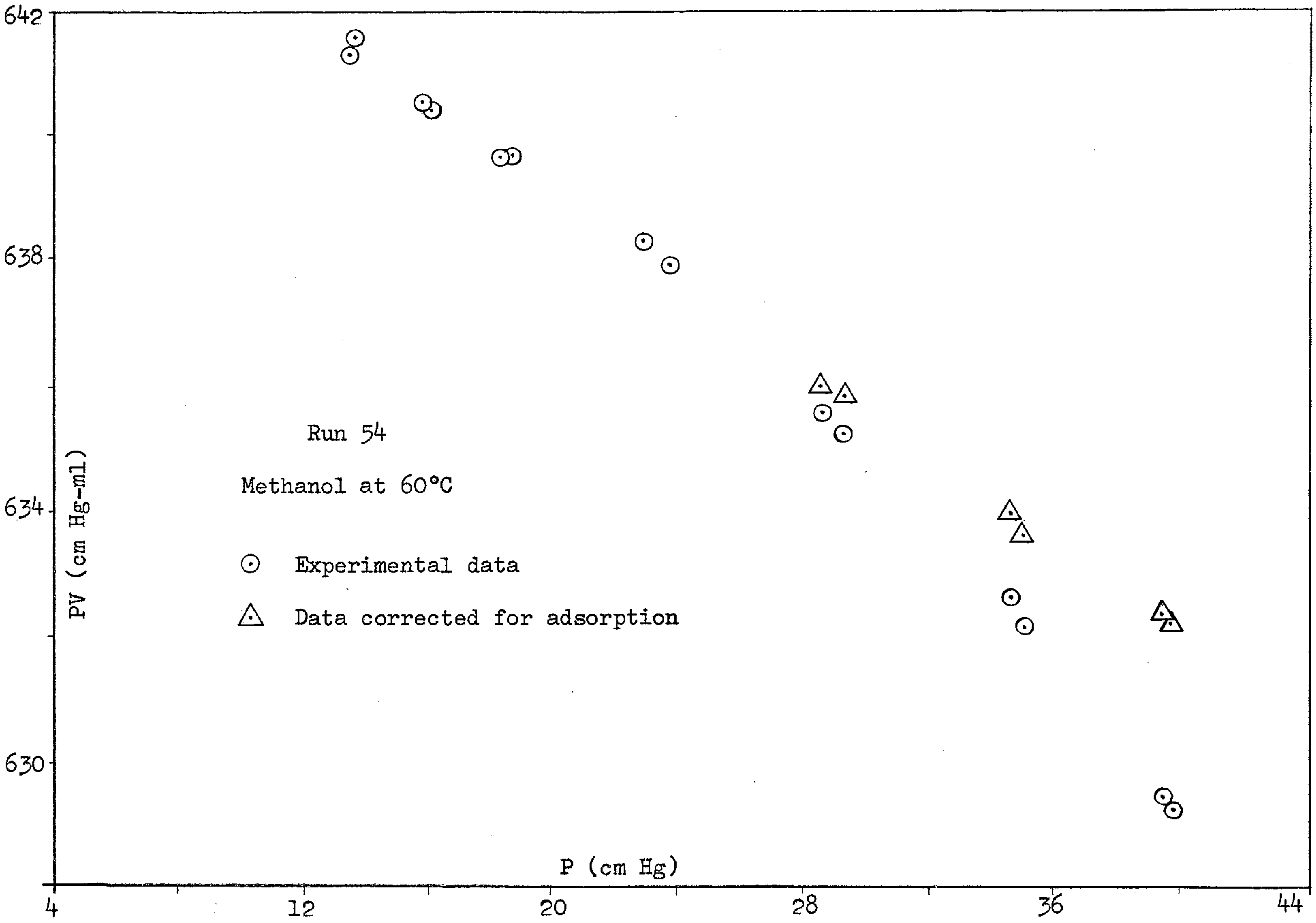

Figure 24. Relationship Between PV and P for Run 54

TABLE VI

SECOND VIRIAL COEFFICIENTS CORRECTED FOR ADSORPTION

Run Number	Second Virial Coefficient (ml/mole) Uncorrected	Corrected
57	-1581	-1093
56	-1509	-1115
55	-1467	-1285
54	-1398	-1169
53	-1480	-1128

Runs were all made with methanol at 60°C where the acceptable value from the literature is -1220 ml/mole.

could probably be accounted for by some of the errors which were discussed in Appendix C.

VITA

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