A LABORATORY INVESTIGATION OF STEAM ADSORPTION IN GEOTHERMAL RESERVOIR ROCKS

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By
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I certify that I have read this report and that in my opinion it is fully adequate, in scope and quality, as a report for the degree of Master of Science.

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ABSTRACT

Some vapor-dominated geothermal reservoirs and low-permeability gas reservoirs exhibit anomalous behavior that may be caused by surface adsorption. For example, geothermal reservoirs in the Larderello area of Italy and reservoirs in the The Geysers Geothermal Field, California produce little, if any, liquid. Yet to satisfy material balance constraints, another phase besides steam must be present. If steam adsorption occurring in significant amounts is not accounted for, the reserves will be grossly under-estimated. In addition, well tests may be misinterpreted because the pressure response is delayed owing to the adsorbed material leaving or entering the gaseous phase.

In the present research the role of adsorption in geothermal reservoirs is investigated. Two sets of laboratory equipment were constructed to measure adsorption isotherms of cores from Berea sandstone, Larderello, and The Geysers. Seven experimental runs were completed using nitrogen on the low temperature apparatus at -196 °C. Eight runs were conducted using steam on the high temperature apparatus at temperatures ranging from 150 °C to 207 °C. The largest specific surface area and the greatest nitrogen adsorption isotherm were measured on the Berea sandstone, followed by a core from Larderello and then The Geysers. Difficulties in determining whether a system had reached equilibrium at the end of each step lead to questions regarding the magnitude of adsorption measured by the steam runs. Nevertheless, adsorption was observed and the difficulties themselves were useful indicators of needed future research.

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1.0 INTRODUCTION

In the highly competitive atmosphere of the energy industry, the objective, as in any business, is to make a profit. Once a resource is discovered, two issues must be addressed: whether the reserves warrant development and if *so,* the design of the optimum development scheme. To respond to these issues one should have an understanding of the natural production mechanism. Unfortunately there exist a variety of unknowns which greatly complicate the matter. One of these, the phenomenon of adsorption, has a significant impact on vapor-dominated geothermal reservoirs and evidently on low-permeability natural gas reservoirs as well.

This report describes the equipment, experimental procedures, and analysis techniques needed to generate and evaluate adsorption data. Some adsorption isotherms, plots of adsorption per gram of sample versus relative vapor pressure at constant temperature, are presented for experimental runs conducted on actual field samples. This work is not intended to provide a statistical basis for definitive conclusions about these reservoirs, but rather to set the stage for more extensive investigations in the future.

1.1 THE ADSORPTION PHENOMENON

One of the difficulties in understanding adsorption is the confusion regarding terminology and nomenclature. Adsorption and the related subject of capillarity have been studied in different scientific disciplines for many years. The focus and the approach vary according to the discipline as do the terms and symbols. The use in this report of important terms is outlined in the ensuing paragraphs.

Adsorption may be defined as the adhesion of molecules of gases, solutes or pure liquids in an extremely thin layer to the surfaces of solid bodies or liquids with which they are in contact. The material that is adsorbed is called the adsorbate, while the material on which the adsorption takes place is called the adsorbent. In contrast to adsorption, absorption in simply the movement of one substance into the bulk of another by some transport mechanism such as convection or diffusion. Though sometimes used to describe these phenomena in general, adsorption and absorption can refer to the processes in the forward direction only. Sorption also describes the forward direction of either process while desorption does the same in the backward direction.

Adsorption may be physical or chemical in nature, or a combination of both. Physical adsorption, also called physisorption, tends to dominate at low temperatures. The heat of adsorption is similar to the heat of condensation because the intermolecular forces involved are the same type as those responsible for the condensation of vapor to liquid. These forces are described in detail in the doctoral dissertation of Hsieh **(1980).** Normally the time to attain equilibrium, that state in which the mass of adsorption remains fixed, is short. However, the low mass transport rates in low-permeability cores lengthen this time considerably. Unlike physical adsorption, chemisorption involves chemical reactions causing it to be much more active at higher temperatures. Correspondingly, the adsorption energy is higher and the equilibrium time depends much more on the reaction kinetics. In addition, chemisorption is more likely to cause irreversible changes in both the adsorbent and adsorbate. An example of this phenomenon is found with oxygen adsorbed on solid carbon. Because of the strength of the bond between the two, heating results in the release of CO and CO_2. If the magnitude of the adsorption energy is similar to that of the surface energy of the adsorbent on a per molecular unit basis, then the adsorbent surface is apt to undergo structural changes. In short, a rock surface is less likely to be altered due to adsorption if the primary mechanism is physical. A chemisorbed bed tends to be monomolecular; however, it is possible for a multi-layer physisorbed bed to form on top. Much of the experimental work is at either end of the spectrum where one or the other process dominates. For the present research physical adsorption dominates even though the use of distilled water adds complexity because of inherent polar effects.

While the same type of forces causing adsorption also cause capillary condensation, the two phenomena are not the same. In studies of capillarity it is assumed that enough molecules are present to model thermodynamically with the Kelvin equation (Eq. 3.1). Figure 1.1 illustrates the progression from adsorption to a combination of capillarity and adsorption. Consider the surface of two adjacent sand grains as a gas is brought into contact with them (Fig. 1.1A). Initially, the gas is adsorbed as a monolayer. As more gas is introduced, the number of layers increases. The converging pore walls where the grains meet promote adsorption preferentially. When the number of adsorbed molecular layers is high enough, the concepts and equations of capillarity begin to apply (Fig. 1.1B). The question of how to model these systems is addressed in the next two chapters.

Confusion in terminology is compounded by the close relationship of adsorption and capillarity. For example, adsorption isotherms in general do not show adsorption

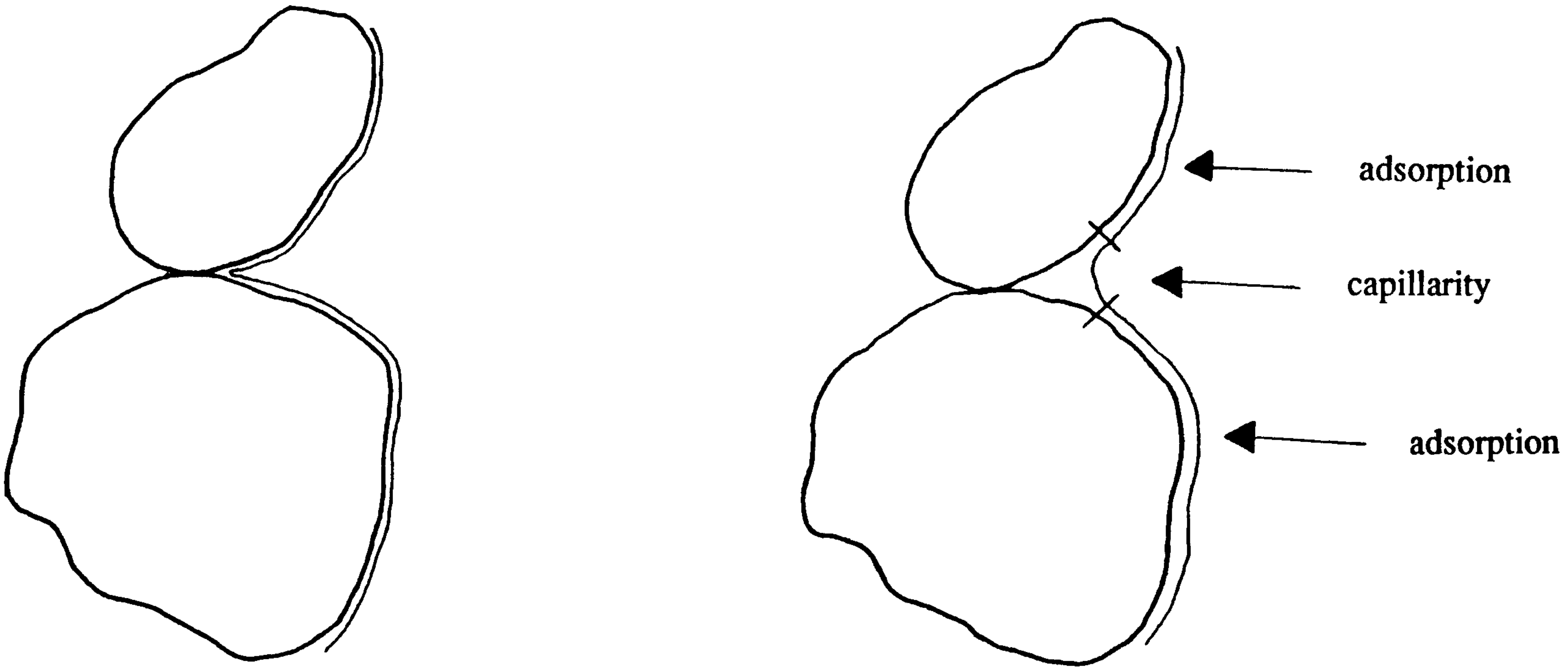

Figure 1.1A Monolayer Adsorption

Figure 1.1B Adsorption Plus Capillarity

FIGURE 1.1 Progression from Monolayer Adsorption to Adsorption Plus Capillary Condensation

alone. They usually include all the molecules clinging to the surface and to each other in a phase composed of adsorbate and capillary condensation. Indeed, it is this total quantity which is so important in estimating reserves. Capillary condensation often does not make a significant contribution until relative pressures are very high as will be shown in Section **2.1.** For simplicity, the total quantity will often be referred to in this report in terms of "adsorption" or even as the "condensed" or "dense" phase to differentiate it from the free gas phase. It should be understood that not all the molecules are condensed in the sense of changing from vapor to liquid. The concept of liquid no longer has meaning on the scale of micropores; yet, the molecules are compressed into a denser packing. Any discussion here requiring differentiation between the effects of adsorption and capillary condensation should be evident from the treatment given.

1.2 VAPOR-DOMINATED GEOTHERMAL SYSTEMS

Steam was once thought to be the only significant constituent of vapor-dominated reservoirs exemplified by The Geysers in California and the Larderello area in Italy. An early model, proposed by James (1968) and extended by White *et al.* (1971), suggests that the vapor zone is underlain by a liquid zone and that any vapor that condenses percolates downward. There may in fact be reservoirs with distinct zones where one or the other phase dominates. There is, however, an increasing amount of evidence to support the idea that a dense H_2O phase is adsorbed within the vapor-dominated zones even though pressures are below saturation pressures.

Gravity measurements conducted at The Geysers by Denlinger, Isherwood, and Kovach **(1981)** show a significant reduction in mass caused by fluid withdrawal at a depth within the steam producing horizon. If steam was the **only** phase in that zone, its removal alone would not account for the magnitude of the reduction observed. Furthermore, Sanyal **(1980)** reported abnormally high neutron log measurements for some vapor-dominated reservoirs. Adsorbed water might account for the anomaly because of the elevated hydrogen concentration. In experiments on porous media saturated with superheated steam, Macias-Chapa **(1981)** observed radon emanations far exceeding the levels expected for a gaseous phase alone.

Laboratory studies of the effect of adsorption in porous media were conducted by the United States Geological Survey (U.S.G.S.) as well as by Hsieh and Ramey **(1983).** Their findings indicate that a large mass of water can exist as an adsorbed phase even at pore pressures below the saturation vapor pressure. In addition, the work of the **U.S.G.S.** examines adsorption during transient flow of steam. Atkinson and Moench **(1978)** developed a numerical steam flow model that was modified by Moench and Herkelrath **(1978)** to include adsorption. **By** using the model in conjunction with adsorption isotherms determined in the laboratory, Herkelrath, Moench, and O’Neal **(1983)** attained reasonable agreement with data from their transient flow experiments. This work demonstrates analytically and experimentally that adsorption tends to delay the fluid pressure response during a flow test.

The most significant result of these studies is that reserve estimates which assume steam to be the only existing phase are too low. According to Economides and Miller **(1985),** the estimates may be as much as a full order of magnitude too low. This error in material balance propagates throughout the reservoir calculations used to predict future behavior. The problem **is** compounded if **a** well test which felt the cushioning effect of adsorption is analyzed without accounting for the resultant time lag. Consequently, the technical and economic evaluations, upon which important decisions are based, may promote a view of the resource which is misleading.

1.3 NATURAL GAS SYSTEMS

Two kinds of natural gas systems exhibit anomalous behavior that could be explained by adsorption: gas storage reservoirs and certain natural tight gas reservoirs. In a gas storage reservoir, the pressure increases with the injection of gas. One might assume that producing until the pressure decreases to its original value would yield a gas volume equal to that injected. Yet, the produced volume is usually less than the injected volume for the same pressure change. Likewise, low permeability gas systems often show some time delay between the production of gas and the average pressure drop in the reservoir. This behavior was noticed in the late 1950's by Ramey*. Under conditions of no water encroachment, he saw that many $\frac{p}{z}$ versus cumulative-gas-produced graphs were still concave upward instead of linear **as** expected. Though adsorption is a possible explanation, flow of gas from very tight sands within the system and peripheral to the drainage area may also account for **this** phenomenon.

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* Information **gained** through **personal** communication, fall **1985.**

1.4 STATEMENT OF THE PROBLEM

Adsorption can have a large potential impact on the validity of traditional methods for assessing vapor-dominated geothermal reservoirs and certain natural gas reservoirs. Evaluations that underestimate reserves and incorporate erroneous well test interpretations can be misleading when employed in the decision-making process. The experimental work completed thus far identifies adsorption as a topic worthy of further research. The ultimate goal is to provide enough information to allow for integration of adsorption effects into technical and economic evaluations.

This research effort builds on the work of Hsieh (1980), who determined that adsorption and capillary condensation were responsible for vapor pressure lowering in porous materials. He then conducted experiments to generate adsorption isotherms for nitrogen, steam, and natural gas using Berea sandstone almost exclusively. While the results of his work with natural gas work were inconclusive because of the low pressures used, the steam results were far more encouraging because more adsorbate is formed from steam at low pressures than from natural gas. The general purpose of the present research is to develop the equipment and methodology to generate more isotherms with actual field cores under extended ranges of pressures and temperatures. Specific goals are three-fold: (1) to construct the apparatus and test it, the procedures, and the analysis techniques; (2) to identify potential problems and limitations of the apparatus, procedures, and analysis and to suggest improvements; and (3) to identify areas of interest suitable for further research.

2.0 LITERATURE SURVEY

As the previous section indicates, capillary condensation and adsorption significantly impact many disciplines, the result being a plethora of literature on these subjects. This survey provides a general overview of the development of some fundamental theories. The histories of capillarity and adsorption are traced separately until about the mid-1970's. Thereafter, they are reviewed jointly with an emphasis on the work pertinent to this research. Though mathematical equations are mentioned in this section, details are reserved for Chapter 3.

While the effect of capillary condensation on **porous** solids has been studied for about ***250*** years, the Kelvin equation was not developed until 1871. This important basic equation was not derived on the basis of rigorous thermodynamics as the condition for chemical equilibrium between phases had not yet been set **forth** by Gibbs. was unknown at the time. Lord Kelvin (Thomson) assumed the vapor to be ideal and the liquid to be incompressible. Nonetheless, since its first application to data on porous solids by Zsigmondy (1911), the Kelvin equation has remained a useful tool. **A** great volume of material on this subject has been published during the twentieth century. Some important publications which include literature reviews are McBain (1932), Brunauer (1943), and Melrose (1986). **A** modified Kelvin equation with a rigorous thermodynamic derivation was developed by Melrose in 1966. **A** year later, he applied the idea of pendular rings based on Gibbs dividing surfaces to the problem of capillary-held liquid. Further theoretical refinement came in 1986 followed by experimental work in 1987. He found that the relation was valid for capillary pressures as high as 4000 psi and that the corrections to the classical form are negligible below a capillary pressure of about 1450 psi.

The vapor pressure at a plane surface of gas-liquid phase separation is higher than the vapor pressure at a curved surface of phase separation. Thus, the vapor pressure in **a porous** medium is lower than the vapor pressure in a non-swelling, non-porous container. Observed by Edelfson and Anderson (1943), the vapor pressure lowering (VPL) effect was also noticed by Calhoun and his co-workers in their landmark studies on core plugs in 1949. Stanford University began its investigations into the matter in 1966. Cady (1969) and Bilhartz (1971) discovered that VPL was not significant in unconsolidated sands. In contrast, consolidated sands studied by Strobel (1973) and Chicoine (1975) did show significant lowering. Later research by Hsieh (1980) demonstrated that although capillary condensation is a factor, adsorption also makes a contribution.

Unlike investigations of capillary condensation, adsorption studies are more a product of this century. Langmuir presented a theory in 1918 based on the kinetic theory that works best for monolayers. Brunauer, Emmett, and Teller (1938) applied the BET equation to multi-layered systems. It is often used to find surface areas and has been widely used because of its simplicity. Chapter 3 details this equation **as** well as a modified form presented by Drain and Morrison (1953).

In general, three approaches have been used to develop theoretical equations that would fit adsorption isotherm behavior: the Langmuir-BET type, the two dimensional equation of state treatment, and the potential method. This last method suggests that the adsorbed layer is **similar** to the atmosphere surrounding a planet in that the density decreases with an increase in distance **from** the surface. **A** field of potential may be defined by a potential function which represents the amount of work done in bringing an adsorbed molecule from the surface to a specific distance above the surface. The major difference between the approaches lies not in how they fit the isotherm data, but in how they agree with the heats and entropies of adsorption. Adamson (1982) compares and contrasts these methods, though the discussion is by his own admission "restrained because it turns out that for nearly all systems studied an ovemding effect makes it virtually impossible to make an experimental verification of the validity of the model or to set up any but remotely austere fundamental theoretical treatments". (Adamson 1982, 573-574) He is referring to surface heterogeneity.

The present research employs the BET equation; however, there is another quation called the Frenkel-Halsey-Hill (FHH) equation which is often mentioned in the literature. It is one of the potential models, and its basic form was suggested first by Frenkel (1946). Halsey (1948), Hill (1952) and McMillan and Teller (1951) extended that work. As with the BET equation, many modifications and justifications were presented in the years after its inception.

Since about 1978 there has been an increasing amount of attention focused on the effect of adsorption and associated capillarity on the petroleum and geothermal industries. Stanford University's research on the VPL effect revealed a significant contribution by adsorption. Hsieh (1980) calculated a minimum relative pressure below which capillary condensation is not important using the Kelvin equation and a minimum radius the size of a water molecule. He discovered that some of the data of Calhoun *et al.* (1949) was below this level as was that of the foregoing Stanford researchers. He began to measure adsorption isotherms for Berea sandstone using nitrogen, steam and to a small extent natural gas and used a BET analysis. As mentioned earlier, the natural gas results were inconclusive because the pressures and temperatures were too low. The steam information revealed a significant mass of a dense phase even at pressures below the vapor pressure. In 1983, Economides incorporated this extra source of reserves into a vapor-dominated geothermal reservoir model.

Other research investigations similar to those of Economides and Hsieh were in progress since 1978 at the United States Geological Survey. A numerical model for a vapor-dominated geothermal reservoir with radial steam flow was developed by Moench and Atkinson (1978). Soon thereafter, Moench and Herkelrath (1978) **modified** the model to include adsorption and the **VPL** effect. Herkelrath *et al.* (1983) then conducted experiments to verify the model. **Using** methods similar to Hsieh, they generated adsorption isotherms to be entered into the model. Next, they repeated the classic transient flow experiments of Aronofsky (1954) and Wallick and Aronofsky (1954) to test their equipment. Finally, they ran transient flow experiments with steam and noticed a definite time delay in the pressure response. The agreement between the model and the data was within acceptable limits.

Morrow and his associates (1984, 1985) measured desorption isotherms for water vapor in low permeability gas sands at room temperature. Kelvin capillary pressures were calculated from about 10,150 psi (700 bar) to 200 psi (14 bar). Comparisons with high-speed centrifuge data for pressures below 800 psi (55 bar) were favorable suggesting that the Kelvin equation was valid for 800-200 psi.

Melrose, who derived the corrected form of the Kelvin equation, recently studied the effects of capillary condensation in the presence of adsorption (1986, 1987). Using the pendular **ring** approach and a modified form of the FHH adsorption theory, the model calculates the quantity of liquid held **by** capillary effects with respect to the total quantity of adsorbate. It also allows for a comparison of the mercury extrusion curve at high pressures which excludes adsorption with the appropriate curve which includes adsorption. Melrose contends **that** the contribution of capillary condensation to the adsorption isotherm is somewhat larger than Hsieh **(1980)** suggested because **of** uncertainties in the surface tension and the liquid phase specific volume. However, the major contribution **does** not occur until the very high relative pressure ranges.

3.0 ANALYTICAL PROCEDURES

3.1 BACKGROUND

In deference to the close link between adsorption and capillarity, the Kelvin equation is discussed in Sub-Section 3.1.1 with focus on its range of applicability. Sub-Section 3.1.2 provides a derivation of the BET equation. Although the thermodynamics of adsorption is important, it is not of immediate interest in the current research. For a discussion of adsorption thermodynamics, the reader is referred to Hsieh (1980) or to a general reference such as Adamson (1982).

3.1.1 THE KELVIN EQUATION

In the last 100 years, the Kelvin equation has been applied successfully to many different capillary systems. Several mathematical forms using the same basic relationship have evolved over the years. A form used freqently is

$$\ln \frac{p}{p_o} = - \frac{\gamma V_L}{R T} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \tag{3.1}$$

where $\frac{p}{p_o}$ = relative vapor pressure

γ = interfacial tension

V_L = volume per mole of liquid

R = gas constant

T = absolute temperature

r_1 and r_2 = the two principal radii of curvature

When the two radii are nearly equal, the term $\frac{1}{r_1} + \frac{1}{r_2}$ is often replaced by $\frac{2}{r_m}$ where r_m is defined by the mean radius of curvature.

The classical Kelvin equation assumes an ideal gas phase and an incompressible liquid phase. Melrose **(1966,** 1986) examined the phenomenon from a rigorous thermodynamic standpoint using Gibbs' condition for a chemical equilibrium between phases. The Gibbs condition had not yet been discovered when Lord Kelvin (Thomson) developed his equation. The corrected form suggested by Melrose has two additional terms which are insignificant for air/brine capillary pressures less than about **1450** psi (Melrose, **1987).** He found the corrected form to be valid for capillary pressures as high as about 4000 psi. Yet, at some point even the corrected form is not applicable because of the increase in liquid compressibility with the decrease in vapor pressure and liquid density. This equation coupled with an extrapolation of various PVT data for water (Speedy, 1982) provides a theoretical limit on thermodynamic stability. This limit at room temperature is about - **30,000** psi, which corresponds to a capillary pressure of about the same magnitude, a p/p_o of about **0.22,** and a Kelvin radius of ***2.5*** molecular diameters. The diameter of a water molecule is approximately **2 °*A*** **(2 x** 10^{-10} m).

Negative pressures have been measured in various experiments, though never so low as the theoretical limit. Values as low as **-4000** psi were observed by Briggs

(1950) with the accompanying values of 0.82 for the relative vapor pressure and 19 molecular diameters, roughly 40 Å for water, for the Kelvin pore radius. Later experiments on cyclohexane by Fisher and Isrealachvili (1979, 1981) achieved negative pressures of about -870 psi which indicates a relative pressure of 0.76 and a Kelvin pore radius of 16 molecular diameters.

The model adsorption isotherm presented in Fig. 3.1 reflects the progression from adsorption alone to adsorption plus capillary condensation (Fig. 1.1). Region A represents adsorption alone. The corrected Kelvin equation suggests that Region B between the theoretical and experimental limits of p/p_0 has at least some capillarity. In Region C, the contribution of capillarity begins growing, particularly for very high relative pressures like 0.98 or 0.99.

The Kelvin equation is appropriate for cases in which capillarity totally dominates or merely contributes significantly. In the latter case, the adsorption and capillarity may be treated separately provided that some method exists to differentiate between the two. Indeed, more than one such method exists. An approach used by Melrose (1986) is based on the concept of dividing surfaces. His model (Fig. 3.2) has two solid spheres with an adsorbed film of constant thickness and capillary liquid held between the converging pore walls.

The dividing surface for the gas and the capillary-held liquid is not a circular arc, but rather a nodoid, or a pendular ring. This surface is assumed to be tangent to and continuous with the surface for the gas and adsorbed film. Because the pore structure has converging walls instead of parallel ones, Melrose developed a minor modification to the Kelvin equation.

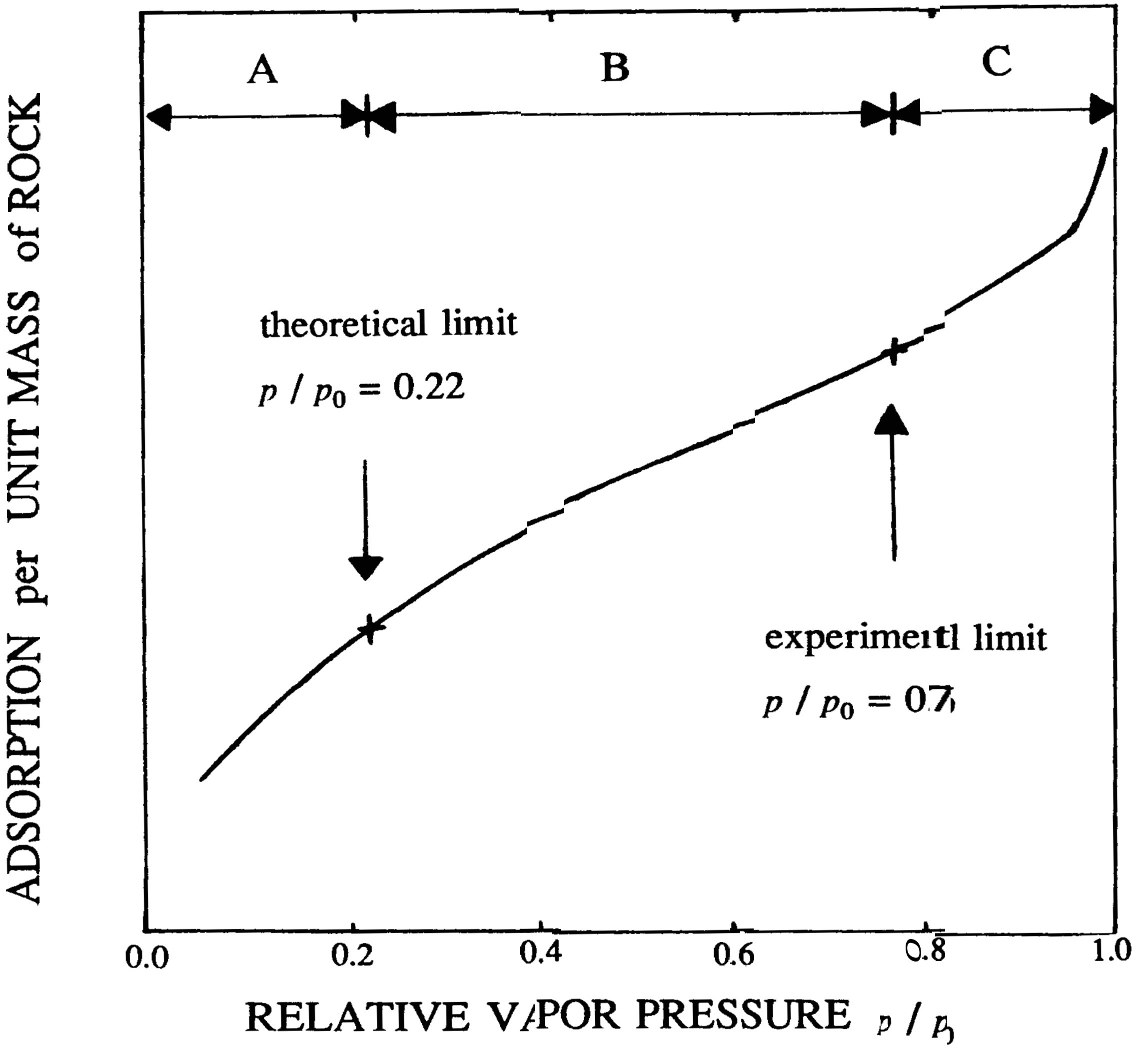

FIGURE 3.1 Model Adsorption Isotherm

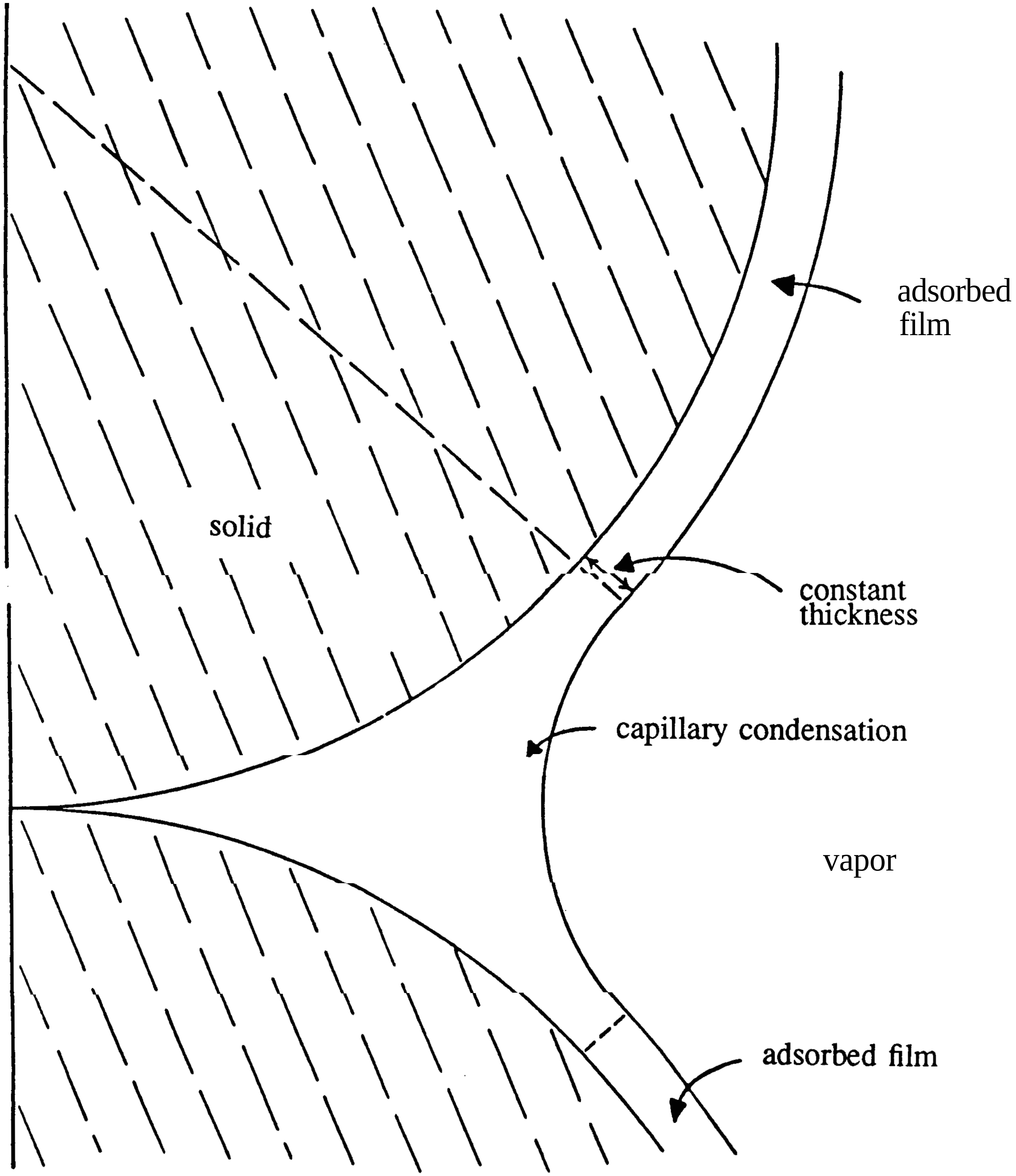

FIGURE 3.2 Schematic of Two Spheres with Adsorption and Capillary Condensation

(from Melrose, **1986, with modifications)**

The adsorbed film may be analyzed by several different methods. Melrose (1986, 1987) used a modified FHH equation with satisfactory results. In the present research, the BET equation was found to be simpler to apply and sufficient for this purpose.

3.1.2 LANGMUIR - BET TYPE EQUATIONS

Langmuir (1918) applied the kinetic theory to surface adsorption, but his equation can only be applied to monolayers. Brunauer, Emmett and Teller (1938), following the same principles, developed the BET equation for multi-layered systems. Later, this equation was modified to accommodate specific numbers of layers.

The following assumptions are required to formulate this modified BET equation:

1. The surface of the solid is uniform. The possible sites of adsorption are identical and can only accept one gas molecule at a time.

2. A gas phase molecule will be adsorbed upon striking an unoccupied site.

3. If a site is already occupied, the gas phase molecule will be adsorbed on top as a next-layer molecule.

4. There are n possible layers at each site.

5. Adsorbed molecules will rejoin the gas phase under conditions of desorption. If there is more than one layer, the uppermost layer will evaporate first, followed by the next, and so on.

6. All layers above the first layer have the same physical properties.

Consider a surface with a total number of adsorption sites, S, and let S_0 denote the unoccupied sites. In addition, let the number of sites covered by one layer be S_1, the number of sites with two layers be S_2, the number of sites with three layers be S_3, and so on. Thus, S_i refers to the number of sites with i layers.

The rate of condensation to the i-th layer, N_{a_i}, depends partly on the pressure of the gas phase and the amount of surface covered by the $i-1$ layer:

$$N_{a_i} = p\, a_i\, S_{i-1} \tag{3.2}$$

where a_i = coefficient of condensation for the i-th layer

i = layer index ranging from 0 to n.

Similarly, an equation may be written for the rate of evaporation from the i-th layer:

$$N_{b_i} = b_i \, S_i \tag{3.3}$$

where b_i = coefficient of evaporation for the i-th layer.

Consider the system at equilibrium when the rates of condensation and evaporation are equal. Combining Eqs. 3.2 and 3.3 yields

$$p \;\; a_i \, S_{i-1} = b_i \, S_i \tag{3.4}$$

from which

$$\frac{S_i}{S_{i-1}} = \frac{p \; a_i}{b_i} = \frac{\theta_i}{\theta_{i-1}} \tag{3.5}$$

where $\theta_i = \dfrac{S_i}{S}$, the fraction of surface covered by i layers. The sum of the surface fractions from 0 to n equals unity. The sixth assumption states that all the physical properties of the layers above the first are identical:

$$a_2 = a_3 = a_4 = \cdots = a_n = a \tag{3.6}$$

and

$$b_2 = b_3 = b_4 = \cdots = b_n = b \quad . \tag{3.7}$$

Only two nontrivial expressions result from writing Eq. **3.5** for every layer. Let

$$\alpha = \frac{\theta_1}{\theta_0} = \frac{p\, a_1}{b_1} \tag{3.8}$$

and

$$\beta = \frac{\theta_2}{\theta_1} = \frac{\theta_3}{\theta_2} = \cdots = \frac{\theta_n}{\theta_{n-1}} = \frac{p\, a}{b} = \frac{\alpha}{C} \tag{3.9}$$

where C is a constant equal to $\frac{b\, a_1}{a\, b_1}$ for a specific fluid at a specific temperature. From Eqs. **3.8** and **3.9,**

$$\theta_i = \alpha\, \beta^{i-1}\, \theta_0 = C\, \beta^i\, \theta_0 \quad . \tag{3.10}$$

If the total number of moles of adsorbate is **X,** then

$$X = X_m\, (\, \theta_1 + 2\, \theta_2 + 3\, \theta_3 + \cdots + n\, \theta_n\,) \quad . \tag{3.11}$$

where X_m equals the number of moles of adsorbate in the first layer if that layer fully covers the surface. It is often called the monolayer adsorption. Substitution of Eq. **3.10** into Eq. **3.11** yields

$$X = X_m C (\beta + 2 \beta^2 + 3 \beta^3 + \cdots + n \beta^n)$$

$$X = X_m C \sum_{i=1}^{n} i \beta^i \tag{3.12}$$

The summation term may be evaluated as follows:

$$\sum_{i=1}^{n} i \beta^i = \frac{d}{d\beta} \sum_{i=2}^{n+1} \beta^i - \sum_{i=1}^{n} \beta^i$$

$$\sum_{i=1}^{n} i \beta^i = \frac{d}{d\beta} \left[\frac{\beta^2 (1 - \beta^n)}{1 - \beta} \right] - \frac{\beta - \beta^{n+1}}{1 - \beta}$$

$$\sum_{i=1}^{n} i \beta^i = \frac{\beta - (n+1) \beta^{n+1} - n \beta^{n+2}}{(1 - \beta)^2} \tag{3.13}$$

Thus,

$$X - X_m C \theta_0 \frac{\beta - (n+1) \beta^{n+1} - n \beta^{n+2}}{(1 - \beta)^2} \quad . \tag{3.14}$$

The term θ_0 may be eliminated with the realization that $\sum_{i=0}^{n} \theta_i = 1$. Therefore, Eq. 3.10 may be reduced:

$$\theta_0 (1 + C \beta + C \beta^2 + \cdots + C \beta^n) = 1$$

$$\theta_0 + C \theta_0 \left(\frac{\beta - \beta^{n+1}}{1 - \beta} \right) = 1$$

$$\theta_0 = \frac{1}{1 + C \left(\frac{\beta - \beta^{n+1}}{1 - \beta} \right)}$$

$$\theta_0 = \frac{1 - n}{1 + (C - 1) \beta - C \beta^{n+1}} \qquad \textbf{(3.15)}$$

Substituting the right-hand side of **Eq.** **3.15** for θ_0 in **Eq. 3.14** yields

$$\frac{X}{X_m} = \frac{C \beta}{1 - \beta} \left[\frac{1 - (n+1) \beta^n + n \beta^{n+1}}{1 + (C - 1) \beta - C \beta^{n+1}} \right] \quad . \qquad (3.16)$$

Equation **3.16** relates the total adsorption, X, to X_m, n, C, and β. The parameter **β** is physically significant in that it equals the relative vapor pressure. If a flat interface has a saturation vapor pressure identical to the equilibrium vapor pressure, p, then $n = \infty$ and $\beta = 1$. **From** the definition of **β** (Eqn. 3.9),

$$\frac{p_0 \, a}{b} = 1 \quad . \qquad \textbf{(3.17)}$$

Thus,

$$\beta = \left(\frac{p \, a}{b} \right) \left(\frac{b}{p_0 \, a} \right) = \frac{p}{p_0} \quad . \qquad (3.18)$$

The values **of** X **and β** are determined experimentally; then a least squares fit **of** Eq. **3.16** will give X_m, n, and C.

In many situations, the number of layers will be large. The BET relation results from evaluating *Eq.* 3.16 for $n = \infty$. **As** $\beta < 1$, β^n and β^{n+1} tend to zero giving

$$\frac{X}{X_m} = \frac{C\,\beta}{(1-\beta)(1+C\,\beta-\beta)} \tag{3.19}$$

This simplification is valid for the range $0.05 < \beta < 0.30$ (Hiemenz 1986, 521-523). In some instances, the upper limit may be extended to approximately 0.35 which was the value used in the present research.

The initial assumptions upon which Eq. 3.19 is based cause the equation at times to be invalid. Generally, surfaces are energetically non-uniform resulting in adsorption at the most favorable sites first. There may also be interaction between molecules of the same layer. Furthermore, the prospect for adsorption may diminish as the distance from the surface increases. If so, the physical properties of the layers above the first would not be identical as assumed.

3.2 ADSORPTION CALCULATIONS

The adsorption calculations indicate the amount of condensed phase at a particular pressure and temperature per unit mass of the porous medium under investigation. The objective is to determine the total number of molecules in the dead volume -- the annular space in the coreholder plus the pore space and tubing space up to Valve C (Fig. 4.1) -- and subtract the molecules existing as a free gas. Those remaining are ascribed to adsorption and capillary condensation. This method assumes that the only significant condensation is within the core itself.

The **first** step is to calculate the dead volume (DV). The data, collected in an adsorption-like run described in Sub-section **4.2.4,** can be analyzed with the ideal gas law. For Step *1*, the appropriate expression is

$$DV = \frac{p_1 V_1}{p_2} - V_1 = V_1 \left(\frac{p_1}{p_2} - 1 \right) \quad \textbf{(3.20)}$$

where p_1 = equilibrium pressure in sampling bottle section near the beginning of the step with all valves closed

p_2 = equilibrium pressure in DV and V_1 at the end of a step Valve **C** open

V_1 = sampling bottle volume **plus** tubing volume.

Each additional step yields another estimate **of** DV; however, these steps begin with some molecules already in the system, under which conditions the correct equation is

$$DV = V_1 \left(\frac{p_1 - p_2}{p_2 - p_2'} \right) \quad \textbf{(3.21)}$$

where p_2' is the equilibrium pressure in DV and V_1 at the end of the immediately preceding step. The slight pressure change that occurs in DV and V_1 when Valve ***C*** is closed in preparation for the next step is assumed to be negligible in the current research. The average of the estimates for DV is taken as the final value.

Low and high temperature runs cannot be analyzed until the dead volume is known. Although pressure versus time is recorded during the entire adsorption run, only the final equilibrium pressures of p_1 and p_2 are used to obtain the isotherm plots. The analysis depends on accurately accounting for the movement of molecules in and out of DV by examining the movement in and out of V_1. Let

n_{tot} = total number of micromoles inside of DV at p_2 at the end of a particular step;

$n_{tot}{}'$ = n_{tot} at the end of the immediately preceding step; and

An = net entry into DV of new molecules, expressed in micromoles.

Then $n_{tot} = n_{tot}{}' + An$. To determine An, it is evident that

An = (micromoles in V_1 at p_1) - (micromoles in V_1 at p_2) .

Applying the real gas law,

$$A\,n = \frac{p_1\,V_1}{Z_1\,R\,T} - \frac{p_2\,V_1}{Z_2\,R\,T} \tag{3.22}$$

where Z_1 is the compressibility factor at p_1, Z_2 is the compressibility factor at p_2, and temperature, T, is constant. Substituting for An, Eq. 3.22 can be put in the form

$$n_{tot} = n_{tot}{}' + \left(\frac{p_1}{Z_1} - \frac{p_2}{Z_2} \right) \frac{V_1}{R\,T} \quad . \tag{3.23}$$

The number of micromoles existing as a gas in DV is

$$n_{gas} = \frac{p_2\,(DV)}{Z_2\,R\,T} \tag{3.24}$$

Thus, the mass of adsorbed gas in DV is given by

$$n_{ads} = n_{tot} - n_{gas} \quad . \tag{3.25}$$

For the low temperature runs with nitrogen, it is assumed that the compressibility factor, Z, is constant at about **0.95** and the saturation vapor pressure, p_0, is 1 atm (taken as **14.7 psi).** For steam, values for Z_1, Z_2, and p_0 are calculated for each step. If the mass of the rock sample is m_r, the adsorption isotherms are then plotted as n_{ads} / m_r versus the relative vapor pressure, p_2 / p_0.

3.3 DETAILS OF THE BET ANALYSIS

The **BET** analysis is based on the straight line form of the **BET** equation:

$$\frac{\beta}{X\,(\,1-\beta\,)} = \frac{1}{C\,X_m} + \frac{C-1}{C\,X_m}\,\beta \tag{3.26}$$

where β = relative vapor pressure, p_2/p_0

X = adsorption (same as n_{ads}), micromoles

C = fitting factor, 1/micromoles

X_m = monolayer adsorption, micromoles

slope = $(C-1) / (C X_m)$

intercept = $1/(C X_m)$

Only data from the proper range for β are analyzed, the adsorption side being examined separately from the desorption side. The desorption results are likely to be less accurate as more experimental cumulative errors are involved. A least squares fit provides the slope and intercept. Simple algebra can then give values for C and X_m

The surface area is found by multiplying X_m by Avogadro's number, N_a, and the cross-sectional area, A_x, of the molecule. A nitrogen molecule has a cross-sectional area of about 16.2 °A or 16.2×10^{-20} m^2 (Adamson 1982, 573). The value of A_x for a liquid water molecule is given by

$$A_x = \pi \left(\frac{3 V_L}{4 \times N_a} \right)^{2/3} \qquad (3.27)$$

in which V_L is the liquid mole volume and Avogadro's Number equals 6.023×10^{17} molecules/micromole. Adamson (1982) gives a similar equation expressing A_x in terms of area per mole. The specific surface area is simply the surface area divided by the mass of the sample.

3.4 DEVELOPMENT OF COMPUTER PROGRAM

The equations described in the two previous sections have been incorporated into a computer program written in fortran. This program has been designed for easy use. The documentation enhances understanding of its present form and would facilitate any future modification.

The program consists of three parts: one input section and two calculation and output sections. For input of data, the program relies on one input file containing the values of p_1 and p_2 as well as a series of questions to be answered during execution by the user. Once the proper information has been entered, the amount of adsorption for each step is calculated and the results are sent to an output file. To aid in the construction of adsorption isotherms, a second output file is created containing the relative vapor pressure and the amount of adsorption or desorption per unit mass of core Sample. The program then proceeds to the BET analysis and prints the results in a third output file.

Additional details on the structure and use of the analysis program are located in Appendix A.

4.0 APPARATUS AND PROCEDURES

4.1 APPARATUS

Hsieh's work provided a foundation for the apparatus designed as a part of the present research. Two similar sets of equipment are used to measure adsorption. One set is **for** fluids with a boiling temperature below room temperature such as nitrogen (Fig. 4.1), and the other is for fluids such as steam with a boiling temperature above room temperature (Fig. **4.2).**

4.1.1 THE LOW TEMPERATURE SYSTEM

The principal features of the low temperature system are the sampling bottle and the coreholder sections. Often, the different components of the apparatus such as the sampling bottle section are referred to by the names Hsieh originated to maintain consistency with **his** work. The sampling bottle section is a not a place to take fluid samples, but rather a storage reservoir that allows for calculation of the flow of gas into and out of the dead volume. A supply line feeds gas into this section; a vacuum line takes gas out. The section itself consists of a stainless steel sampling bottle and 1/8 inch tubing. All joints **are** sealed with apoxy to prevent leaks. The coreholder section consists of the coreholder and 1/4 inch tubing. Bellows-type valves and Swagelok fittings are used in both the low and high temperature systems. **A** two-stage mechanical pump with **a** cold trap provides the necessary vacuum which in turn is monitored with a McLeod gauge. The pressure in the sampling bottle volume is measured with a

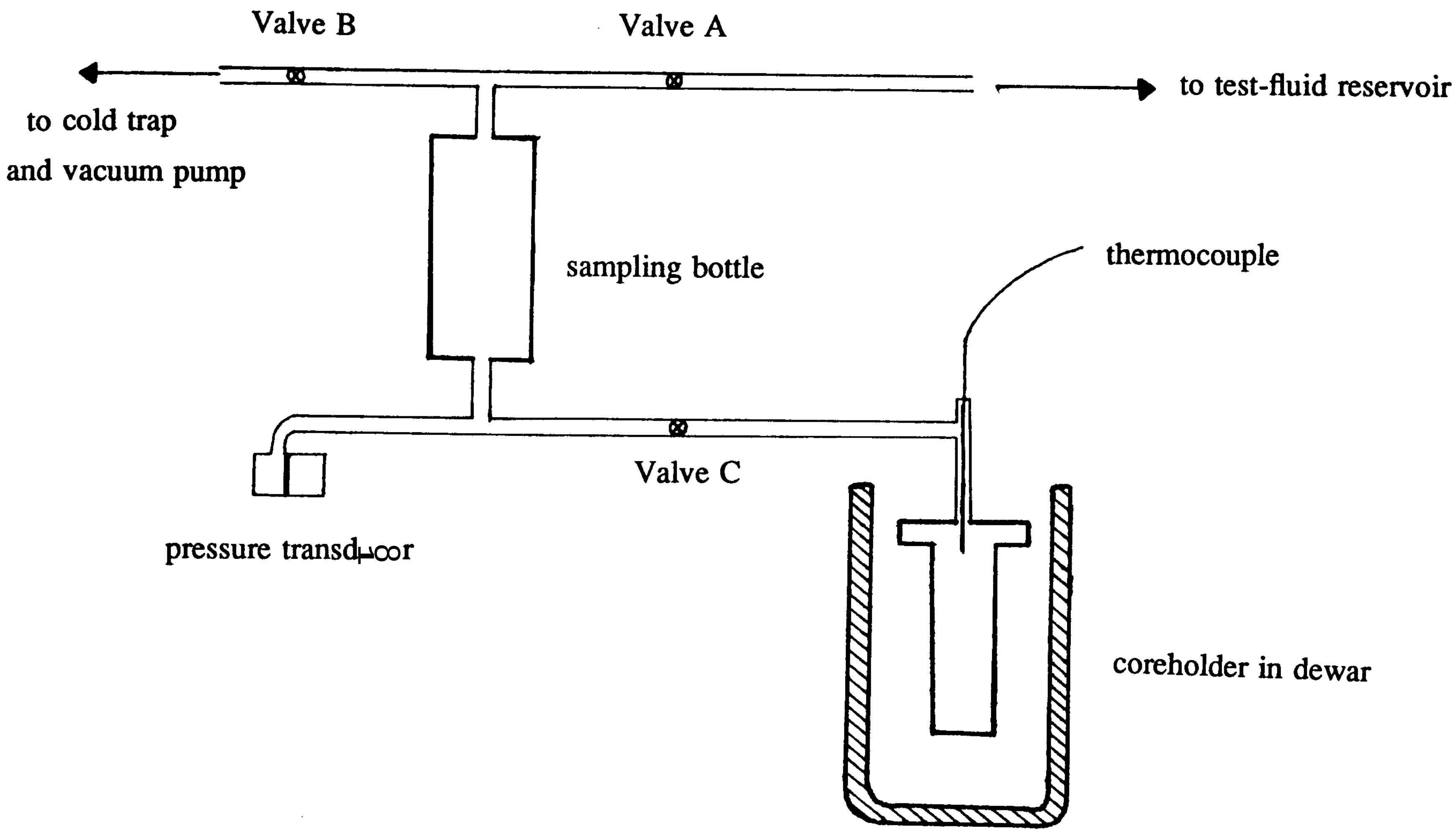

FIGURE 4.1 Schematic of the Low Temperature System

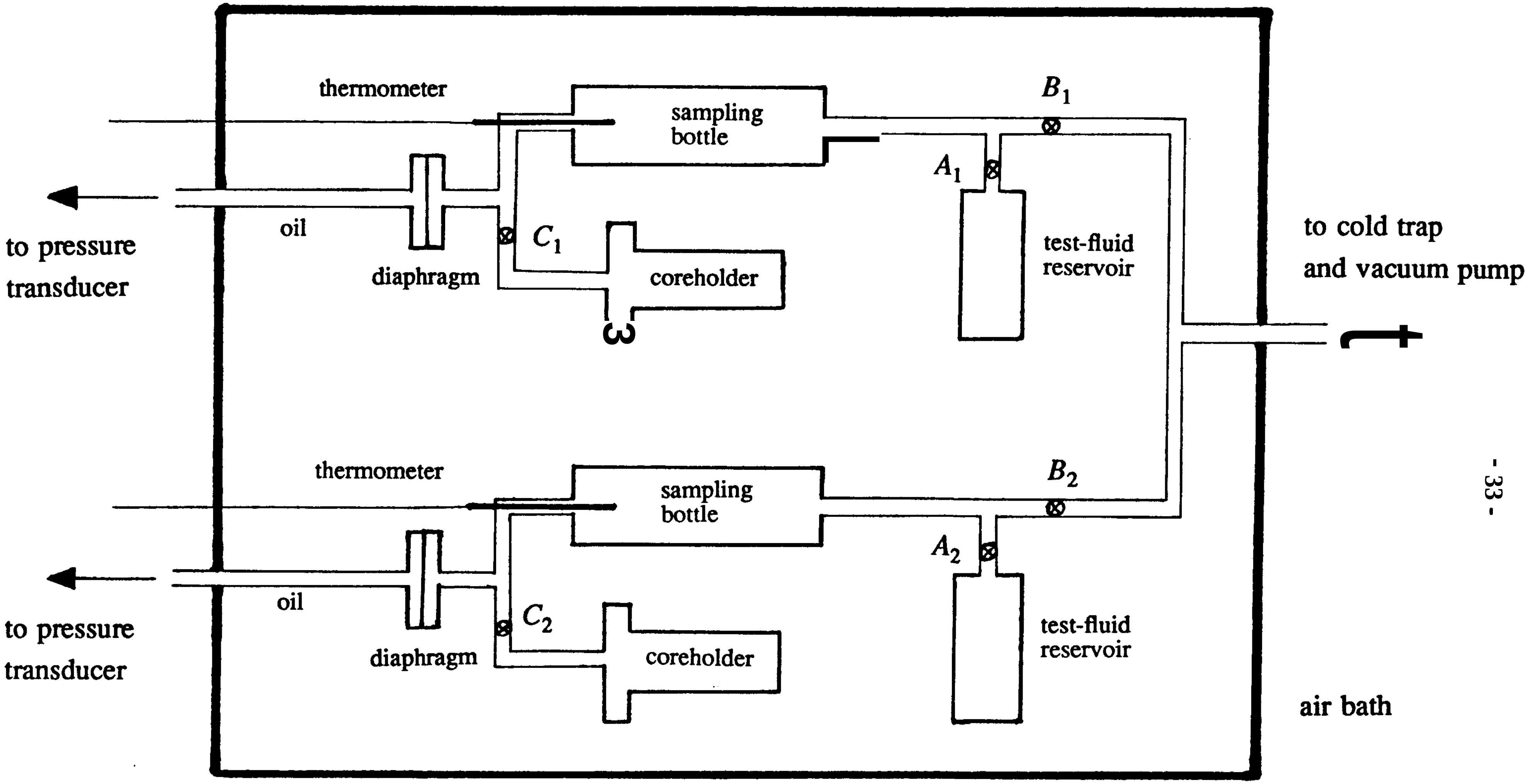

FIGURE 4.2 Schematic of the High Temperature System

reluctance type plate transducer. The plate has a 25 psi differential capacity and the signal from the instrument is in volts. A thermocouple is placed inside a modified coreholder to monitor temperature.

This system can be used to determine the dead volume as well as the amount of adsorption. The dead volume measurements are performed at room temperature, but during the adsorption measurements, the coreholder is immersed in a dewar filled with liquid nitrogen.

4.1.2 THE HIGH TEMPERATURE SYSTEM

The principal elements of the low temperature system are also found in the high temperature system. When the measurements of the dead volume and low temperature adsorption are completed, the coreholder section is transferred intact from the low temperature system to the high temperature system. Refemng to Fig. 4.2, this system has been doubled to accommodate two coreholders at the same time. The oven houses the test-fluid reservoirs which are connected to the sampling bottles which are in turn connected to their respective coreholders. The tubing is all 1/4 inch. A single line leading outside the oven **links** the sampling bottles to a two-stage mechanical pump and a cold trap.

Although the valves are the same type used in the low temperature system, the control **knobs** must be outside the air bath while the valves themselves must be inside.

Thus, long steel rods must be joined to the valve stems with couplings on the inside and also joined to the knobs on the outside. The couplings must be able to withstand the large torque required to fully close the valves at elevated temperatures.

Elevated temperatures also create complications with respect to the pressure measurement instruments. Following the lead of Hsieh, thin steel diaphragms are used to transfer the pressure responses outside the oven to standard reluctance plate transducers. The pressure differential for these transducers is 500 psi. An improved diaphragm design, shown in Fig. 4.3, has several advantages over its predecessor. The plate, normally .003-.004 inches thick, has a larger diameter for enhanced sensitivity. No longer soldered into place, it is held by the pressure of two sides of the unit bolted together. In this way, the diaphragm assembly can be taken apart, inspected, cleaned, and if necessary the plate can be replaced. The entire unit is stainless steel. One chamber is filled with the test gas. The opposite one is filled with diffusion pump silicon oil of high quality, as is the tubing that connects the chamber to the transducer. This oil can withstand high temperature without significant degradation or vaporization. It must, however, go through a long period of outgassing before enough light ends are drawn off to achieve the desired characteristics. A lower grade oil would require even more time. Replacing a broken plate is fairly easy; replacing and outgassing the oil consumes the most time. Thus, a spare diaphragm unit and tubing are filled with oil and attached to a vacuum pump in readiness for emergencies. Figure 4.4 shows the configuration of the pressure measurement system outside the oven. For safety reasons, there is an overflow oil reservoir which is separated from the two transducers by valves. When warming or cooling the oven, the valves are opened to avoid unnecessary stress on the plates. Although this method of measuring pressure is valid,

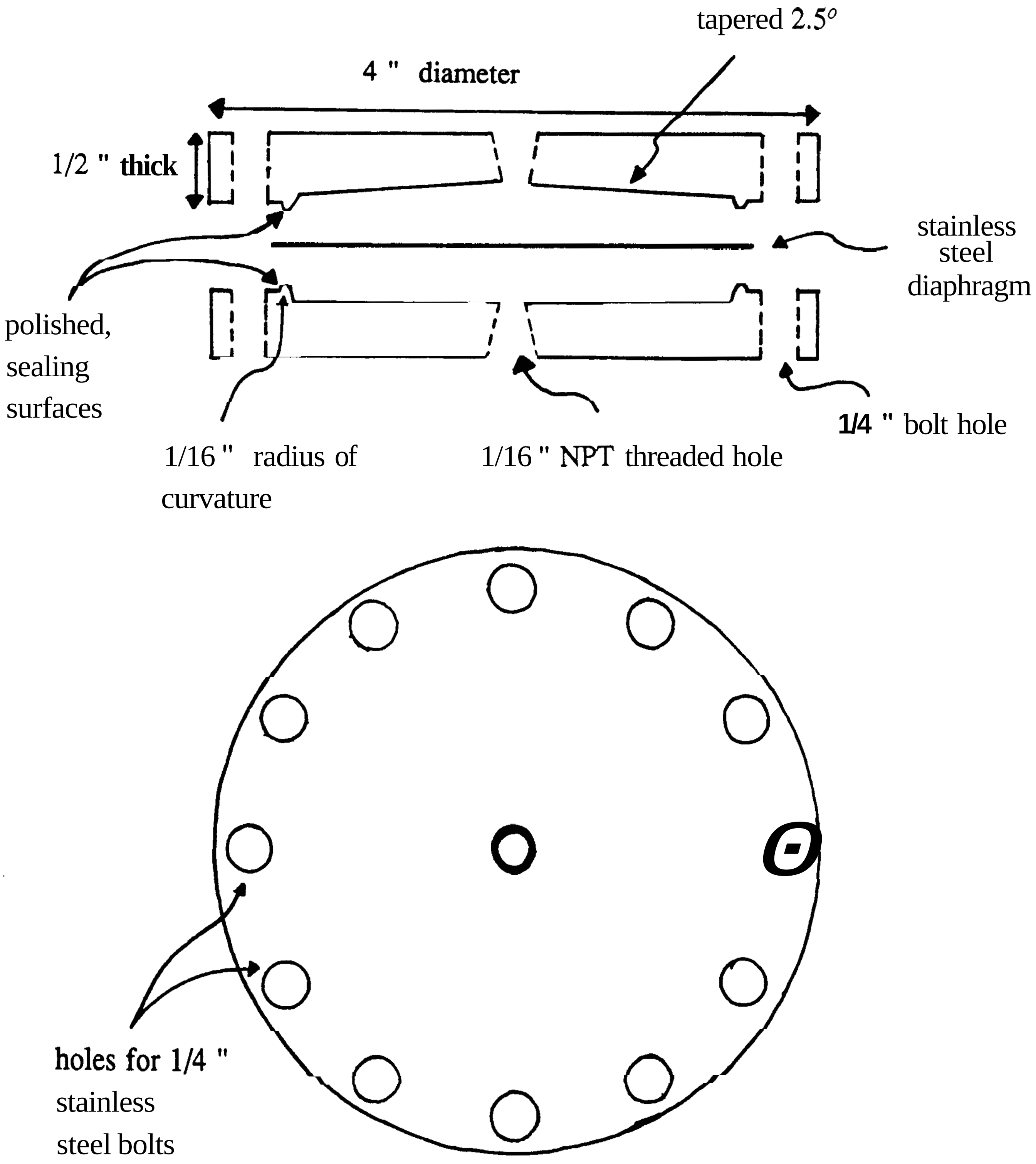

FIGURE 4.3 Schematic of Modified Diaphragm Assembly

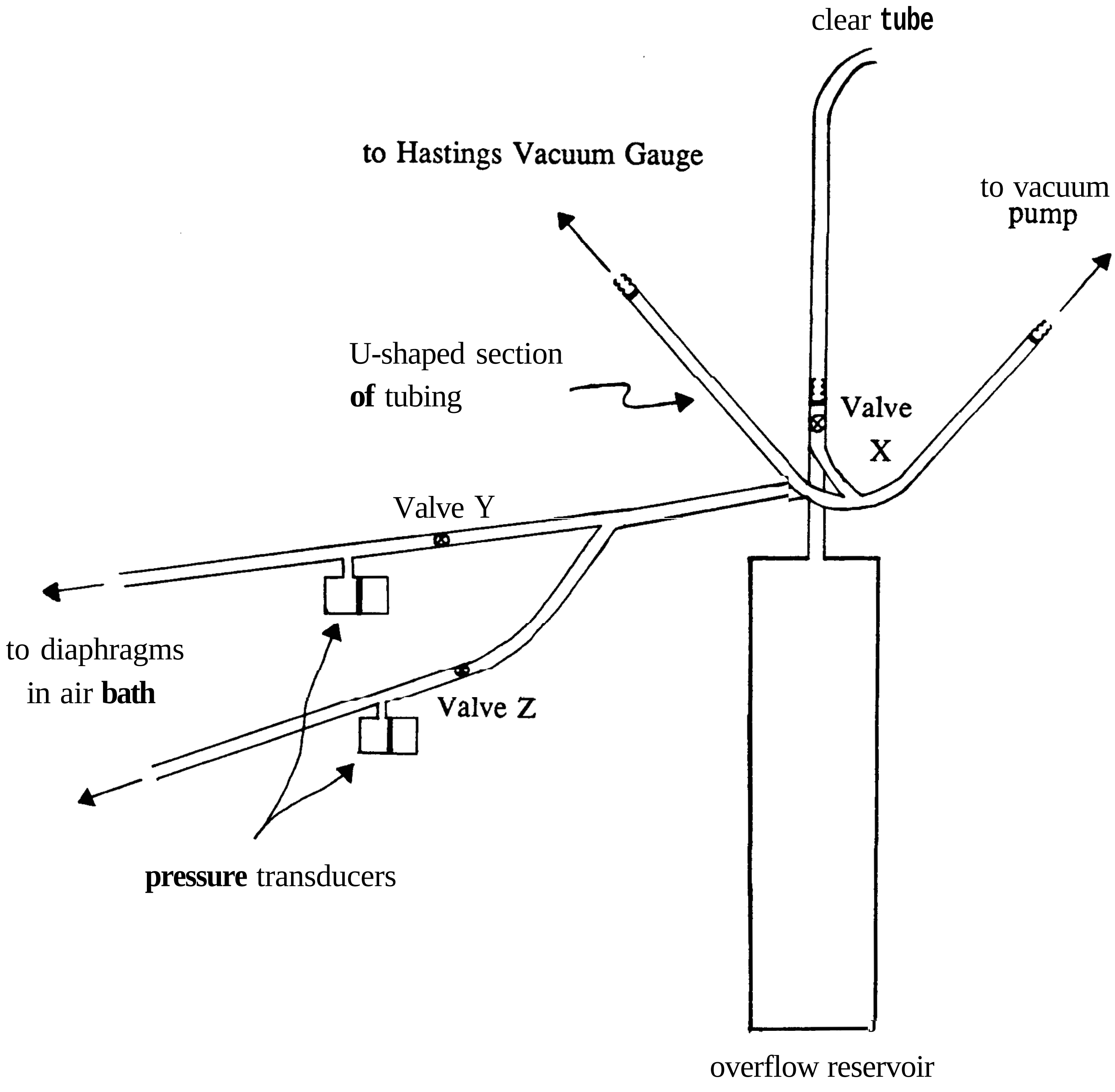

FIGURE 4.4 Schematic of Pressure-Measurement System Outside of Air Bath

the time and effort required to use it can be counter-productive, and hence, high temperature pressure transducers are recommended as a replacement.

Constant temperature is assumed to simplify the data analysis. To determine how well **this** constraint is met, the temperature is monitored at various places throughout the equipment. Platinum resistance thermometers constructed by Hsieh are located inside the sampling bottles. **A** constant current generator sends a current through the thermometers and the voltage drops are measured. The resistances can be calculated and the corresponding temperatures found **using** Tables 4.1a - 4.1c. First, one must find the calculated resistance in the main part of the appropriate table. For example, the value of 108.855 ohms is located in Table 4.1a in the third row, second column of the resistance entries. By following the row to the base temperature column, one can see that the base temperature is 20 °C. By following the column up from the resistance entry, one can see that the temperature increment is **3** °C. The actual temperature is the sum of these values, namely **23** °C. Because of the structure of the tables, the only interpolation necessary is between two adjacent values of the same row. Further information on Hsieh's platinum resistance thermometers are available in hist doctoral thesis (1980). The temperature of the air bath is checked with a thermocouple next to an inside wall of the oven, and if necessary, the room temperature can be recorded as well. Sometimes the oven temperature varies with large fluctuations in room temperature. These variations, usually related to day and night changes, become significant when one considers that an experimental run can last a week or more. When these monitoring devices indicate the need, a heater or an air-conditioner are used to provide a stable room temperature.

TABLE 4.1a Correlation of Temperature (0-129 °C) Versus Resistance for a Platinum Resistance Thermometer

Base Temperature	Temperature Increment Above Base Temperature, C									
°C	0	1	2	3	4	5	6	7	8	9
	Resistance in Ohms									
0	100.000	100.385	100.770	101.155	101.540	11.925	102.310	102.695	103.080	103.465
10	103.850	104.235	104.620	105.005	105.390	105.775	106.160	106.545	106.930	107.315
20	107.700	108.085	108.470	108.855	109.240	109.625	110.01	110.395	110.780	111.165
30	111.550	111.935	112.320	112.705	113.090	113.475	113.860	114.245	114.630	115.015
40	115.400	115.785	116.170	116.555	116.940	117.325	117.710	118.095	118.480	118.865
50	119.250	119.635	120.020	120.405	120.790	121.175	121.560	121.945	122.330	122.715
60	123.100	123.485	123.870	124.255	124.640	125.025	125.410	125.795	126.180	126.565
70	126.950	127.335	127.720	128.105	128.490	128.875	129.260	129.645	130.300	130.415
80	130.800	131.185	131.570	131.955	132.340	132.725	133.110	133.495	133.880	134.265
90	134.650	135.035	135.420	135.805	136.190	136.575	136.960	137.345	137.730	138.115
100	138.500	138.885	139.270	139.655	140.040	140.425	140.810	141.195	141.580	141.965
110	142.350	142.735	143.120	143.505	143.890	144.275	144.660	145.045	145.430	145.815
120	146.200	146.585	146.970	147.355	147.740	148.125	148.510	148.895	149.280	149.665

TABLE 2b Correlation of Temperature (120-249 °C) Versus Resistance for a Platinum Resistance Thermometer

Base Temperature °C	Temperature Increment Above Base Temperature, C									
	0	1	2	3	4	5	6	7	8	9
	Resistance in Ohms									
120	146.200	146.585	146.970	147.355	147.740	148.125	148.510	148.895	149.280	149.665
130	150.050	150.435	150.820	151.205	151.590	151.975	152.360	152.745	153.130	153.515
140	153.900	154.285	154.670	155.055	155.440	155.825	156.210	156.595	156.980	157.365
150	157.750	158.135	158.52	158.905	159.290	159.675	160.060	160.445	160.830	161.215
160	161.600	161.985	162.370	162.755	163.140	163.525	163.910	164.295	164.680	165.065
170	165.450	165.835	166.220	166.605	166.990	167.375	167.760	168.145	168.530	168.915
180	169.300	169.685	170.070	170.455	170.840	171.225	171.610	171.995	172.380	172.765
190	173.150	173.535	173.920	174.305	174.690	175.075	175.460	175.845	176.230	176.625
200	177.000	177.385	177.770	178.155	178.540	178.925	179.310	179.695	180.080	180.465
210	180.850	181.235	181.620	182.005	182.390	182.775	183.160	183.545	183.930	184.315
220	184.700	185.085	185.470	185.855	186.240	186.625	187.010	187.395	187.780	188.165
230	188.550	188.935	189.320	189.705	190.090	190.475	190.860	191.245	191.630	192.015
240	192.400	192.785	193.170	193.555	193.940	194.325	194.710	195.095	195.480	195.865

TABLE 4.1c Correlation of Temperature (240-49 °C) Versus Resistance for a Platinum Resistance Thermometer

Base Temperature °C	Temperature Increment Above Base Temperature, °C									
	0	1	2	3	4	5	6	7	8	9
	Resistance in Ohms									
240	192.400	192.785	193.170	193.555	193.940	194.325	194.710	195.095	195.480	195.865
250	196.250	196.635	197.020	197.405	197.790	198.175	198.560	198.945	199.330	199.715
260	220.100	200.485	200.870	201.255	201.640	202.025	202.41	202.795	203.180	203.565
270	203.950	204.335	204.720	205.105	205.490	205.875	206.260	206.645	207.030	207.415
280	207.800	208.185	208.570	208.955	209.340	209.725	210.110	210.495	210.880	211.365
290	211.650	212.035	212.420	212.805	213.190	213.575	213.950	214.345	214.730	215.115
300	215.500	215.885	216.270	216.655	217.040	217.425	217.810	218.195	218.580	218.965
310	219.350	219.735	220.120	220.505	220.890	221.275	221.660	222.045	222.430	222.815
320	223.200	223.585	223.970	224.355	224.740	225.125	225.510	225.895	226.280	226.665
330	227.050	227.435	227.820	228.205	228.590	228.975	229.360	229.745	230.130	230.515
340	230.900	231.285	231.670	232.055	232.440	232.825	233.210	233.595	233.980	234.365
350	234.750	235.135	235.520	235.905	236.290	236.625	237.060	237.445	237.830	238.215

4.1.3 DATA LOGGING

Adsorption experiments, especially those involving a relatively large molecule such as steam, tend to be time-consuming and tedious. Automating the experiment would increase the quality and quantity of data as well as free the operator for other tasks. There are two areas in which to automate: the actual apparatus and the data aquisition system.

The high temperature apparatus presents a problem because of the valves. Normally, one would use pressure actuated valves that can respond to a computer signal, but those that are commercially available cannot withstand the high temperatures used in the present research. In contrast, the data aquisition system can be automated with commercially available equipment. An IBM Portable in conjunction with the LabMaster cards by Tecmar reads pressures and temperatures in terms of voltage input and converts to digital output. The major limitation is that the cards cannot always read all the voltage signals simultaneously.

4.2 PROCEDURES

The quality of experimental data does not depends solely on the apparatus design; it also depends on how that apparatus is used. The procedures are outlined in detail in the *six* sub-sections.

Basic Procedures for an Experimental Run

describes the basic tasks required during an experimental run.

General Equipment Preparation and Maintenance

describes some of the activities **required** to ensure that the machinery **is** ready for an experimental run.

Core Preparation

describes what is done to the core sample prior to a run.

Dead Volume Determination

describes how to obtain the data for the dead volume calculations.

Low Temperature Adsorption

describes how to obtain the adsorption data for substances with relatively **low** boiling temperatures.

High Temperature Adsorption

describes how to obtain the adsorption data **for** substances with relatively high boiling temperatures.

4.2.1 BASIC PROCEDURES FOR AN EXPERIMENTAL RUN

The routine followed for any experimental run involves three time periods: before, during and after the run. Regardless of the type of experiment -- dead volume determination, low temperature adsorption, or high temperature adsorption -- the activities during the run itself are almost identical. Initially, the system should be at operational temperature and the coreholder and sampling bottle sections should be exposed to the vacuum pump. Consequently, Valves A and C are open and B is closed (Fig. 4.1 and Fig. 4.2). The basic procedures are outlined below.

1. Close Valves A and C.

2. Open Valve B until pressure nears desired p_1 and then close. Adjustments can be make with Valve A as well if too much test gas is allowed in. Wait a few minutes for a stable p_1.

3. Open Valve C to allow contact between the sampling bottle and coreholder. Wait for a stable p_2. Depending on sample permeability, equilibrium may require one hour, 20 hours, or more.

4. Close Valve C. This action marks the end of one step.

5. Repeat Numbers 2 - 4 until peak of cycle is obtained (i.e. the point of greatest p_2 and the end of adsorption).

6. Open Valve **A** to decrease pressure in sampling bottle; then close.
   Make any adjustments necessary to bring pressure near desired
   p_1 and wait for equilibrium.

7. Open Valve C and wait for equilibrium.

8. Close Valve C.

9. Repeat Numbers **6 - 8** until cycle and run are completed.

The Data Checklist shown in Tables 4.2a and 4.2b prompts the operator to record the pertinent data and stores the information in an orderly fashion. The experimental temperature is determined by a thermocouple in the coreholder **for** the low temperature system. For the high temperature system, platinum resistance thermometers in the sampling bottles are used as well as a thermocouple inside the oven. **As** the temperature **is** assumed to be constant, appreciable variations should be noted. For the present research, the atmospheric pressure was measured with a mercury-filled, brass manometer. The height of the mercury column depends on temperature because of the thermal properties of brass. Consequently, the atmospheric pressures are corrected for room temperature so that they can be reported using a standard of 0 °C. Copies of the Data Checklists for each of the experimental runs are in Appendix B.

Table 4.2a **DATA CHECKLIST**

DATE ____________

SAMPLE NAME ______________________ RUN NUMBER ________

SAMPLE WEIGHT ________ gm

COMMENTS

____

____

____

____

____

CIRCLE TYPE OF EXPERIMENT AND MEDIUM USED (E.G. ADSORBATE)

dead volume low temperature high temperature

helium nitrogen steam natural gas ________

other medium ____________

TEMPERATURE OF EXPERIMENT ________ C or K

DEAD VOLUME (if already known) ________ cc

SAMPLING BOTTLE VOLUME (circle one)

low T system 45.07 cc

high T system: Number 1 158.62 cc OR Number **2** 513.30 cc

other __________ cc

PRESSURE TRANSDUCER CALIBRATION INFORMATION:

plate differential: **25** psi 100 psi 500 psi other ______

atmospheric pressure (corrected for room T): _________ psia

vacuum pressure: __________ psia _________ volts

Table 4.2b

RAW EQUILIBRIUM PRESSURE DATA

STEP	p_1* (volts)	$P2$* (volts)	COMMENTS

* Entries are in volts for computer program which converts to psia.

4.2.2 GENERAL EQUIPMENT PREPARATION AND MAINTENANCE

Experimental research requires a continuous effort to preserve the integrity of the equipment. The question arises as to what tasks are required to ensure that the apparatus is truly ready for an experimental run. This sub-section addresses that question in part; further details are discussed later.

While some tasks are repeated prior to every run, others are repeated at more irregular intervals. Leak checks, for example, are carried out when the equipment has been idle for too long or when the pressure data looks suspicious. Obviously a failure to maintain pressure, above or below atmospheric, in a supposedly isolated volume at equilibrium suggests a problem. An added complication is the fact that some leaks occur within a discreet temperature range. The high temperature system sometimes exhibits this behavior. The longer the test, the less tolerance there is for a leak -- be it past a valve to another chamber or directly to the atmosphere. For a lengthy run, even a pinhole leak in the tubing can adversely affect the data. Thus, identifying and repairing leaks is crucial to the quality of the test.

Another task which requires attention at irregular intervals is that of removing corrosion and impurities from the interior of the system. As with leak checks, a thorough examination is conducted when the equipment has been idle for too long or when the data or external evidence so indicates. Care must be taken when choosing a solvent, especially when cleaning the rubber vacuum hoses. Some solvents such as acetone will actually be absorbed by the rubber, thereby forcing a long period of outgassing before a suitable vacuum can be achieved. In some instances, there is no choice but to replace the affected part.

The need for replacement also applies when repairs are impossible on a part that has failed or is about to fail. A supply of crucial, hard-to-obtain parts should be kept in the laboratory, especially those that are prone to failure. If unprepared, something as small as a broken rod coupling on a valve can result in a premature finish to the run and several days delay while acquiring parts, building and installing a replacement, and preparing for a new run. Moreover, parts such as the diaphragm unit from a machine shop or the pressure transducers from a manufacturer can take weeks to be delivered. Thus, planning ahead is important.

One of the primary concerns for any operator is that the measurement devices be reliable. Two types of devices are used to monitor temperature. Whereas the thermocouples are fairly easy to maintain and use, the platinum resistance thermometers may pose problems. Vulnerable parts of these thermometers include the wiring, switches, and constant current generator. The constant current generator presently in use is sometimes difficult because a small change in the setting produces a large change in the temperature calculations. The current was normally set as near a possible to 100 microamps to make the calculations simpler. With data logging, the only constraint is that the level be consistent with the input capabilities of the computer card. Unfortunately, the initial current setting tends to drift requiring the operator to make the appropriate adjustments.

The pressure-measurement devices used are vacuum gauges, reluctance plate pressure transducers, and steel diaphragm assemblies. Both the vacuum gauges are susceptible to poisoning by impurities. The gauge tube of the Hastings Vacuum Gauge is particularly vulnerable to substances released from the core or elsewhere in the system at elevated temperatures. This situation is encountered during the baking out process described in the next sub-section (Core Preparation). The reliability of the transducers depends on whether the plates have a well-behaved deformation pattern. As a safety precaution, the differential pressure that the plates can withstand should be marked clearly on the outside of the transducers and should be kept in mind at all times. Ideally, the plates should deform in such a way that the relationship between the voltage reading and the pressure is linear. This linearity makes the conversion from volts to psia very simple. Thus, upon installation the transducers are checked with a deadweight tester at experimental temperatures. Subsequent checks are performed whenever that linearity is in doubt. The question of plate strength as well as linearity applies also to the thin steel plates in the diaphragm assemblies. The first check is carried out once the devices are in place and the silicon oil has been properly outgassed. Later checks occur whenever there is a significant change such as a new diaphragm. Of course, Valves Y and Z (Fig. 4.4) leading to the overflow reservoir should be closed when putting pressure on the diaphragms.

The purpose of outgassing the silicon oil is to draw off the more volatile components, thereby reducing the compressibility. The oil can then transfer the pressure response from the diaphragms to the transducers with greater accuracy. The procedure is simple, but generally time-consuming. Boiling the oil before placing it in the system may accelerate the process.

The outgassing procedures can be described by first referring to Fig. **4.4.** Valve **X** and a clear tube are shown above the U-shaped section and the overflow reservoir. During periods of disuse, this valve is closed and the ends of the U-shaped section are plugged. For outgassing, **a** vacuum pump is attached to one end and the Hastings Gauge to other. The Hastings gauge tube is connected to the left-hand end of the U-shaped tubing and is higher as a precaution against contamination. All the valves are closed initially, exposing only the reservoir section to the pump, and thereafter the system is periodically back-flushed until the vacuum **is** about 50 microns or less. To back-flush the system, the pump is turned off and the connecting hose to the gauge tube **is** removed from the steel tubing. Then **a** slight suction is created in the clear tubing above the reservoir by sucking on it. Valve **X is** opened all the way to allow gas bubbles to reach the liquid surface. Drawing the liquid level some distance up the tube and letting it drop **again** helps the process because the bubbles will drop more slowly than the liquid. The valve is closed just before the surface disappears from view.

Once the reservoir section is outgassed, one of the diaphragm sections can be added by opening Valve Y or **Z.** The same procedure is followed until the entire volume is outgassed -- a **task** which can require as much as a few months. Turning on the oven and **using** the heat gun sometimes reduces the time element. One of the advantages of **adding** the diaphragm sections on separately **is** that one may check each section for leaks in addition to the outgassing.

In view of the prospect for delays and problems inherent in the pressure- measurement system consisting of all the equipment shown in **Fig 4.4** plus the diaphragms shown in Fig. 4.2, it is recommended that high temperature pressure transducers be used instead. Not only would this change simplify the process, it would also facilitate any experiments done in the future on transient flow behavior.

Before every run, the transducers (Fig. 4.4) must be calibrated *so* that the voltage readings can be converted to pressure units. The first step is to measure the atmospheric pressure inside the room and if necessary correct to 0 °C and convert to psia. The zero on the voltmeter should correspond to zero plate deflection. For the current research, zero plate deflection was chosen as atmospheric pressure. To set the span, a strong vacuum is applied *so* the reading becomes negative. The expected voltage for this vacuum is calculated in the following manner:

$$\frac{span}{fill\ voltage\ range} = \frac{atmospheric\ pressure\ (psia)}{full\ differential\ plate\ pressure\ (psia)}$$

Thereafter, the voltage corresponds to pressure in psig. The computer program can convert all the readings in volts to psia.

4.2.3 CORE PREPARATION

The samples for the present research have been provided by outside organizations from Iceland, Italy, Mexico, and the United States. Some are cuttings or cores from wells, while others are from outcrops. Though several different reservoirs are represented in the collection thus far, the current research emphasis is on Larderello, Italy and The Geysers, California. The Larderello field is composed largely of various limestone units as well as some anhydrites. The sample from Montiverdi Well #2 is a micaschist. The Geysers is a naturally fractured reservoir of greywacke with low matrix porosity and permeability. Berea sandstone is included in the tests because of the relatively high porosity and permeability and because it allows for comparison with the work of Hsieh (1980). Permeability and porosity data were collected on test core samples to gain added information of the reservoir rocks.

Because adsorption depends in part on the nature of the rock surfaces, the treatment of a sample prior to an experiment can significantly affect the results. As there is no control over that treatment while the sample is in the possession of the outside organization, it is important to learn as much as possible about the history of the sample. For example, some drilling fluids can change the surface characteristics as can certain tests to determine other parameters such as porosity found by mercury injection.

Preparations for an adsorption experiment are not complicated. First, the sample size is adjusted to fit the coreholder. For large cores, a drill press is used to cut plugs that are about an inch in diameter and six inches long. Some coreholders can accommodate a slightly larger diameter. If one continuous plug is impossible, two or three pieces are used to fill the volume. Large, irregular cuttings may require a rotary saw to provide the proper shape. Next the sample is dried out in a small oven under a vacuum. When dry, it is weighed and placed inside the coreholder which is then attached to the low temperature system. A heating tape is placed around the coreholder to heat it to the desired temperature. Once this temperature has been attained, the coreholder is left open overnight to the vacuum pump and cold trap. Impurities still in the coreholder at this stage are released, so it is important to keep the trap filled with liquid nitrogen. The last step preceding the dead volume test is to turn off and remove the heating tape and allow the temperature to return to ambient conditions.

4.2.4 DEAD VOLUME DETERMINATION

Eqs. 3.20 and **3.21** which involve only pressures and volumes can be applied to calculate the dead volume as described in Section **3.2.** A simple experimental approach is to vacuum out the system, close all valves, allow some gas into the sampling bottle volume, and measure p_1. Then open Valve C (Fig. 4.1), wait for equilibrium and measure p_2. These actions together constitute one step of the adsorption procedures (Sub-section 4.2.1). Therefore, one can follow the general pattern of an adsorption run, generating one estimate per step. Unlike adsorption runs, the relationship of consecutive p_2 values does not matter and the operational temperature is room temperature.

Originally, helium was used for the dead volume determination, but scatter in the estimates prompted further examination. A second run often produced data with better agreement; however, subsequent work with nitrogen proved it to be more satisfactory for these measurements.

An alternate method of determining the dead volume exists which might yield more accurate results because of the higher pressures used. Attach pressure transducers with plate differentials of 500 psi to the sampling bottle and coreholder sections. Now pressures in each section can be recorded after Valve C is closed, thereby eliminating the need for equilibrium prior to closing the valve and accounting for the slight volume change upon closing. Helium is supplied to both sections until the pressure reaches approximately 400 psi. Valves **B** and C are closed and Valve **A** opened to evacuate the sampling bottle volume. Then Valve C is opened to allow some expansion into the sampling bottle and closed again. By applying the real gas law with the known sampling bottle volume and the appropriate pressures, one estimate for DV can be obtained. As with the first method, more estimates can be obtained by continuing the experiment in the same manner and modifying the analysis slightly.

4.2.4 LOW TEMPERATURE ADSORPTION

A low temperature adsorption run is different from the dead volume determination in two respects. First, the coreholder is immersed in a dewar filled with the liquid form of the test fluid. Second, the consecutive p_2 values must increase during adsorption and decrease during desorption. Otherwise, the computer program will not operate properly. **Thus** far, only nitrogen has been used as an test fluid, though other substances such as argon are possible. After the system is vacuumed out, the basic procedures shown in Sub-section 4.2.1 can be applied.

It is important that the coreholder be isolated from the vacuum and supply lines. During the course of a run, the liquid level in the dewar must be as close as possible to constant as even small changes can cause an appreciable difference in the pressure readings. Insulation fiber on top of the dewar retards evaporation; however, liquid must still be added periodically.

4.2.6 HIGH TEMPERATURE ADSORPTION

Like the low temperature system, the high temperature system can accommodate a variety of substances, including steam and hydrocarbon gases. In the present research, only distilled water has been used. The adsorption of brines cannot be determined with the current apparatus.

Although the basic procedures for an adsorption test are independent of temperature, the high temperature tests present more problems. The valves are more difficult to operate and the chances of something breaking or leaking are increased. Moreover the equipment must be properly warmed prior to the test and cooled afterwards. It often takes a few days to prepare, a week or more for a test and a day or so to cool the equipment.

The procedures required to prepare the equipment safely are outlined below. Those activities already described in Sub-section 4.2.2 as general preparation. While the order of some steps is arbitrary, others obviously must occur in the order given.

1. Fill the test-fluid reservoirs to capacity.
2. Set the current for the platinum resistance thermometers, adjusting to obtain reasonable readings.
3. Make sure the oven damper is open and that all foreign objects are removed.
4. Open Valves **Y** and **Z** next to the transducers to allow for expansion during heating (Fig. 4.4).
5. Vacuum most of the gas out of the system leaving only enough to help with the heating.
6. Close all valves inside the oven.
7. Close oven doors and commence heating.
8. Once proper temperature has been reached throughout the system, close Valves **Y** and Z.
9. Vacuum out the system starting with one sampling bottle volume.
10. Once that volume has a vacuum of about 10 - 50 microns, close off the valve (B_1 or B_2 in Fig. 4.2).
11. Wait for a few minutes, then open the valve and at the same time check the gauge for a loss in vacuum. A loss indicates a possible leak.
12. Continue in this manner adding onto the volume section by section until the entire system with the exception of the test-fluid reservoirs has been vacuumed.

The method of vacuuming described in Steps 9 - 12 also serves as a final leak check.

Regarding the run itself, the directions given in Sub-section 4.2.1 may be applied to both parts of the system. In other words, when Valve A is mentioned, one should mentally substitute A, and A_2, likewise for the other valves. To avoid confusion, keep both cores on the same step at the same time. This allows for a comparison of the transient behavior in the two cores.

Operating the valves is more difficult in the high temperature system. Greater force is required to fully close the valves which, in turn, means that greater force also is required to open them. Wrenches are often necessary, but must be used with care. The knob on a valve should not be forced all the way open, but left loose as an indication of the open status. Sometimes, especially when there are several operators working in shifts, a knob that has been forced open is mistaken for one that has been forced closed. This situation can result in breakage.

A problem arises during the desorption process because of the distance between the diaphragms and Valves B_1 and B_2. When one of those valves is opened wide, the sudden surge of molecules away from the diaphragm causes a large pressure drop. If, however, the valve is quickly closed in response to that drop, the many molecules still remaining in the volume move back towards the diaphragm. The pressure reading goes up until equilibrium is reached. Many times the new pressure is only slightly lower than the old pressure. A better method is to crack the valve open slowly, never opening it all the way. The molecules then move in a slower, more controlled manner and the pressure reading decreases accordingly. When the reading nears the desired p_1, the valve can be closed again.

The criterion for determining whether or not equilibrium has been attained is a constant pressure. This choice leads to **some** significant problems, some of which will be discussed in more detail in the next section (Limitations of Apparatus and Procedures). In general, one must consider those things causing pressure changes that are not directly related to the equilibrium process. **Leaks** are an obvious source of changes, though the effects may be subtle and difficult to detect. If the run is continued despite a suspected leak, **all** pertinent information should be recorded under "Comments" in the Data Checklist (Table **4.2).** Fluctuations in room temperature may also cause small pressure changes regardless of the equilibrium status. The link may be established by comparing a trace of room temperature versus time and a trace of coreholder pressure and temperature versus time.

The final issue in terms of test procedures is that of keeping the cold trap in good operating condition. For some test fluids, this requirement is easily satisfied. Steam, however, presents a problem when it condenses because it tends to emulsify the vacuum pump oil. The steam also causes the liquid nitrogen to evaporate quickly, so the trap must be refilled fairly often. Moreover, if present in sufficient quantities, the water freezes in the cold trap and completely blocks access to the pump. The trap must then be removed, cleaned, and reinstalled before the pump is used again on the next step.

Once the test is completed, the cooling down process **starts** by exposing the sampling bottles and coreholders to the vacuum pump. Evacuating the system becomes especially important if the test fluid changes to a condensed phase **at** room temperature. After the vacuuming is completed, Valves A_1 and A_2 may be closed or open and the pump turned off. Valves Y and Z near the transducers must be opened to allow for the change in oil volume with cooling. Then the oven is turned off. After room temperature is restored, Valves *Y* and Z are closed, and the ends of the U-shaped tubing should be plugged. These precautions minimize the contact between the atmosphere and the oil, thereby reducing the effects of reabsorption of air in the oil.

4.3 LIMITATIONS OF APPARATUS AND PROCEDURES

When conducting experimental research, one must eventually consider the various factors which have an impact on the quality and usefulness of the final data. For this research effort, these factors may be grouped into the following categories: events unrelated to the phenomenon under investigation; equipment design; core selection and preparation; test-fluid selection; and procedures.

The first category includes all those Occurrences that can change the data but have nothing to do with adsorption in a core sample. For example, corrosion in the system would result in inflated values for adsorption in the core since it was assumed that no signification adsorption occurs on the steel walls contacted by the test fluid. One of the most significant problems is that of subtle leaks. Large leaks are troublesome; yet they are also comparatively easy to identify and repair. Small leaks that go undetected can cause the adsorption estimates to be too high -- a discrepancy that increases with time. A hysteresis loop on an adsorption isotherm may merely be the result of such a leak.

Limitations resulting from the present equipment design affect the scope of investigation as well as data quality. Difficulties manipulating the valves, a sensitivity to the liquid nitrogen level in the dewar on the low temperature system and a sensitivity of the high temperature system to room temperature are some of the features that affect data quality. The design of the test-fluid reservoirs is the major limitation to the scope of investigation. Brines cannot be tested because salt would remain in solution while the water vaporized. In addition, the highest pressure that can be achieved in theory is the vapor pressure inside the reservoir. In practice, however, that pressure is difficult to reach. Measurements at relative pressures above 0.9 are possible, but the adsorption isotherm curve tends to change quickly in that region. Detailed studies of that region would require high data resolution that can be difficult to obtain.

The degree to which the data are useful depends in part on the core selection. Using a general rock type is not as reliable as testing the appropriate outcrop sample which in turn is not as reliable as testing a core from the zone of interest. Once the core is chosen, the preparations must not disturb its surfaces to any significant extent as already discussed in Sub-section 4.2.3. Two main considerations are the effect of washing and drying on clays and the effect of breaking the sample into small pieces to reduce the testing time.

Just as the core itself has an impact on data quality, so too does the test fluid have an effect. The choice of distilled water complicates matters because it is a polar fluid with different interaction behavior than a non-polar fluid. As a result of the added forces, the thickness of the adsorbed layer tends to be slightly greater. If clays are present in significant quantities, the interactions become even more complex.

Unfortunately, of the substances of interest to the geothermal industry, distilled water and some noncondensable gases are only test fluids that can be used in the present apparatus.

Applying the experimental procedures incorrectly will obviously lead to incorrect data. Although the procedures, applied correctly, should lead to reliable data, there is one major area of concern: the equilibration of p_2.

Equilibrium is determined by observing when the change in pressure becomes negligible with time. The low temperature system can record changes as low as 0.0025 psi, though it is more accurate above 0.01 psi. The high temperature system can measure a change as low as about 0.5 psi. The difficulty comes in deciding what constitutes a negligible amount and whether the equilibration process is indeed the source of change. A rate of 0.05 psi per hour may seem small, but it has a significant impact if it continues for a day or more. Were the operator to end a step too early, the equilibrium estimate would be off by at least 1.2 psi. Unfortunately, small changes in the direction of equilibrium may also be caused by a leak, a fluctuation in room temperature, a drop in the liquid nitrogen level, or by some other cause.

An alternate approach to the equilibrium problem which depends on the use of early transient data may be possible. Figure 4.5 is an idealized graph of pressure versus time such as that obtained during the first few steps of an adsorption experiment. Initially, the pressure in the sampling bottle is at a vacuum. Then gas is introduced to the sampling bottle when a valve is opened and closed again. In response the pressure increases sharply until it reaches a stable level designated p_1. After a short

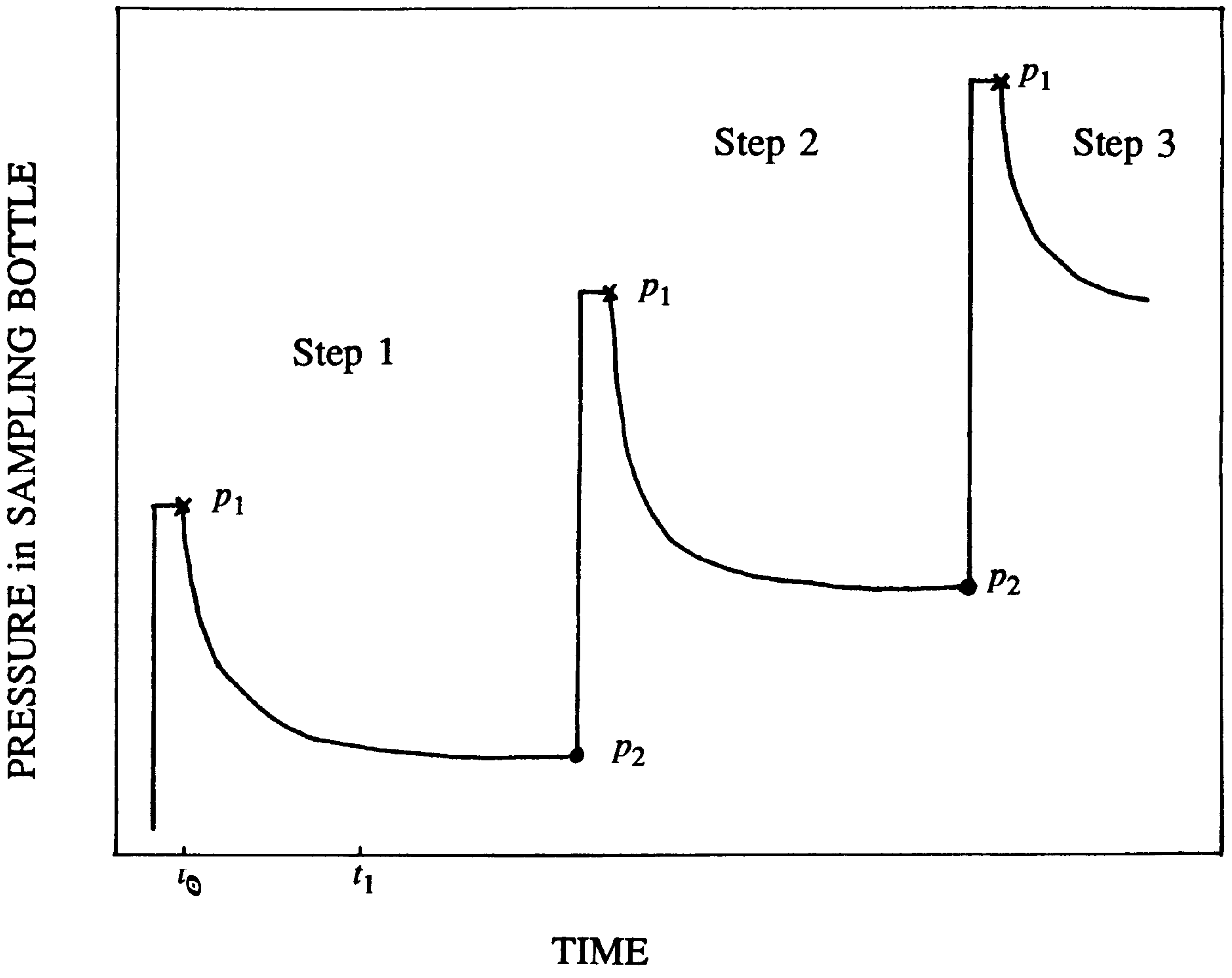

FIGURE 4.5 Idealized Pressure Versus Time Showing the First Steps of an Adsorption Experiment

time, the valve to the coreholder is opened. The pressure drops quickly at first, then more gently as the pressure-time slope nears zero. Eventually, when p_2 is reached, the valve between the two volumes (V, and DV) is closed again. The next step begins when the valve **(A)** to the test-fluid reservoir is opened. The current analysis uses only p_1 and p_2. Transient pressure data on the pressure-time curve could also be collected in more detail and analyzed.

Closer examination of Fig. **4.5** reveals that the general shapes are similar to those for various well tests: draw-down, build-up, and injectivity. To draw the parallel further, the adsorption side is something like successive periods of injection followed by shut-in, while the desorption side is more like draw-downs and shut-ins. The field of well testing has the techniques to predict equilibrium pressures from early transient data. Conceivably, the same type of techniques could be developed for adsorption/desorption **data.** If so, p_2 could be predicted after only **a** fraction of the equilibrium time has elapsed.

The immediate advantage of such a development is that the operator would have an advance target pressure for p_2. **A** leak or some other problem would be indicated if the pressure remained unstable beyond the target value.

If the analytical techniques could be modifies to the extent that it is not necessary to attain an equilibrium pressure before progressing to the next step, the savings in time and effort would be enormous. Figure **4.6** is the same type of graph as Fig. **4.5** except that each step is terminated before p_2 is reached. If Step 1 proceeds until time, t_1, as in **Fig 4.5,** there could be enough data **to** predict p_2 with modified analytical

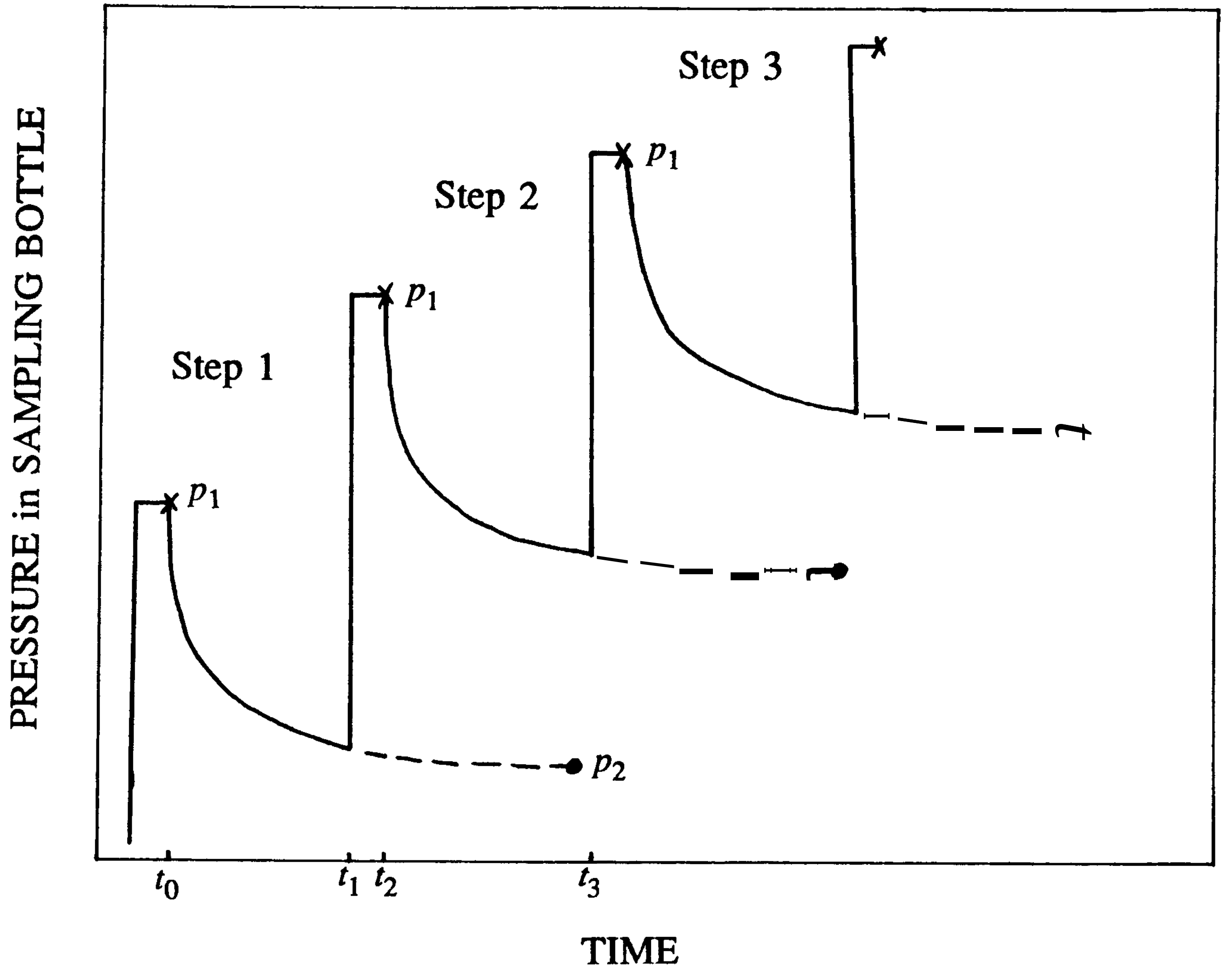

FIGURE 4.6 Idealized Pressure Versus Time Showing an Adsorption Experiment with Estimated Equilibrium Pressures

techniques. The dashed line shows how the curve might have continued to p_2 if left undisturbed. Now Valve C to the coreholder is closed and because the system is not at equilibrium, there are fewer molecules in the dead volume than there were at the end of Step 1 in Fig. 4.5. The difference could be calculated simply by measuring the pressure in the sampling bottle section. This volume would still be important in accounting for the flow in and out of the dead volume. Nonetheless, the difference causes a problem since the predicted p_2 corresponds to the n_{tot} of the old method. For clarity, let n^*_{tot} denote the actual number of moles in DV when the valve is closed before equilibrium.

One solution is to estimate what n_{tot} as well as p_2 would have been had the valve been left open. Step 2 begins much as before leaving the dead volume a little more time to equilibrate, but without the addition of new molecules. Once Valve C is opened at t_2, the pressure responds to the new influx into DV and to the disturbance of Step 1. If left long enough, the entire system would reach a state identical to the end of Step 2 in Fig. 4.5. If that p_2 and n_{tot} can be predicted from the data before $t3$, Valve C may be closed and Step 3 started. Again, there will be a difference between the n^*_{tot} in DV and the predicted value, n_{tot}. The experiment would continue in this manner using superposition to combine the effects of the current step with those of the previous steps. This approach would, in theory, reproduce the same points to generate the isotherm as the present method of waiting for equilibrium.

The second solution presupposes the same experimental conditions as the first. Though more closely related to the real physical situation, it too uses an imaginary state, namely that state arising from closing Valve C and then waiting for equilibrium in DV. Now the important prediction is that of the equilibrium pressure, p_2^*, which corresponds to n_{tot}^*. Pressure data taken from inside the dead volume between t_0 and t_2 may be required for such a prediction. During the first part of Step 2 the core is still isolated, but after t_2 the perturbation begins again. Like the other solution, the superposition principle would be needed to analyze the pressure responses of the remaining steps. This method should also produce the same isotherm but with a different set of data points.

In the future, measurement of adsorption isotherms may well be a routine matter for geothermal and low permeability natural gas reservoirs. The data may be widely used for reserve estimates as well as for reservoir simulations and well test analyses. Advancements in technique such as those suggested would require much effort, but would be well worthwhile.

5.0 DATA ANALYSIS AND INTERPRETATION

Thus far, five samples from among Berea, The Geysers, and Larderello cores were used to conduct a total of fifteen adsorption experiments. Though more samples were available from these and other sources, time constraints limited the quantity that could actually tested. High Temperature Runs 1, 2 and **3** at 169 °C, 207 °C, and 150 °C respectively were completed on Sample #1 of Berea sandstone. Sample #2 **of** the Berea had one high temperature run at 167 °C as well as three low temperature runs (LT1, LT2, and LT4) at -196 °C. LT3 was aborted due to equipment failure. Only one sample from The Geysers was used for the following tests: LT1 at -196 °C, **HT1** at 153 °C, HT2 at 200 °C, and HT3 at 180 °C. Like the Berea, two samples from Montiverdi Well **2** in Larderello, Italy have been used in this study. Though Sample #1 has not yet been tested, Sample #2 has been subjected to three low temperature tests, while Sample #3, which has been crushed into large fragments, has been used for one high temperature run at 180 °C.

Permeability and porosity were measured for small, cylindrical plugs that were cut from four samples: Sample #1 of Berea, Sample #1 **of** The Geysers, Sample #1 of Montiverdi **Well #2,** and Sample #2 of Montiverdi Well #2. **A** Ruska Gas Permeameter was used to determine permeability. The pore volume was determined by finding the difference between weight of the plug when saturated with distilled water and the weight when ***dry.*** Vernier calipers were used to measure the plug dimensions from which the **bulk** volume was calculated. **As** expected, the Berea has the highest values of permeability and porosity at 212 md and 18.35 %. The values for the other three samples are quite similar. For example, the porosity of The Geysers, Sample #1 is 1.34 %, while for Samples #1 and #2 of Montiverdi Well #2 the porosity is 1.15 % and 1.28 % respectively. Unfortunately, the Ruska Gas Permeameter could only provide an upper limit for the permeabilities of these plugs. Sample #1 of The Geysers has a permeability less than 0.743 md. Samples #1 and #2 of Montiverdi Well #2 have permeabilities less than 0.777 md and 0.768 md respectively.

Chapter 4 describes the equipment and experimental procedures required to generate the data. The resultant Data Checklists (example shown in Table 4.2) are given in Appendix B. Sections 3.2 and 3.3 present the equations important to the analysis, and Section 3.4 and Appendix A present the corresponding computer program. In the next section, the application of the analytical procedures is examined for one experimental run.

5.1 APPLICATION OF ANALYTICAL PROCEDURES

The Low Temperature Run #1 (LT1) conducted on Sample #2 of Montiverdi Well #2 continued for about 22 hours, yielding a record of pressure and time enabling the operator to choose the values of p_1 and p_2 for each step. Figure 5.1 is a graph of the raw data in which the voltage signals from the pressure transducers have been converted to pressure in psia. Initially, the apparatus is evacuated; then, the pressure rises quickly to p_1 indicating that some gas has been introduced into the sampling bottle volume. The pressure declines sharply as the valve to the coreholder is opened

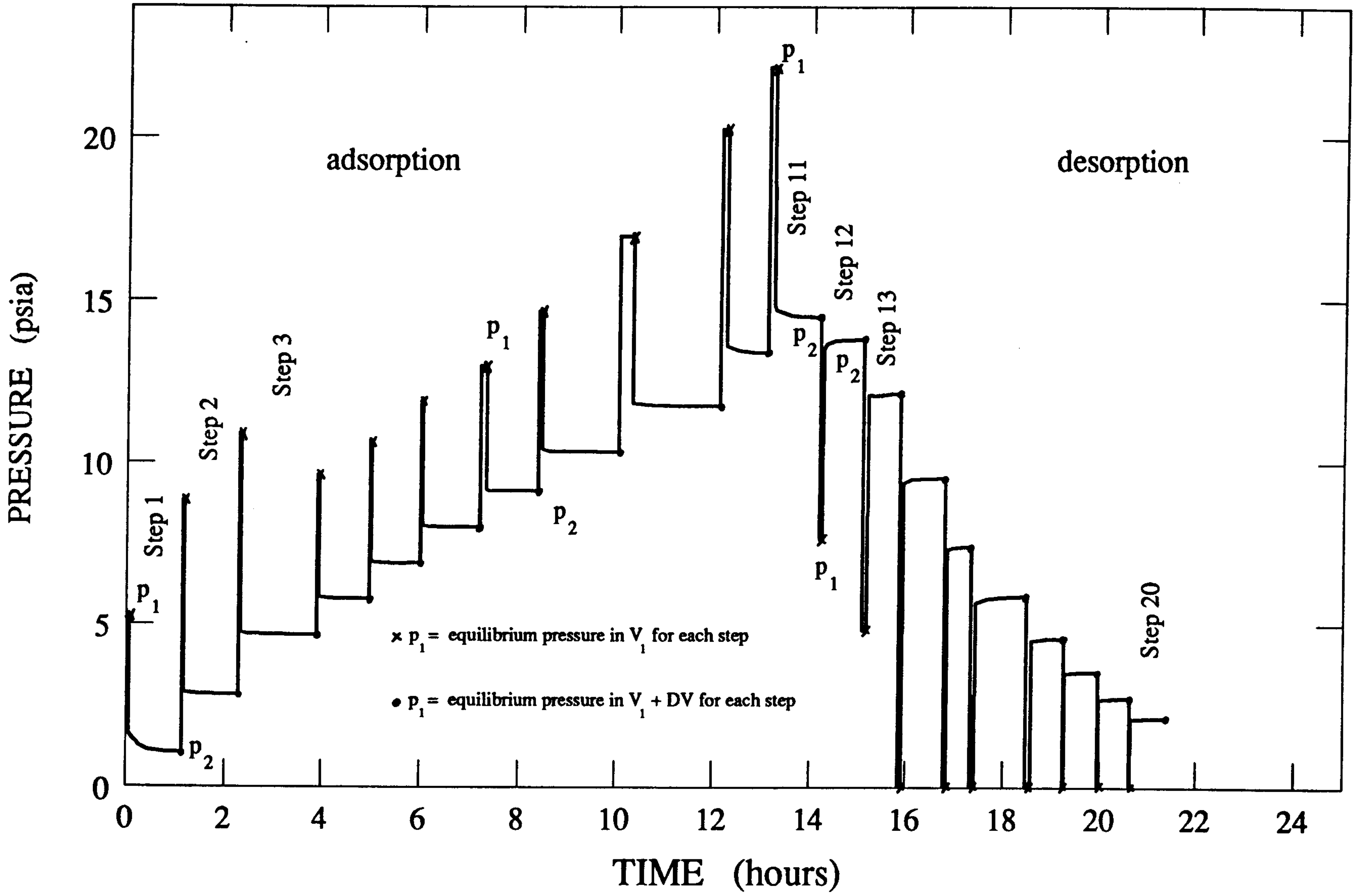

FIGURE 5.1 Raw Data from Nitrogen Run #1 at -196°C on Core

Sample #2 from Montiverdi Well #2

allowing gas to flow into DV. Eventually the system stablizes yielding p_2 and the valve is closed again ending Step 1. When more gas is sent into the sampling bottle, the pressure rises dramatically and levels off at p_1 for Step 2. The process of adsorption continues through Step 11 with ever-increasing p_2 values. Just over 14 hours into the experiment, desorption begins with step 12. Now gas is taken out of the sampling bottle at the beginning of the step which decreases the pressure. When p_1 is established and the valve to the coreholder is opened, gas moves into the sampling bottle volume and the pressure rises. If there were a transducer in the coreholder instead of the sampling bottle volume, it would show the pressure decreasing as the gas exits. As a result, the p_2 for Step 12 is lower than that of Step 11, consistent with the fact that desorption is taking place. The process continues until Step 20 when the run was terminated.

Using the values of p_1 and p_2, the amount of adsorption was calculated with the results shown in Table 5.1. Columns (5), (6), and (7) have the following relationship: $n_{tot} - n_{gas} = n_{ads}$. All values are positive indicating that they are realistic from a physical standpoint. Negative values are discussed in Section 5.2. The adsorption isotherm, Fig. 5.2, is generated with Columns (2) and (8). In Column (8), n_{ads} is equivalent to X in the BET analysis. The desorption curve denoted by a dashed line is slightly above the adsorption curve denoted by a solid line. Hysteresis of comparable magnitude was observed by Hsieh (1980), and similar to Hsieh's results, both curves are nearly linear. In the high pressure ranges, however, the curves become increasingly nonlinear. This behavior is usually evident when there is sufficient resolution for the higher values of p_2/p_o.

TABLE 5.1 Nitrogen Run 1 at -1%°C on Sample #2 from Montiverdi Well #2

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Step	Pressure Data			Amount of Nitrogen in DV			
	p_2/p_0	p_1	p_2	n_{tot}	n_{gas}	n_{ads}	n_{ads} / m_r
	[dimensionless)	(psia)	(psia)	(μmoles)	moles)	(μmoles)	(μmoles/gm)
1	0.07238	5.1965	1.0640	2102.637	511.111	1591.526	8.927
2	0.19347	8.8440	2.8440	5155.468	1366.165	3789.302	21.255
3	0.31881	10.8965	4.6865	8315.147	2251.243	6063.905	34.014
4	0.39517	9.6165	5.8090	10252.423	2790.455	7461.968	41.856
5	0.47034	10.6465	6.9140	12151.538	3321.261	8830.276	49.531
6	0.54585	11.8915	8.0240	14119.342	3854.469	10264.872	57.579
7	0.62238	12.9865	9.1490	16071.882	4394.883	11676.999	65.500
8	0.70452	14.6740	10.3565	18268.648	4974.927	13293.722	74.568
9	0.80146	16.9865	11.7815	20916.979	5659.451	15257.528	85.584
10	0.91286	20.2415	13.4190	24388.301	6446.053	17942.248	100.643
11	0.98701	22.1290	14.5090	28265.3%	6969.653	21295.744	119.454
12	0.93990	9.2340	13.8165	25933.797	6636.999	19296.799	108.241
13	0.82612	4.8440	12.1440	22219.520	5833.584	16385.936	91.913
14	0.64942	0.0515	9.5465	17388.414	4585.829	12802.585	71.813
15	0.50503	0.0440	7.4240	13633.433	3566.249	10067.184	56.470
16	0.40112	0.0315	5.8965	10649.291	2832.488	7816.804	43.847
17	0.31201	0.0290	4.5865	8330.412	2203.206	6127.207	34.369
18	0.24143	0.0340	3.5490	6541.962	1704.825	4837.137	27.133
19	0.18735	0.0340	2.7540	5158.012	1322.932	3835.080	21.512
20	0.14500	0.0340	2.1315	4090.793	1023.904	3066.890	17.203

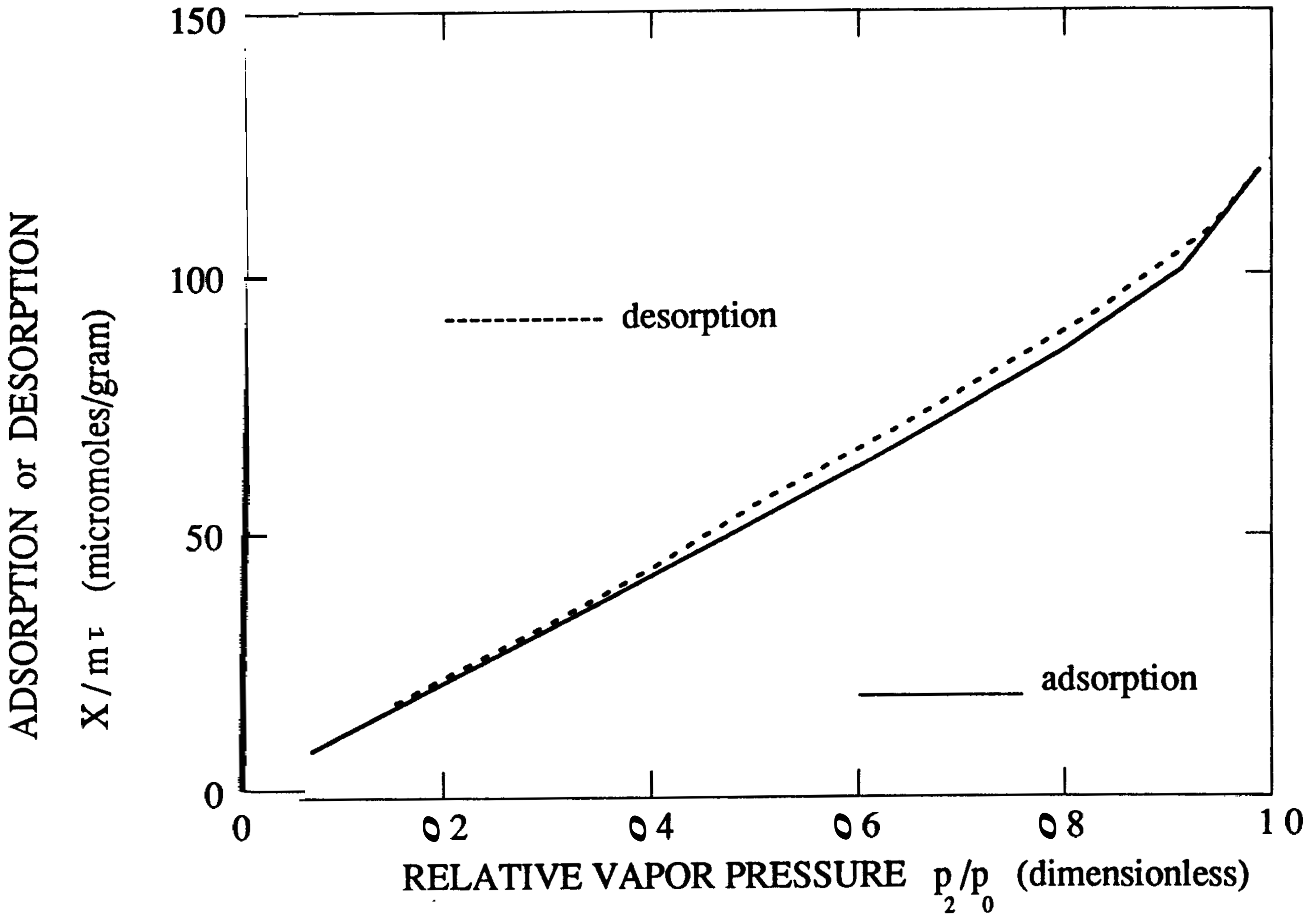

FIGURE 5.2 Adsorption Isotherm of Nitrogen Run #1 at -196°C on Core Sample #2 from Montiverdi Well #2

The adsorption and desorption parts provide for two BET analyses given in Table 5.2. Because the straight line form of the BET equation is used, the two variables, β and $\beta/\{X(1-\beta)\}$, are provided followed by the "C" factor, the monolayer adsorption, the sample weight, the surface area, and the specific surface area. In this case, the adsorption and desorption analyses agree fairly well with specific surface areas of 3.538 m^2/gm and 3.633 m^2/gm respectively.

5.2 ADSORPTION RESULTS

The focus of this section is on adsorption isotherms. Tables similar to Table 5.1 for all runs are presented in Appendix C. Tables 5.3 and 5.4 appear in the present section for convenience.

As stated previously, there were three nitrogen tests on Sample #2 of Berea, one on Sample #1 of The Geysers, and three on Sample #2 of Montiverdi Well #2. Of all the nitrogen experiments conducted, LT1 of Berea, Sample #2 is the only run with negative values as seen in Columns (5), (7), and (8) of Table 5.3. Because it was the first run attempted, experimental errors and/or operator errors may have been factors. The problem of negative values was confronted in many of the high temperature runs. This topic is addressed further when the steam data are discussed.

Figure 5.3, the isotherm of LT4, is typical of the two positive value tests on Berea, Sample #2. A small hysteresis exists as well as a turn upwards at high relative

TABLE 5.2 BET Results of Nitrogen Run 1 at -196 °C on Sample #2 from Montiverdi Well #2

*** Analysis Based on Adsorption ***

Rel. Pressure, β	the factor $\beta/\{X(1-\beta)\}$ in 1/mole
0.0723810	49.0276
0.1934694	63.3041
0.3188095	77.1810

The value of "C" factor in BET analysis **is**	3.7921	1/micromoles
The monolayer adsorption is	6446.0050	micromoles
The weight of the sample is	178.2760	grams
The total surface area is	628.9535	square meters
The specific surface area is	3.5280	square meters/gram

*** Analysis Based on Desorption ***

Rel. Pressure, β	the factor $\beta/\{X(1-\beta)\}$ in 1/mole
0.3120068	74.0146
0.2414286	65.7967
0.1873469	60.1128
0.1450000	55.2973

The value of "C" factor in BET analysis is	3.8518	1/micromoles
The monolayer adsorption **is**	6638.4812	micromoles
The weight of the sample is	178.2760	grams
The total surface area is	647.7339	square meters
The specific surface area is	3.6333	square meters/gram

TABLE 5.3 Nitrogen Run 1 at -196°C on Sample #2 of Berea Sandstone

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Step	Pressure Data			Amount of Nitrogen in DV			
	p_2/p_0	p_1	p_2	n_{tot}^*	n_{gas}	n_{ads}^*	n_{ads} / m_r^*
	(dimensionless)	(psia)	(psia)	(µmoles)	(µmoles)	(µmoles)	(µmoles/gm)
1	0.06122	1.5825	0.9000	347.259	468.634	-121.374	-0.799
2	0.11378	2.4625	1.6725	749.216	870.877	-121.662	-0.801
3	0.16803	3.2975	2.4700	1170.252	1286.139	-115.887	-0.763
4	0.32058	5.1475	4.7125	1391.582	2453.817	-1062.235	-6.995
5	0.40714	7.2850	5.9850	2053.029	3116.413	-1063.385	-7.002
6	0.48180	8.2125	7.0825	2627.978	3687.886	-1059.907	-6.979
7	0.55646	9.3025	8.1800	3199.112	4259.358	-1060.246	-6.982
8	0.62942	10.3475	9.2525	3756.254	4817.813	-1061.560	-6.990
9	0.77483	13.5675	11.3900	4864.177	5930.818	-1066.642	-7.024
10	0.88690	14.6700	13.0375	5694.801	6788.678	-1093.876	-7.203
11	0.83707	11.5200	12.3050	5295.389	6407.262	-1111.873	-7.321
12	0.76582	10.1975	11.2575	4756.056	5861.825	-1105.769	-7.281
13	0.69235	9.0800	10.1775	4197.642	5299.465	-1101.823	-7.255
14	0.60867	7.7125	8.9475	3569.268	4658.999	-1089.731	-7.176
15	0.53180	6.6650	7.8175	2982.870	4070.603	-1087.733	-7.163
16	0.43673	5.0050	6.4200	2262.911	3342.919	-1080.009	-7.112
17	0.35442	3.9800	5.2100	1637.080	2712.868	-1075.787	-7.084
18	0.27228	2.8075	4.0025	1029.058	2084.118	-1055.059	-6.947
19	0.19915	1.8125	2.9275	461.741	1524.361	-1062.620	-6.997
20	0.13197	0.9275	1.9400	-53.425	1010.166	-1063.590	-7.004

* Negative values are physically unrealistic. For further discussion, see Section 5.2.

pressures. Figure 5.4 comparing the adsorption curves from LT2 and LT4 shows close agreement of the two.

The nitrogen run conducted on The Geysers yields and isotherm, Fig. 5.5, which exhibits very little hysterisis. The smoothness of the curves reflect the increased resolution of data compared to other runs. The changing slope at the top is still evident, though less pronounced than before.

Sample #2 from Montiverdi 2 was the subject of three nitrogen tests, the first having been the focus of Section 5.1. An isotherm typical of the runs has already appeared as Fig. 5.2. In Fig. 5.6, the adsorption curves of LT2 and LT1 constitute the high and low boundaries while LT3 falls between them slightly above LT1.

Because adsorption behavior depends partly upon the properties of each core Sample, examining isotherms of different samples should provide a comparison of the properties of one in relation to another. In Fig. 5.7, the following adsorption curves are shown: LT4 on Sample #2 of Berea, a nitrogen run conducted by Hsieh (1980) on his Sample #1 of Berea, LT1 of The Geysers Sample #1, and LT1 on Sample #2 of Montiverdi 2. The highest curve by far is that of Sample #2 of Berea, followed in descending order by Sample #2 of Montiverdi 2, Sample #1 of The Geysers, and Hsieh's Sample #1 of Berea. Thus, for the same relative vapor pressure, more nitrogen per gram of sample is adsorbed on Sample #2 of Berea than on any other core. This outcome suggests that the specific surface areas should follow a similar pattern, and upon inspection, the BET analyses do indeed indicate that Sample #2 of Berea has the largest specific surface area followed in order by the others (Table 5.5, next section).

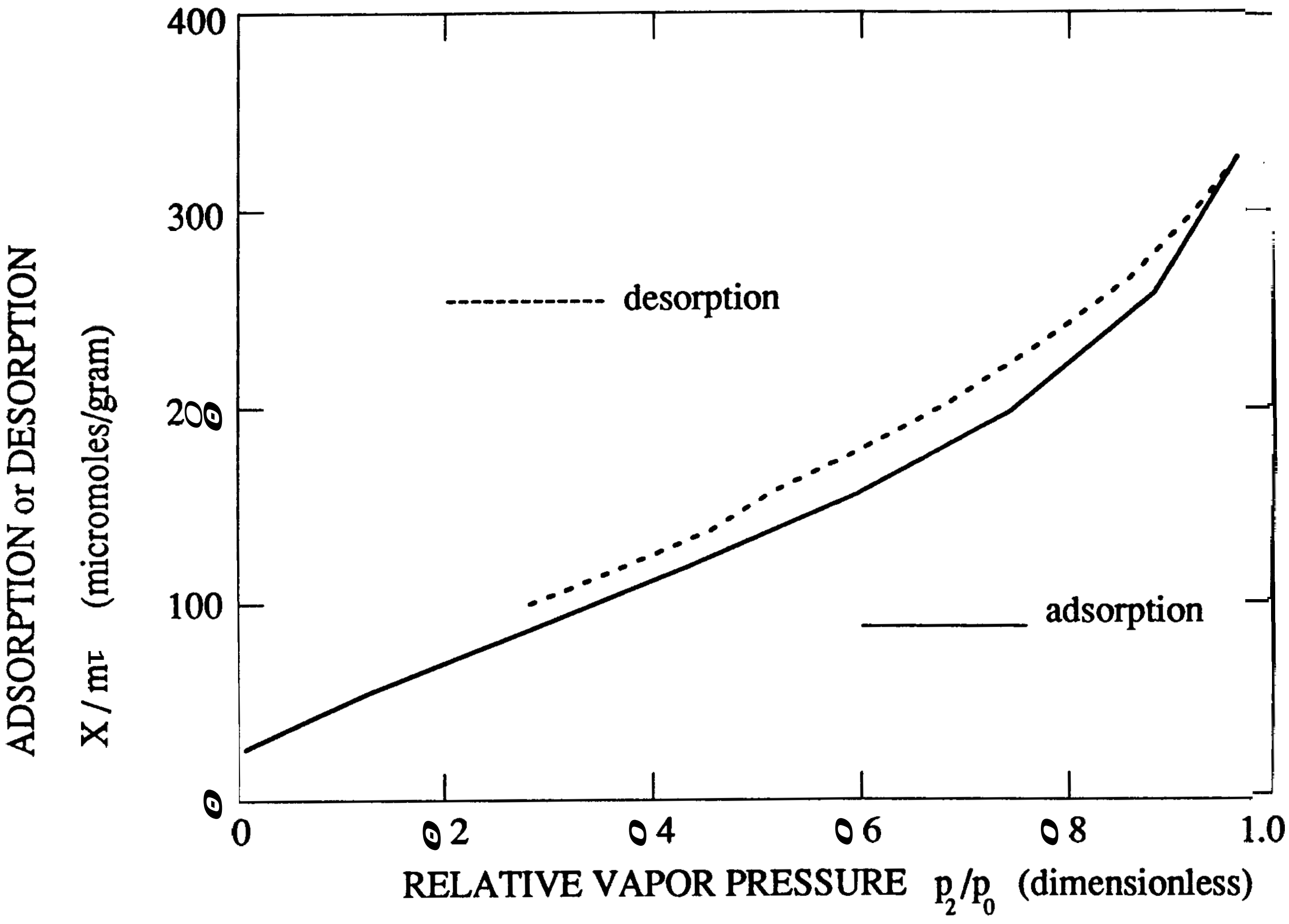

FIGURE 5.3 Adsorption Isotherm of Nitrogen Run #4 at -196°C on Core Sample #2 of the Berea Sandstone

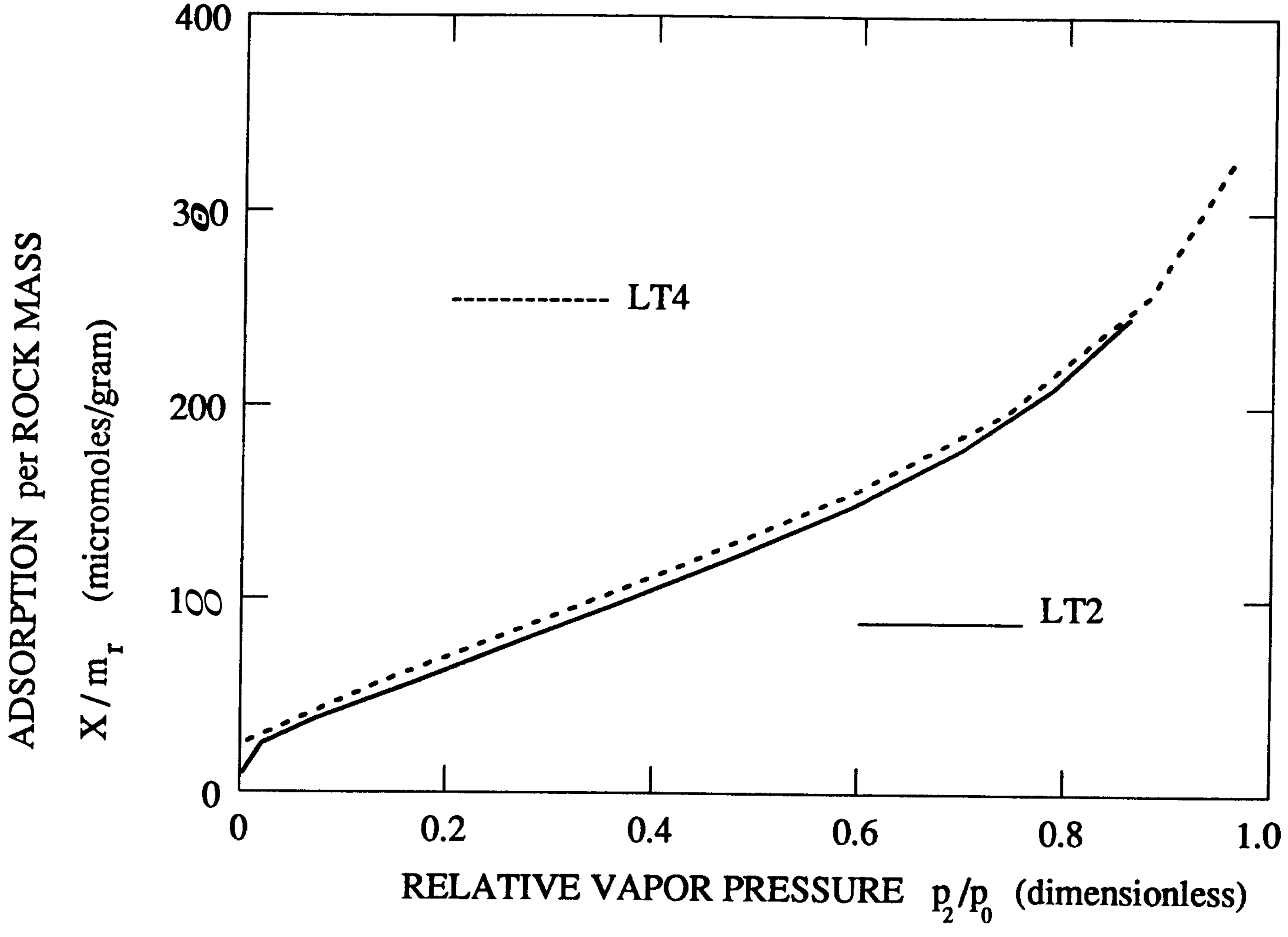

FIGURE 5.4 Comparison of the Adsorption Curves of LT2 and LT4 at -196°C on Core Sample #2 of the Berea Sandstone

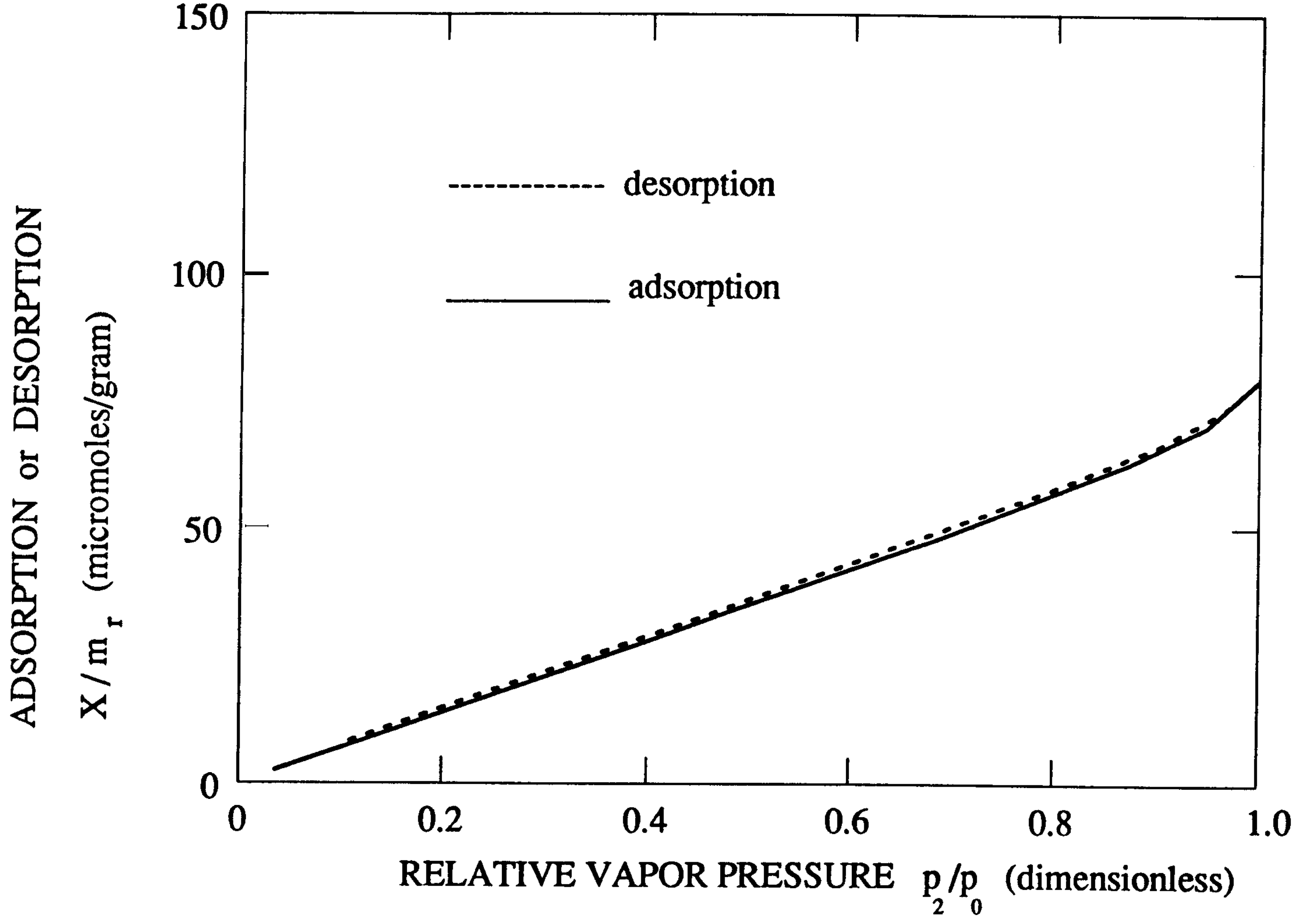

FIGURE 5.5 Adsorption Isotherm of Nitrogen Run #1 at -196°C

on Core Sample #1 from The Geysers

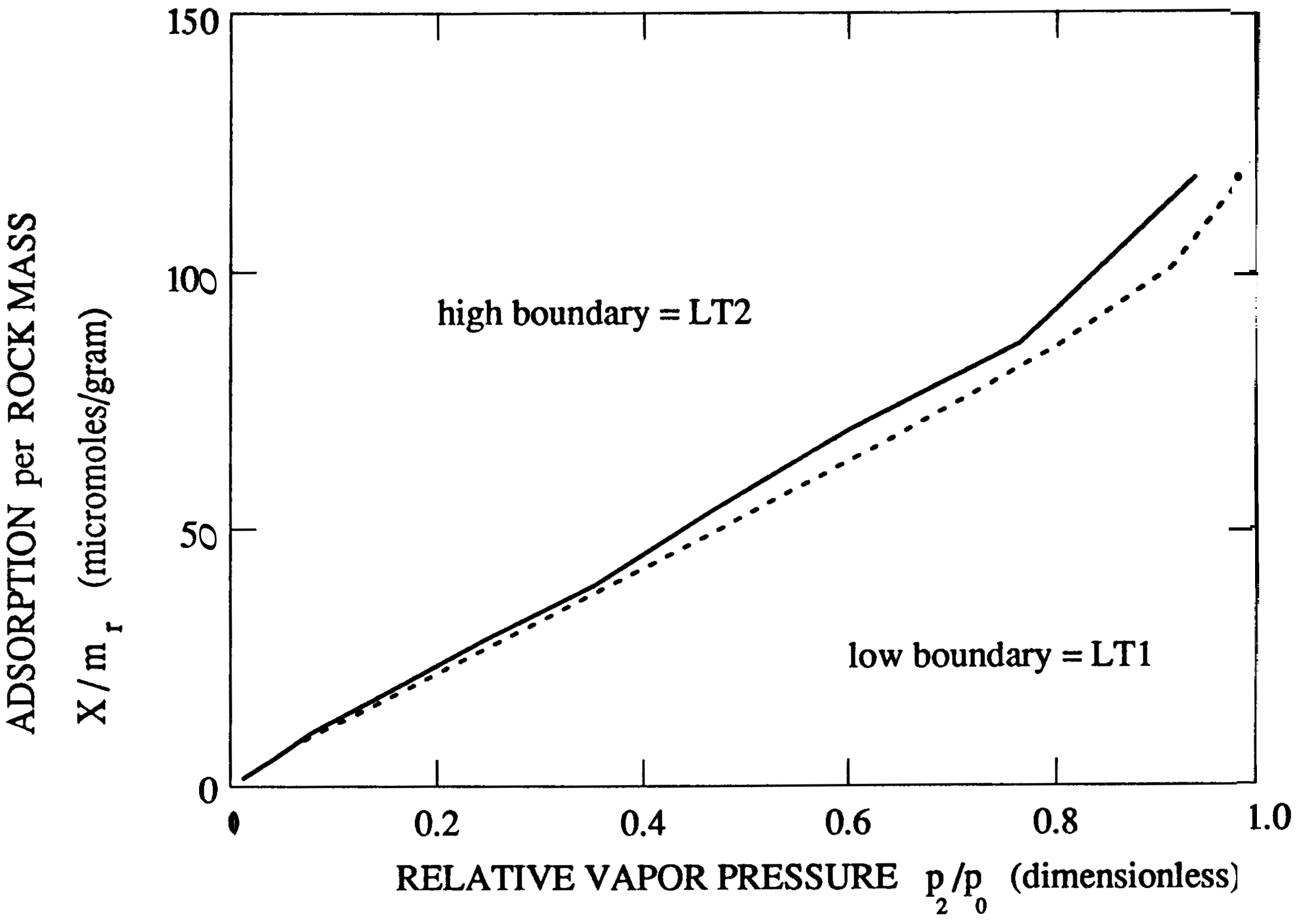

FIGURE 5.6 Comparison of the Adsorption Curves from the Nitrogen Runs on Core Sample #2 from Montiverdi Well #2

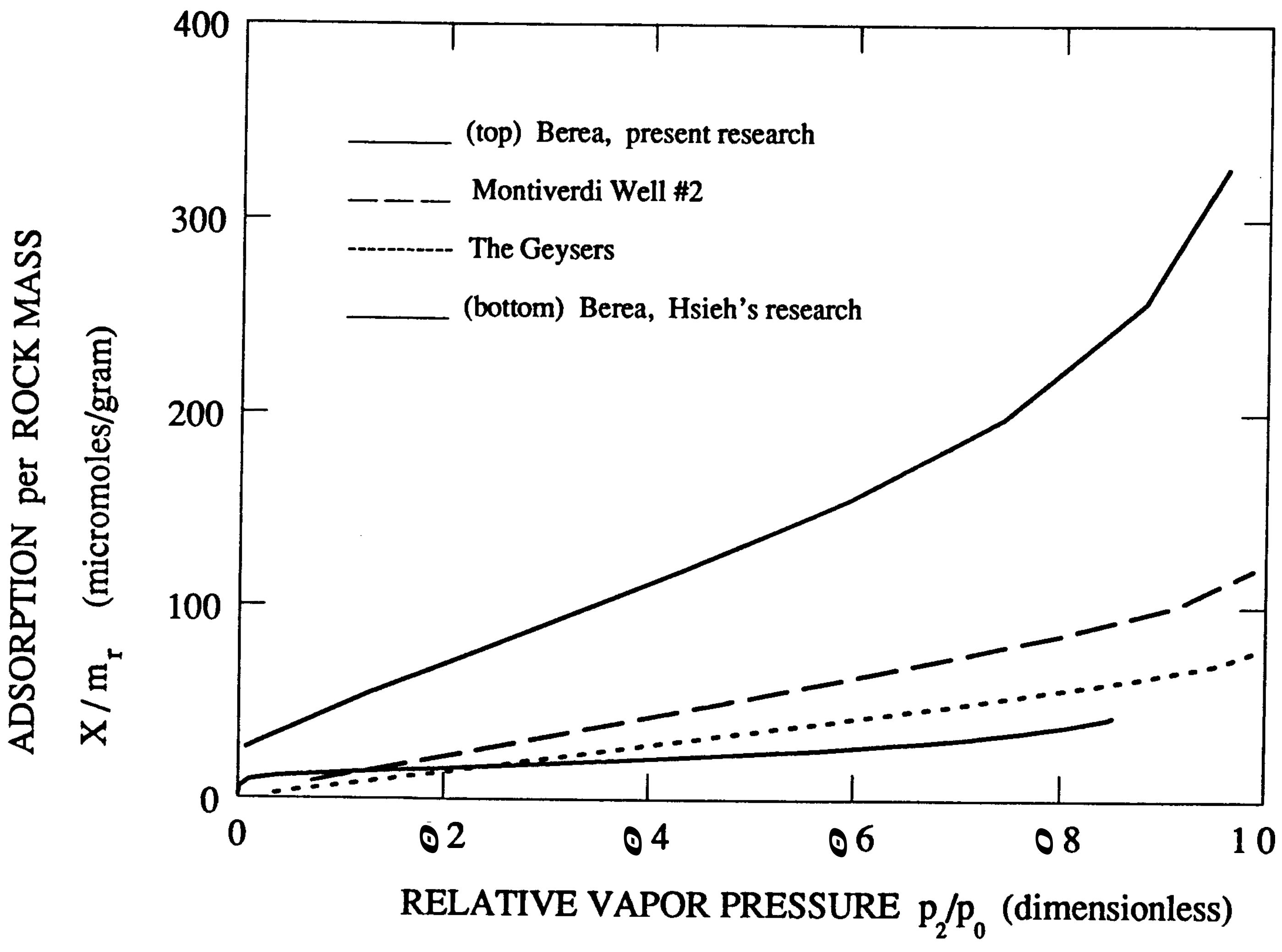

FIGURE 5.7 Comparison of the Adsorption Curves of LT4 on Sample #2 of Berea, LT1 on Sample #2 from Montiverdi Well #2, LT1 on Sample #1 from The Geysers, and a Low Temperature Run from Hsieh (1980) on Sample #1 of Berea

Eight high temperature runs were made using four of the five samples. Unlike the nitrogen tests, the steam tests yield results that are anomalous yet not without pattern. The shapes of the adsorption curves are as expected, but many are translated downward such that negative values of adsorption result. Moreover, the desorption curves fall below the corresponding adsorption curves contrary to the expected hysteresis pattern. In his tabular data, Hsieh (1980) reported similar behavior with all his samples -- three samples of Berea, one unconsolidated silica sandpack, and two field cores from an unspecified field -- when he used methane at room temperature as the test fluid. Several of his steam runs using the silica sandpack exhibited the same tendencies.

High Temperature Run #1 (HT1) conducted at 167 °C on Sample #2 of Berea is indicative of this anomalous behavior, as may be seen in Fig. *5.8.* The adsorption results provided in Table **5.4** include negative values in Columns **(5),** (7), and **(8)** that are physically unrealistic. Even the positive values are too small if the entire isotherm is depressed. Because of the relationship between Columns (5), *(6)* and (7), a negative quantity *in* (7) suggests that *(5)* is too small and/or (6) is too large. The negative value in *(5)* at Step 17 indicates that at the very least n_{tot} is too **small.**

Examination of the equations used to calculate n_{tot} **and** n_{gas} provides some insight regarding the occurrence **of** negative values. **As** seen in Eq. **3.23,**

$$n_{tot} = n_{tot}' + \left(\frac{p_1}{Z_1} - \frac{p_2}{Z_2} \right) \frac{V_1}{R\,T} \qquad , \tag{3.23}$$

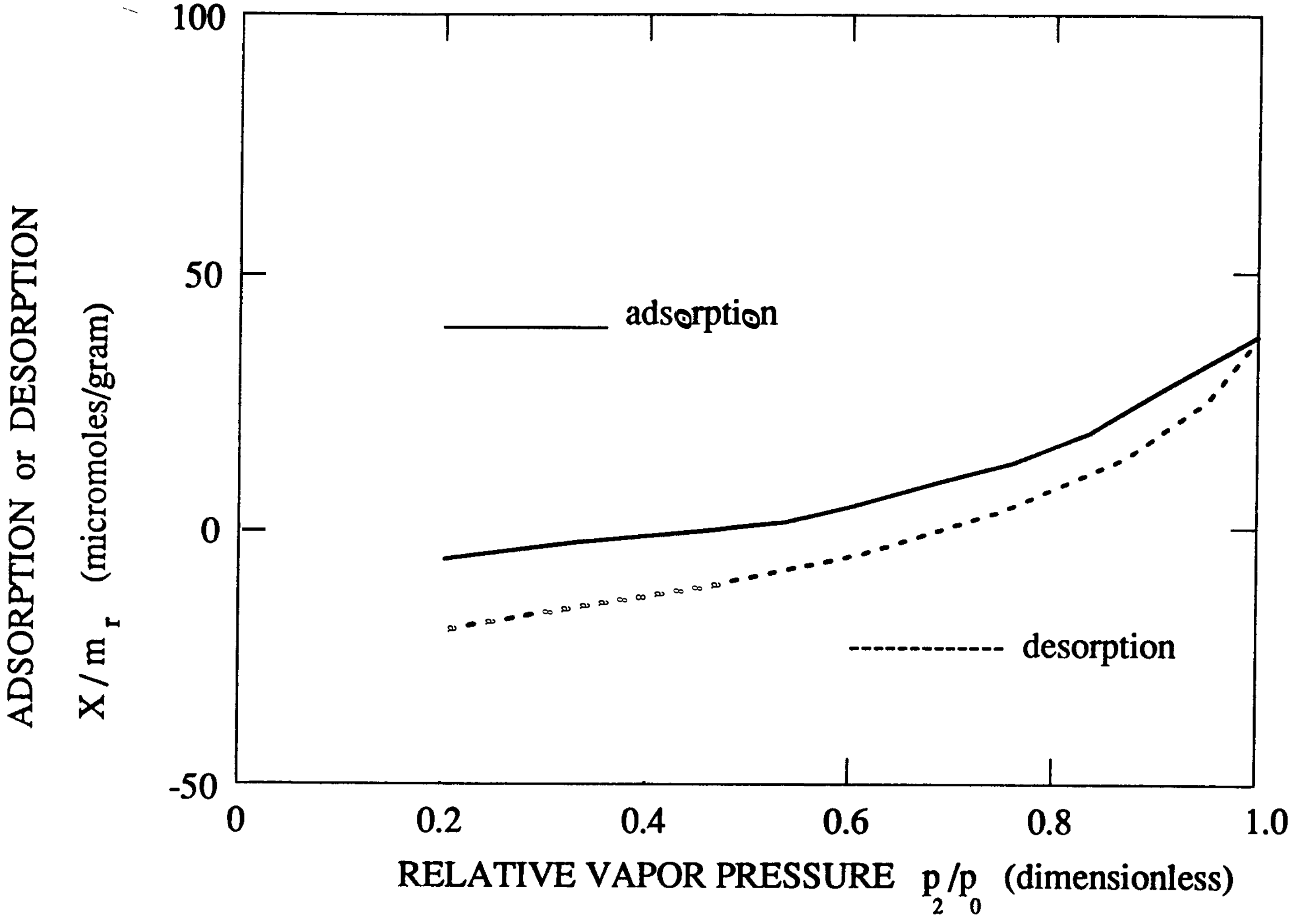

FIGURE 5.8 Adsorption Isotherm of Steam Run #1 at 167°C

on Core Sample #2 of Berea

TABLE 5.4 Steam Run #1 at 169°C on Sample #1 of Berea Sandstone

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
	Pressure Data			Amount of Nitrogen in DV			
Step	p_2/p_0	p_1	p_2	n_{tot}*	n_{gas}	n_{ads}*	n_{ads}/m_r*
	(dimensionless)	(psia)	(psia)	(poles)	(poles)	(µmoles)	(µmoles/gm)
1	0.21226	25.9040	22.6540	994.998	1988.552	-993.553	-8.419
2	0.30549	36.1540	32.6040	2093.675	2876.735	-783.060	-6.635
3	0.39450	45.7040	42.1040	3219.691	3733.741	-514.050	-4.356
4	0.48960	56.1040	52.2540	4438.274	4659.569	-221.294	-1.875
5	0.59220	67.5040	63.2040	5817.703	5670.774	146.929	1.245
6	0.68356	76.9040	72.9540	7100.115	6582.569	517.546	4.385
7	0.78006	87.4540	83.2540	8482.271	7558.089	924.182	7.831
8	0.87095	97.2540	92.9540	9916.054	8488.919	1427.135	12.092
9	0.95106	105.6540	101.5040	11316.257	9319.632	1996.625	16.918
10	1.04757	117.1040	111.8040	13132.761	10333.740	2799.021	23.716
11	1.24714	139.1040	133.1040	15258.429	12480.472	2777.957	23.538
12	1.13002	105.6040	120.6040	10127.246	11212.285	-1085.039	-9.194
13	0.96746	91.1040	103.2540	6064.233	9490.884	-3426.651	-29.034
14	0.83253	81.2540	88.8540	3564.151	8094.000	-4529.849	-38.382
15	0.65029	60.7040	69.4040	774.201	6249.302	-5475.101	-46.391
16	0.52755	50.6040	56.3040	-1028.406	5032.041	-6060.447	-51.351
17	0.42308	40.5540	45.1540	-2465.501	4010.817	-6476.318	-54.875
18	0.32657	30.6540	34.8540	-3763.047	3078.901	-6841.948	-57.973
19	0.23194	20.7040	24.7540	-5000.955	2175.227	-7176.182	-60.805
20	0.18977	18.2540	20.2540	-5610.062	1775.709	-7385.771	-62.581

* Negative values are physically unrealistic. **For** further discussion, **see** Section *5.2.*

the accuracy of n_{tot} depends on the determination of p_1 and p_2. Moreover, the error for each step is added into the next step because of the term n'_{tot}, thereby causing the error to accumulate. Though an incorrect p_2 introduces error into n_{gas}, that error is confined to its own step as shown by Eq. 3.24:

$$n_{gas} = \frac{p_2 \, (DV)}{Z_2 \, R \, T} \tag{3.24}$$

Two possible sources of error are (1) leaks and (2) choosing p_1 and p_2 before equilibrium has been attained. In both instances, the error caused in p_1 is likely to be small because of the shorter time required for equilibrium. Suppose, however, that there is a significant error in p_2 denoted by δp_2 such that the measured value is $(p_2 + \delta p_2)$. Then the equations become

$$n_{tot} = n_{tot}{}' + \left(\frac{p_1}{Z_1} - \frac{p_2 + \delta p_2}{Z_2} \right) \frac{V_1}{R \, T} \tag{5.1}$$

and

$$n_{gas} = \frac{(p_2 + \delta p_2)\,(DV)}{Z_2 \, R \, T} \tag{5.2}$$

The cumulative error in n_{tot} for a particular step is

$$- \sum_{i=1}^{step\ \#} \delta p_{2_i} \frac{V_t}{Z_{2_i} \, R \, T} \tag{5.3}$$

while the error in n_{gas} for each step is simply

$$\delta p_2 \frac{(DV)}{Z_2 \, R \, T} \tag{5.4}$$

Thus, the error for n_{ads} becomes

$$error_i = -\sum_{i=1}^{step\,\#} \delta p_{2_i} \cdot Z_{2_i} \frac{V_1}{R \, T} - \delta p_{2_i} \frac{(DV)}{Z_{2_i} \, R \, T} \tag{5.5}$$

If a leak is present, the measured p_2 is too low indicating that δp_2 is negative. The calculations for n_{tot} become more inflated with each step and the values for n_{gas} are are consistently low with the result that the adsorption is over-estimated by continually increasing amounts. On an isotherm, this effect would exaggerate height, especially for the desorption curve, causing a hysteresis loop where there might otherwise have been none. Thus, a leak could not be the cause of the negative adsorption estimates.

The effect of choosing p_2 before equilibrium has been established may result in negative values with the desorption curve below the adsorption curve depending on the value of the error terms for desorption. Figure 5.1, a typical raw data graph, shows that the pressure decreases towards a stable p_2 during adsorption. Thus, choosing a value too soon would mean that the δp_2's are positive and the p_2's are too high. The corresponding values of n_{tot} are increasingly under-estimated, and the n_{gas} values are over-estimated leading to n_{ads} values that are increasingly under-estimated. When desorption begins, gas is taken out of the sampling bottle so the pressure is low. Then the valve to the coreholder opens and the pressure rises. Normally the expected trend is a continued slow rise in pressure. In this case, it seems that moving to the next step prematurely would yield a p_2 that is too low and a δp_2 that is negative leading to a compensation of errors. The amount of compensation would depend on the particular δp_2 values.

Figures 5.9 and 5.10 illustrate two extreme idealized cases -- that of no compensation and that of full compensation for δp_2. The depictions include for both cases (1) the same assumed true isotherm for reference, and (2) the same adsorption path for the measured isotherms. This path slopes more gently than the true path yielding the apparent maximum error at the top. When there is virtually no compensation, Fig. 5.9, the desorption curve parallels the true desorption curve but is displaced downward by an amount equal to the apparent maximum error. However, when there is full compensation as in Fig. 5.10, the desorption eventually rejoins its true path.

These characteristics would change, of course, if the δp_2 values did not become negative at the outset. Suppose that the error at the top of the isotherm is large due to poor penetration. In this instance, the measured adsorption occurs on the outside surfaces of the sample and on surfaces some small distance within. At the beginning of desorption, some of the gas that would have been adsorbed is taken out. The initial response when the valve is opened remains the same, yet if there are sufficient molecules left in the system, conditions may still favor adsorption over desorption. Thus, the δp_2 would be smaller but still positive, and the difference between the true and the measured desorption curves would increase with decreasing relative pressure. Eventually the δp_2's may become zero or even negative resulting in a gentler slope,

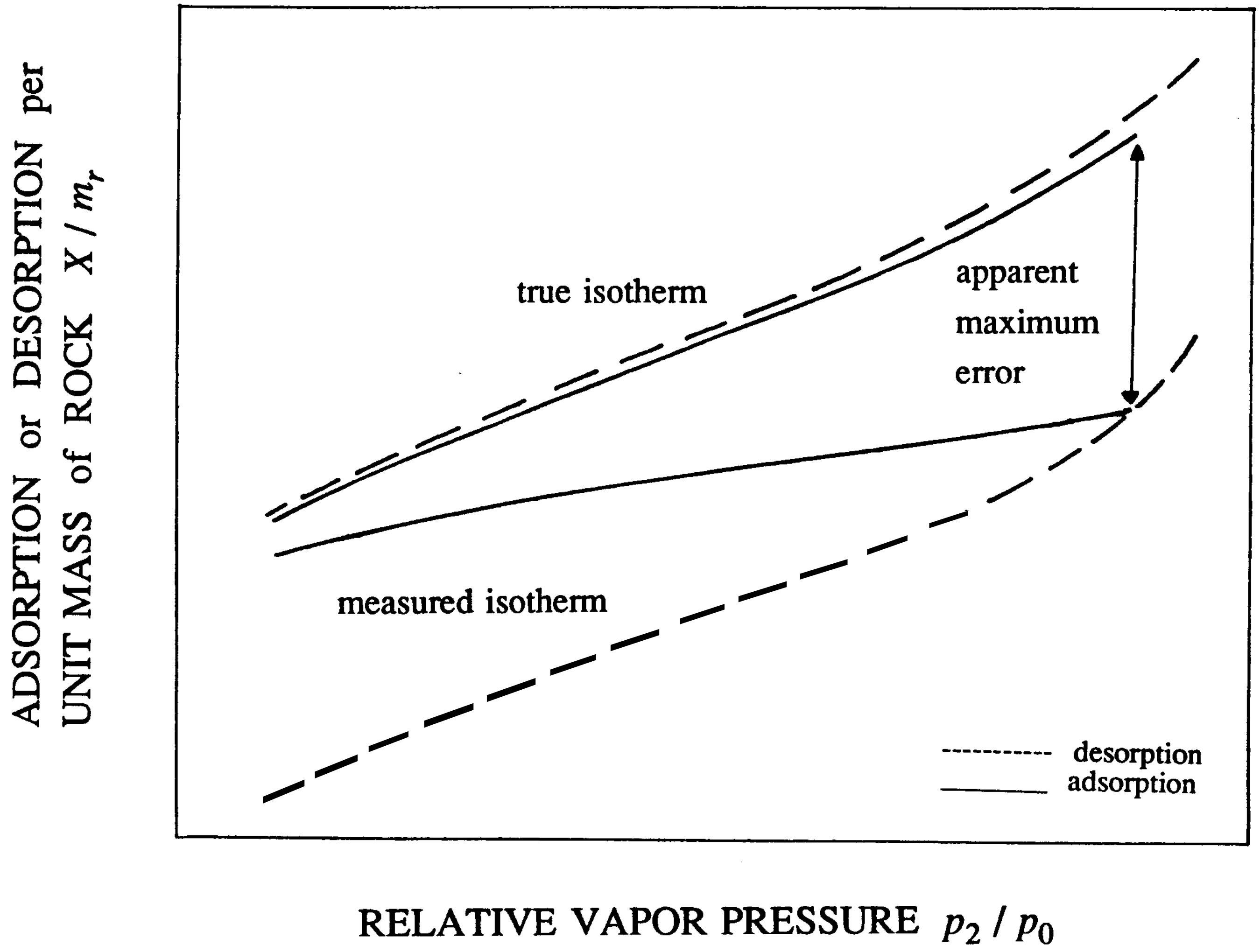

FIGURE 5.9 Idealized Case in which $\delta p_2 = 0$ for Desorption Resulting in No Compensation

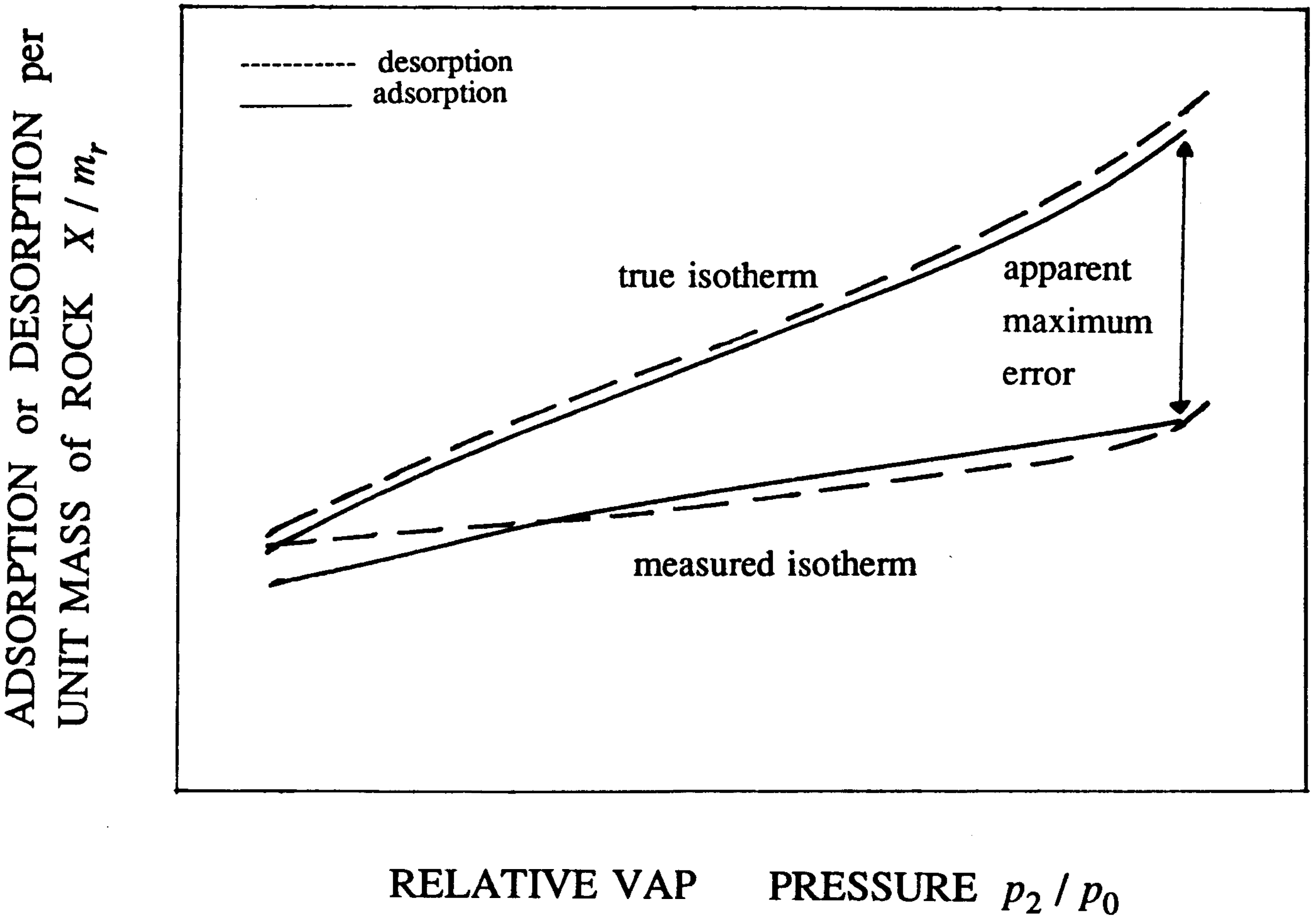

FIGURE 5.10 Idealized Case in which the δp_2 Values Fully Compensate on the Last Step

but the measured desorption curve would still fall below the measured adsorption curve. Although this theory appears to explain the anomalous behavior of steam isotherms such as Fig. 5.8, it is not unlikely that other factors may contribute to this phenomenon.

Three high temperature runs were conducted on Sample #1 of Berea sandstone, whereas only one was completed on Sample #2 of the Berea. The isotherm of the latter is given in Fig. 5.8. A comparison of the four runs provided by Fig. 5.11 shows a band of results in which the high boundary is formed by the adsorption curve of HT2 at 207 °C on Sample #1 and the low boundary is formed by the adsorption curve of HT3 at 150 °C on Sample #1.

Although the HT1 at 153 °C on Sample #1 from The Geysers is similar to those completed for Berea and Montiverdi Well #2, the other two high temperature runs for that sample are distinct in that the values for the adsorption curve are all positive. Figure 5.12 is the isotherm for HT2 conducted at 200 °C which, as seen in Fig. 5.13, compares quite favorably with the adsorption curve of HT3 conducted at 180 °C. Comparison of the time allowed for equilibrium for each run supports the theory that in most cases the steps were ended prematurely. For HT1 the average waiting time was only an hour, while for HT2 the time varied from six to eight hours and for HT3 the time varied from eight to twelve hours.

Sample #3 consisting of crushed fragments from Montiverdi Well #2 was the subject of one steam run at 180 °C. The isotherm in Fig. 5.14 has a rather flat adsorption curve, but the desorption curve has a significant slope change from very steep at

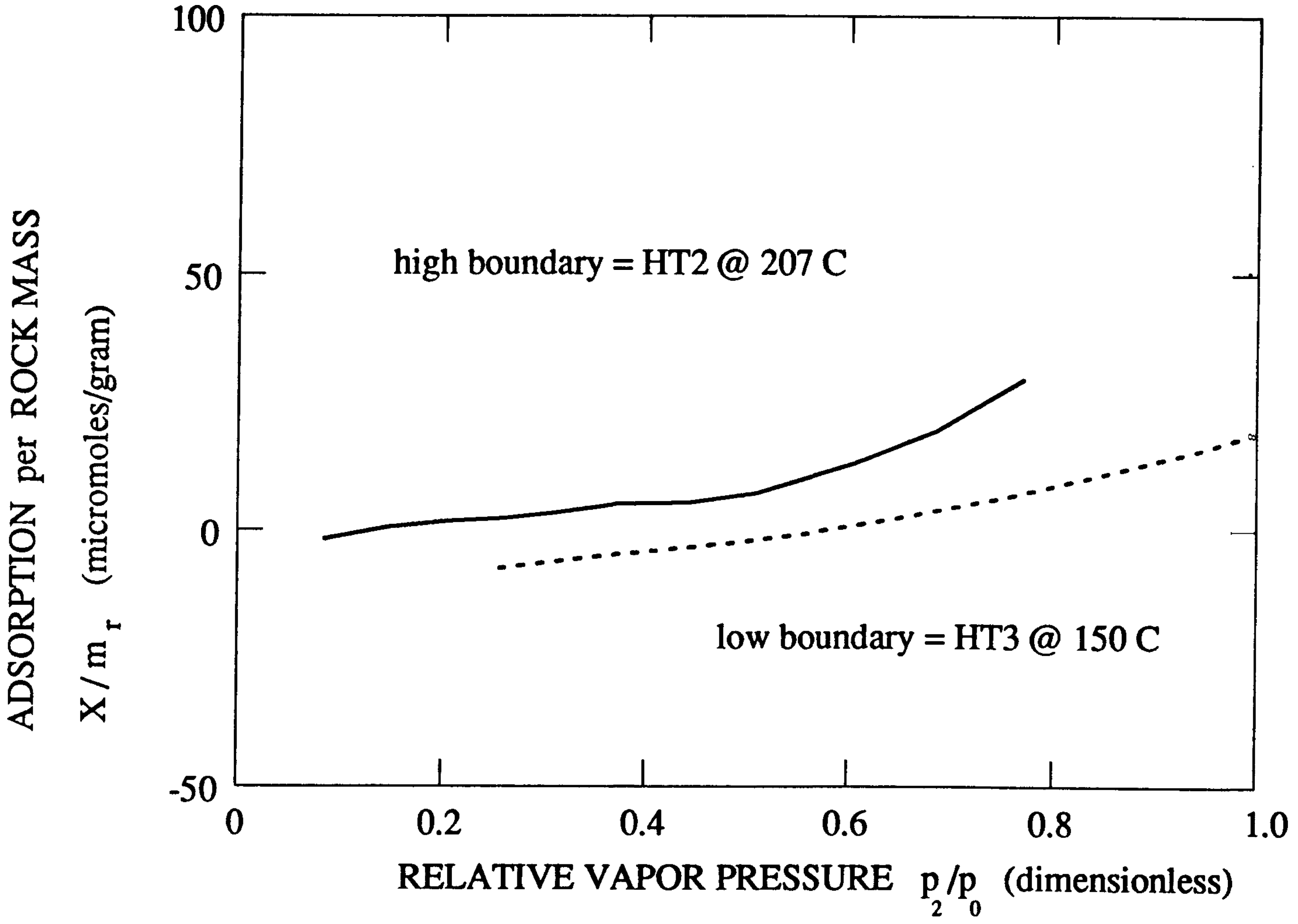

FIGURE 5.11 Comparison of the Adsorption Curves from the Steam

Runs on Core Samples #1 and #2 of Berea

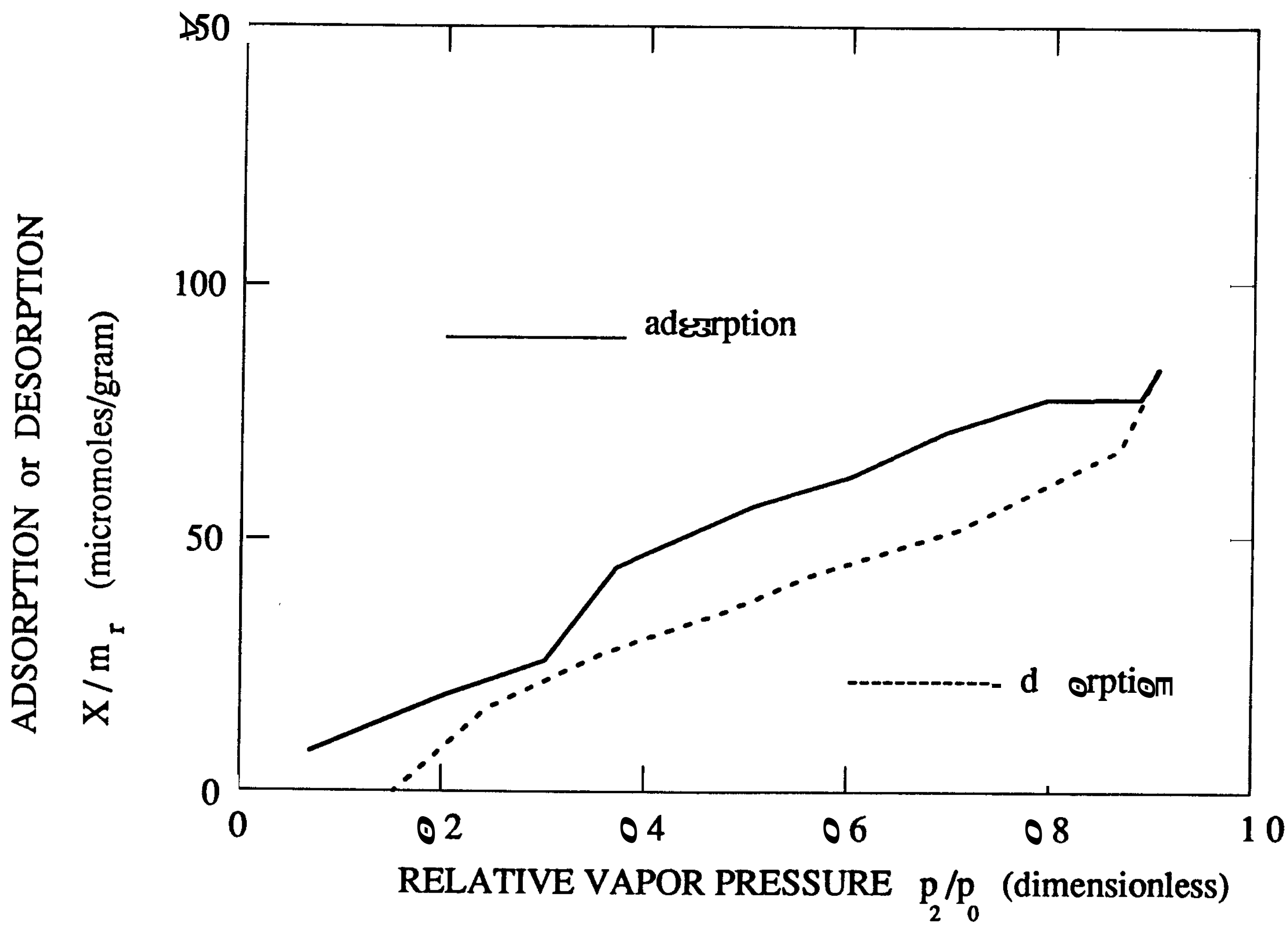

FIGURE 5.12 Adsorption Isotherm of Steam Run #2 at 200°C

on Core Sample #1 from The Geysers

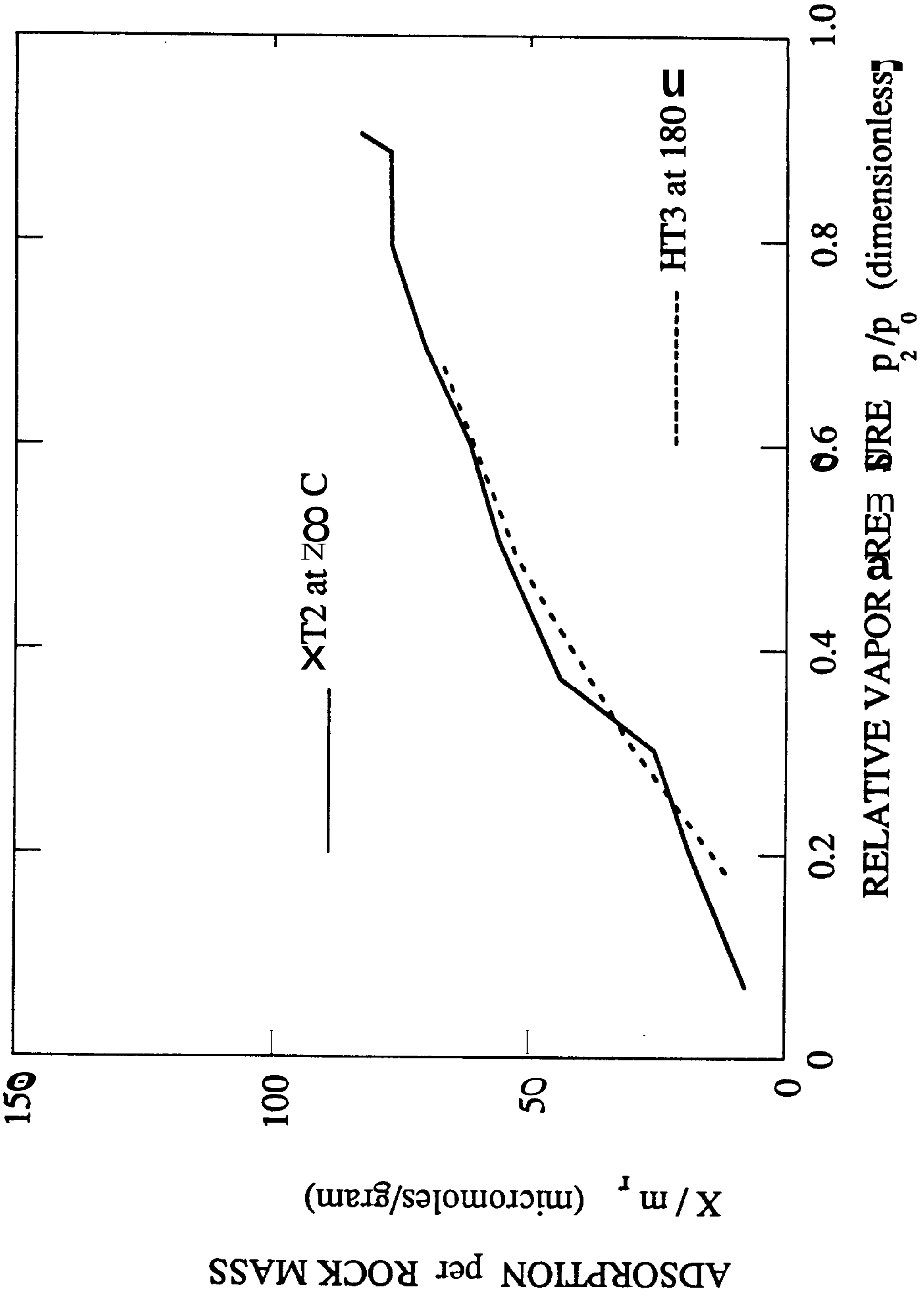

FIGURE 5.13 Comparison of Adsorption Curves of HT2 at 200°C and HT3 at 180°C on Core Sample #1 from The Geysers

high relative pressures to more moderate at lower relative pressures. As already mentioned **this** behavior may occur if δp_2 is positive when desorption begins, but diminishes with time until it becomes negative.

5.3 BET RESULTS

The results of the BET analysis consist of estimates of the "C" factor in the BET equation, the monolayer adsorption, the surface area, and the specific surface area. An example **of** the results for one run, namely the LT1 on Sample #2 from Montiverdi Well **#2,** has already been presented in Table **5.2.** A complete listing of results, excluding those **from** runs or **parts** of runs having negative values, is given in Appendix D. Because of the above restriction on negative values, the majority of the tests presented are nitrogen tests.

Table ***5.5*** highlights the similarities between the BET results for the same core as well **as** contrasts between cores. The "C" factor, monolayer adsorption per weight and specific surface area from **a** variety of runs are given for Sample #2 of Berea, Sample #1 of Berea **from** Hsieh's work (1980), Sample #1 of The Geysers, and Sample #2 from Montiverdi Well **#2.** As mentioned in the previous section, Sample #2 of Berea has the largest specific surface area and the highest isotherm, followed in descending order by Sample #2 of Montiverdi Well **#2,** Sample #1 of The Geysers, and Hsieh's Sample #1 of Berea.

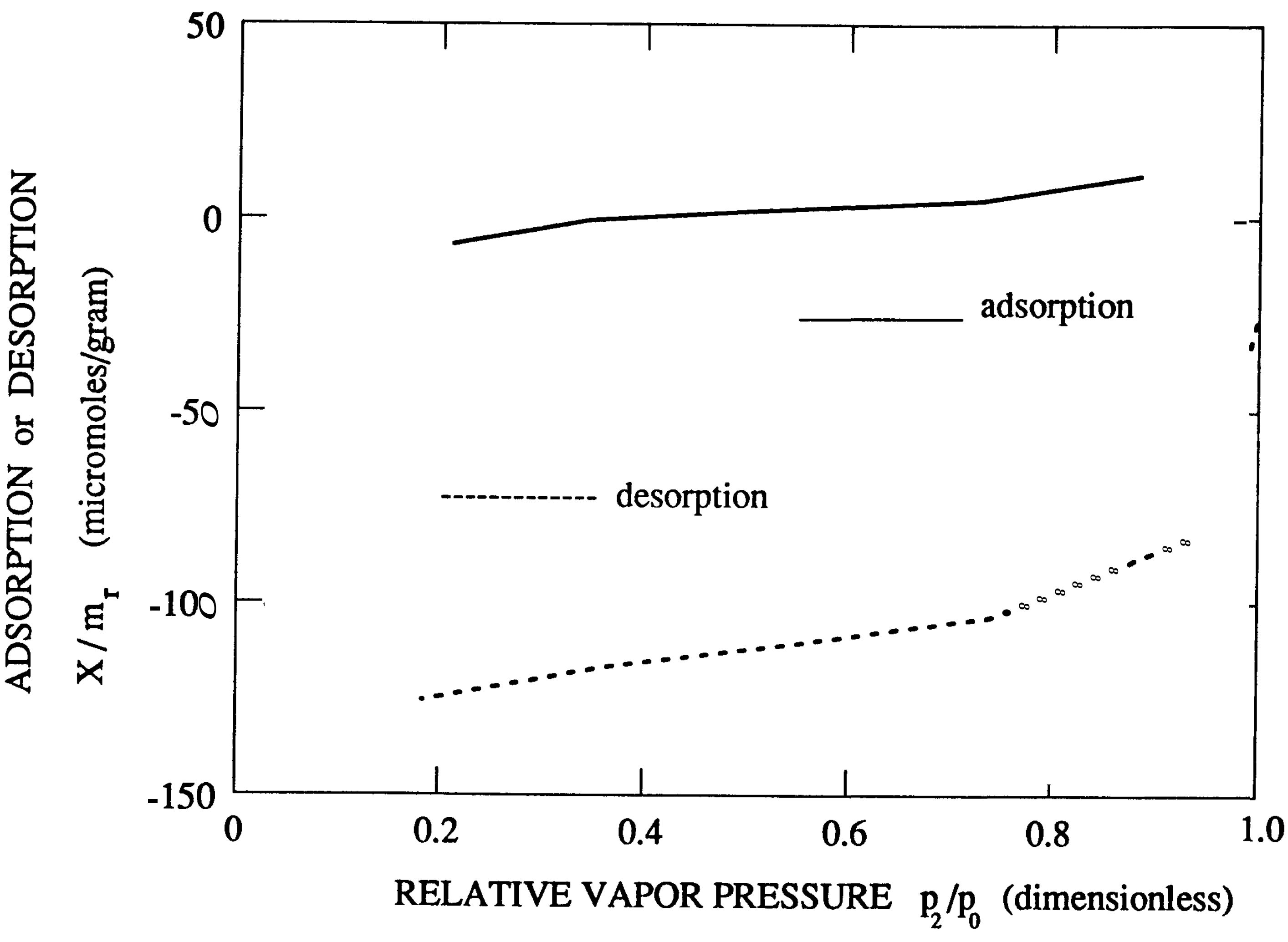

FIGURE 5.14 Adsorption Isotherm of Steam Run #1 at 180°C on Core Sample #3 from Montiverdi Well #2

TABLE 5.5 Comparison of BET Results

Sample & Run	"C" factor	Monolayer Adsorption/Weight	specific Surface Area
	(1/μmole)	(μmoles/gram)	(m^2/gram)
Berea			
Sample #2			
LT2 - ads.	12.3224	68.228	6.6572
LT4 - ads.	11.5873	75.941	7.4098
LT4 - des.	17.4894	82.027	8.0036
Hsieh's Berea *			
Sample #1			
LT - ads.	100.2559	13.050	1.2733
LT - des.	126.8745'	13.400	1.3075
HT -ads.	6.8615	16.015	1.3075
(107 °C) des.	5.2691	17.001	1.2316
HT -ads.	6.7979	13.985	1.0763
(195 °C) des.	66.3525	21.667	1.6674
The Geysers			
Sample #1			
LT1 - ads.	2.6224	27.564	2.6895
LT1 - des.	3.2250	26.353	2.5713
HT2 - ads.	4.9360	26.583	2.0818
Montiverdi Well #2			
Sample #2			
LT1 - ads.	3.7921	36.157	3.5280
LT1 - des.	3.8518	37.237	3.6333
LT2 - ads.	3.8958	37.997	3.7075
LT3 - ads.	3.3077	40.120	3.9146
LT3 - des.	4.3935	38.235	3.7307

* Data **for** Hsieh's Berea #1 **from** Hsieh's doctoral thesis (1980).

6.0 CONCLUDING REMARKS

Although the main objective of the present research was to construct laboratory equipment to determine adsorption isotherms for nitrogen and steam on various geothermal reservoir **rocks,** only a part of this objective could be achieved. Considerably more success was gained with the nitrogen experiments than with the steam.

Nitrogen was chosen as one of the test fluids because it is a relatively small molecule, it is easily available, it is fairly safe to handle, and it has been widely used by researchers studying adsorption. The rocks tested were Berea sandstone, core material from Larderello wells and core material from The Geysers wells. The constant temperature used in the nitrogen experiments varied slightly from one experiment to another but was in all instances within 1 °C from the critical temperature. The relative vapor pressure (p_2/p_o) ranged from as low as 0.003 to unity.

The configuration of the nitrogen isotherms developed in these experiments was what would be expected considering earlier investigations of other researchers. However, they were higher on the X/m_r vs. p_2/p_o graphs than those obtained by Hsieh (1980). This discrepancy could be due to differences in experimental procedures.

Significantly, no physically impossible results such as negative adsorption were obtained with nitrogen except for the first run which may have been performed incorrectly. Such was not the case with steam. The nitrogen experiments indicate that the low temperature apparatus was functioning as intended and that confidence could be placed in it for further experimentation.

The experiments with steam yielded mixed results. With the exception of one additional sample from Larderello, the same rocks were used with steam as were used with nitrogen. The tests were run at eight different constant temperatures, the lowest being 150 °C and the highest 207 °C. The relative pressures ranged from 0.064 to approximately unity.

The adsorption part of the hysteresis loop for two experiments on The Geysers core material yielded results that were close to what might be expected. However, negative adsorption was recorded for the desorption part of this loop corresponding to lower p_2/p_o values. The whole loop may be too low on the X/m_r vs. p_2/p_o graph. Thus, the positive adsorption curve must represent a lower limit.

As was shown analytically in Chapter 5.0, leaks cause a cumulative error such that both the adsorption and desorption curves would rise with the desorption part rising more. Thus, leaks could not cause negative-adsorption results.

A critical factor in the experimentation is the determination of p_2, the final pressure in the sampling bottle and coreholder. It is an equilibrium pressure. If p_2 is assigned before equilibrium has been attained, then the assigned value would differ from the true value by an amount δp_2 which becomes a cumulative error as the experiment progresses from step to step. This cumulative error depresses the adsorption curve over its entire extent because δp_2 is positive. The experiments showed three possible effects of δp_2 on the desorption curve. First, the sign of δp_2 reverses at the beginning of desorption becoming negative and the cumulative error diminishes. It continues to do so throughout the desorption process until such time, if ever, that the error is nullified. Second, δp_2 may remain positive at the start of desorption but diminish in magnitude until it becomes zero and thereafter become increasingly negative. Third, δp_2 may remain approximately zero throughout the desorption process.

At this point, it is clearly evident that a main objective of future research with the kind of apparatus described herein should be to make every effort to reduce δp_2 to a negligible quantity.

In essence the findings and recommendations considered most important as a result of the present research are the following:

1. Berea sandstone has the largest specific surface area and the greatest nitrogen adsorption isotherm followed by Montiverdi Well #2 from Larderello and then The Geysers.

2. Steam adsorption was observed; however, the true magnitude is still in question probably due to difficulties in establishing equilibrium.

3. Modifications which may help eliminate negative-adsorption results should be investigated. These include the alternative technique for determining dead volume, placing a pressure transducer in the coreholder section, and using high temperature pressure transducers in the high temperature system.

4. Among important topics requiring further study are techniques for

establishing equilibrium values of p_2, core preparation, and the use of brines as test fluids.

Once laboratory studies have progressed to the point where adsorption data can be generated with a high degree of confidence, the information should be applied on a reservoir engineering level. If it becomes possible to shorten each step by predicting p_2 from early-time transient data, the duration of the experiments will be greatly reduced. In time, perhaps a correlation between adsorption properties and rock type might be developed which enables an engineer to make an approximation of the impact of adsorption on a particular field. Laboratory tests could then provide a more complete picture resulting in better performance predictions and reserve estimates.

7.0 NOMENCLATURE

a	coefficient of condensation for any adsorbed layer excluding the first
a_i	coefficient of condensation for the i-th layer
A_x	cross-sectional area of a molecule
b	coefficient of evaporation for any adsorbed layer excluding the first
b_i	coefficient of evaportation for the i-th layer
C	constant in BET equation for a specific adsorbate at a specific set of conditions
DV	dead volume, i.e. annular volume in coreholder plus pore volume plus tubing volume to valve C
HT1, 2, 3, ...	high temperature run 1, 2, 3, ...
i	index ranging from 0 to n which may refer to specific layer or step number depending on context
LT1, 2, 3, ...	low temperature run 1, 2, 3, ...
m_r	mass of the rock sample
n	maximum number for index i or amount of gas (usually in poles)
n_{ads}	amount of adsorption (usually in pmoles) at p_2, same as X in BET equation

n_{gas}	amount of gas (usually in pmoles) at p_2 in DV
n_{tot}	total amount of material (usually in pmoles) at p_2 in DV
$n_{tot}{}^{I}$	total amount of material (usually in pmoles) at $p_2{}'$ in DV, i.e. at the end of the immediately preceding step
$n_{tot}{}^{*}$	total amount of material in DV at $p_2{}^{*}$ if valve C is opened and then closed again before the end of the step
N_a	Avogadro's number, **6.023 * 10^{17}** molecules/μmole
N_{a_i}	rate of condensation to i-th layer
N_{b_i}	rate of evaporation from i-th layer
P	curved or flat interface pressure of gas phase
Po	saturation vapor pressure for flat interface
p_1	equilibrium pressure of gas in sampling bottle section when all valves are closed
$P2$	equilibrium pressure of gas in system near end of step when only Valve C is open
$P2{}'$	same as p_2 but for immediately preceding step
$P2{}^{*}$	predicted equilibrium pressure in DV if valve C is opened and then **closed** before the end of the step, corrensponds to $n_{tot}{}^{*}$
r_m	mean radius of curvature

r_1	one of two principal radii of curvature found in the Kelvin equation
r_2	same as above
R	gas constant, 1206.2379 * 10^{-6} cc-psia/(gm-µmole-K)
S	total number of adsorption sites on a surface
S_i	number of adsorption sites covered by i layers
t_0, t_1, t_2, ...	specific points in time during the experiment, found in Figure 4.8
T	temperature
V_L	volume per mole of liquid
V_1	sampling bottle volume plus tubing volume
X	total amount of adsorption, in micromoles
X_m	the monolayer adsorption, in micromoles
Z_1	compressibility factor at p_1
Z_2	compressibility factor at p_2
a	ratio of 8, to θ_2
β	ratio of θ_i to θ_{i-1} where $i > 1$, also relative vapor pressure, p_2 / p_0
γ	interfacial tension

Δn	net entry of new molecules (usually in poles) into DV
δp_2	amount of error in p_2 estimate
θ_i	fraction of surface covered by i layers
π	pi, 3.1416...

8.0 REFERENCES

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9.0 APPENDICES

9.1 APPENDIX A -- COMPUTER PROGRAM

The analysis program located at the end of this appendix consists of a main program with six subroutines. Variable descriptions and comments are provided throughout. The main program consists of three general sections, all of which have some computations. The first is an input section while the latter two are output sections.

The input section allows the program to obtain and manipulate parameter values in readiness for the adsorption calculations. Much of the data are entered by the user in response to questions asked during execution. The Data Checklists of Appendix B contain the pertinent information for each run. If the dead volume (DV) is already known, it is entered directly. Otherwise, it is calculated by the subroutine DEDVOL. Because there are usually several estimates of DV, the user has the option of combining all or part of those estimates to obtain the final figure. The pressures are read in volts from an input file designated "p1p2" which has p_1 values in the first column and p_2 values in the second. Subroutine **PSIA** changes all pressure tranducer signals from volts into psia. Near the end of this section are options to "echo" the data and to allow for re-entry if necessary.

The second section of the main program emphasizes the adsorption calculations described in Section 3.2. It uses the subroutine VOLUME to evaluate the specific volume and the 2-factor of superheated steam and the subroutine SVAPP to calculate the saturation vapor pressure. NTOT, NGAS, NADS, B (the array for the relative vapor pressure), and XW (the array for NADS/weight) are calculated and sent to a file named "results" along with P1 and P2. A second output file named "isoplot" records the number of steps for adsorption and desorption and their respective B and XW values. In addition, the values needed for the straight line form of the BET equation are calculated and stored in the arrays F, G, F1, and G1.

The last section uses the BET equation to determine the surface area. The adsorption arrays G and F correspond to the x and y values of a straight line that is analyzed by the method of least squares with subroutine LSTSQ. For steam tests, subroutine VOLIQD provides the specific volume of liquid water. Once the adsorption data are processed, the desorption arrays G1 and F1 are transferred to G and F so the same calculation commands may be used again. The results are sent to a file named "BET".

```
C     PROGRAM ADS.F
C
C
C
C     CREATED JUNE 1986 BY JERALYN LUETKEHANS TO RUN A BET ANALYSIS
C     ON STEAM OR NITROGEN ADSORPTION DATA
C
C
C
C     EXPLANATION OF KEY VARIABLES
C
C     W              weight of sample in gm (1 can be entered if W unknown)
C     N              number of steps in run
C     DV             dead volume in cc - pore volume, annular space in coreholder
C                    and tubing space
C     V1             sampling bottle volume in cc (usu. 45.07 cc on NIT system)
C     ANS1,2,...     decision variables that allow the user to choose certain
C                    options
C     PI             the mathematical constant 3.14...
C     PO             saturated steam vapor pressure for nonporous container
C     P1             array for pressures in the sampling bottle - before valve C
C                    is opened - entered in volts
C     P2             array for pressures in DV + V1 (i.e. equilibrium pressure) -
C                    entered in volts
C     Z              "Z" or compressibility factor for the gas in question-when
C                    constant, esp. for nitrogen (assumed about 0.95)
C     Z1             "Z" factor at P1 -- esp. for high T runs
C     22             "Z" factor at P2 -- esp. for high T runs
C     T              temperature in Kelvin (for NIT run usu. 77.3 K)
C     TC             temperature in Centigrade
C     R              gas constant (1206.2379*1.0E-6 cc-psia/(gm-umole-K))
C     ZRT            Z*R*T
C     NTOT           total umoles in dead volume
C     NGAS           umoles as gas in dead volume
C     NADS           umoles adsorbed in dead volume
C     XW             array for NADS/W -- needed for isotherm plot
C     B              array for BETA in BET EQN (i.e. relative pressures)
C     F              array for the factor  B/(X(1-B)) in 1/mole in BET range for
C                    adsorption
C     F1             same but for desorption
C     G              array for BETA in BET range (.05<B<.35) for adsorption
C     G1             same but for desorption
C     CF             "C" factor in BET EQN
C     XM             Xm in BET EQN - monolayer adsorption in umoles
C     XA             cross-sectional area of a liquid water molecule -- units
C                    taken care of in program
C     V              specific volume -- changed later in program to molar volume
C     SA             surface area in square meters
C     SA1            specific surface area in square meters/gm (SA1=SA when
C                    weight is unknown and entered as 1 gm)
C
C
C
C
C
C
      Implicit Real*8(a-h,o-z)
      Integer  ANS,ANS1,ANS2,ANS3,ANS4
      Real NADS,NGAS,NTOT
      Dimension P1(100),P2(100),B(100),F(30),F1(30),G(30),G1(30)
      Dimension XW(100)
C
C
C     Initialize variables and constants
C
```

```
10      Do 20 I=1,100
             P1(I)=0.0
             P2(I)-0.0
             B(I)=0.0
20      Continue
        Do 30 I=1,30
             F(I)=0.0
             F1(I)=0.0
             G(I)=0.0
             G1(I)=0.0
30      Continue
C       Default value for constant Z factor set for nitrogen
        Z=0.95
        R=1206.2379E-6
C
C       Enter basic information
C
        Write(6,3)
3       Format('What is the weight of the sample in gm?',/)
        Read(5,*)W
        Write(6,4)
4       Format('Is this a nitrogen run (enter 0) or a steam run (enter
     #  1)',/)
        Read(5,*)ANS
        Write(6,5)
5       Format('What is the sampling bottle volume, V1, in cc (for NIT usu.
     #  45.07 cc)?',/)
        Read(5,*)V1
        Write(6,6)
6       Format('How many steps are there?',/)
        Read(5,*)N
        Write(6,7)
7       Format('Do you need to calculate the dead volume?(0=no,1=yes)',/)
        Read(5,*)ANS1
        If (ANS1.EQ.0) then
             Write(6,8)
8            Format('Enter the dead volume in cc.',/)
             Read (5,*)DV
        Else
             Call DEDVOL(V1,DV)
C            DEDVOL will calculate dead volume
        Endif
        Write(6,9)
9       Format('Do you want to enter temperature in centigrade (enter 0)
     #  or Kelvin (enter 1)?',/)
        Read(5,*)ANS2
        Write(6,11)
11      Format('What is the temperature?', /)
        If (ANS2.EQ.0) then
             Read(5,*)TC
             T = TC + 273.16
        Else
             Read(5,*)T
             TC = T - 273.16
        Endif
        Open(unit=4,file='p1p2',status='old')
        Do 41 I=1,N
              Read(4,*)P1(I),P2(I)
41      Continue
C
C       Option to echo input data and make changes
C
        Write(6,16)
16      Format('Do you want to echo input data?(0=no,1=yes)',/)
        Read(5,*)ANS3
        If (ANS3.EQ.0) go to 60
```

```
      Write(6,17)
17    Format(/,'weight (gm)  V1 (cc)  DV (cc)',/)
      Write(6,*)W,V1,DV
      Write(6,18)T,TC
18    Format('T = ',F7.3,2x,'K and ',F7.3,2x,'C',//)
      Write(6,19)
19    Format ('Step        P1  (VI       P2 (v) ',//)
      Do 50 I=1,N
         Write(6,21)I,P1(I),P2(I)
21       Format(I4,F10.4,F10.4,/)
50    Continue
60    Write(6,22)
22    Format ('Do you want to change input?(0=no,1-yes)' ,/)
      Read(5,*)ANS4
      If (ANS4.EQ.1) go to 10
C
C
C     Change pressures to psia - data in volts is replaced by psia form
C     to save space.
C
      Call PSIA (N,P1,P2)
C
C     Output headings for adsorption table.
C
      Open(unit=1,file='results',status='new')
      If (ANS.EQ.0) then
         Write(1,24)
      Else
         Write(1,51)
      Endif
24    Format('Step', x, 'Pressure Data', x, 'Amount of Nitrogen in DV' ,/)
51    Format('Step', x, 'Pressure Data',x, 'Amount of Steam in DV' ,/)
      Write(1,25)
25    Format('$p sub 2$/$p sub 0$',x,'Sp sub 1$',x,'$p sub 2$',x,
     # 'Total',x, 'Free Gas' ,x, 'Adsorption', X,'Ads./Weight', /)
      Write(1,52)
52    Format(' (dimensionless)',x,'(psia)',x,'(psia)',x,'($mu$moles)',
     # x,'($mu$moles)',x,'($mu$moles)',x,'($mu$moles/gm)',/)
C
C     Calculation of B, NTOT, NGAS, NADS, and XW for isotherm
C     B and XW are arrays that are saved. Only last value of other 3 will
C     be saved.  B and B/{X(1-B)} are saved in arrays for BET range.
C     Adsorption and desorption are stored separately.
C
      J-0
      J1=0
      NTOT=0.0
      NUP=0
      NDOWN=0
      If (ANS.EQ.1) call SVAPP(TC,P0)
C
C     SVAPP calculates the saturation vapor pressure for steam.
C
      Do 90 I=1,N
         If (ANS.EQ.0) go to 70
C
C        Steam calculations follow. For nit. jump down to 70.
C
         Call VOLUME(TC,P1(I),V,Z1)
         Call VOLUME(TC,P2(I),V,Z2)
C
C        VOLUME finds V and Z for a given T (in C) and P (in psia).
C        Calculations for moles are based on real gas law keeping track
C        of flow in and out of DV.
C
         A = V1/(R*T)
```

```
            C = P1(I)/Z1
            D = P2(I)/Z2
            NTOT = NTOT + (C-D)*A
            NGAS = P2 (I)*DV/(Z2*R*T)
            NADS = NTOT - NGAS
            XW(I) = NADS/W
            B(I) = P2(I)/P0
            Go to 80
C
C           Nitrogen calculations with constant 2-0.95.
C
70          ZRT = Z*R*T
            NTOT = NTOT + (P1 (I)-P2 (I))*V1/ZRT
            NGAS = P2 (I)*DV/ZRT
            NADS = NTOT - NGAS
            XW(I) = NADS/W
            B(I) = P2(I)/14.7
C
C           Assume P0 for nit. is 14.7 psia.  Rest calc. OK for steam & nit.
C
80          Write(1,26)I,B(I),P1(I),P2(I),NTOT,NGAS,NADS,XW(I)
26          Format(I2,x,F7.5,x,F8.4,x,F8.4,x,F10.3,x,F9.3,x,
     #      F10.3,x,F8.3,/)
            If (P2(I).LT.P2(I+1)) then
                 NUP=NUP+1
            Else
                 NDOWN=NDOWN+1
            Endif
C
C           Check values to see if they are in BET range. If not, jump to
C           bottom of DO LOOP.
C
            If (B(I).LT.0.05) go to 90
            If (B(I).GT.0.35) go to 90
C
            If (P2(I).LT.P2(I+1)) then
C                true for adsorption
                 J = J+1
                 F(J) = B(I)*1.0E6/(NADS*(1.0-B(I)))
                 G(J) = B(I)
            Else
C                true for desorption
                 J1 = J1+1
                 F1(J1) = B(I)*1.0E6/(NADS*(1.0-B(I)))
                 G1(J1) = B(I)
            Endif
90       Continue
         Open (unit-2,file='isoplot' ,status='new')
         Write (2,*)NUP
         Do 160 I=1,NUP
              Write (2,*)B(I),XW(I)
160      Continue
         Write (2,*)NDOWN
         Do 170 I=1,NDOWN
              Write (2,*)B(I+NUP),XW(I+NUP)
170      Continue
C
C        Analysis of BET data -- starts with adsorption section
C
         If (J.EQ.0) go to 130
         Open(unit=3,file='BET',status='new')
         Write(3,27)
27       Format(/,'*** Analysis Based on Adsorption ***',//)
C
C        Desorption section jumps back to here for calculations.
C
```

```
100    Write(3,28)
28     Format(11x,'Rel. Pressure, $beta$',10x,
     # 'the factor $beta$/{X(1-$beta$)} in 1/mole',//)
C
C      X and NADS are the same variable.
C
       Do 110 I=1,J
            Write(3,29)G(I),F(I)
29          Format(F24.7,F32.4)
110    Continue
       If (J.EQ.1) go to 130
       Call LSTSQ(J,G,F,S,YINT)
C
C      LSTSQ is a least squares routine to find the slope and y-intercept
C      of the BET eqn.
C
       CF = S/YINT + 1.0
       XM = 1.0E6/(YINT*CF)
C
C      Surface area calculations for nitrogen use Avogadro's  No. and a
C      cross-sectional area of 16.2 angstroms.
C
       If (ANS.EQ.0) then
            SA = XM*0.006023*16.2
            Go to 120
       Endif
C
C      Steam SA calculations
C
       Call VOLIQD(TC,PO,V)
C
C      VOLIQD finds the specific volume of liq. water. V is then changed to
C      molar volume.
C
       V = V*180.0/6.023
       PI = 3.141593
       POW = 2.0/3.0
       XA = ((V*3.0/(4.0*PI))**POW) * PI
       SA = XM*0.006023*XA
120    Continue
       SA1 = SA/W
C
C      Output of results
C
       Write(3,31)CF
31     Format(//,'The value of "C" factor in BET analysis is ',
     # F16.4,2x,'1/micromoles',/)
       Write(3,32)XM
32     Format('The monolayer adsorption is ',F31.4,2x,'micromoles',/)
       Write(3,33)W
33     Format ('The  weight of the sample is ',F31.4,2x,'grams', /)
       Write(3,34)SA
34     Format ('The  total surface area is ',F33.4,2x,'square meters', /)
       Write(3,35)SA1
35     Format('The specific surface area is',F31.4,2x,
     # 'square meters/gram',/)
C
C      Desorption analysis -- if no desorption data is left, the analysis of
C      the run is done.
C
130    If (J1.EQ.0) go to 150
       Write(3,36)
36     Format(/,'*** Analysis Based on Desorption ***',//)
C
C      Reset variables so they will work in adsorption section calculations.
C
```

```
      J = J1
      J1 = 0
      DO 140 I=1,J
         G(I) = G1(I)
         F(I) = F1(I)
140   Continue
C
C     Go back to calculations under adsorption section
C
      Go to 100
C
150   Continue
      STOP
      END
```

```
      SUBROUTINE DEDVOL(V1,DV)
C
C     This subroutine calculates the dead volume -- i.e. the space in the
C     coreholder section that can be occupied by a gas.  The gas is assumed
C     to be an ideal gas.
C
C     Input: V1
C     Output: DV
C
C     Explanation of variables
C
C     V1      known volume -- usu. sampling bottle volume
C     DV      dead volume in cc
C     NUM     number of steps
C     PR1     array of P1 values in volts
C     PR2     array of P2 values in volts
C     PRV     pressure at vacuum
C     DDV     array to keep track of DV estimates
C     ANS...  decision variables
C     OPT     decision variable
C     CC      keeps track of sum of DDV's for average
C     AA      numerator for DV calculations
C     BB      denominator for DV calculations
C     AVG     arithmetic average of DV estimates
C     SN      array to keep track of step numbers of estimates used in avg
C
C
C
      Implicit Real*8 (a-h,o-z)
      Dimension PR1(15),PR2(15),DDV(15),SN(15)
C
C     Zero out arrays
C
      Do 10 I=1,15
           PR1(I) = 0.0
           PR2(I) = 0.0
           DDV(I) = 0.0
           SN(I) = 0.0
10    Continue
C
C     Enter data
C
      Write(6,1)
1     Format('How may steps are there?' ,/)
      Read (5,*)NUM
      Write(6,2)
2     Format('Enter pressures, PR1 and PR2, in volts by step
     # number.', /)
      Do 20 I=1,NUM
           Write(6,3)I
3          Format('Step', 2x,14,/)
           Read(5,*)PR1(I),PR2(I)
20    Continue
      Write(6,4)
4     Format('What is the pressure in volts for a vacuum?',/)
      Read (5,*)PRV
C
      Call PSIA(NUM,PRV,PR1,PR2)
C
C     PSIA changes pressure from volts to psia.
C     Step 1 estimate of DV
C
      DDV(1) = V1*(PR1(1)/PR2 (1)-1.0)
      CC = DDV(1)
      Write(6,5)DDV(1)
5     Format('Estimates for DV in cc',//,'Step',3x,'1',F15.4,/)
```

```
C
C       Estimates for other steps
C
        Do 30 I=2,NUM
             AA = PR1(I) - PR2(I)
             BB = PR2(I) - PR2(I-1)
             DDV(I) = V1*AA/BB
             CC = CC + DDV(I)
             Write(6,6)I,DDV(I)
6            Format(’Step’,I4,F15.4,/)
30      Continue
C
C       Calculation of arithmetic average
C
        AVG = CC/NUM
        Write(6,7)AVG
7       Format(’The arithmetic average is ’,F18.4,2x,’cc’,/)
        Write(6,8)
8       Format(’Do you wish to use this average for DV? (0=no, 1=yes)’,/)
        Read(5,*)ANS
        If (ANS.EQ.l) then
             DV = AVG
             Return
        Endif
        Go to 200
C
C       Repeat output of DDV when viewing options more than once.
C
100     Write(6,9)
9       Format(’Estimates for DV in cc’,/)
        Do 40 I=1,NUM
             Write(6,11)I,DDV(I)
11           Format(’Step’,I4,F15.4,/)
40      Continue
C
C       List of options
C
200     Write(6,12)
12      Format(’You have the following options:’,/,’1. Use any one
      # estimate for DV’,/,’2. Throw out questionable values and
      # calculate new average.’,/)
        Read(5,*)OPT
        If (OPT.EQ.2) go to 300
        Write(6,13)
13      Format(’Enter step number of estimate to be used as DV.’,/)
        Read(5,*)K
        DV = DDV(K)
        Return
C
C       Continues here only if new average calculated.
C
300     Write(6,14)
14      Format(’How many points would you like to include in the
      # new AVG?’,/)
        Read(5,*)L
        Write(6,15)
15      Format ('Enter  the step numbers of the values to be used.’,/)
        Do 50 I=1,L
              Read(5,*)SN(I)
50      Continue
        cc-0 .0
        Do 60 I=1,L
             M=SN (I)
             CC=CC+DDV(I)
60      Continue
        AVG=CC/L
```

```
      Write(6,16)AVG
16    Format('The new average is',F18.4,2x,'cc',/)
      Write(6,17)
17    Format('Do you wish to use this average for DV? (0=no, 1=yes)',/)
      Read(5,*)ANS1
      If (ANS1.EQ.1) then
           DV=AVG
           Return
      Endif
C
C     If new AVG is not acceptable, the program goes back to print out
C     estimates and options again.
C
      Go to 100
C
C
      END
```

```
      SUBROUTINE PSIA(N,1,P2)
C
C     This subroutine replaces all pressures in volts with pressures in psia.
C     The values in volts are not saved. The calibration is based on ambient
C     P, the plate differential, and the voltage range (set at 10 V default).
C     It is assumed to be linear, so the P measurement system must be checked
C     out to see that it complies reasonably well with that assumption.
C
C     Input :  N,P1,P2
C     Output : P1,P2 (new values)
C
C     Explanation of variables
C
C     N       number of steps
C     P1      array P1 in main program
C     P2      array P2 in main program
C     PA      ambient pressure -- must already be corrected for temperature and
C             entered in psia
C     DIFF    plate differential in psi of the pressure transducer
C     VOLT    voltage range (in positive direction) set at default of 10 V
C
C
C
      Implicit Real*8 (a-h,o-z)
      Dimension P1(100),P2(100)
C
C     Enter information
C
      Write(6,1)
 1    Format(/,'What is the plate differentia1 in psi of the P
     # transducer?', /)
      Read(5,*)DIFF
      Write(6,2)
 2    Format('What is the ambient pressure in psia (with temperature
     # correction if needed)?' ,/)
      Read(5,*)PA
      VOLT=10.0
C
C     Change to psia
C
      Do 10 I=1,N
         P1(I) = P1(I)*DIFF/VOLT + PA
         P2(I) = P2(I)*DIFF/VOLT + PA
 10   Continue
C
C     Output results
C
      Write(6,3)
 3    Format(///,10x,'Pressure in psia',//,2x,'Step',15x,'P1',15x,
     # 'P2',/)
      Do 20 I-l,N
         Write(6,4)I,P1 (I),P2 (I)
 4       Format(2x,I4,10x,F10.4,7x,F10.4)
 20   Continue
      Return
      End
```

```
      SUBROUTINE SVAPP(T,P0)
C
C     This subroutine will calculate the saturated steam vapor pressure for
C     a nonporous container by using the 1968 IFC formula for scientific and
C     research purposes.  It was copied from Hsieh's  program.
C
C     Input: T
C     output: PO
C
C     Explanation of variables
C
C     T      temperature in Centigrade
C     PO     saturated steam vapor pressure in psia
C
C
C
      Implicit Real*8 (a-h,o-z)
C
      F1 = -741.9242
      F2 = -29.72100
      F3 = -11.55286
      F4 = -0.8685635
      F5 = 0.1094098
      F6 = 0.439993
      F7 = 0.2520658
      F8 = 0.05218684
      X = 0.65 - 0.01*T
      S = (((F8*X + F7)*X + F6)*X + F5)*X + F4)*X
      S = ((S + F3)*X + F2)*X + F1
      P0 = exp(0.01/(T + 273.15)*(374.136 - T)*S)
      PO = P0*3203.599344
      Return
      END
```

```
      SUBROUTINE VOLUME(T,P,V,Z)
C
C     This subroutine calculates the specific volume and Z factor of
C     superheated steam by using a 1967 formula for industrial utilization.
C     Copied from program Hsieh wrote.
C
C     Input:  T,P
C     output: V,Z
C
C     Explanation of variables
C
C     T      temperature in Centigrage
C     P      pressure in psia
C     V      specific volume
C     Z      Z factor
C
C
C
      Implicit Real*8 (a-h,o-z)
C
      If (P.GT.1.0E-5) go to 10
      Z=1.0
      V=1.0E5
      Return
 10   TH = (T+273.15)/647.3
      B = P/3208.2335
      X = exp(2.29*(1.0-TH)/3.0)
      x2 = x*x
      x3 = X2*X
      X6 = X3*X3
      X8 = X2*X6
      X10 = X8*X2
      X11 = X10*X
      X14 = X6*X8
      X16 = X8*X8
      X27 = X11*X16
      B2 = B*B
      B3 = B*B2
      B4 = B2*B2
      B5 = B2*B3
      B6 = B3*B3
      B7 = B6*B
      TO = 4.260321148*TH/B
      T1 = -X3*(0.06670375918*X10 + 1.388983801)
      T2 = 0.08390104328*X16 + 0.02614670893
      T2 = -2.0*B*(T2*X2 - 0.03373439453*X)
      T3 = -3.0*B2*(0.4520918904*X8 + 0.1069036614)*X10
      T4 = 4.0*B3*(0.5975336707*X11 + 0.08847535804)*X14
      T5 = 0.5958051609*X10*X8 - 0.5159303373*X14 + 0.2075021122*X10
      T5 = -5.0*B4*T5*X14
      AUX = 1.0/B4 + 0.4006073948*X14
      AUX = AUX*AUX
      T6 = -4.0/B5*(0.1190610271*X - 0.09867174132)*X11/AUX
      AUX = 1.0/B5 + 0.08636081627*X11*X8
      AUX = AUX*AUX
      T8 = -6.0/B7*(0.006552390126*X10 + 0.0005710218649)*X14/AUX
      T9 = ((527.5718623*X - 2693.088365)*X - 5745.984054)*X
      T9 = (((T9 - 6508.211677)*X + 4126.607219)*X - 1388.522425)*X
      TT = (B/(15.74377327 - 34.17061978*TH + 19.31380707*TH*TH))**10
      TT = 11.0*TT
      T9 = TT*(T9 + 193.6587558)
      V = T9 + T8 + T7 + T6 + T5 + T4 + T3 + T2 + T1 + TO
      Z = V/T0
      V = V*3.17
      Return
      END
```

```
      SUBROUTINE LSTSQ(N,X,Y,S,YINT)
C
C     This subroutine uses the least squares method to find the slope and
C     y intercept of an equation of the form
C                 Y = YINT + SX
C
C     Input :  X, Y, N
C     Output : S, YINT
C
C     Explanation of variables
C
C     X       array of X values corresponding to B of BET eqn
C     Y       array of Y values corresponding to B/{X(1-B)} of BET eqn
C     S       slope corresponding to (CF-1)/XM of BET eqn
C     YINT    y intercept corresponding to 1/(CF*XM) of BET eqn
C     A       sum of x*x
C     C       sum of X
C     D       sum of Y
C     E       sum of X*Y
C     N       number of data points
C     DEN     denominator  needed in calculations
C
C
C
      Implicit Real*8 (a-h,o-z)
      Dimension X(30),Y(30)
C
C
      A = 0.0
      C = 0.0
      D = 0.0
      E = 0.0
      Do 10 I=1,N
           A = A + X(I)*X(I)
           C = C + X(I)
           D = D + Y(I)
           E = E + X(I)*Y(I)
10    Continue
      DEN = N*A - C*C
      S = (N*E - C*D)/DEN
      YINT = (A*D - C*E)/DEN
      Return
      END
```

```
      SUBROUTINE VOLIQD(T,P,V)
C
C     This subroutine calculates the specific volume of liquid water for a
C     given temperature and pressure.  It was copied from Hsieh's  program.
C
C     Input : T,P
C     output: V
C
C     Explanation of variables
C
C     T      temperature in Centigrade
C     P      pressure in psia
C     V      specific volume of liquid water in cc/gm
C
C
C
      Implicit Real*8 (a-h,o-z)
C
      TH = (T + 273.15)/647.3
      BT = P*6894.76/22120000.0
      All = 7.982692717
      A12 = -0.02616571843
      A13 = 0.00132241179
      A14 = 0.02284279054
      A15 = 242.1647003
      A16 = 1.269716E-10
      A17 = 2.0748383-7
      A18 = 2.174020E-8
      A19 = 1.105710E-9
      A20 = 12.93441934
      A21 = 0.00001308119072
      A22 = 6.047626E-14
      Y = 1.0 - 0.8438375405*TH*TH - 0.005362162162/TH**6
      Z = 1.72*Y*Y - 0.14684556978*TH + 0.099517174*BT
      Z = Y + SQRT(Z)
      T1 = A11*0.0497585887*Z**(-5.0/17.0)
      T2 = (A14*TH + A13)*TH + A12 + A15*(0.6537154 - TH)**10
      T2 = T2 + A16/(1.15E-6 + TH**19)
      T3 = ((3.0*A19*BT + 2.0*A18)*BT + A17)/(1.51E-5 + TH**11)
      T4 = A20*TH**18*(0.14188 + TH*TH)
      T4 = T4*(-3.0/(7.002753165 + BT)**4 + 0.0002995284926)
      T5 = (4.0*A22*(TH**(-20))*BT + 3.0*A21*(0.204 - TH))*BT*BT
      V = (T1 + T2 + T3 + T4 + T5)*3.17
      Return
      END
```

9.2 APPENDIX B -- DATA CHECKLISTS

The Data Checklist was designed as a convenient means of recording data during an experimental run that will later be used by the analysis program. The first page identifies the date, the sample name, its weight, and the run number as well as providing space for any comments about the run. It also shows the type of experiment and test fluid, the temperature, the dead volume, the sampling bottle volume, and information about the pressure transducer calibration. The second page has places to list the step number, p_1, p_2, and any comments about the step. The present computer program assumes a constant temperature equal to the experiment temperature listed on the first page, thereby neglecting any variations in core temperature from one equilibrium state to the next. Though optional, recording the core temperature allows one to judge the validity of the constant temperature assumption. It also makes the information available for any future analysis which includes varations.

The following Data Checklists contain information from the fifteen experiemntal runs conducted for this study.

DATA CHECKLIST

DATE ____________

SAMPLE NAME Berea , Sample #1 RUN NUMBER DV1 & DV2

SAMPLE WEIGHT 118.02 gm

COMMENTS

DV1 *is* best. Let DV - 084 cc .

CIRCLE TYPE OF EXPERIMENT AND MEDIUM USED (E.G ADSORBATE)

[✓ dead volume] low temperature high temperature

[✓ helium] nitrogen steam natural gas ________

other medium ____________

TEMPERATURE OF EXPERIMENT room C or K

DEAD VOLUME (if already known) ________ cc

SAMPLING BOTTLE VOLUME (circle one)

low T system [✓ 45.07 cc]

high T system: Number 1 158.62 cc OR Number 2 513.30 cc

other __________ cc

PRESSURE TRANSDUCER CALIBRATION INFORMATION:

plate differential: [✓ 25 psi] 100 psi 500 psi other ________

#1,

atmospheric pressure (corrected for room T): 14.683 psia 14.704 #2

#1

vacuum pressure: __________ psia -5.873 volts

-5.882 #2

RAW EQUILIBRIUM PRESSURE DATA

STEP	p_1 (volts)	p_2 (volts)	COMMENTS
1	-4.850	-5.367	DV1
2	-3.841	-4.615	
3	-2.865	-3.750	
4	-1.841	-2.806	
5	-0.491	-1.658	average = 46.084 cc
			DV2
1	-4.793	-5.652	
2	-3.751	-5.230	
3	-2.994	-4.722	
4	-2.191	-4.155	
5	-1.345	-3.521	
6	-0.424	-2.816	average = 157.268

DATA CHECKLIST

DATE 7/24/85

SAMPLE NAME Berea, Sample #1 **RUN NUMBER** HT1

SAMPLE WEIGHT 118.02 **gm**

COMMENTS

CIRCLE TYPE OF EXPERIMENT AND MEDIUM USED (E.G. ADSORBATE)

dead volume **low temperature** [✓ **high temperature**]

helium **nitrogen** [✓ steam] **natural gas** ____

other medium ____

TEMPERATURE OF EXPERIMENT 169 [✓ C] **or K**

DEAD VOLUME (if already known) 46.084 **cc**

SAMPLING BOTTLE VOLUME **(circle one)**

low T system 45.07 cc

high T system: Number 1 [✓ **158.62 cc**] **OR** **Number 2 513.30 cc**

other ____ **cc**

PRESSURE TRANSDUCER CALIBRATION INFORMATION:

plate differential: 25 psi **100 psi** [✓ 500 psi] **other** ____

atmospheric pressure (corrected for room T): 14.604 **psia**

vacuum pressure: ____ **psia** -0.292 **volts**

RAW EQUILIBRIWM PRESSURE DATA

STEP	p_1 (volts)	p_2 (volts)	COMMENTS
1	0.226	0.161	average equilibrium time about
2	0.431	0.360	40 minutes
3	0.622	0.550	
4	0.830	0.753	
5	1.058	0.972	
6	1.246	1.167	
7	1.457	1.373	
8	1.653	1.567	
9	1.821	1.738	
10	2.050	1.944	
11	2.490	2.370	
			beginning of desorption
12	1.820	2.120	
13	1.530	1.773	
14	1.333	1.485	
15	0.922	1.096	
16	0.720	0.834	
17	0.519	0.611	
18	0.321	0.405	
19	0.122	0.203	
20	0.073	0.133	

DATA CHECKLIST

DATE 8/8/85

SAMPLENAME Berea, Sample #1 RUN NUMBER HT2

SAMPLE WEIGHT 118.02 gm

COMMENTS

CIRCLE TYPE OF EXPERIMENT AND MEDIUM USED (E.G. ADSORBATE)

dead volume low temperature [✓ high temperature]

helium nitrogen [✓ steam] natural gas

other medium

TEMPERATURE OF EXPERIMENT 207 [✓ C] or K

DEAD VOLUME (if already known) 46.084 cc

SAMPLING BOTTLE VOLIJME (circle one)

low T system 45.07 cc

high T system: Number 1 [✓ 158.62 cc] OR Number 2 513.30 cc

other cc

PRESSURE TRANSDUCER CALIBRATION INFORMATION:

plate differential: 25 psi 100 psi [✓ 500 psi] other

atmospheric pressure (corrected for room T): 14.675 psia

vacuum pressure: psia -0.294 volts

RAW EQUILIBRIUM PRESSURE DATA

STEP	p_1 (volts)	p_2 (volls)	COMMENTS
1	0.276	0.163	average equilibrium time about
2	0.585	0.476	45 minutes
3	0.886	0.786	
4	1.167	1.078	
5	1.416	1.334	
6	1.768	1.660	
7	2.130	2.023	
8	2.491	2.375	
9	3.049	2.866	
10	3.455	3.287	
11	3.925	3.727	
12	4.518	4.448	
			beginning of desorption
13	1.826	3.218	
14	1.548	2.031	
15	1.316	1.503	
16	1.143	1.237	
17	0.936	1.014	
18	0.734	0.805	
19	0.533	0.601	
20	0.332	0.399	
21	0.134	0.202	
22	-0.025	0.038	

DATA CHECKLIST

DATE 8/13/85

SAMPLE NAME Berea, Sample #1 RUN NUMBER HT3

SAMPLE WEIGHT 118.02 gm

COMMENTS

____

____

____

____

____

CIRCLE TYPE OF EXPERIMENT AND MEDIUM USED (E.G. ADSORBATE)

dead volume low temperature [✓ high temperature]

helium nitrogen [✓ steam] natural gas ________

other medium ____________

TEMPERATURE OF EXPERIMENT 150 [✓ C] or K

DEAD VOLUME (if already known) 46.084 cc

SAMPLING BOTTLE VOLUME (circle one)

low T system 45.07 cc

high T system: Number 1 [✓ 158.62 cc] OR Number 2 513.30 cc

other __________ cc

PRESSURE TRANSDUCER CALIBRATION INFORMATION:

plate differential: 25 psi 100 psi [✓ 500 psi] other ______

atmospheric pressure (corrected for room T): 14.760 psia

vacuum pressure: __________ psia -0.295 volts

RAW EQUILIBRIUM PRESSURE DATA

STEP	p_1 (volts)	p_2 (volts)	COMMENTS
1	0.105	0.059	
2	0.230	0.179	
3	0. 382	0. 325	
4	0.521	0.464	
5	0.670	0.607	
6	0.812	0.744	
7	0. 953	0.881	
8	1.091	1.017	
9	1.267	1.173	
10	1.297	1.282	
			beginning of desorption
11	1.174	1.221	
12	0.999	1.089	
13	0.815	0.920	
14	0.719	0.792	
15	0.577	0.649	
16	0.439	0.512	
17	0.299	0.360	
18	0.137	0.213	
19	-0.001	0.067	

DATA CHECKLIST

DATE 6/25/85

SAMPLE NAME Berea, Sample #2 RUN NUMBER DV1 & DV2

SAMPLE WEIGHT 151.865 gm

COMMENTS

Best average DV is 46. 124 cc.

CIRCLE TYPE OF EXPERIMENT AND MEDIUM USED (E.G. ADSORBATE)

[✓ dead volume] low temperature high temperature

[✓ helium] nitrogen steam natural gas ________

other medium ____________

TEMPERATURE OF EXPERIMENT 77.3 C or [✓ K]

DEAD VOLUME (if already known) ________ cc

SAMPLING BOTTLE VOLUME (circle one)

low T syste 5.07 cc

high T system: Number 1 158.62 cc OR Number 2 513.30 cc

other __________ cc

PRESSURE TRANSDUCER CALIBRATION INFORMATION:

plate differential: [✓ 25 psi] 100 psi 500 psi other ______

atmospheric pressure (corrected for room T): 14. 68 psia for DV2

vacuum pressure: __________ psia -5. 865 volts

RAW EQUILIBRIUM PRESSURE DATA

STEP	p_1 (volts)	P_2 (volts)	COMMENTS
			DV1 -- estimates **for** each step given
1	-3.173	-5.450	249.088 cc
2	-1.665	-4.760	202.815 cc
3	0.565	-3.720	185.697 cc
4	2.309	-2.498	177.293 cc
5	4.130	-1.115	170.927 cc
6	6.521	0.494	168.823 cc
			DV2
1	-4.850	-5.368	46.322 cc
2	-3.840	-4.614	46.265 cc
3	-2.865	-3.750	46.165 cc
4	-1.841	-2.807	46.169 cc
5	-0.491	-1.657	45.697 cc
			average = 46.124 cc

DATA CHECKLIST

DATE 6/27/85

SAMPLE NAME Berea, Sample #2 RUN NUMBER LT1

SAMPLE WEIGHT 151.865 gm

COMMENTS

CIRCLE TYPE OF EXPERIMENT AND MEDIUM USED (E.G. ADSORBATE)

dead volume [✓ low temperature] high temperature

helium [✓ nitrogen] steam natural gas ____

other medium ____

TEMPERATURE OF EXPERIMENT 77.3 C or [✓ K]

DEAD VOLUME (if already known) 46.124 cc

SAMPLING BOTTLE VOLUME (circle one)

low T system [✓ 45.07 cc]

high T system: Number 1 158.62 cc OR Number 2 513.30 cc

other ____ cc

PRESSURE TRANSDUCER CALIBRATION INFORMATION:

plate differential. [✓ 25 psi] 100 psi 500 psi other ____

atmospheric pressure (corrected for room T): 14.932 psia

vacuum pressure: ____ psia -5.973 volts

RAW EQUILIBRIUM PRESSURE DATA

STEP	p_1 (volts)	p_2 (volts)	COMMENTS
1	-5.340	-5.613	
2	-4.988	-5.304	
3	-4.654	-4.985	
4	-3.914	-4.088	
5	-3.059	-3.579	
6	-2.688	-3.140	
7	-2.252	-2.701	
8	-1.834	-2.272	
9	-0.546	-1.417	
10	-0.105	-0.758	
			beginning of desorption
11	-1.365	-1.057	
12	-1.894	-1.470	
13	-2.341	-1.902	
14	-2.888	-2.394	
15	-3.307	-2.846	
16	-3.971	-3.405	
17	-4.381	-3.889	
18	-4.850	-4.372	
19	-5.248	-4.802	
20	-5.602	-5.197	

DATA CHECKLIST

DATE 4/10/85

SAMPLE NAME Berea, Sample #2 RUN NUMBER LT2

SAMPLE WEIGHT 151.865 gm

COMMENTS

Run aborted after adsorption section because of a leak. Therefore, there is no desorption section.

CIRCLE TYPE OF EXPERIMENT AND MEDIUM USED (E.G. ADSORBATE)

dead volume [✓ low temperature] high temperature

helium [✓ nitrogen] steam natural gas ________

other medium ____________

TEMPERATURE OF EXPERIMENT 77.3 C or [✓ K]

DEAD VOLUME (if already known) 46. 124 cc

SAMPLING BOTTLE VOLUME (circle one)

low T system [✓ 45.07 cc]

high T system: Number 1 158.62 cc OR Number 2 513.30 cc

other __________ cc

PRESSURE TRANSDUCER CALIBRATION INFORMATION:

plate differential [✓ 25 psi] 100 psi 500 psi other ______

atmospheric pressure (corrected for room T): 14.72 psia

vacuum pressure: __________ psia -5.888 volts

RAW EQUILIBRIUM PRESSURE DATA

STEP	P_1 (volts)	p_2 (volts)	COMMENTS
1	-4.705	-5.870	
2	-3.846	-5.764	
3	-3.638	-5.460	
4	-1.965	-4.880	
5	-1.093	-4.279	
6	-0.544	-3.681	
7	0.289	-3.061	
8	1.338	-2.403	
9	2.415	-1.782	
10	3.062	-1.257	
11	3.944	-0.826	
12	4.705	0.505	
			Run aborted at this point due to leak.

DATA CHECKLIST

DATE ____________

SAMPLE NAME Berea, Sample #2   RUN NUMBER LT4

SAMPLE WEIGHT 151.865 gm

COMMENTS

CIRCLE TYPE OF EXPERIMENT AND MEDIUM USED (E.G. ADSORBATE)

dead volume   [✓ low temperature] ~~low temperature~~   high temperature

helium   [✓ nitrogen]   steam   natural gas ________

other medium ____________

TEMPERATURE OF EXPERIMENT 77.3 C or [✓ K]

DEAD VOLUME (if already known) 46.124 cc

SAMPLING BOTTLE VOLUME (circle one)

low T system [✓ 45.07 cc]

high T system: Number 1 158.62 cc OR Number 2 513.30 cc

other __________ cc

PRESSURE TRANSDUCER CALIBRATION INFORMATION:

plate differential: [✓ 25 psi] 100 psi 500 psi other _______

atmospheric pressure (corrected for room T): 14.657 psia

vacuum pressure: __________ psia -5.863 volts

RAW EQUILIBRIUM PRESSURE DATA

STEP	p_1 (volts)	p_2 (volts)	COMMENTS
1	-2.655	-5.818	
2	-0.982	-5.114	
3	0.409	-4.228	
4	1.505	-3.318	
5	3.020	-2.365	
6	4.410	-1.489	
7	7.333	-0.682	
8	8.468	-0.217	
			beginning of desorption
9	-4.074	-0.467	
10	-5.124	-0.849	
11	-5.843	-1.326	
12	-5.848	-1.829	
13	-5.860	-2.354	
14	-5.860	-2.843	
15	-5.860	-3.190	
16	-5.862	-3.599	
17	-5.862	-3.952	
18	-5.862	-4.260	

DATA CHECKLIST

DATE 5/30/85

SAMPLE NAME Berea, Sample #2 RUN NUMBER HT1

SAMPLE WEIGHT 151.865 gm

COMMENTS

CIRCLE TYPE OF EXPERIMENT AND MEDIUM USED (E.G. ADSORBATE)

dead volume low temperature [✓ high temperature]

helium nitrogen [✓ steam] natural gas ________

other medium ____________

TEMPERATURE OF EXPERIMENT 167.4 [✓ C] or K

DEAD VOLUME (if already known) 46.124 cc

SAMPLING BOTTLE VOLUME (circle one)

low T system 45.07 cc

high T system: Number 1 [✓ 158.62 cc] OR Number *2* 513.30 cc

other ___________ cc

PRESSURE TRANSDUCER CALIBRATION INFORMATION:

plate differential: 25 psi 100 psi [✓ 500 psi] other _______

atmospheric pressure (corrected for room T): 14.744 psia

vacuum pressure: ___________ psia __________ volts

RAW EQUILIBRIUM PRESSURE DATA

STEP	p_1 (volts)	p_2 (volts)	COMMENTS
1	0.210	0.144	
2	0.521	0.412	
3	0.783	0.683	
4	0.929	0.862	
5	1.080	1.007	
6	1.273	1.181	
7	1.427	1.344	
8	1.604	1.504	
9	1.815	1.679	
10	2.010	1.868	
			beginning of desorption
11	1.604	1.755	
12	1.431	1.584	
13	1.146	1.321	
14	0.847	1.018	
15	0.560	0.709	
16	0.235	0.380	
17	0.029	0.139	

DATA CHECKLIST

DATE 6/17/85

SAMPLE NAME The Geysers, Sample #1 **RUN NUMBER** DV1, DV2, & DV3

SAMPLE **WEIGHT** 197.55 gm

COMMENTS

DV1 average = 36.578 cc

DV2 average = **bad** numbers because **of** a leak

DV3 average = **37.388** cc --- **best** estimate

CIRCLE TYPE OF EXPERIMENT AND MEDIUM USED (E.G.ADSORBATE)

[✓ **dead volume**] **low** temperature high temperature

[✓ **helium**] **nitrogen** steam natural gas

other medium

TEMPERATURE OF EXPERIMENT 77.3 *C* or [✓ K]

DEAD VOLUME (if already **known)** cc

SAMPLING BOTTLE VOLUME (circle one)

low T system: [✓ **45.07 cc**]

high T system: Number 1 **158.62** cc OR Number **2** **513.30** cc

other *cc*

PRESSURE TRANSDUCER CALIBRATION INFORMATION:

plate differential: [✓ **25 psi**] 100 psi ***500*** psi other

atmospheric pressure (corrected for room **T**): 14.687 psia

vacuum pressure: **psia** -5.875 volts

RAW EQUILIBRIUM PRESSURE DATA

STEP	p_1 (volts)	p_2 (volts)	COMMENTS
			DV1 estimates
1	-4.273	-4.982	35.783 cc
2	-3.480	-4.152	36.490 cc
3	-2.394	-3.185	36.867 cc
4	-0.311	-1.610	37.172 cc
			DV1 average = 36.578 cc
			DV2 estimates
1	-3.693	-5.280	Bad results due to a **leak.**
2	-2.680	-4.555	
3	-1.910	-3.815	
4	-0.866	-3.812	
5	-0.001	-2.148	
			DV3 estimates done at room temperature
1	-5.016	-5.419	37.053 cc
2	-4.081	-4.690	37.651 cc
3	-3.054	-3.798	37.592 cc
4	-1.997	-2.812	37.254 cc
5	-0.461	-1.527	37.389 cc
			DV3 average = 37.388 cc ---- best estimate

DATA CHECKLIST

DATE 6/85

SAMPLE NAME The Geysers, Sample #1 RUN NUMBER LT1

SAMPLE WEIGHT 197.55 gm

COMMENTS

CIRCLE TYPE OF EXPERIMENT AND MEDIUM USED (E.G. ADSORBATE)

dead volume [✓ low temperature] high temperature

helium [✓ nitrogen] steam natural gas ________

other medium ____________

TEMPERATURE OF EXPERIMENT 77.3

DEAD VOLUME (if already known) 37.388 cc

SAMPLING BOTTLE VOLUME (circle one)

low T system [✓ 45.07 cc]

high T system: Number 1 158.62 cc OR Number 2 513.30 cc

other __________ cc

PRESSURE TRANSDUCER CALIBRATION INFORMATION:

plate differential: [✓ 25 psi] 100 psi 500 psi other ______

atmospheric pressure (corrected for room T): 14.71 psia

vacuum pressure: __________ psia -5.884 volts

RAW EQUILIBRIUM PRESSURE DATA

STEP	P1 (volts)	p_2 (volts)	COMMENTS
1	-5.116	-5.673	average equilibrium time about
2	-4.673	-5.400	30 minutes
3	-3.941	-4.998	
4	-3.388	-4.559	
5	-2.806	-4.082	
6	-2.205	-3.572	
7	-1.784	-3.093	
8	-0.925	-2.503	
9	-0.176	-1.872	
10	0.232	-1.328	
11	0.950	-0.745	
12	1.200	-0.302	
13	1.637	-0.010	beginning of desorption
14	-1.266	-0.204	
15	-1.971	-0.577	
16	-3.025	-1.190	
17	-4.268	-2.002	
18	-5.116	-2.837	
19	-5.883	-3.659	
20	-5.878	-4.260	
21	-5.877	-4.699	
22	-5.874	-5.020	
23	-5.879	-5.252	

DATA CHECKLIST

DATE 8/20/85
SAMPLE NAME The Geysers. Sample #1 RUN NUMBER HT1

SAMPLE WEIGHT 197.55 **gm**

COMMENTS

average equilibrium time about one hour

CIRCLE TYPE OF EXPERIMENT AND MEDIUM USED (E.G. ADSORBATE)

dead volume low temperature [✓ **high temperature**]

helium nitrogen [✓ steam] natural gas ________

other medium ____________

TEMPERATURE **OF** EXPERIMENT 153 [✓ C] or K

DEAD VOLUME (if already known) 37.388 cc

SAMPLING BOTTLE VOLUME (circle one)

low T system **45.07** cc

high T system: Number **1** [✓ **158.62 cc**] **OR** Number 2 **513.30** cc

other __________ cc

PRESSURE TRANSDUCER CALIBRATION INFORMATION:

plate differential: **25** psi **100 psi** [✓ *00* psi] other ______

atmospheric pressure (corrected for room T): 14.696 psia

vacuum pressure: __________ **psia** -0.294 volts

RAW EQUILIBRIUM PRESSURE DATA

STEP	p_1 (volts)	p_2 (volu)	COMMENTS
1	0.129	0.098	
2	0.257	0.211	
3	0.390	0.338	
4	0.526	0.457	
5	0.655	0.571	
6	0.792	0.696	
7	1. 124	0.990	
8	1.266	1.219	
			beginning of desorption
9	1.119	1.138	
10	1.09’7	1. 128	
11	0.949	0.990	
12	0.812	0. 855	
13	0. 672	0.727	
14	0.501	0.568	
15	0. 328	0.249	
16	0. 160	0.249	
17	0.008	0.310	

DATA CHECKLIST

DATE 3/20/86

SAMPLE NAME The Geysers. Sample #1 RUN NUMBER HT2

SAMPLE WEIGHT 197.55 gm

COMMENTS

average equilibrium time usually 6-8 hours. though as high as 12 hours

CIRCLE TYPE OF EXPERIMENT AND MEDIUM USED (E.G ADSORBATE)

dead volume low temperature [✓ high temperature]

helium nitrogen [✓ steam] natural gas ________

other medium ____________

TEMPERATURE OF EXPERIMENT 200 [✓ C] or K

DEAD VOLUME (if already known) 37.388 cc

SAMPLING BOTTLE VOLUME (circle one)

low T system 45.07 cc

high T system: Number 1 [✓ 158.62 cc] OR Number 2 513.30 cc

other __________ cc

PRESSURE TRANSDUCER CALIBRATION INFORMATION:

plate differential: 25 psi 100 psi [✓ 500 psi] other ______

atmospheric pressure (corrected for room T): 14.851 psia

vacuum pressure: __________ psia -0.246 volts

RAW EQUILIBRIUM PRESSURE DATA

STEP	p_1 (volts)	p_2 (volts)	COMMENTS
1	0.1998	0.0186	
2	0.9117	0.6192	
3	1.2257	1.0711	
4	1.6926	1.3765	
5	2.278	1.983	
6	2.589	2.416	
7	3.046	2.839	
8	3.468	3.287	
9	3.785	3.723	
10	3.859	3.773	
			beginning of desorption
11	3.385	3.611	
12	2.525	2.897	
13	1.982	2.252	
14	1.668	1.858	
15	1.073	1.314	
16	0.532	0.802	
17	0.190	0.462	
18	-0.068	0.160	
19	-0.121	0.034	

DATA CHECKLIST

DATE 7/3/86

SAMPLE NAME The Geysers, Sample #1 RUN NUMBER HT3

SAMPLE WEIGHT 197.55 gm

COMMENTS

Average equilibrium time about 12 hours.

CIRCLE TYPE OF EXPERIMENT AND MEDIUM USED (E.G. ADSORBATE)

dead volume low temperature [✓ high temperature]

helium nitrogen [✓ steam] natural gas ________

other medium ____________

TEMPERATURE OF EXPERIMENT 180 [✓ C] or K

DEAD VOLUME (if already known) 37.388 cc

SAMPLING BOTTLE VOLUME (circle one)

low T system 45.07 cc

high T system: Number 1 [✓ 158.62 cc] OR Number 2 513.30 cc

other __________ cc

PRESSURE TRANSDUCER CALIBRATION INFORMATION:

plate differential: 25 psi 100 psi [✓ 500 psi] other ______

atmospheric pressure (corrected for room T): 14.905 psia

vacuum pressure: __________ psia __________ volts

RAW EQUILIBRIUM PRESSURE DATA

STEP	p_1 (volts)	p_2 (volts)	COMMENTS
1	0.511	0.223	
2	0.934	0.602	
3	1.516	1.123	
4	1.985	1.677	
5	2.530	2.482	
6	1.988	2.238	
7	1.494	1.790	
8	1.001	1.299	
9	0.504	0.790	

DATA CHECKLIST

DATE 6/17/85

SAMPLE NAME Montiverdi 2, Sample #2 RUN NUMBER DV1 & DV2

SAMPLE WEIGHT 178.276 gm

COMMENTS

DV2 better than DV1. Average DV2 = 42.551 cc.

CIRCLE TYPE OF EXPERIMENT AND MEDIUM USED (E.G.ADSORBATE)

[✓ dead volume] low temperature high temperature

[✓ helium] nitrogen steam natural gas ______

other medium ______

TEMPERATURE OF EXPERIMENT 23 [✓ C] or K

DEAD VOLUME (if already known) ______ cc

SAMPLING BOTTLE VOLUME (circle one)

low T system [✓ 45.07 cc]

high T system: Number 1 158.62 cc OR Number 2 513.30 cc

other ______ cc

PRESSURE TRANSDUCER CALIBRATION LNFORMATION:

plate differential [✓ 25 psi] 100 psi 500 psi other ______

atmospheric pressure (corrected for room T): 14.708 psia

vacuum pressure: ______ psia -5.883 volts

RAW EQUILIBRIUM PRESSURE DATA

STEP	p_1 (volts)	p_2 (volts)	COMMENTS
			DV1 estimates
1	-3.803	-5.382	289.291 cc
7	-2.631	-4.626	118.935 cc
3	-2.286	-4.035	133.380 cc
4	-2.635	-3.675	130.177 cc
			estimates diverge too much
			DV2 estimates
1	-3.606	-4.709	41.775 cc
2	-2.957	-3.809	42.666 cc
3	-1.945	-2.852	42.715 cc
4	-0.976	-1.886	42.457 cc
5	-0.058	-0.952	43.140 cc
			DV2 average = 42.551 cc

DATA CHECKLIST

DATE 5/25/85

SAMPLE NAME Montiverdi 2, Sample #2 RUN NUMBER LT1

SAMPLE WEIGHT 178.276 gm

COMMENTS

CIRCLE TYPE OF EXPERIMENT AND MEDIUM USED (E.G. ADSORBATE)

dead volume [✓ low temperature] high temperature

helium [✓ nitrogen] steam natural gas ______

other medium ______

TEMPERATURE OF EXPERIMENT 77.3 C or [✓ K]

DEAD VOLUME (if already known) 42.551 cc

SAMPLING BOTTLE VOLUME (circle one)

low T system [✓ 45.07 cc]

high T system: Number 1 158.62 cc OR Number 2 513.30 cc

other ______ cc

PRESSURE TRANSDUCER CALIBRATION INFORMATION:

plate differential: [✓ 25 psi] 100 psi 500 psi other ______

atmospheric pressure (corrected for room T): 14.684 psia

vacuum pressure: ______ psia -5.873 volts

RAW EQUILIBRIUM PRESSURE DATA

STEP	p_1 (volts)	p_2 (volls)	COMMENTS
1	-3.795	-5.448	
2	-2.336	-4.736	
3	-1.515	-3.999	
4	-2.027	-3.550	
5	-1.615	-3.108	
6	-1.117	-2.664	
7	-0.679	-2.214	
8	-0.004	-1.731	
9	0.921	-1.161	
10	2.223	-0.506	
11	2.978	-0.070	
			beginning of desorption
12	-2.180	-0.347	
13	-3.936	-1.016	
14	-5.853	-2.055	
15	-5.856	-2.904	
16	-5.861	-3.515	
17	-5.862	-4.039	
18	-5.860	-4.454	
19	-5.860	-4.772	
20	-5.860	-5.021	

DATA CHECKLIST

DATE 2/1/86

SAMPLE NAME Montiverdi 2, Sample #2 **RUN NUMBER** LT2

SAMPLE WEIGHT 178.276 **gm**

COMMENTS

CIRCLE TYPE OF EXPERIMENT AND MEDIUM USED (E.G. ADSORBATE)

dead volume [✓ **low temperature**] high temperature

helium [✓ **nitrogen**] **steam** natural gas ____

other **medium** ____

TEMPERATURE OF EXPERIMENT 77.3 **C** or [✓ K]

DEAD VOLUME **(if** already **known)** 42.551 cc

SAMPLING BOTTLE VOLUME (circle one)

low T system: [✓ 45.07 cc]

high T system: Number **1** **158.62** cc **OR** Number **2** **513.30** cc

other ____ cc

PRESSURE TRANSDUCER CALIBRATION INFORMATION:

plate differential: [✓ **25 psi**] **100** psi **500** psi other ____

atmospheric pressure (corrected for room T): 14.67 psia

vacuum pressure: ____ psia -5.865 volts

RAW EQUILIBRIUM PRESSURE DATA

STEP	p_1 (volts)	p_2 (volts)	COMMENTS
1	-5.500	-5.790	
2	-4.950	-5.620	
3	-4.500	-5.410	
4	-3.420	-4.970	
5	-2.460	-4.410	
6	-1.710	-3.790	
7	-0.490	-3.125	
8	0.650	-2.330	
9	1.860	-1.370	
10	5.050	-0.370	
			beginning of desorption
11	-5.860	-1.300	
12	-5.820	-2.280	
13	-5.860	-3.030	
14	-5.860	-3.670	last point had very short equilibrium time

DATA CHECKLIST

DATE 2/13/86

SAMPLE NAME Montiverdi 2. Sample #2 RUN NUMBER LT3

SAMPLE WEIGHT 178.276 gm

COMMENTS

CIRCLE TYPE OF EXPERIMENT AND MEDIUM USED (E.G. ADSORBATE)

dead volume [✓ low temperature] high temperature

helium [✓ nitrogen] steam natural gas ________

other medium ____________

TEMPERATURE OF EXPERIMENT 77.3

DEAD VOLUME (if already known) 42.551 cc

SAMPLING BOTTLE VOLUME (circle one)

low T system: [✓ 45.07 cc]

high T system: Number 1 158.62 cc OR Number 2 513.30 cc

other __________ cc

PRESSURE TRANSDUCER CALIBRATION INFORMATION:

plate differential: [✓ 25 psi] 100 psi 500 psi other ______

atmospheric pressure (corrected for room T): 14.67 psia

vacuum pressure: __________ psia -5.868 volts

RAW EQUILIBRIUM PRESSURE DATA

STEP	p_1 (volts)	p_2 (volts)	COMMENTS
1	-5.030	-5.700	
2	-4.360	-5.420	
3	-3.560	-5.010	
4	-2.760	-4.510	
5	-1.020	-3.710	
6	0.250	-2.820	
7	2.250	-1.690	
8	4.070	-0.600	
			beginning of desorption
9	-1.850	-0.860	
10	-3.020	-1.320	
11	-4.260	-1.980	
12	-5.500	-2.740	
13	-5.780	-3.410	
14	-5.790	-3.920	
15	-5.790	-4.330	

DATA CHECKLIST

DATE ____________

SAMPLE NAME Montiverdi 2, Sample #3 RUN NUMBER HT1

SAMPLE WEIGHT 95.6 gm

COMMENTS

CIRCLE TYPE OF EXPERIMENT AND MEDIUM USED (E.G. ADSORBATE)

dead volume low temperature [✓ high temperature]

helium nitrogen [✓ steam] natural gas ________

other medium ____________

TEMPERATURE OF EXPERIMENT 180 [✓ C] or K

DEAD VOLUME (if already known) 61.478 cc

SAMPLING BOTTLE VOLUME (circle one)

low T system 45.07 cc

high T system: Number 1 [✓ 158.62 cc] OR Number 2 513.30 cc

other __________ cc

PRESSURE TRANSDUCER CALIBRATION INFORMATION:

plate differential: 25 psi 100 psi [✓ 500 psi] other ______

atmospheric pressure (corrected for room T): 14.692 psia

vacuum pressure: __________ psia -0.294 volts

RAW EQUILIBRIUM PRESSURE DATA

STEP	p_1 (volts)	p_2 (volts)	COMMENTS
1	0.513	0. 322	average equilibrium time
2	0. 894	0. 708	about 20-24 hours
3	1.403	1.200	
4	2.082	1. 828	
5	2.483	2.276	
6	2.657	2.648'	
			beginning of desorption
7	1. 970	2.450	
8	1.501	1.864	
9	1.006	1.282	
10	0.499	0.748	
11	-0.013	0.242	

9.3 APPENDIX C -- TABLES OF ADSORPTION RESULTS

Appendix C presents the tables of adsorption results from all fifteen experimental runs, starting with those conducted at low temperatures. Each table lists the pressure data gathered during the experiment as well as the values of p n_{gas}, and n_{ads} obtained from the analysis. The interpretation of these results is found in Section 5.2 as is a discussion on the issue of negative adsorption values. The tables also include the parameters required to construct adsorption isotherms: the relative vapor pressure, p_2/p_0, and the amount of adsorption or desorption per unit mass of the sample. Theoretically, the values of p_2/p_0 should be less than unity. Values exceeding unity are due to small instrument errors.

TABLE C.1 Nitrogen Run 1 at -196°C on Sample #2 of Berea Sandstone

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Step	Pressure Data			Amount of Nitrogen in DV			
	p_2/p_0	p_1	p_2	n_{tot}*	n_{gas}	n_{ads}*	n_{ads}/m_r*
	(dimensionless)		(psia)	(µmoles)	(µmoles)	(µmoles)	(µmoles/gm)
1	0.06122	1.5825	0.9000	347.259	468.634	-121.374	-0.799
2	0.11378	2.4625	1.6725	749.216	870.877	-121.662	-0.801
3	0.16803	3.2975	2.4700	1170.252	1286.139	-115.887	-0.763
4	0.32058	5.1475	4.7125	1391.582	2453.817	-1062.235	-6.995
5	0.40714	7.2850	5.9850	2053.029	3116.413	-1063.385	-7.002
6	0.48180	8.2125	7.0825	2627.978	3687.886	-1059.907	-6.979
7	0.55646	9.3025	8.1800	3199.112	4259.358	-1060.246	-6.982
8	0.62942	10.3475	9.2525	3756.254	4817.813	-1061.560	-6.990
9	0.77483	13.5675	11.3900	4864.177	5930.818	-1066.642	-7.024
10	0.88690	14.6700	13.0375	5694.801	6788.678	-1093.876	-7.203
11	0.83707	11.5200	12.3050	5295.389	6407.262	-1111.873	-7.321
12	0.76582	10.1975	11.2575	4756.056	5861.825	-1105.769	-7.281
13	0.69235	9.0800	10.1775	4197.642	5299.465	-1101.823	-7.255
14	0.60867	7.7125	8.9475	3569.268	4658.999	-1089.731	-7.176
15	0.53180	6.6650	7.8175	2982.870	4070.603	-1087.733	-7.163
16	0.43673	5.0050	6.4200	2262.911	3342.919	-1080.009	-7.112
17	0.35442	3.9800	5.2100	1637.080	2712.868	-1075.787	-7.084
18	0.27228	2.8075	4.0025	1029.058	2084.118	-1055.059	-6.947
19	0.19915	1.8125	2.9275	461.741	1524.361	-1062.620	-6.997
20	0.13197	0.9275	1.9400	-53.425	1010.166	-1063.590	-7.004

* Negative values are physically unrealistic. For further discussion, see Section 5.2.

TABLE C.2 Nitrogen Run 2 at -196°C on Sample #2 of Berea Sandstone

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Step	Pressure Data			Amount of Nitrogen in DV			
	p_2/p_0	p_1	p_2	n_{tot}	n_{gas}	n_{ads}	n_{ads} / m_r
	(dimensionless)	(psia)	(psia)	(μmoles)	moles)	(μmoles)	(μmoles/gm)
1	0.00306	2.9575	0.0450	1481.895	23.432	1458.463	9.604
2	0.02109	5.1050	0.3100	3921.615	161.418	3760.197	24.760
3	0.07279	5.6250	1.0700	6239.223	557.153	5682.069	37.415
4	0.17143	9.8075	2.5200	9947.140	1312.174	8634.966	56.859
5	0.27364	11.9875	4.0225	13999.772	2094.532	11905.241	78.394
6	0.37534	13.3600	5.5175	17990.076	2872.984	15117.092	99.543
7	0.48078	15.4425	7.0675	22251.318	3680.075	18571.244	122.288
8	0.59269	18.0650	8.7125	27009.918	4536.633	22473.285	147.982
9	0.69830	20.7575	10.2650	32348.557	5345.026	27003.531	177.813
10	0.78759	22.3750	11.5775	37842.379	6028.450	31813.930	209.488
11	0.86088	24.5800	12.6550	43909.879	6589.509	37320.371	245.747
12	1.08724	26.4825	15.9825	49252.332	8322.151	40930.180	269.517

TABLE C.3 Nitrogen Run 4 at -196°C on Sample #2 of Berea Sandstone

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
	Pressure Data			Amount of Nitrogen in DV			
Step	p_2/p_0	p_1	p_2	n_{tot}	n_{gas}	n_{ads}	$n_{ads}\ /\ m_r$
	(dimensionless)	(psia)	(psia)	moles)	moles)	(µmoles)	(µmoles/gm)
1	0.00762	8.0195	0.1120	4023.376	58.319	3965.058	26.109
2	0.12735	12.2020	1.8720	9279.333	974.758	8304.575	54.684
3	0.27803	15.6795	4.01870	15177.656	2128.117	13049.539	85.929
4	0.43279	18.4195	6.3620	21312.574	3312.719	17999.855	118.525
5	0.59486	22.2070	8.7445	28162.363	4553.296	23609.068	155.461
6	0.74384	25.6820	10.9345	35665.969	5693.638	29972.332	197.362
7	0.88109	32.9895	12.9520	45861.152	6744.158	39116.996	257.577
8	0.96017	35.8270	14.1145	56908.582	7349.476	49559.105	326.337
9	0.91765	4.4720	13.4895	52320.434	7024.036	45296.398	298.268
10	0.85269	1.8470	12.5345	46882.578	6526.764	40355.816	265.735
11	0.77156	0.0495	11.3420	41136.895	5905.824	35231.070	231.989
12	0.68602	0.0370	10.0845	36024.676	5251.039	30773.637	202.638
13	0.59673	0.0070	8.7720	31564.998	4567.615	26997.383	177.772
14	0.51357	0.0070	7.5495	27727.336	3931.055	23796.281	156.694
15	0.45456	0.0070	6.6320	24331.063	3479.344	20851.719	137.304
16	0.38500	0.0020	5.61595	21452.498	2946.924	18505.574	121.855
17	0.32497	0.0020	4.7770	19022.953	2487.403	16535.551	108.883
18	0.27259	0.0020	4.0070	16985.189	2086.461	14898.729	98.105

TABLE C.4 Nitrogen Run 1 at -196°C on Sample #1 from The Geysers

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
	Pressure Data			Amount of Nitrogen in DV			
itep	p_2/p_0	p_1	p_2	n_{tot}	n_{gas}	n_{ads}	n_{ads}/m_r
	[dimensionless)	(psia)	(psia)	(µmoles)	@moles)	(µmoles)	(µmoles/gm)
1	0.03588	1.9200	0.5275	708.5 11	222.646	485.866	2.459
2	0.0823 1	3.0275	12100	1633.265	510.713	1122.552	5.682
3	0.15068	4.8575	22 150	2977.782	934.900	2042.882	10.341
4	0.22534	6.2400	3.3125	4467.309	1398.130	3069.180	15.536
5	0.30646	7.6950	4.5050	6090.397	1901.456	4188.941	21.204
6	0.39320	9.1975	5.7800	7829.239	2439.604	5389.635	27.282
7	0.47466	10.2500	6.9775	9494.304	2945.04 1	6549.263	33.152
8	0.57500	12.3975	8.4525	11501.540	3567.604	7933.936	40.162
9	0.6823 1	14.2700	10.0300	13658.874	4233.431	9425.443	47.712
10	0.77483	15.2900	11.3900	15643.214	4807.455	10835.759	54.851
11	0.87398	17.0850	12.8475	17799.275	5422.632	12376.644	62.65 1
12	0.94932	17.7100	13.9550	19709.838	5890.082	13819.756	69.956
13	0.99898	18.8025	14.6850	21804.844	6198.198	15606.646	79.001
14	0.96599	11.5450	14.2000	20453.967	5993.491	14460.477	73.199
15	0.90255	9.7825	13.2675	18680.781	5599.904	13080.877	66.216
16	0.79830	7.1475	11.7350	16346.638	4953.072	11393.566	57.674
17	0.66020	4.0400	9.7050	13464.257	4096.255	9368.002	47.421
18	0.5 1820	1.9200	7.6 175	10565.340	3215.170	7350.170	37.207
19	0.37840	0.0025	5.5625	7736.383	2347.802	5388.581	27.277
20	0.27619	0.0150	4.0600	5678.267	1713.632	3964.635	20.069
21	0.20153	0.0175	2.9625	4 179.835	1250.403	2929.433	14.829
22	0.14694	0.0250	2.1600	3093.537	911.686	2181.851	11.045
23	0.10748	0.0125	1.5800	2295.985	666.88 1	1629.103	8.247

TABLE C.5 Nitrogen Run 1 at -196°C on Sample #2 from Montiverdi Well #2

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
	Pressure Data			Amount of Nitrogen in DV			
Step	p_2/p_0	p_1	p_2	n_{tot}	n_{gas}	n_{ads}	n_{ads} / m_r
	(dimensionless)	(psia)	(psia)	(µmoles)	(poles)	(µmoles)	(µmoles/gm)
1	0.07238	5.1965	1.0640	2102.637	511.111	1591.526	8.927
2	0.19347	8.8440	2.8440	5155.468	1366.165	3789.302	21255
3	0.31881	10.8965	4.6865	8315.147	2251.243	6063.905	34.014
4	0.39517	9.6165	5.8090	10252.423	2790.455	7461.968	41.856
5	0.47034	10.6465	6.9140	12151.538	3321.261	8830.276	49.531
6	0.54585	11.8915	8.0240	14119.342	3854.469	10264.872	57.579
7	0.62238	12.9865	9.1490	16071.882	4394.883	11676.999	65.500
8	0.70452	14.6740	10.3565	18268.648	4974.927	13293.722	74.568
9	0.80146	16.9865	11.7815	20916.979	5659.451	15257.528	85.584
10	0.91286	20.2415	13.4190	24388.301	6446.053	17942.248	100.643
11	0.98701	22.1290	14.5090	28265.3%	6969.653	21295.744	119.454
12	0.93990	9.2340	13.8165	25933.797	6636.999	19296.799	108.241
13	0.82612	4.8440	12.1440	22219.520	5833.584	16385.936	91.913
14	0.64942	0.0515	9.5465	17388.414	4585.829	12802.585	71.813
15	0.50503	0.0440	7.4240	13633.433	3566.249	10067.184	56.470
16	0.40112	0.0315	5.8965	10649.291	2832.488	7816.804	43.847
17	0.31201	0.0290	4.5865	8330.412	2203.206	6127.207	34.369
18	0.24143	0.0340	3.5490	6541.962	1704.825	4837.137	27.133
19	0.18735	0.0340	2.7540	5158.012	1322.932	3835.080	21.512
20	0.14500	0.0340	2.1315	4090.793	1023.904	3066.890	17203

TABLE C.6 Nitrogen Run 2 at -196°C on Sample #2 from Montiverdi Well #2

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Step	Pressure Data			Amount of Nitrogen in DV			
	p_2/p_0	p_1	p_2	n_{tot}	n_{gas}	n_{ads}	n_{ads} / m_r
	(dimensionless)	(psia)	(psia)	(µmoles)	moles)	(µmoles)	(µmoles/gm)
1	0.01327	0.9200	0.1950	368.884	93.672	275.212	1.544
2	0.04218	2.2950	0.6200	1221.132	297.828	923.304	5.179
3	0.07789	3.4200	1.1450	2378.664	550.021	1828.643	10.257
4	0.15272	6.1200	2.2450	4350.284	1078.425	3271.859	18.353
5	0.24796	8.5200	3.6450	6830.709	1750.940	5079.769	28.494
6	0.35340	10.3950	5.1950	9476.4%	2495.510	6980.987	39.158
7	0.46650	13.4450	6.8575	12828.250	3294.121	9534.130	53.480
8	0.60170	16.2950	8.8450	16618.848	4248.851	12369.997	69.387
9	0.76497	19.3200	11.2450	20727.449	5401.733	15325.716	85.966
10	0.93503	27.2950	13.7450	27621.758	6602.652	21019.105	117.902
11	0.77687	0.0200	11.4200	21821.379	5485.798	16335.581	91.631
12	0.61020	0.1200	8.9700	17318.453	4308.897	13009.556	72.974
13	0.48265	0.0200	7.0950	13718.657	3408.208	10310.449	57.834
14	0.37381	0.0200	5.4950	10932.949	2639.620	8293.329	46.520

TABLE C.7 Nitrogen Run 3 at -196°C on Sample #2 from Montiverdi Well #2

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Step	Pressure Data			Amount of Nitrogen in DV			
	p_2/p_0	p_1	p_2	n_{tot}	n_{gas}	n_{ads}	n_{ads} / m_r
	(dimensionless)	(psia)	@silk)	moles)	(µmoles)	(µmoles)	(µmoles/gm)
1	0.02857	2.0950	0.4200	852.249	201.754	650.494	3.649
2	0.07619	3.7700	1.1200	2200.582	538.012	1662.571	9.326
3	0.14592	5.7700	2.1450	4045.001	1030.388	3014.613	16.910
4	0.23095	7.7700	3.3950	6271.023	1630.848	4640.176	26.028
5	0.36701	12.1200	5.3950	9692.738	2591.583	7101.155	39.832
6	0.51837	15.2950	7.6200	13597.817	3660.401	9937.417	55.742
7	0.71054	20.2950	10.4450	18609.549	5017.439	13592.109	76.242
8	0.89592	24.8450	13.1700	24549.850	6326.441	18223.408	102.220
9	0.85170	10.0450	12.5200	23290.557	6014.202	17276.355	96.908
10	0.77347	7.1200	11.3700	21128.135	5461.779	15666.355	87.877
11	0.66122	4.0200	9.7200	18227.945	4669.173	13558.772	76.055
12	0.53197	0.9200	7.8200	14717.189	3756.475	10960.715	61.482
13	0.41803	0.2200	6.1450	11702.520	2951.859	8750.661	49.085
14	0.33129	0.1950	4.8700	9323.855	2339.390	6984.465	39.178
15	0.26156	0.1950	3.8450	7466.717	1847.013	5619.704	31.522

TABLE C.8 Steam Run 1 at 169°C on Sample #1 of Berea Sandstone

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
	Pressure Data			Amount of Nitrogen in DV			
Step	p_2/p_0	p_1	p_2	n_{tot}*	n_{gas}	n_{ads}*	n_{ads} / m_r*
	[dimensionless)	(psia)	(psis)	moles)	moles)	(µmoles)	(µmoles/gm)
1	0.21226	25.9040	22.6540	994.998	1988.552	-993.553	-8.419
2	0.30549	36.1540	32.6040	2093.675	2876.735	-783.060	-6.635
3	0.39450	45.7040	42.1040	3219.691	3733.74 1	-514.050	-4.356
4	0.48960	56.1040	52.2540	4438.274	4659.569	-221.294	-1.875
5	0.59220	67.5040	63.2040	5817.703	5670.774	146.929	1.245
6	0.68356	76.9040	72.9540	7100.115	6582.569	517.546	4.385
7	0.78006	87.4540	83.2540	8482.271	7558.089	924.182	7.831
8	0.87095	97.2540	92.9540	9916.054	8488.919	1427.135	12.092
9	0.95106	105.6540	101.5040	11316.257	9319.632	1996.625	169 18
10 .	1.04757	117.1040	111.8040	13132.761	10333.740	2799.021	23.716
11	1.247 14	139.1040	133.1040	15258.429	12480.472	2777.957	23.538
12	1.13002	105.6040	120.6040	10127.246	11212.285	-1085.039	-9.194
13	0.96746	91.1040	103.2540	6064.233	9490.884	-3426.65 1	-29.034
14	0.83253	81.2540	88.8540	3564.151	8094.000	-4529.849	-38.382
15	0.65029	60.7040	69.4040	774.201	6249.302	-5475.101	-46.391
16	0.52755	50.6040	56.3040	-1028.406	5032.041	-6060.447	-51.351
17	0.42308	40.5540	45.1540	-2465.501	4010.817	-6476.318	-54.875
18	0.32657	30.6540	34.8540	-3763.047	3078.901	-6841.948	-57.973
19	023 194	20.7040	24.7540	-5000.955	2175.227	-7176.182	-60.805
20	0.18977	18.2540	20.2540	-5610.062	1775.709	-7385.771	-62.58 1

* Negative values are physically unrealistic. For further discussion, see Section **5.2.**

TABLE C.9 Steam Run 2 at 207°C on Sample #1 of Berea Sandstone

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
	Pressure Data			Amount of Nitrogen in DV			
itep	p_2/p_0	p_1	p_2	n_{tot}*	n_{gas}	n_{ads}*	n_{ads} / m_r*
	(:dimensionless)	(psia)	(psia)	moles)	(µmoles)	(µmoles)	(µmoles/gm)
1	0.08770	28.4750	22.8250	1574.716	1830.192	-255.476	-2.165
2	0.14783	43.9250	38.4750	3110.67	3101.945	8.732	0.074
3	0.20738	58.9750	53.9750	4535.869	4375.786	160.083	1.356
4	0.26348	73.0250	68.5750	5818.333	5589288	229.045	1.941
5	0.31266	85.475	81.3750	7011.842	6664.563	347.279	2.943
6	0.37528	103.0750	97.6750	8605.901	8050.005	555.896	4.710
7	0.44502	121.1750	115.8250	10210.042	9615.114	594.928	5.041
8	0.51264	139.2250	133.4250	11977.239	11156.704	820.535	6.953
9	0.60697	167.1250	157.9750	14835.479	13349.114	1486.364	12.594
10	0.68784	187.4250	179.0250	17514.506	15270.854	2243.652	19.011
11	0.77237	210.9250	201.0250	20748.832	17323.926	3424.906	29.020
12	0.91088	240.5750	237.0750	21935.451	20796.021	1139.430	9.655
13	0.67459	105.9750	175.5750	628.267	14953.111	-14324.844	-121.376
14	0.44656	92.0750	116.2250	-6523.989	9649.884	-16173.873	-137.043
15	0.34512	80.4750	89.8250	-9249.594	7380.472	-16630.066	-140.909
16	0.29402	71.8250	76.5250	-10607.702	6255.853	-16863.555	-142.887
17	0.25118	61.4750	65.3750	-11725.251	5322.151	-17047.402	-144.445
18	0.21103	51.3750	54.9250	-12734.607	4454.337	-17188.945	-145.644
19	0.17184	41.3250	44.7250	-13694.097	3613.843	-17307.939	-146.653
20	0.13304	31.2750	34.6250	-14632.617	2787.769	-17420.387	-147.605
21	0.09519	21.3750	24.7750	-15578.524	1987.886	-17566.410	-148.843
22	0.06368	13.4250	16.5750	-16449.994	1326.201	-17776.195	-150.620

* Negative values are physically unrealistic. **For further** discussion, see Section **5.2.**

TABLE C.10 Steam Run 3 at 150% on Sample #1 on Berea Sandstone

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
	Pressure Data			Amount of Nitrogen in DV			
Step	p_2/p_0	p_1	p_2	n_{tot}*	n_{gas}	n_{ads}*	n_{ads}/m_r*
	(dimensionless)	(psia)	(psia)	moles)	(poles)	(poles)	(µmoles/gm)
1	0.25662	20.0100	17.7100	731.081	1615.765	-884.684	-7.4%
2	0.34356	26.2600	23.7100	1547.937	2171.148	-623.211	-5.281
3	0.44934	33.8600	31.0100	2469.813	2852.635	-382.822	-3.244
4	0.55005	40.8100	37.9600	3400.368	3507.569	-107.201	-0.908
5	0.65220	48.2600	45.0100	4472.294	4178.286	294.008	2.491
6	0.75291	55.3600	51.9600	5605.080	4846.024	759.056	6.432
7	0.85217	62.4100	58.8100	6816.937	5510.771	1306.166	11.067
8	0.95070	69.3100	65.6100	8075.583	6177.434	1898.149	16.083
9	1.06373	78.1100	73.4100	9695.554	6950.803	2744.750	23.257
10	1.14270	79.6100	78.8600	9955.521	7496.890	2458.630	20.832
11	1.09850	73.4600	75.8100	9147.005	7190.690	1956.315	16.576
12	1.00287	64.7100	69.2100	7617.40	6533.199	1084.204	9.187
13	0.88042	55.5100	60.7600	5856.647	5701.245	155.402	1.317
14	0.78769	50.7100	54.3600	4642.559	5078.167	-435.608	-3.691
15	0.68408	43.6100	472100	3457.245	4388.942	-931.697	-7.894
16	0.58482	36.7100	40.3600	2266.864	3735.166	-1468.302	-12.441
17	0.47470	29.7100	32.7600	1281.860	3016.974	-1735.114	-14.702
18	0.36820	21.6100	25.4100	66.876	2329.277	-2262.400	-19.170
19	0.26242	14.7100	18.1100	-1010.572	1652.661	-2663.233	-22.566

* **Negative** values are physically unrealistic. **For** further discussion, see Section **5.2.**

TABLE C.11 Steam Run 1 at 167.4°C on Sample #2 of Berea Sandstone

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Step	Pressure Data			Amount of Nitrogen in DV			
	p_2/p_0	p_1	p_2	n_{tot}*	n_{gas}	n_{ads}*	n_{ads}/m_r*
	(dimensionless)	(psia)	(psis)	(µmoles)	(µmoles)	(µmoles)	(µmoles/gm)
1	0.20360	25.2440	21.9440	1008.562	1925.365	-916.803	-6.037
2	0.32793	40.7940	35.3440	2700.303	3122.632	-422.329	-2.781
3	0.45365	53.8940	48.8940	4275.915	4351.244	-75.329	-0.496
4	0.53669	61.1940	57.8440	5341.717	5173.250	168.467	1.109
5	0.60396	68.7440	65.0940	6513.426	5845.543	667.883	4.398
6	0.68468	78.3940	73.7940	8007.143	6660.20	1346.939	8.869
7	0.76030	86.0940	81.9440	9368.590	7431.508	1937.082	12.755
8	0.83452	94.9440	89.9440	11027.381	8196.604	2830.776	18.640
9	0.91571	105.4940	98.6940	13313.490	9042.876	4270.614	28.121
10	1.00339	115.2440	108.1440	15733.317	9968.430	5764.888	37.961
11	0.95097	94.9440	102.4940	13206.944	9413.580	3793.364	24.979
12	0.87164	86.2940	93.9440	10676.896	8582.223	2094.674	13.793
13	0.74963	72.0440	80.7940	7834.371	7322.184	512.188	3.373
14	0.60906	57.0940	65.6440	5108.106	5896.786	-788.680	-5.193
15	0.46571	42.7440	50.1940	2773.669	4470.111	-1696.442	-11.171
16	0.31309	26.4940	33.7440	542.528	2978.769	-2436.241	-16.042
17	0.20128	16.1940	21.6940	-1130.337	1903.18	-3033.526	-19.975

* Negative values are physically unrealistic. **For** further discussion, **see** Section **5.2.**

TABLE C.12 Steam Run 1 at 153°C on Sample #1 from The Geysers

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
	Pressure Data			Amount of Nitrogen in DV			
itep	p_2/p_0 (dimensionless)	p_1 (psia)	p_2 (psia)	n_{tot} (μmoles)	n_{gas} (μmoles)	n_{ads}* (μmoles)	n_{ads}/m_r* (μmoles/gm)
1	0.26218	21.1460	19.5960	489.749	1441.360	-951.610	-4.817
2	0.33777	27.5460	25.2460	1221.879	1863.201	-641.322	-3.246
3	0.42272	34.1960	31.5960	2056.331	2340.850	-284.519	-1.440
4	0.50233	40.9960	37.5460	3172.800	2791.931	380.869	1.928
5	0.57859	47.4460	43.2460	4543.058	3227.363	1315.695	6.660
6	0.66221	54.2960	49.4960	6123.22	3708.656	2414.565	12.223
7	0.85888	70.8960	64.1960	8379.224	4857.350	3521.874	17.828
8	1.01207	77.9960	75.6460	9181.742	5769.360	3412.382	17.274
9	0.95789	70.6460	71.5960	8860.143	5444.967	3415.175	17.288
10	0.95120	69.5460	71.0960	8336.063	5405.058	2931.005	14.837
11	0.85888	62.1460	64.1960	7650.250	4857.350	2792.900	14.138
12	0.76857	55.2960	57.4460	6938.003	4326.899	2611.104	13.217
13	0.68295	48.2960	51.0460	6035.494	3828.655	2206.839	11.171
14	0.57658	39.7460	43.0960	4948.295	3215.862	1732.434	8.770
15	0.46955	31.0960	35.0960	3664.190	2605.771	1058.419	5.358
16	0.36319	22.6960	27.1460	2250.265	2005.721	244.544	1.238
17	0.27020	15.0960	20.1960	644.111	1486.019	-841.908	-4.262

* Negative values are physically unrealistic. For further discussion, see Section 5.2.

TABLE C.13 Steam Run 2 at 200°C on Sample #1 from The Geysers

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
	Pressure Data			Amount of Nitrogen in DV			
itep	p_2/p_0 (dimensionless)	p_1 (psia)	p_2 (psia)	n_{tot}* (μmoles)	n_{gas} (poles)	n_{ads}* (poles)	n_{ads}/m_r* (μmoles/gm)
1	0.07003	24.8412	15.7812	2555.259	1039.638	1515.620	7.672
2	0.20329	60.4362	45.8112	6786.004	3051.913	3734.091	18.902
3	0.30132	77.6012	67.9012	9637.902	4562.732	5075.170	25.691
4	0.37132	99.4812	83.6762	14361.588	5658.791	8702.798	44.054
5	0.50589	128.7512	114.0012	18893.643	7809.281	11084.362	56.109
6	0.60196	144.3012	135.6512	21600.750	9382.540	12218.210	61.849
7	0.69581	167.1512	156.8012	24915.115	10952.791	13962.324	70.677
8	0.79522	188.2512	179.2012	27883.555	12654.697	15228.857	77.089
9	0.88641	204.6012	199.7512	29508.789	14254.031	15254.758	77.220
10	0.90305	207.8012	203.5012	30955.701	14550.030	16405.67	83.046
11	0.86710	184.1012	195.4012	27223.619	13912.309	13311.311	67.382
12	0.70868	141.1012	159.7012	21339.600	11170.810	10168.790	51.475
13	0.56557	113,9512	127.4512	17194.340	8782.745	8411.595	42.580
14	0.47815	98.2512	107.7512	14325.571	7361.157	6964.414	35.254
15	0.35745	68.5012	80.5512	10777.375	5440.482	5336.893	27.015
16	0.24385	41.4512	54.9512	6887.440	3673.747	3213.693	16.268
17	0.16841	24.3512	37.9512	3020.331	2520.747	499.584	2.529
18	0.10140	11.4512	22.8512	-187.415	1509.288	-1696.704	-8.589
19	0.07345	8.8012	16.5512	-2360.976	1090.669	-3451.645	-17.472

* Negative values are physically unrealistic. For further discussion, see Section 5.2.

TABLE C.14 Steam Run 3 at 180°C on Sample #1 from The Geysers

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Step	Pressure Data			Amount of Nitrogen in DV			
	p_2/p_0	p_1	p_2	n_{tot}	n_{gas}	n_{ads}*	n_{ads} / m_r*
	(dimensionless)	(psia)	(psia)	moles)	moles)	(µmoles)	(µmoles/gm)
1	0.18271	40.4550	26.5550	4156.388	1837.542	2318.846	11.738
2	0.30965	61.6050	45.0050	9216.763	3140.759	6076.004	30.757
3	0.48888	90.7050	71.0550	15383.369	5021.665	10361.704	52.451
4	0.67947	114.1550	98.7550	20360.059	7079.964	13280.095	67.224
5	0.95641	141.4050	139.0050	21169.363	10193.699	10975.664	55.559
6	0.87246	114.3050	126.8050	17059.631	9233.238	7826.393	39.617
7	0.71834	89.6050	104.4050	12329.806	7507.833	4821.973	24.409
8	0.54943	64.9550	79.8550	7696.822	5668.724	2028.098	10.266
9	0.37433	40.1050	54.4050	3363.801	3813.736	-449.935	-2278

* Negative values are physically unrealistic. **For** further discussion, see Section **5.2.**

TABLE C.15 Steam Run 1 at 180°C on Sample #3 from Montiverdi Well #2

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Step	Pressure Data			Amount of Nitrogen in DV			
	p_2/p_0	p_1	p_2	n_{tot}^*	n_{gas}	n_{ads}^*	n_{ads} / m_r^*
	(dimensionless)	(psia)	(psia)	(poles)	@moles)	@moles)	(µmoles/gm)
1	0.21 186	40.3420	30.7920	2861.171	3510.334	-649.164	-6.790
2	0.34465	59.3920	50.0920	5700.209	5761.999	-61.790	-0.646
3	0.51391	84.8420	74.6920	8881.432	8695.757	185.675	1.942
4	0.72995	118.7920	106.0920	13015.294	12556.296	458.998	4.801
5	0.88407	138.8420	128.4920	16475.582	15399.341	1076.24 1	11.258
6	1.01205	147.5420	147,0920	16628.785	17822.727	-1 193.941	-12.489
7	0.94393	113.1920	137.1920	8691.073	16525.457	-7834.384	-81.950
8	0.74234	89.7420	107,8920	2878.266	12781.881	-9903.615	-103.594
9	0.54212	64.9920	78.7920	-1410.305	9192.158	-10602.464	-110.904
10	0.35841	39.6420	52.0920	-5 177.585	5997.766	-11175.352	-116.897
11	0.18434	14.0420	26.7920	-8944.318	3048.807	-11993.126	-125.451

* Negative values are physically unrealistic. For further discussion, see Section 5.2.

9.4 APPENDIX D -- TABLES OF BET RESULTS

The BET analysis is used primarily to determine the amount **of** monolayer adsorption and the specific surface area. Appendix C presents the analysis results, and Section **53** their interpretation. Each table of Appendix **D** separates the information pertaining to adsorption from that pertaining to desorption, though desorption is sometimes absent due to a lack **of data** within the proper range ($0.05 \ c \ \beta \ c \ 0.35$ where β is the relative vapor pressure). The two parameters used in the straight line form **of** the BET equation *are* given **as** well. **as** the "C" factor, the monolayer adsorption, the weight **of** the sample, the surface area and the specific surface area.

Because negative adsorption values have no physical significance, the first nitrogen test conducted on sample #2 of Berea and all the steam tests except HT2 (high temperature run **2)** and **HT3** (high temperature run ***3)*** using sample #1 from The Geysers **are** excluded from this appendix. The desorption section **of HT2** seen in Table **D.7** shows the consequences of analyzing negative adsorption values. The *irregularities* present in the analysis of HT3 (Table **D.8)** result **from** the shape **of** the BET function itself. Though unusual, a similar phenomenon was recorded by Hsieh (1980) when unconsolidated silica sand was tested.

TABLE D.l BET Results of Nitrogen Run 1 at -1%°C on Sample 2 from Berea Sandstone

*** Analysis **Based** on Adsorption ***

Rel. **Pressure, β**	**the** factor β/{X(1-β)} in 1/mole
0.0727891	13.8160
0.1714286	23.9603
0.2736395	31.6438

The value of "C" factor in **BET analysis is**	12.3224	1/micromoles
The monolayer adsorption **is**	10361.4181	micromoles
The weight **of** the sample **is**	151.8650	grams
The **total** surface area **is**	1010.9906	**square** meters
The specific surface area **is**	6.6572	square **meters/gram**

TABLE D.2 BET Results of Nitrogen Run 4 at -1%°C on Sample #2 from Berea Sandstone

*** Analysis **Based** on Adsorption ***

Rel. Pressure, β	the factor β/{X(1-β)} in 1/mole
0.1273469	17.5723
0.2780272	29.5101

The **value of** ***"C"*** factor in **BET** analysis is 11.5873 1/micromoles

The monolayer adsorption **is** 11532.7994 micromoles

The weight of the sample **is** 151.8650 **grams**

The **total** surface **area is** 1125.2853 **square** meters

The **specific** surface **area** is 7.4098 square meters/gram

*** Analysis **Based on** Desorption ***

Rel. Pressure, β	the factor β/{X(1-β)} in 1/mole
0.3249660	29.1 134
0.2725850	25.1519

The value **of "C"** factor in **BET** analysis is 17.6719 1/micromoles

The monolayer adsorption is 12474.1029 micromoles

The weight of the sample **is** 151.8650 *grams*

The **total** surface **area is** 1217.1307 **square** meters

The **specific** surface **area is** 8.0146 square meters/gram

TABLE D.3 BET Results of Nitrogen Run 1 at -196°C on Sample #1 from The Geysers

*** Analysis Based on Adsorption ***

Rel. Pressure, β	the factor β/{X(1-β)} in 1/mole
0.0823129	79.9037
0.1506803	86.8444
0.2253401	94.7775
0.3064626	105.4881

The value of "C" factor in BET analysis is	2.6224 1/micromoles
The monolayer adsorption is	5445.2220 micromoles
The weight of the sample is	197.5500 grams
The total surface area is	531.3045 square meters
The specific surface area is	2.6895 square meters/gram

*** Analysis Based on Desorption ***

Rel. Pressure, β	the factor β/{X(1-β)} in 1/mole
0.2761905	96.2457
0.2015306	86.1587
0.1469388	78.9462
0.1074830	73.9222

The value of "C" factor in BET analysis is	32250 1/micromoles
The monolayer adsorption is	5206.0115 micromoles
The weight of the sample is	197.5500 grams
The total surface area is	507.9641 square meters
The specific surface area is	2.5713 square meters/gram

TABLE D.4 BET Results of Nitrogen Run 1 at -196 °C on Sample #2 from Montiverdi Well 2

*** Analysis **Based** on Adsorption ***

Rel. Pressure, β	the factor β/{X(1-β)} in 1/mole
0.0723810	49.0276
0.1934694	63.3041
0.3188095	77.1810

The value of "C" factor in BET analysis is	3.7921 1/micromoles
The monolayer adsorption is	6446.0050 micromoles
The weight of the sample is	178.2760 grams
The total surface area is	628.9535 square meters
The specific surface area is	3.5280 square meters/gram

*** Analysis **Based** on Desorption ***

Rel. Pressure, β	the factor β/{X(1-β)} in 1/mole
0.3120068	74.0146
0.2414286	65.7967
0.1873469	60.1128
0.1450000	55.2973

The value of "C" factor in BET analysis is	3.8518 1/micromoles
The monolayer adsorption is	6638.4812 micromoles
The weight of the sample is	178.2760 grams
The total surface area is	647.7339 square meters
The specific surface area is	3.6333 square meters/gram

TABLE D.5 BET Results of Nitrogen Run 2 at -1%°C on Sample #2 from Montiverdi Well #2

*** Analysis Based on Adsorption ***

Rel. Pressure, β	the factor β/{X(1-β)} in 1/mole
0.0778912	46.1931
0.1527211	55.0907
0.2479592	64.9075

The value of "C" factor in BET analysis is	3.8958 1/micromoles
The monolayer adsorption is	6774.0261 micromoles
The weight of the sample is	178.2760 grams
The total surface area is	660.9594 *square* meters
The specific surface area is	3.7075 *square* meters/gram

TABLE D.6 BET Results of Nitrogen Run 3 at -196°C on Sample #2 from Montiverdi Well #2

*** Analysis Based on Adsorption ***

Rel. Pressure, β	the factor β/{X(1-β)} in 1/mole
0.0761905	49.6065
0.1459184	56.6734
0.2309524	64.7194

The value of "C" factor in BET analysis is	3.3077 1/micromoles
The monolayer adsorption is	7152.4423 micromoles
The weight of the sample is	178.2760 grams
The total surface area is	697.8824 square meters
The specific surface area is	***3.9146* square meters/gram**

*** Analysis Based on Desorption ***

Rel. Pressure, β	the factor β/{X(1-β)} in 1/mole
0.3312925	70.9320
0.2615646	63.0308

The value of "C" factor in BET analysis is	4.3935 1/micromoles
The monolayer adsorption is	6816.3462 micromoles
The weight of the sample is	178.2760 grams
The total surface area is	665.0886 square meters
The specific surface area is	3.7307 square meters/gram

TABLE D.7 BET Results of Steam Run 2 at 200°C on Sample #1 from The Geysers

*** Analysis Based on Adsorption ***

Rel. Pressure, β	the factor β/{X(1-β)} in 1/mole
0.0700300	49.6849
0.2032898	68.3330
0.3013155	84.9747

The value of "C" factor in BET analysis is	4.9360	
The monolayer adsorption is	5251.3935	micromoles
The weight of the sample is	197.5500	grams
The total surface area is	411.2543	square meters
The specific surface area is	2.0818	square meters/gram

*** Analysis Based on Desorption ***

Rel. Pressure, β	the factor β/{X(1-β)} in 1/mole
0.2438491	100.3479
0.1684106	405.3709
0.1014035	-66.5093
0.0734469	-22.9656

The value of "C" factor in BET analysis is	-13.4718	
The monolayer adsorption is	801.8721	micromoles
The weight of the sample is	197.5500	grams
The total surface area is	62.7973	square meters
The specific surface area is	0.3179	square meters/gram

TABLE D.8 BET Results of Steam Run 3 at 180 C on Sample #1 from The Geysers

*** Analysis Based on Adsorption ***

Rel. Pressure, β	the factor β/{X(1-β)} in 1/mole
0.1827081	96.4070
0.3096509	73.8219

The value of "C" factor in BET analysis is -0.3801 1/micromoles

The monolayer adsorption is -20407.3531 micromoles

The weight of the sample is 1975500 grams

The total surface area is -1575.9440 square meters

The specific surface area is -7.9774 square meters/gram