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Determination of the pore structure of porous materials using electrical conductance

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Determination of the pore structure of porous materials using electrical conductance

by

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INTRODUCTION

The pore-volume distribution of a porous solid as a function of pore size has become progressively more important in understanding chemical and physical behavior of porous materials. The purpose of this dissertation is to introduce a new method for determining pore size distributions and demonstrate the significance of this new methodology to the field of civil engineering materials. This method has been called conductometric phase transition porosimetry (CPTP).

The methodology combines the plastic ice model for solid-liquid phase transitions of pore water with relationships between electrical conductance and temperature, and conductance and pore structure. With measurements of the electrical conductance and the corresponding temperature of a material subjected to a cycle of capillary freezing and thawing, a pore size distribution is obtainable.

It is well-known that the liquid to solid and solid to liquid phase transitions of water in capillaries occurs at temperatures below $0^{o}C$, the normal melting point of bulk water. The plastic ice model gives a thermodynamic relationship between the effective pore radii and the temperatures at which these phase transitions occur. For the solid to liquid phase transition, the radius given by this relationship is the pore body radius, while for the liquid to solid transition it is the radius of the pore constriction or neck.

In addition, many porous materials consist of a nonconducting solid phase which has a void system consisting of randomly intersecting

capillaries of various sizes. If the material is saturated, the pore solution generally will exhibit electrolytic conductance which results from the mobility of ions in the pore solution. In CPTP, it is assumed that the conductance through the solid phase, including ice in frozen pores, is negligible when compared to the electrolytic conductance of the unfrozen pore solution. Thus, when the temperature of a mass of saturated porous material is lowered from $0^{o}C$, the pore solution will freeze and a decrease in conductance will be observed. Capillaries will begin to freeze with larger sizes freezing at higher temperatures in accordance with the plastic ice theory.

An automated Conductometric Phase Transition Porosimeter has been built and used to determine the pore size distribution of a porous Vycor glass sample and a comparative analysis of these results with those obtained by mercury porosimetry and phase transition porosimetry is presented.

In addition, since perhaps the greatest advantage this method of porosimetry has over other available methods is the ability to test much larger samples, example results obtained from the testing of 4-inch diameter by 4-inch high portland cement mortar and concrete cylinders are also presented. For the cement mortar tested, the pore size distribution obtained is compared with the pore size distribution obtained from mercury porosimetry.

The ability to evaluate the pore size distributions of heterogeneous conglomerate materials such as portland cement concrete should provide a

valuable new tool for investigating the physical and chemical behavior of these materials.

REVIEW OF LITERATURE AND THEORY

Pore Structure Analysis Methods

As stated in the introduction, the pore-volume distribution of a porous solid as a function of pore size has become progressively more important in understanding chemical and physical behavior of porous materials. In order to understand and predict the macrobehavior and properties of an engineering material, it is often necessary to investigate the microstructure of the material. For many porous engineering materials, including soil, concrete, stone and brick, the void space of the material greatly effects the mechanical properties of the material. Thus, an analysis of the microstructure of these materials must include the determination of the pore-size distribution to accurately predict their macro-behavior.

Two independent methods which have found large scale application exist for pore size distribution analysis. They are capillary condensation and mercury porosimetry.

Capillary condensation

The first, capillary condensation, is also often referred to as gas or vapor absorption. For this method, total pore volume and pore-size distributions are determined from gas-adsorption isotherms. The pore volume is the volume of condensed adsorbate at the saturation vapor pressure. When the pressure is reduced, the adsorbate evaporates from the larger capillaries first as dictated by the Kelvin equation. The Kelvin equation can be expressed as (Gregg and Sing, 1967):

$$RT \ln \left(\frac{p}{p_o}\right) = -\gamma V_L \left(\frac{1}{r_1} + \frac{1}{r_2}\right) \quad (1)$$

where p is the vapor pressure and p_o is the normal vapor pressure of the adsorbate. Also, T is the temperature (expressed in ^oK), γ and V_L are the surface tension and the molar volume of the adsorbate in liquid form, respectively, and R is the molar gas constant. The terms r_1 and r_2 are the principal radii of curvature of the meniscus. The effective radius or Kelvin radius, r_k, is defined to be equal to the pore radius, r_p, minus the film thickness of adsorbed vapor in the pores, t (see Figure 1a). Considering adsorption and desorption separately for an open-ended cylindrical pore as depicted in Figure 1a and 1b, and assuming the solid phase is completely wettable, then the appropriate values for r_1 and r_2 in equation 1 are r_k and ∞ during adsorption. During adsorption, for cylindrical pores with openings at only one end and for all cylindrical pores which remain filled with adsorbate during desorption, the appropriate values for r_1 and r_2 are r_k. From this, it can be shown that for a given volume, (p/p_o) during adsorption will be greater than it is for desorption. This difference is one source of the hysteresis loop that typically occurs between adsorption and desorption curves. Figure 2 illustrates typical adsorption and desorption isotherms.

Another source of hysteresis occurs in bottle-necked pores (see Figure 1c). With this type of pore, during adsorption condensation occurs in the neck of the pore first in accordance with the Kelvin equation and later in the body. However, during desorption evaporation in the pore body is inhibited by the presence of liquid in the pore neck

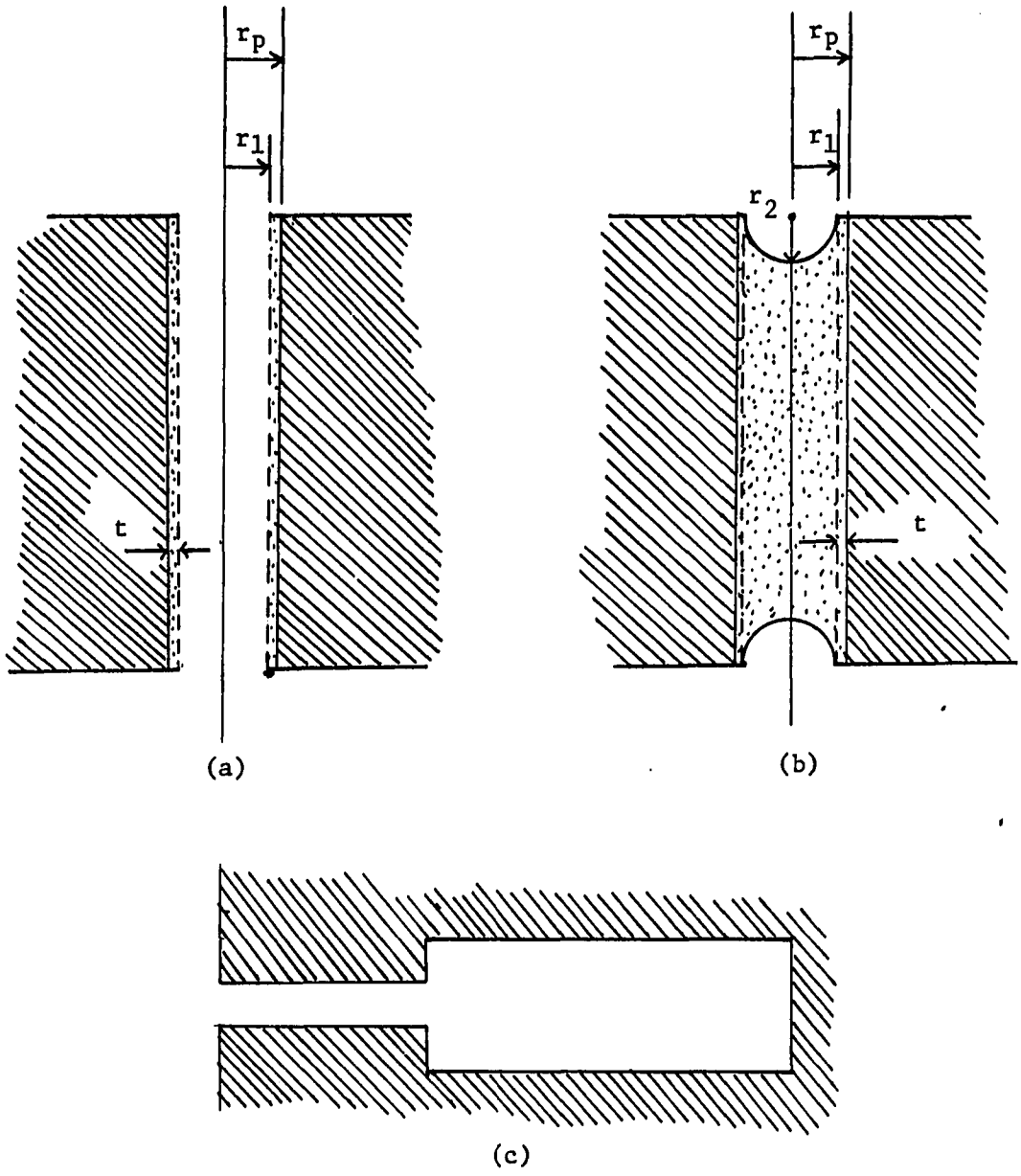


Figure 1. Illustration of capillary condensation: (a) adsorption in, and (b) desorption out of a cylindrical pore with two open ends and (c) example of a bottle-necked pore

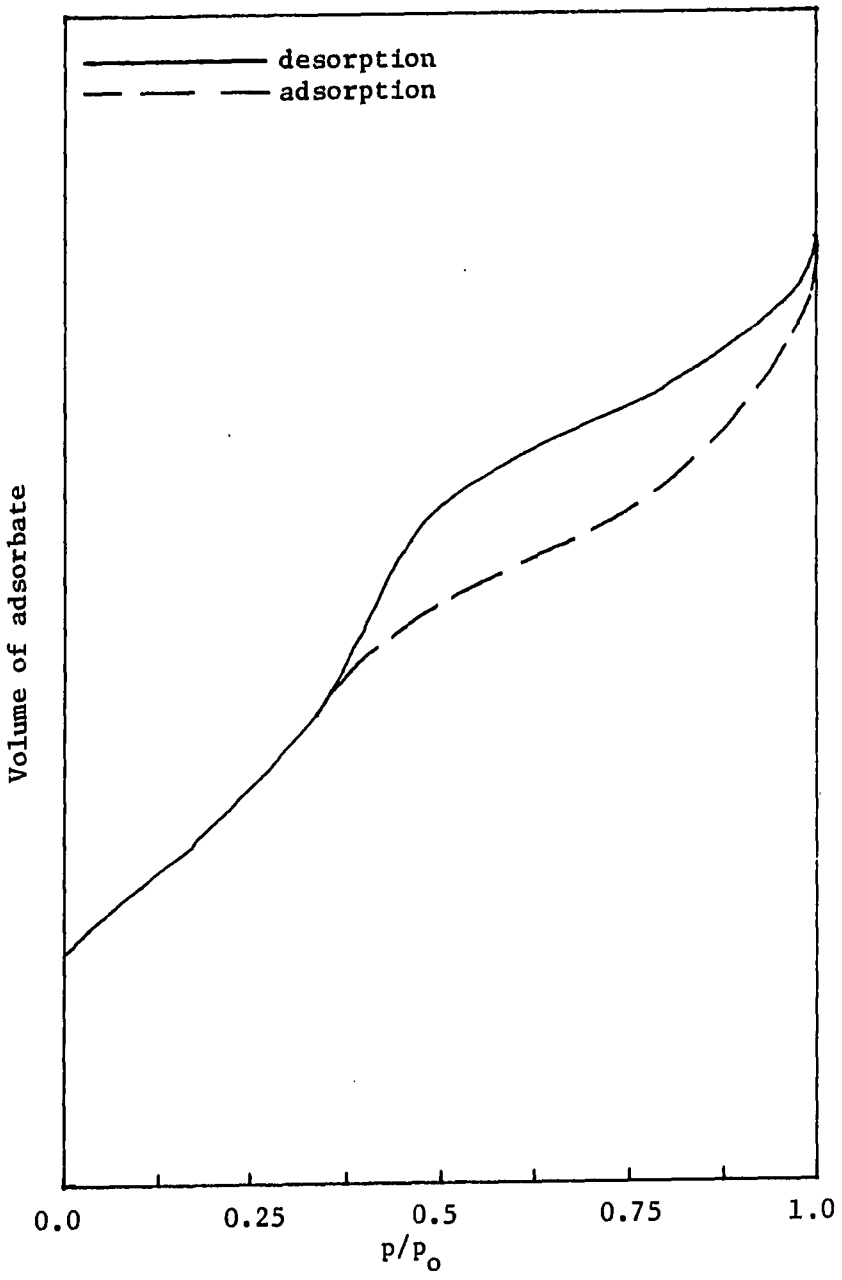


Figure 2. Example of adsorption and desorption isotherms

and will not occur until evaporation occurs in the neck in accordance with the Kelvin relationship. Due to diverse views over the explanation of the hysteresis loop for a particle pore system, the identification of the true equilibrium branch of sorption isotherms of porous solids has long been a subject of debate (O'Neil, 1985; Brunauer et al., 1967a; Brunauer, 1943).

Using the Kelvin equation, the value of r can be calculated for any given point on the isotherm. If the amount absorbed on the walls is neglected, then the volume at that point on the isotherm would be equal to the volume of all the pores which have radii up to and including r. A graph of volume versus radius could be made and the pore size distribution would result. When allowances for the thickness of the adsorbed film, t, are made, the relevant Kelvin radius is equal to r_p - t. Then, a determination of the adsorbed film thickness becomes necessary.

Wheeler (1951) first proposed the sorption isotherm method and considered the thickness to be equal to the monolayer capacity as calculated from BET theory (Brunauer et al., 1938). A method introduced by Barrett et al. (1951) and expanded by others (Pierce, 1953; Cranston and Inkley, 1957) has found universal acceptance and is known as the BJH method. The appropriate values for film thickness are still a matter of debate. This is evident in the work of O'Neil (1985), in which parameters affecting the calculation of pore volume distributions are investigated.

Brunauer and co-workers (Brunauer et al., 1967a; 1967b; Mikhail et

al., 1968a; 1968b; Hagymassy et al., 1969; Skalny et al., 1971) broadened the range of pore sizes measurable by adsorption isotherms and eliminated some uncertainties by introducing two new methods for the analysis of isotherm data. The micropore analysis method (also referred to as the MP method) allows the size distributions of pores with radii smaller than 16 angstroms to be determined. The second method, the corrected modeless method, introduced the concept of hydraulic radius which is defined as the volume of pores divided by the surface area of pores. If this method is used, no assumption need be made regarding pore shape. The Kelvin radius in the Kelvin equation is replaced with hydraulic radius and the adsorbed film thickness is based on the value of the BET parameter.

Enüstün (1981) points out that vapor pressures of various liquids in capillaries of a few micron in diameter are considerably smaller than those predicted by the Kelvin equation and states that these deviations cannot be attributed entirely to multilayer adsorption at the solid/vapor interface. He states that additional deviations are primarily due to increases in the liquid/vapor interfacial tension near the solid surface. This causes perturbations in the liquid/vapor meniscus such that the meniscus is not spherical but rather the radius of curvature is greater near the sides of a capillary than it is near the center of the capillary.

A researcher must evaluate the net effect of the aforementioned uncertainties for a particular pore system in order to identify the true equilibrium branch for that system if indeed one does exist. The desorption branch has found large-scale acceptance in the literature as

being representative of the size of the pore constrictions, while the adsorption branch has generally been assumed to represent the size of the pore bodies.

Currently, commercially available sorption instruments are capable of determining pore size distributions for pores ranging from smaller than 16 angstroms to approximately 5000 angstroms and costs range from about $25,000 for simple models to about $100,000 for top of the line models.

Mercury porosimetry

The second method, mercury injection porosimetry, was suggested by Washburn (1921) and later developed by Ritter and Drake (1945) and Drake (1949), and further developed by Winslow and Shapiro (1959). Since most materials are non-wettable by mercury, a minimum pressure, p, is required to force mercury through a constriction. The pressure required for intrusion into a circular pore of radius r is given by the Young and Laplace equation and may be written as (Allen, 1975):

$$p = \frac{2\gamma \cos \theta}{r} \qquad (2)$$

where γ is the surface tension of mercury and θ the angle of contact between the meniscus and the walls of the capillary.

The pore-volume distribution is determined by measuring the volume of mercury intruded into a sample as the pressure is increased. Measured values for pressure are converted to pore radii using equation 2.

As with sorption isotherms, the intrusion and extrusion branches of

mercury penetration tests do not follow the same path giving rise to a hysteresis loop. For mercury porosimetry, the hysteresis problem is further complicated because the hysteresis loop does not close for many materials due to entrapment of mercury. Figure 3 illustrates a typical mercury penetration cycle for which the hysteresis loop does not close.

Recently two theories have been advanced to explain the hysteresis and the entrapment of mercury after extrusion. Hill (1960) states that intrusion advances axially while extrusion advances radially. Assuming this premise to be correct, Hill shows that the extrusion pressure should be equal to half the intrusion pressure for a cylindrical pore. Hill also presents experimental evidence in support of this theory. This theory also predicts that if the neck radius is less than half the body radius for a system of essentially cylindrical pores, then entrapment of mercury will occur in the pore bodies.

The second theory has been introduced by Lowell and Shields (1984). They state that after intrusion, mercury atoms fall into the potential field of the walls of the capillary and they acquire a lower free energy than possessed during intrusion. Therefore, extrusion occurs at a lower pressure with a lower contact angle than during extrusion. The theory also states that extrusion stops when the interfacial free energy near a pore constriction equals the pore potential. This in turn results in the entrapment of mercury in the pore bodies.

Additional controversies exist with regard to mercury porosimetry beyond the effects of constrictions on intrusion and extrusion. These include debates about the effect of kinetic hysteresis due to hydraulic

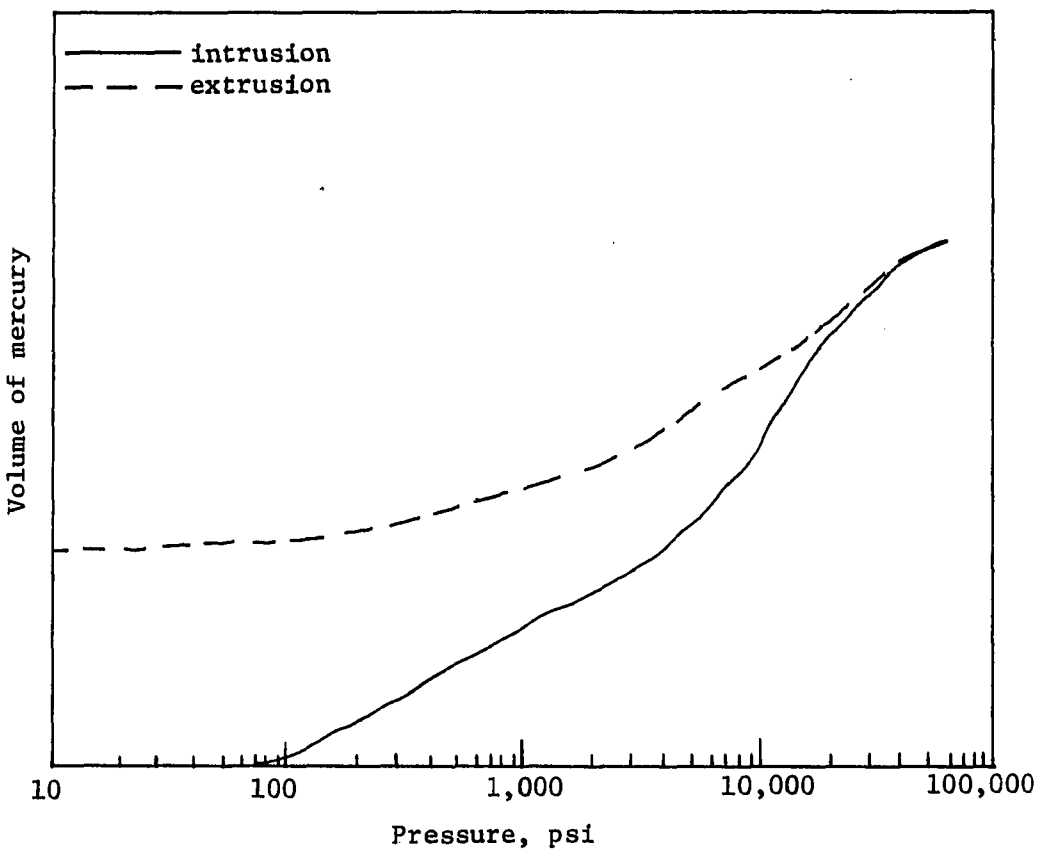


Figure 3. Example of intrusion and extrusion branches from mercury porosimetry

drag, the effect of the magnitude of the contact angle, and the effect of differences between contact angles for advancing and retreating menisci (Conner et al., 1984).

In spite of the aforementioned problems associated with hysteresis loops, the intrusion cycle has generally been assumed to represent the size of the pore constrictions and the extrusion cycle, the pore bodies. Often, due to problems associated with entrapment of mercury, the extrusion cycle is ignored.

In an effort to better interpret the information obtained from the extrusion cycle, Cebeci et al. (1978) refined a technique applied by Hill (1960) and Caro and Freeman (1961) in which, after extrusion, a specimen is intruded a second time. Cebeci et al. (1978) suggest this technique to distinguish the distribution of uniform pores from that of pores with mercury entrapping constrictions.

Mercury porosimetry has been reviewed in more detail by Rootare (1968). Currently commercially available instruments are capable of measuring pore size distributions for pores ranging form 18 to 10,000 angstroms and like capillary condensation instruments are quite expensive, with prices starting at around $40,000.

The purpose of this section is not to provide a complete literature review of these two powerful methods of porosimetry, but rather to point out that the measurement of the pore structure of a material is not a routine analysis. Thus, when researchers refer to materials of known pore size distributions, they are generally overstating the analysis and should actually be using terminology such as pore size distribution as

determined by mercury porosimetry or nitrogen sorption. Researchers should fully understand the nature and limitations of the analysis technique used to be able to give correct interpretations.

Phase transition porosimetry

Recently, a method was developed based on observation of the liquid-solid phase transition point of pore water in a porous sample at the saturated state by dilatometric measurements (Enüstün et al., 1985a; 1985b; Eckrich et al., 1986). This method has been referred to as ice porosimetry or phase transition porosimetry. A similar method has been proposed by Brun et al. (1977). This method has been referred to as thermoporometry and is based on calorimetrically measured freezing points of water in a saturated porous material. Brun assumes freezing is initiated by homogeneous in-situ nucleation. It is in this latter respect that phase transition porosimetry differs from thermoporometry. It has been shown previously (Enüstün et al., 1978; 1985a; 1985b) that the plastic ice model put forward by Everett (1961) is applicable to freezing and melting of the pore water in a saturated porous material. A discussion of the plastic ice theory is included later in this dissertation. With phase transition porosimetry, the process of the phase change is followed by measuring the volume change of the sample. The principles of phase transition porosimetry are discussed in detail by Enüstün et al. (1985a; 1985b) and Eckrich et al. (1986).

Commercially produced phase transition porosimeters are not yet available, but laboratory prototypes are capable of determining pore size

distributions for pores ranging from about 12 to 5000 angstroms.

Importance to Civil Engineering Materials

The determination of pore size distributions is important in the characterization of a wide variety of materials. Rootare (1968) cites published papers reporting pore size distribution data for a variety of materials including paper, soft woods, textiles, leather, PVC resins, macroreticular ion exchange resins, carbons, coal, coke, membrane filters, Florida filter clays, clay building bricks, petroleum reservoir rocks, phosphate rocks and triple super phosphate, refractory materials, porous iron, aluminum oxides, catalysts and other porous materials.

In the field of civil engineering materials, investigations of the pore structure of portland cement paste and mortar, aggregates, and soils have been undertaken.

Mikhail et al. (1964) and Bodor et al. (1970) introduced and developed procedures for the analysis of the pore structure of hydrated cement pastes from nitrogen sorption isotherms. Odler et al. (1972) and Hagymassy et al. (1972) introduced experimental techniques for determining the pore size distribution of hydrated portland cement pastes by water vapor adsorption. Litvan (1976) states specific surface areas of hydrated portland cement pastes computed form water adsorption isotherms are generally much larger than those calculated from nitrogen isotherms. This difference is attributed by Litvan, not to deficiencies of the measuring methods, but to real difference evoked by the particular drying technique used. Drying techniques explored by Litvan included

drying over a desiccant; vacuum drying; storage in methyl alcohol and/or pentane, followed by vacuum distillation at room temperature, evaporation, or vacuum distillation above the critical point of the adsorbate. Elapsed time for the different combinations used ranged from 6.5 hours to 134 days and results measured by nitrogen adsorption varied form 69.6 to 249.4 m/g. Water sorption surface area sample preparation included allowing the sample to equilibrate at approximate atmospheric relative humidity for 133 days followed by vacuum drying. The water surface area from the desorption isotherm was 286 m/g, while for adsorption, 182 m/g. These results illustrate the importance of sample preparation on surface area determination and thus also on pore distribution determinations for hydrophilic materials like portland cement, soils, clays, and some aggregates. Any method for determining the pore size distributions of these materials which minimizes sample disturbance is more likely to produce results more directly applicable to engineering problems.

Winslow and Diamond (1970) used mercury porosimetry to study the evolution of porosity in portland cement paste and Diamond (1971) presented a critical comparison of mercury porosimetry and capillary condensation pore size distributions of portland cement pastes in which he favored mercury porosimetry. This set off a rather heated debate as to the merits of the two methods (Beaudoin, 1972; Diamond, 1972; Mikhail et al., 1975). Regardless of the relative merits or demerits of the two methods, both necessitate the drying of the sample prior to testing.

Lemish et al. (1958) and Hiltrop and Lemish (1960) first applied

mercury porosimetry to measure the pore size distribution of aggregates and attempted to associate it with the frost durability of concrete. They did not find any close correlation between pore size distribution and service records but stated that knowledge of a rock's pore size distribution might be of value in attempting to predict its service record as an aggregate.

Recent work by researchers at Purdue University illustrates the difficulties encountered when trying to relate measurements of properties of a component of portland cement concrete to behavior of portland cement concrete. In this case, researchers attempted to relate pore size distributions of coarse aggregates to the field service records of concrete containing these aggregates. Kaneuji (1978) introduced an empirical "Expected Durability Factor" which was used to predict the freeze-thaw durability of laboratory concrete specimens. The expected durability factor is defined as:

$$EDF = K_1/PV + K_2(MD) + K_3 \qquad (3)$$

where: EDF = Expected Durability Factor;

PV = mercury intruded pore volume for pores larger than 45 angstroms in diameter, expressed in cc/g;

MD = median diameter of pores larger than 45 angstroms in diameter, expressed in μm;

K_1, K_2, and K_3 are empirical constants with values of 0.579, 6.24, and 3.04, respectively.

Based on a few comparisons with active field performance, Kaneuji set

tentative borderlines for classifying coarse aggregate as durable, nondurable, or marginal. Lindgren (1980) attempted to expand this correlation by testing aggregates taken from 52 highway cores and 5 rock samples. The approach involved determining an average EDF value for aggregate extracted from the concrete cores. Determination of the average value involved selecting representative samples of the various aggregates within a concrete core, determining the EDF for each representative aggregate, determining the percentage of each representative aggregate present, selecting a threshold between durable and nondurable aggregates, and finally selecting what percentage of nondurable aggregate present in the core is detrimental. Nondurable cores were defined as having an EDF value of 50 or less for more than ten percent of the aggregate. Although the author claimed good correlation between serviceability ratings and average durability factor, closer examination of the data indicates 10 of the 52 cores evaluated would be incorrectly evaluated as durable using this approach and four incorrectly evaluated as nondurable.

While the assumption made by these authors that deterioration of portland cement concrete pavements in temperate climates is due largely to the coarse aggregate in the concrete is not a bad one, examination of the pore structure of the coarse aggregate alone precludes the possibility that the deterioration might be due to interactions between the mortar and the aggregate and other factors. Also, with the expanding use of new admixtures, new types of portland cement, and cement substitutes in concretes being placed today, assuming coarse aggregate to

be the sole source of freeze-thaw deterioration in the future is questionable. The ability to evaluate the pore size distribution of a concrete mixture and subsequent changes in this distribution when the concrete is exposed to a set of simulated or actual environmental conditions should be a valuable aid in predicting the serviceability of concrete structures made using that mixture. Available porosimetry methods are incapable of doing this due to their inability to determine pore size distribution of samples large enough to be considered representative of a highly heterogeneous material such as portland cement concrete. The porosimeter introduced in this dissertation, however, is capable of testing large samples, as will be shown later in this document.

Diamond (1970) and Sridharan et al. (1971) first demonstrated that mercury porosimetry could be used to determine the pore size distributions of soils and provide a better understanding of engineering modifications of soil such as compaction. The interpretation of pore size distributions of soil by conventional techniques is hindered by the same limitations mentioned earlier for portland cement concrete. Specifically, the inability to test representative size samples and the effects of sample preparation make interpretation of results difficult. Diamond (1970) infers this when he states that the development of techniques for water removal which do not involve changes in pore structure are necessary and suggests that for weak saturated clays, critical-region drying or freeze-drying may be practical.

In summary, the advent of conductometric phase transition

porosimetry promises significant improvements over conventional porosimetry techniques for the determination of the pore size distribution of civil engineering materials. These include minimal pore structure disturbance due to sample preparation and the ability to determine the pore size distributions of samples much larger than by other methods, thus minimizing sampling errors.

Capillary Freezing and Melting

Two models have been proposed to explain the mechanism of freezing and thawing in capillaries. They are the homogeneous nucleation model and the plastic ice model.

For the homogeneous nucleation model, it is assumed that ice crystals are formed in capillaries in the same manner as in the freezing of bulk water. Crystal growth continues until a capillary wall obstructs the growth. The remaining capillary space is occupied by unfrozen pore water or solution. The theory is consistent with the observed relationship between temperature and capillary freezing in that the smaller the capillary, the lower the freezing temperature. Enüstün et al. (1965) explored the validity of the homogeneous nucleation model experimentally by investigating the electrical conductance of a sample of porous glass saturated with ammonium nitrate solution at temperatures below the normal freezing point and found freezing points predicted by this model to be inaccurate. In discussing this theory, Enüstün et al. (1965) and Hesstvedt (1964) point out that freezing by homogeneous nucleation is a rate process beyond the treatment of equilibrium

thermodynamics and Enüstün later rejects the model in favor of the plastic ice model first rigorously developed by Everett (1961). Continued investigations (Enüstün et al., 1978; 1985a; 1985b) of capillary freezing and melting led to the confirmation of the plastic ice model and subsequently to the development of phase transition porosimetry discussed earlier in this dissertation.

Early development of the plastic ice model can be traced to research done during investigations of frost action in soils by several researchers. Penner (1957), while investigating soil moisture tension and ice segregation, concluded that moisture tensions developed as a result of freezing point depressions and that higher tensions developed in soils with small pores than in soils with large pores because the freezing point decreases with the radius of curvature of the ice/water interface. Penner (1959) and Miller et al. (1960) pointed out that equilibrium thermodynamics could be used to provide a relationship between the freezing point in capillaries and the suction pressure developed in these capillaries. These studies led to the work of Everett (1961) and Everett and Haynes (1965) who developed a rigorous equilibrium thermodynamics formula for capillary freezing and melting. From this beginning, the plastic ice model has been extensively utilized in investigations of frost action in soils.

The plastic ice model relationship between capillary freezing point and capillary size can be developed from fundamental equilibrium thermodynamic principles as follows.

Consider two cylinders, each closed by a piston and joined by a

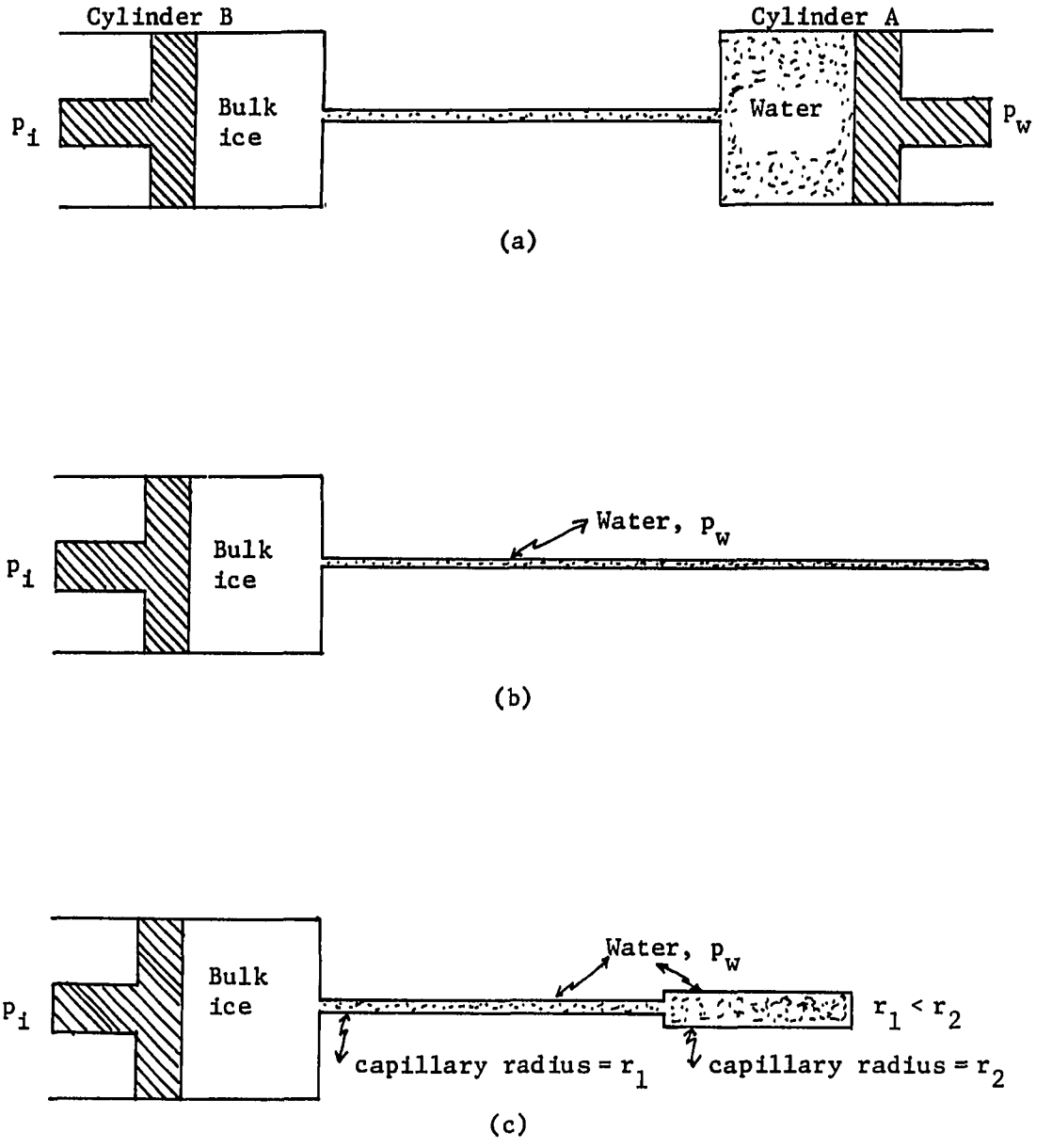


Figure 4. Schematics of capillary freezing and melting

capillary tube (see Figure 4a). If the temperature in both of the cylinders is lowered below $0^{o}C$ and freezing is nucleated in cylinder B only, the accompanying expansion is taken up by the movement of the pistons. The well-known Laplace equation gives a relationship for the pressure difference across a meniscus and can be expressed as:

$$p_i - p_w = \frac{2\gamma_{i,w}}{r_{i,w}} \quad . \tag{4}$$

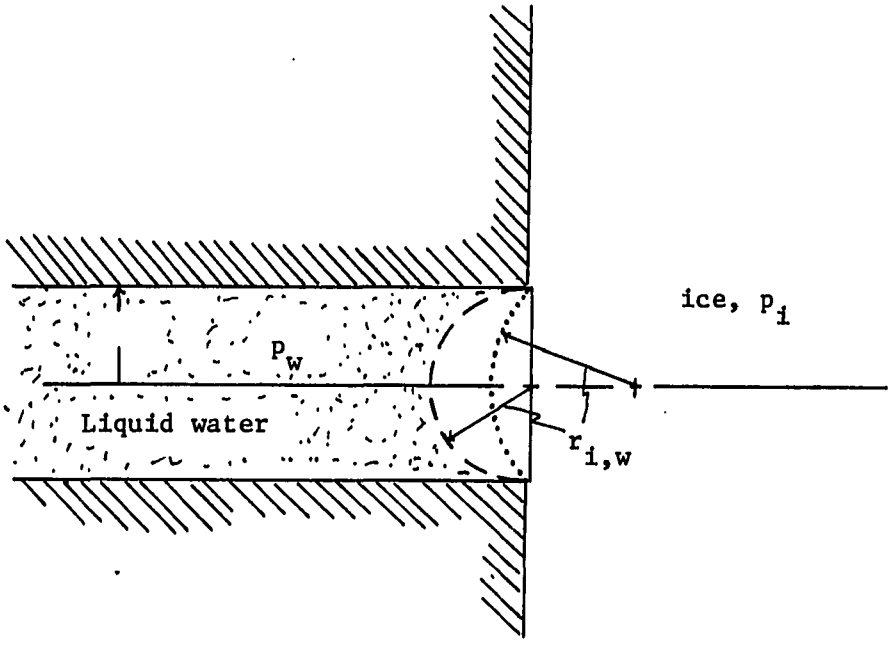
where p_i is the pressure on the ice side of the meniscus, p_w is the pressure on the liquid water side of the meniscus, $\gamma_{i,w}$ is the ice/water interfacial tension, and $r_{i,w}$ is the radius of curvature of the spherical meniscus. As long as the pressures exerted by the pistons are equal to those of equilibrium, the ice/water interface will be a plane and there will be no tendency for ice to penetrate the capillary (see Figure 5). Also, since the chemical potential of the liquid water will be greater than that of the ice, the growth of the bulk ice crystal will continue until all the liquid water is withdrawn from cylinder A. With soils, this type of behavior can occur and is the driving mechanism behind frost heave. The chemical potential of the liquid water, $\mu_w\ (T,p_w)$, at temperature T (^{o}K) and pressure, p_w, can be expressed as:

$$\mu_w\ (T,p_w) = \mu_w{}^{o}\ (T_o,p_o) - \int_{T_o}^{T} S_w{}^{o}\, dT + \int_{p_o}^{p_w} V_w{}^{o}\, dp \tag{5}$$

and the chemical potential of the ice $u_i(T,p_i)$ as:

$$\mu_i\ (T,p_i) = \mu_i{}^{o}\ (T_o,p_o) - \int_{T_o}^{T} S_i{}^{o}\, dT + \int_{p_o}^{p_i} V_i{}^{o}\, dp \tag{6}$$

where:



———— $p_i = p_w$ $r_{i,w} = \infty$

..... $p_i - p_w < 2\gamma/r_{i,w}$ $r_{i,w} > r$

– – – – – – – – $p_i - p_w = 2\gamma/r_{i,w}$ $r_{i,w} = r$
ice will advance into capillary

Figure 5. Equilibrium interface between ice and water

T_o = melting point of ice in ^oK;

p_o = atmospheric pressure;

μ_w^o, μ_i^o = chemical potentials of liquid water and ice at T_o and p_o, respectively;

p_w, p_i = pressures of liquid water and ice, respectively;

S_w^o, S_i^o = molar entropies of liquid water and ice at T_o and p_o, respectively; and

V_w^o, V_i^o = molar volumes of liquid water and ice at T_o and p_o, respectively.

If the capillary is close-ended (see Figure 4b) and the pressure of the ice remains at p_o due to movement of the piston as the temperature of the system is lowered, the transfer of liquid water to ice lowers p_w below p_o; thus, the radius of curvature of the ice/water interface will increase in accordance with the Laplace equation (see Figure 5), and the pressure in the liquid will be $p_o - (2\gamma/r_{i,w})$. Realizing that $\mu_i^o = \mu_w^o$ and that at equilibrium $\mu_i = \mu_w$, equations 4, 5, and 6 can be combined as:

$$-\int_{T_o}^{T} S_i \, dT = -\int_{T_o}^{T} S_w^o \, dT + \int_{p_o}^{p_o - (2\gamma/r_{i,w})} V_w^o \, dp \qquad (7)$$

Neglecting the pressure dependence of V_w^o, equation 7 can be rewritten as:

$$2 V_w^o / r_{i,w} = \int_{T_o}^{T} (S_w^o - S_i^o) \, dT \quad . \qquad (8)$$

Also, from thermodynamics,

$$S_w^o - S_i^o = (L^o/T_o) + \int_{T_o}^{T} ((C_{pw} - C_{pi})/T)\, dT \quad , \tag{9}$$

where L^o is the normal heat of fusion of ice at T_o and p_o, and C_{pw} and C_{pi} are the molar heat capacities at constant pressure of liquid water and ice, respectively. Combining equations 8 and 9 results in:

$$2\, V_w^o/r_{i,w} = L^o(T_o - T)/T_o - \int_{T_o}^{T} \int_{T_o}^{T} ((C_{pw} - C_{pi})/T)\, dT\, dT \quad . \tag{10}$$

Enüstün et al. (1965) pointed out that the double integral portion of this equality can be considered to be negligible. Finally, realizing that the density of water, ρ_w, is equal to the ratio of its molecular weight to its molar volume, V^o, and that the heat of fusion of ice per unit mass, λ, is equal to the molar heat of fusion, L^o, divided by the molecular weight of ice, equation 10 can be reduced to:

$$r_{i,w} = \frac{2\gamma\, T_o}{\rho_w\, \lambda(T_o - T)} \tag{11}$$

Equation 11 correlates the equilibrium temperature, T, with the radius of curvature of the ice/water interface, $r_{i,w}$, in a capillary. When the radius of curvature of the meniscus equals the radius of curvature of the capillary, r (see Figure 5), the water in the capillary will freeze.

Figure 4c shows a bottle-necked capillary. During capillary freezing, the phase transition in the capillary will be controlled by the radius of the pore constriction as the ice cannot intrude into the larger pore body until freezing is initiated in the pore constriction. During

melting, however, the constriction will melt first in accordance with the plastic ice model as will the body, but at a higher temperature.

Hesstvedt et al. (1964) gave the following relationship between the ice/water interfacial tension, γ, and temperature where:

$$\gamma = \gamma_o + k\,(T - T_o) \tag{12}$$

where k is a dimensional constant with a value of 0.25 ergs cm^{-1} K^{-1} and γ_o is the value of γ at T_o. Hesstvedt also gives a value for γ_o of 29 ergs cm^{-2}.

For conductometric phase transition porosimetry, it is helpful to develop a relationship between pore radius, r and the negative inverse of the absolute temperature, X. With this information and substituting the relationship for ice/water interfacial tension given in equation 12, equation 11 can be rewritten as:

$$r = \frac{-2T_o(k - \gamma_o X + kT_o X)}{\rho_w \lambda (1 + T_o X)} \tag{13}$$

where r, T_o, γ_o, k, ρ_w, and λ are as defined earlier and X = (-1/T), where T is the phase transition temperature in ^oK.

The numerical values of the various constants used in the computations contained in this dissertation are as follows:

T_o = 273.16 ^oK;

ρ_w = 1.000 gm cm^{-3}; and

λ = 333.3 J gm^{-1}.

These values can be obtained from standard physical and chemical handbooks.

A possible concern with applying plastic ice model relationships to conductometric phase transition porosimetry is the effect of solute concentration in pore water upon capillary freezing and melting. It is well-known that solute concentration affects the freezing point of bulk pore solution. It may also affect the ice/water interfacial tension. Enüstün et al. (1978) investigated these effects of solute concentration on capillary freezing of four porous Vycor glass samples saturated with distilled water, and 0.02, 0.04, and 0.06 molar ammonium nitrate solutions. They monitored the variation of electrical conductance with temperature during a cycle of capillary freezing and thawing for each of the four samples and from examinations of inflection points of all curves concluded that the presence of solute had no significant effect on the location of inflection points and thus no significant effect on capillary freezing and thawing. These experiments were limited to solutions with relatively low solute concentrations saturating a porous material having a relatively small (approximate modal pore body size = 45 angstroms) and narrow pore size distribution. The effect of solute concentration on the freezing point of solutions in bulk and capillary pores saturated with the solution can be evaluated using fundamental thermodynamic relationships. In the derivation of the plastic ice model equation relating pore freezing temperatures and pore radii (equation 11), it was stated that at equilibrium the chemical potential of water, μ_w, would equal the chemical potential of ice, μ_i. For a nonvolatile solute that does not form a solid solution with a freezing solvent, at the freezing point the chemical potentials of the pure frozen solvent and the

contaminated liquid are equal. The resultant equilibrium relationship can be expressed as (Atkins, 1982):

$$\mu_i = \mu_w^* = \mu_w + RT \ln(x_a) \quad , \tag{14}$$

where μ_w^* is the chemical potential of the pore solution, R is the gas constant, and x_a is mole fraction of solvent in the pore solution. Following the same steps presented earlier results in an equation which relates pore freezing temperatures, pore radii, and solute concentration. This relationship can be expressed as:

$$r = \frac{2\gamma T_o}{\rho_w \lambda (T_o - T) - (\rho_w T_o / M) RT \ln(x_a)} \quad . \tag{15}$$

Column 3 of Table 1 lists values of r calculated for several different values of x_a and T using equation 15. Concentrations selected are .02, .06, .1 and 1 molar ammonium nitrate solutions. It can be seen from the examination of the values listed in Table 1 that for the solute concentrations and pore sizes investigated by Enüstün et al. (1978) (.02 to .06 molar), the effect of the solute is negligible as they had observed experimentally. However, for increased solute concentrations and especially for larger pore sizes, this is not the case. For example, at a temperature of -1.0 ^{o}C, pure water in pores with radii larger than 471 angstroms will freeze. If the pores are saturated with a .1 molar solution of ammonium nitrate, only solution in pores larger than 578 angstroms will freeze. Equation 14 provides the relationship necessary to calculate pore radii from pore freezing points if the solute

concentration is known. At concentrations and temperatures for which no pore radius is indicated in column 3 of Table 1, no freezing will occur as these temperatures are above the freezing point of the bulk solution.

Another relationship can be used to calculate pore radii from pore solution freezing points if the bulk solution freezing point is known. The relationship is nearly the same as the one expressed in equation 11, except the bulk solution freezing point, T_o^*, is substituted for the normal freezing point of water, T_o. The appended relationship is:

$$r_{i,w} = \frac{2\gamma\ T_o^*}{\rho_w\ \lambda(T_o^* - T)} \quad . \tag{16}$$

Column 4 of Table 1 gives values for r calculated for several different values of T_o^* and T. The values of T_o^* selected are those equal to the bulk solution freezing points of .02, .06, .1, and 1 molar ammonium nitrate solutions. These values were calculated using a relationship given by Atkins (1982), where

$$T_o - T_o^* = (R\ (T_o)^2/H_{fus})\ x_b \tag{17}$$

where H_{fus} is the molar enthalpy of fusion for the solvent and x_b is the mole fraction of the solute. Values for T_o^* calculated using equation 16 and a value of 6.008 kJ mol^{-1} for the molar enthalpy of fusion of water are given in Table 2. Comparative examination of the data listed in columns 3 and 4 of Table 1 indicate the relationships expressed in equations 15 and 16 give the same results.

At this point, another advantage phase transition porosimetry

Table 1. Effect of solute concentration on calculation of pore radii from pore solution freezing points for ammonium nitrate solution

Molarity	Temperature, °C	Pore radius, angstroms	
		Equation 14	Equation 15
0	- 0.10	4749.4	4749.4
0	- 0.50	788.1	788.1
0	- 1.00	471.2	471.2
0	-10.00	43.44	43.44
0	-20.00	19.67	19.67
0	-30.00	11.75	11.75
.02	- 0.10	7565.1	7564.1
.02	- 0.50	840.2	840.4
.02	- 1.00	489.4	489.5
.02	-10.00	43.59	43.61
.02	-20.00	19.70	19.71
.02	-30.00	11.76	11.76
.06	- 0.10	--	--
.06	- 0.50	967.8	968.6
.06	- 1.00	530.2	530.7
.06	-10.00	43.91	43.95
.06	-20.00	19.77	19.79
.06	-30.00	11.78	11.80
.1	- 0.10	--	--
.1	- 0.50	1141.1	1142.2
.1	- 1.00	578.4	579.2
.1	-10.00	44.23	44.31
.1	-20.00	19.84	19.88
.1	-30.00	11.81	11.81
1.0	- 0.10	--	--
1.0	- 0.50	--	--
1.0	- 1.00	--	--
1.0	-10.00	52.82	53.69
1.0	-20.00	21.51	21.91
1.0	-30.00	12.42	12.69

Table 2-3. Variation of bulk solution freezing point with solute concentration for ammonium nitrate solutions

Molarity	Bulk solution freezing point (^{o}C)
0.00	0.0000
0.02	-0.0371
0.06	-0.1114
0.10	-0.1855
1.00	-1.8528

methods have over mercury porosimetry can be illustrated. The pressure differential across the meniscus of intruding mercury for a pore with a radius of curvature equal to 18 angstroms is approximately 60,000 psi. Due to the much lower interfacial tension across an ice/water meniscus, the pressure differential across the meniscus of intruding ice for a pore with a radius of curvature of 18 angstroms (-21.5 ^{o}C) is approximately 3800 psi. Thus, mechanical sample degradation due to induced pressures during the determination of pore size distributions will be much less for phase transition porosimetry methods than for mercury porosimetry. However, viscous forces that develop due to flow of ice are higher than those due to flow of mercury because of the higher viscosity of ice. Therefore, rapid freezing and repeated freezing and thawing cycles may cause destruction of samples in phase transition porosimetry.

It is pertinent at this point to discuss some limitations of the plastic ice model. Theoretically, the model provides a relationship for evaluating the size of infinitesimally small pores. However, for pores with extremely small radii, interactions between the solid porous

material and the liquid solution may cause the radius of the penetrating ice to differ significantly from the radius of the penetrated pore. Further, as the size of a pore begins to approach the size of water molecules, the formation of a meniscus and thus applicability of the Laplace equation becomes questionable. The size of pores at which these effects become appreciable is debatable. However, the calculation of pore sizes from their freezing points assuming these affects to be negligible still provides valuable information about the pore structure of materials with extremely small pores. Researchers should bear in mind that the calculated pore radii for these small pores may provide only an index of the size of the pore which, although directly related to the pore size, may not be equal to the actual pore size.

Principles of Electrical Conductance of Porous Materials

Many porous materials consist of a nonconducting solid phase and a void system of randomly intersecting capillaries of various sizes. If the material is saturated, the pore solution generally will exhibit electrolytic conductance, which results from the mobility of ions in the solution.

Archie (1942), Winsauer et al. (1951), and Perkins et al. (1956) used a parameter called resistivity factor in their investigations of the resistivity of porous geomaterials. Consider a cylindrical container of volume V having a cross-sectional area, A, and length, L, made of an insulating material, but with ends of a conducting material and filled with a solution of conductivity, κ. The conductance, C, of the container

is then

$$C = \kappa(A/L) = \kappa(V/L^2) \quad . \tag{18}$$

Let the same container be filled with a porous material saturated with the same solution. The conductance will now be considerably less since the mean length of path traversed by the current is longer and the cross-sectional area which is available to current flow is smaller.

Previous researchers defined the conductance of porous material, C', as

$$C' = \kappa(A'/L') \tag{19}$$

where L' is the effective tortuous path length traversed by the electrical current and A' is the effective conducting cross-sectional area of the material available to current flow. The resistivity factor, F, by definition is equal to C/C'.

Winsauer et al. (1951) and later Perkins et al. (1956) expressed a relationship between resistivity factor, F, and pore structure where

$$F = \tau/\psi \quad , \tag{20}$$

where τ is the tortuosity, defined as the ratio of L' to L, and ψ is the ratio of A' to A. Also, these investigators related the resistivity factor to the tortuosity, τ, and porosity, η, of the sample by

$$F = \frac{\tau^2}{\eta} \quad . \tag{21}$$

In a commentary of the paper by Perkins et al. (1956), Wyllie and de Witte (1956) pointed out that this is true only if porosity equaled tortuosity times ψ, or otherwise stated, the pore volume, V_p, was equal

to the product of A' and L', which is only true for pores with uniform cross-sectional areas.

This can be shown by considering a pore system consisting of one pore with a nonuniform cross-sectional area. If the pore is a right angle truncated cone, a relationship between the conductance of the pore and the pore geometry can be developed as follows. Figure 6 illustrates the geometry of such a cone. The resistance of an infinitesimally small section of the cone, dR, can be expressed as

$$dR = \frac{\rho d\ell}{\pi r^2} = \frac{\rho}{\pi} \frac{d\ell}{(\ell \tan\theta + r_o)^2} \tag{22}$$

where $d\ell$, r, r_o, and θ are as defined in Figure 6 and ρ is the resistivity of the pore solution. Integrating over the length of the pore, L, gives the following relationship,

$$R_c = \frac{\rho}{\pi} \int_0^L \frac{d\ell}{(\ell \tan\theta + r_o)^2} \tag{23}$$

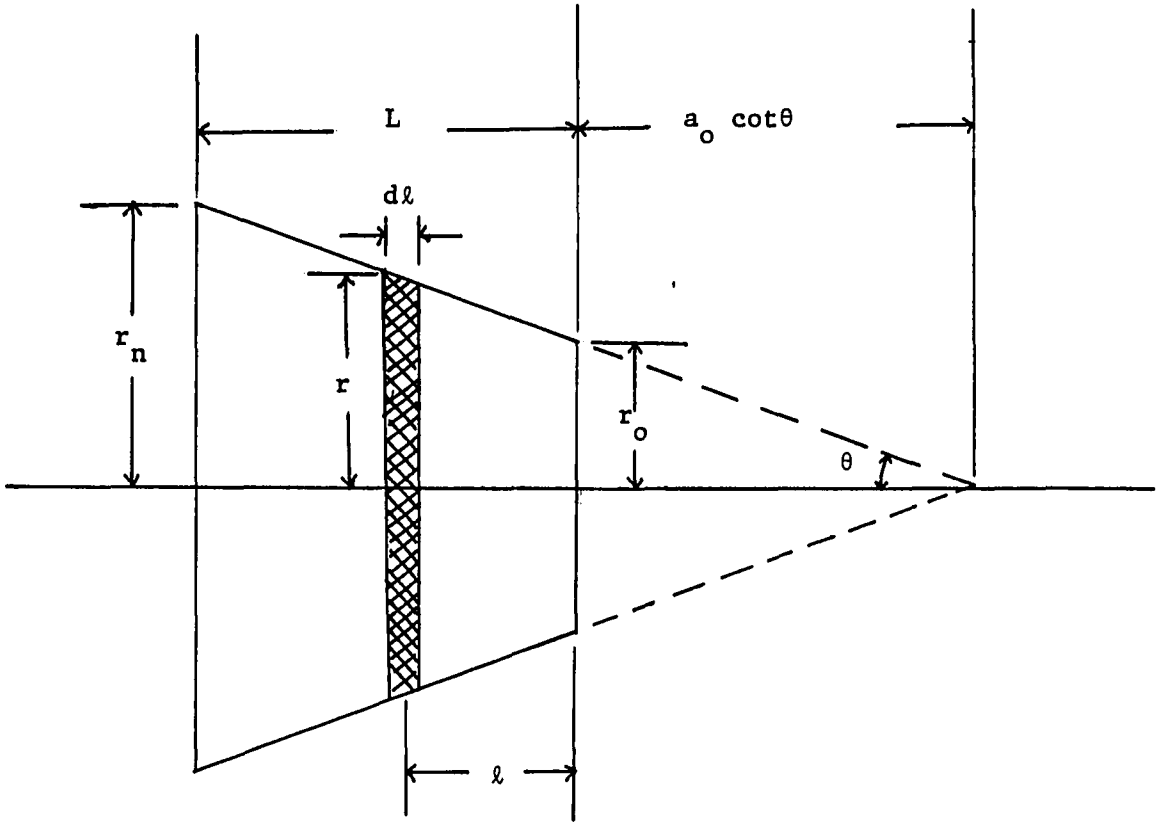
where R_c is the resistance of the cone. Realizing that tan θ equals the quantity, $(r_n - r_o)/L$, and solving the integral yields

$$R_c = \frac{\rho}{\pi} \frac{L}{r_o r_n} \quad . \tag{24}$$

Since conductance, C, is the reciprocal of resistance, R and conductivity, κ, is the reciprocal of resistivity, ρ, equation 24 can be rewritten as

$$C_c = \frac{\kappa(\pi r_n r_o)}{L} \quad , \tag{25}$$

where C_c is the conductance of the cone. Examination of equation 25 with respect to equation 18 indicates that for a pore system consisting of a



$$r = (\ell + r_o \cot\theta) \tan\theta = \ell \tan\theta + r_o$$

Figure 6. Geometry of right angle truncated cone

single right angle truncated cone, A' must equal $\pi r_n r_o$ and L' must equal L. Therefore, in order for the relationship expressed in equation 21 to be correct, the volume of the pore must be equal to $L\pi r_n r_o$. Mensuration tables give the volume of a right angle truncated cone, V_c, as

$$V_c = L\frac{\pi}{3} r_o r_n \left(\frac{r_o}{r_n} + 1 + \frac{r_n}{r_o}\right) \quad . \tag{26}$$

From this, it is clear that the volume of the cone will equal $L\pi r_n r_o$ only when $r_n = r_o$, or otherwise stated, only when the pore has a uniform cross-sectional area.

For conductometric phase transition porosimetry, the conductance of a porous material, C', is redefined as

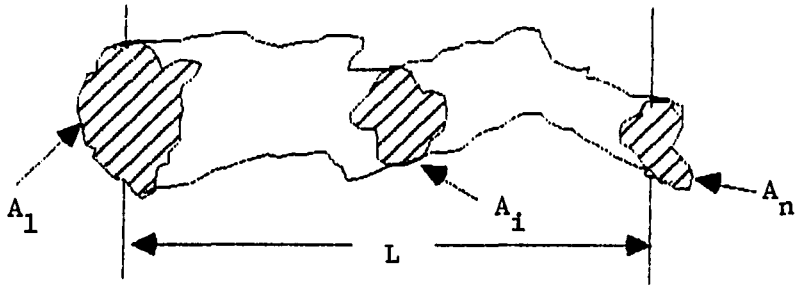
$$C' = \kappa V_p/(L^2\omega) \tag{27a}$$

where κ and L are as defined earlier (equation 18), V_p is the pore volume and ω is a dimensionless pore geometry factor. At this point, some relationships between pore geometry factor and pore geometry will be developed to give some physical significance to this new factor.

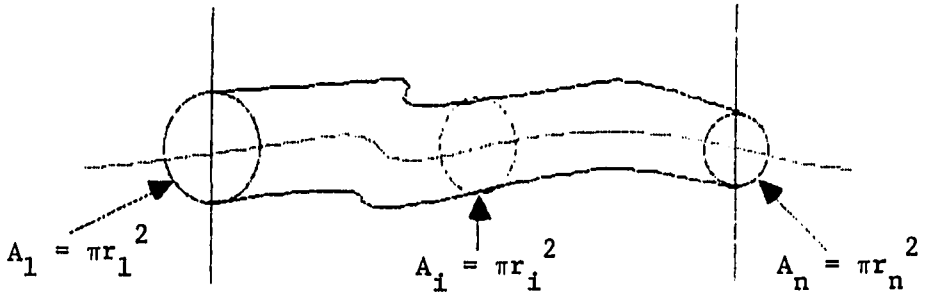
An expression for the conductance of a pore system consisting of x number of parallel conducting pores can be developed from equation 27a and can be expressed as

$$C' = \kappa \frac{V_p}{\omega L^2} = \kappa \sum_{j=1}^{j=x} \frac{V_{pj}}{L^2\omega_j} \quad , \tag{27b}$$

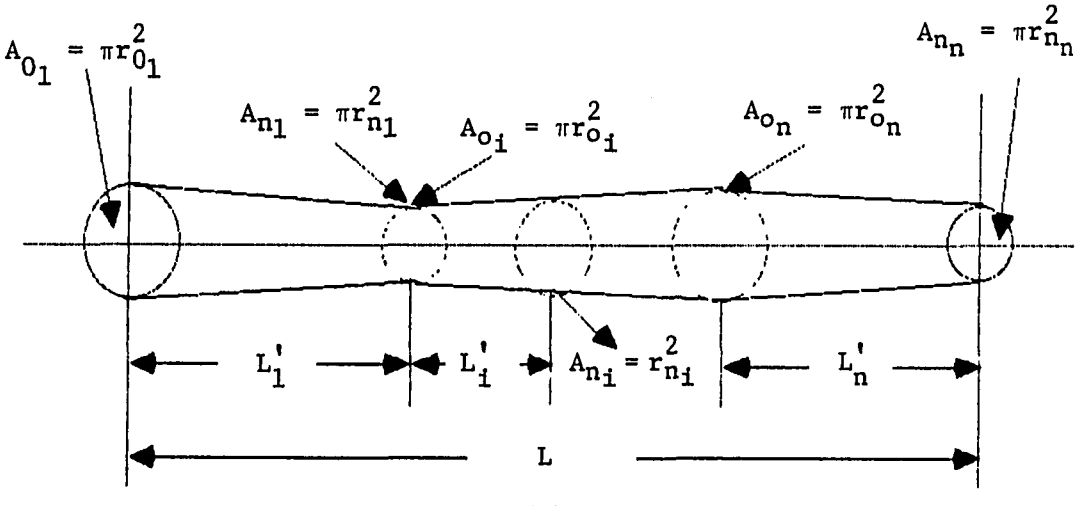
where C', κ, V_p, L, and ω are as defined earlier and V_{pj} and ω_j are the pore volume and pore geometry factor for individual conducting pore j. From this relationship, it can be seen that if the pore geometry factor for each parallel conducting pore, ω_j, is the same, then the pore



(a)



(b)



(c)

Figure 7. Right angle truncated cone modeling of irregular pore

geometry factor for the pore system, ω, is equal to ω_j.

Let us now consider an irregular single conducting pore channel of a porous material as shown in Figure 7a. This pore can be represented by a pore with equivalent circular cross-sectional areas as shown in Figure 7b. Such a pore would have the same volume and conductance as the original irregular pore. If this circular pore is then stretched so the curve connecting the centers of the circular cross-sections is a straight line, the pore can be represented by a series of right angle truncated cones as shown in Figure 7c without a change in the volume or conductance.

By combining equations 25, 26, and 27a, it can be shown that if the pore system of a porous material when stretched consists of a single right angle truncated cone, then the dimensionless pore geometry factor, ω, can be expressed as

$$\omega = \left(\frac{1}{3}\right)\left(\frac{L'}{L}\right)^2 \left(\frac{r_o}{r_n} + 1 + \frac{r_n}{r_o}\right) \tag{28}$$

Using the same approach, the pore geometry factor, ω, for a pore system consisting of a singular irregular pore (represented by z number of right angle truncated cones in a series connection, Figure 7) can be expressed as

$$\omega = \frac{\sum_{i=1}^{i=z} \left(L_i' r_{oi} r_{ni} \left((r_{oi}/r_{ni}) + 1 + (r_{ni}/r_{oi})\right)\right)}{3L^2} \left(\sum_{i=1}^{i=z} L_i'/(r_{oi} r_{ni})\right) \tag{29}$$

The relationship expressed in equation 29 can be greatly simplified for a pore of uniform cross-sectional area. The simplified relationship can be

expressed as

$$\omega = (L'/L)^2 \tag{30}$$

where L' is the sum of the lengths of component cylinders (right angle truncated cones with uniform cross-sectional areas) and L is the distance between the ends of the conducting pores as previously defined. The quantity (L'/L) has been commonly referred to as tortuosity. Also, for a pore consisting of uniformly sized right angle truncated cones (r_{oi} and r_{ni} are constant), equation 29 can be simplified to the relationship expressed in equation 28. Further, if the connected cones lie in a straight line perpendicular to the end planes of the conducting material, L' will equal L and the pore geometry factor will be a function of the ratio of the pore neck radii to the pore body radii only. This ratio will be hereafter referred to as necking. Later in this dissertation, these two fundamental characteristics, tortuosity and necking, will be referred to in a qualitative sense in discussing the importance of the pore geometry factor to conductometric phase transition porosimetry.

Finally, considering any pore system to consist of x number of irregular conducting pore channels connected in parallel, an expression for the pore geometry factor for any pore system as modeled by an agglomeration of right angle truncated cones is

$$\omega = \frac{\sum_{j=1}^{j=x}\left(\sum_{i=1}^{i=z} L_i' r_{oi} r_{ni}\left((r_{oi}/r_{ni}) + 1 + (r_{ni}/r_{oi})\right)\right)_j}{3L^2} \times \left(\sum_{j=1}^{j=x}\left(\left(\sum_{i=1}^{i=z} L_i'/(r_{oi} r_{ni})\right)^{-1}\right)_j\right)^{-1} \tag{31}$$

Equation 31 provides a rather complicated expression for the pore geometry factor for any pore system. The relationship may be seen as largely academic, illustrating the need to be able to determine the pore size distribution of a material in order to characterize the pore structure of a material. A corrected version of equation 21 which relates the measurable parameter resistivity factor, F, to porosity, η, and pore structure can be written by combining equations 18 and 27 and expressed as

$$F = \omega/\eta \quad . \tag{32}$$

Examining this relationship in light of equation 31 illustrates that values for the pore geometry factor determined from singular conductance measurements and measurements of porosity are very difficult to interpret due to the interrelated effect of tortuosity and necking on pore geometry factor. If the parallel conducting pores within a system have equivalent pore geometry factors, the pore geometry factor for the system as well as the individual pores could be evaluated using the relationship given for a single conducting pore (equation 29). This would simplify matters somewhat, but interpretation would still be difficult. Pore systems for which this would be true would contain geometrically similar pores, or otherwise stated, all pores in the system would have the same tortuosity and necking. This does not imply that all the pores in the system are identical but rather that large pores are essentially magnifications of smaller pores.

CONDUCTOMETRIC PHASE TRANSITION POROSIMETRY

In conductometric phase transition porosimetry, it is assumed that the electronic conductance through the solid phase of a porous material is negligible when compared to the electrolytic conductance of the pore solution. Thus, when the temperature of a mass of saturated porous material is raised from sub-freezing temperatures, the frozen pore solution will melt and an increase in electrical conductance will be observed. Capillaries will begin to melt with smaller sizes melting at lower temperatures in accordance with the plastic ice theory.

The theory behind conductometric phase transition porosimetry is developed from a few basic relationships. First, it is assumed the relationship between the electrical conductivity of an electrolyte and the absolute temperature of the electrolyte is an Arrhenius type relationship and can be expressed as

$$\ln \kappa = \frac{-a}{T} + b, \tag{33}$$

where:

κ = electrical conductivity;

T = absolute temperature;

a = physical constant; and

b = physical constant.

Recalling the relationship between conductance and pore volume introduced earlier as equation 27 and combining the same relationship with equation 33 results in the following equation.

$$Y = mX + d + \log_{10} \left(\frac{V_p}{L^2\omega}\right) \tag{34}$$

where L, V_p, and ω are as defined earlier; and

X = -1/(absolute temperature);

Y = $\log_{10}$ (conductance);

m = physical constant; and

d = physical constant.

A plot of the log of the conductance versus the negative inverse of the absolute temperature (Y versus X) for which no phase change occurs will result in a line with a slope equal to m. Below freezing temperatures, the phase changes which occur in a certain range of pores will effectively decrease the volume of conducting pores. Thus, V_p at below freezing temperatures can be considered to be the volume of conducting pores, V_{cp}.

Taking the first derivative of equation 34 yields

$$\frac{dY}{dX} = m + \frac{d(\log_{10} (V_p/(L^2\omega)))}{dX} . \tag{35}$$

Integrating equation 35 over the definite interval, X to X_o, yields the following relationship:

$$\log_{10}\left[\frac{\dfrac{V_{cp}(X_o)}{L^2\omega_{X_o}}}{\dfrac{V_{cp}(X)}{L^2\omega_X}}\right] = \int_X^{X_o} \frac{dY}{dX}\, dX - \int_X^{X_o} m\, dX \quad . \tag{36}$$

The right half of equation 36 can be calculated numerically from

conductance test data and is given the variable name Z. Also, if X_o is the value of X at the pore solution melting point, then $V_{cp}(X_o)$ is simply the total conducting pore volume, V_p.

Figure 8 illustrates graphically the calculation of the parameter Z. Plotted on this graph is the first derivative of the log of the conductance with respect to the negative inverse of the absolute temperature versus the negative inverse of the absolute temperature. The data plotted were obtained from the warming cycle of conductometric phase transition testing of porous Vycor glass (see results and discussion). The integration of these data over finite intervals, as illustrated in Figure 8, gives the parameter Z as a function of the negative inverse of the absolute temperature.

Rearranging equation 36 and referring to pore volume by radius, we obtain

$$\alpha \frac{V_{cp(r)}}{V_p} = 10^{-Z(X,X_o)} \tag{37}$$

where $V_{cp(r)}$ is the volume of the pores with radii smaller than or equal to r containing unfrozen pore solution, V_p is the total pore volume and α is the ratio of the pore geometry factor of the total pore system, ω, to the pore geometry factor of the pores smaller than r, ω_r. The plastic ice model of capillary freezing and melting as expressed earlier in equation 13 provides the necessary relationship between the negative inverse of absolute temperature, X, and pore radius.

If it is assumed that the pore geometry factor, ω, is independent of pore size, then α is equal to unity and equation 37 can be reduced to

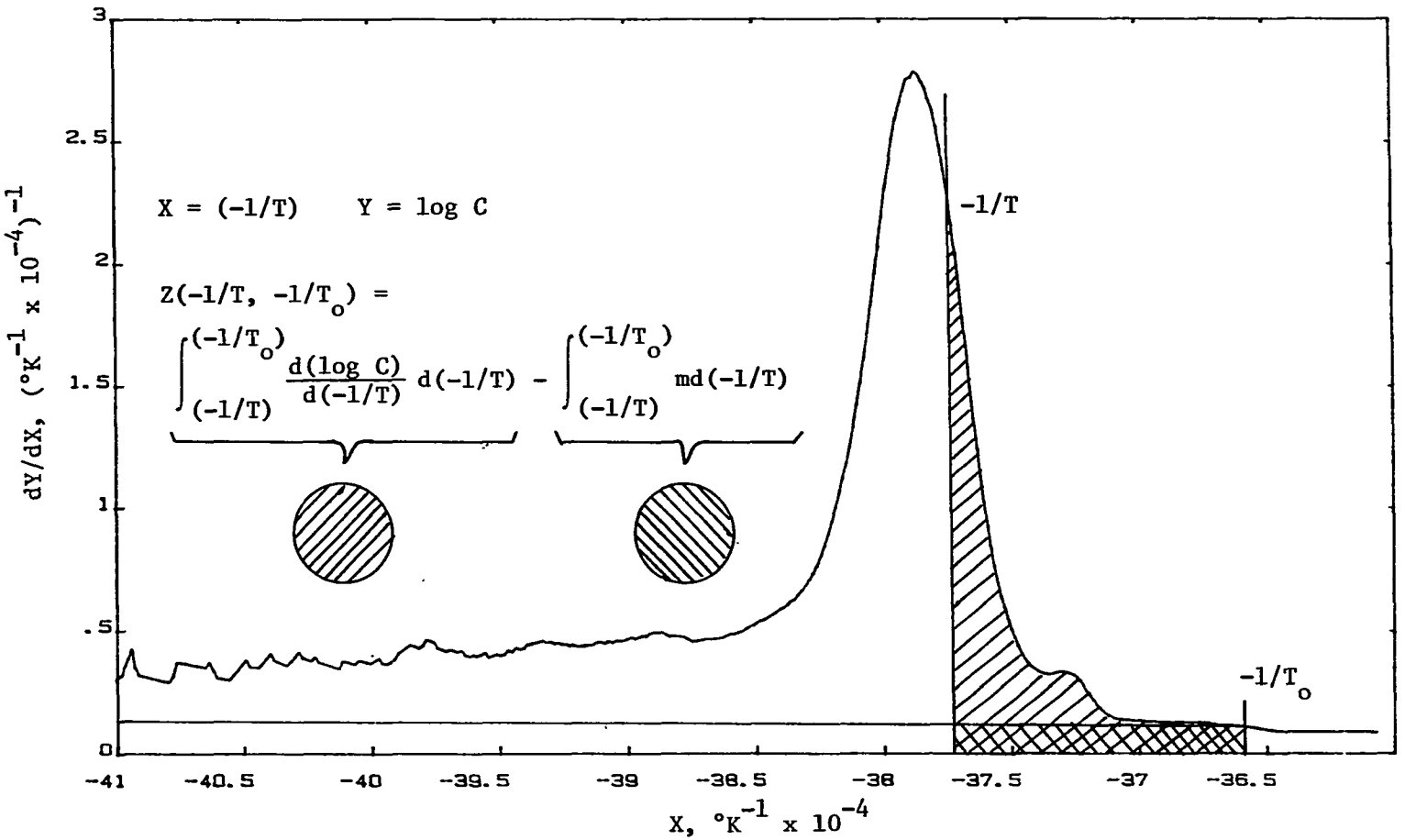


Figure 8. Illustration of the calculation of the parameter Z in conductance phase transition porosimetry

$$\frac{V_{cp(r)}}{V_p} = 10^{-Z(X,X_o)} \tag{38}$$

Assuming a to be equal to unity implies the pore system has a certain degree of homogeneity. This does not imply that all the conducting pores are exactly the same, but rather that the tortuosity and necking inherent to a given pore structure is uniform throughout the pore size distribution.

Examination of equation 37 indicates that the evaluation of the maximum and minimum pore sizes will be unaffected by variations in pore geometry factor. One can examine qualitatively the effect of varying pore geometry factors and such an examination follows.

The expression for the conductance of a pore system of x number of parallel conducting pores expressed in equation 27 can be reduced to

$$\frac{V_p}{\omega} = \sum_{j=1}^{j=x} \frac{V_{pj}}{\omega_j} . \tag{39}$$

where V_{pj} and ω_j are the pore volume and pore geometry factor, respectively, for individual conducting pore j. Errors in the determination of pore size distributions of materials for which the pore geometry factor is dependent of pore size are somewhat reduced by the compensating effect of pore volume on the overall pore geometry factor of a pore system. For example, let's consider a pore system in which the pore geometry factor is a function of pore size with small pores having larger pore geometry factors. Pores containing larger volumes of pore solution will affect the overall pore geometry factor to a greater extent than pores containing smaller volumes of solution. Changing pore

geometry factors will affect the determined size distribution. It will be somewhat skewed towards the larger pores, as illustrated in Figures 9 and 10.

The plots in Figures 9 and 10 labeled actual size distribution are for a hypothetical pore system having a normalized Gaussian distribution with a standard deviation, σ, equal to 0.3 times the mean pore size, R. The pore geometry factor for a range of pore sizes was assumed to be inversely proportional to the pore radius. Calculations necessary to produce the curves labeled conductometry size distribution in Figures 9 and 10 were performed with the aid of a computer spreadsheet and the relationships expressed in equations 37 and 39. Examination of Figure 10 indicates the modal pore sizes as determined by conductometric phase transition porosimetry would be somewhat larger than the actual modal pore size. Table 4 illustrates the effect of standard deviation on this shift in modal pore size. Shown in this table are the errors in modal pore size expressed as a percentage of the actual pore size as calculated for various standard deviations. Also listed are the approximate ratios of the pore geometry factor for the largest pores in the distribution to the pore geometry factor for the smallest pores in the distribution. These ratios will hereafter be referred to as pore geometry factor ratios. The pore geometry factor ratios listed in Table 4 are the ratios of the pore geometry factor for a pore with a radius equal to the mean radius, R, minus three times the standard deviation, σ, to the pore geometry factor for a pore with a radius equal to the mean radius, R, plus three times the standard deviation, σ. Since pore geometry factors

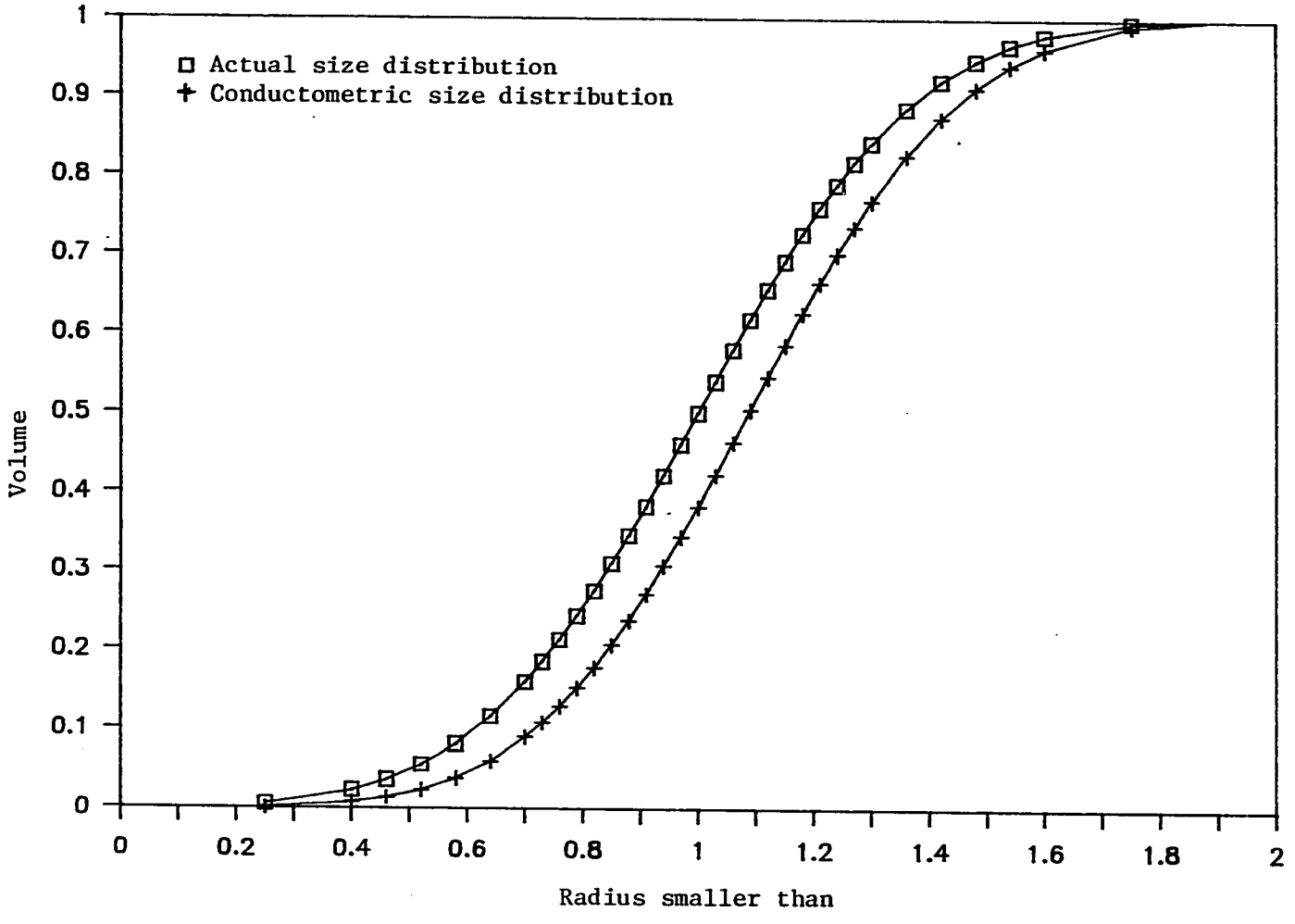


Figure 9. Illustration of error imposed by assuming that pore geometry factor is independent of pore size in CPTP

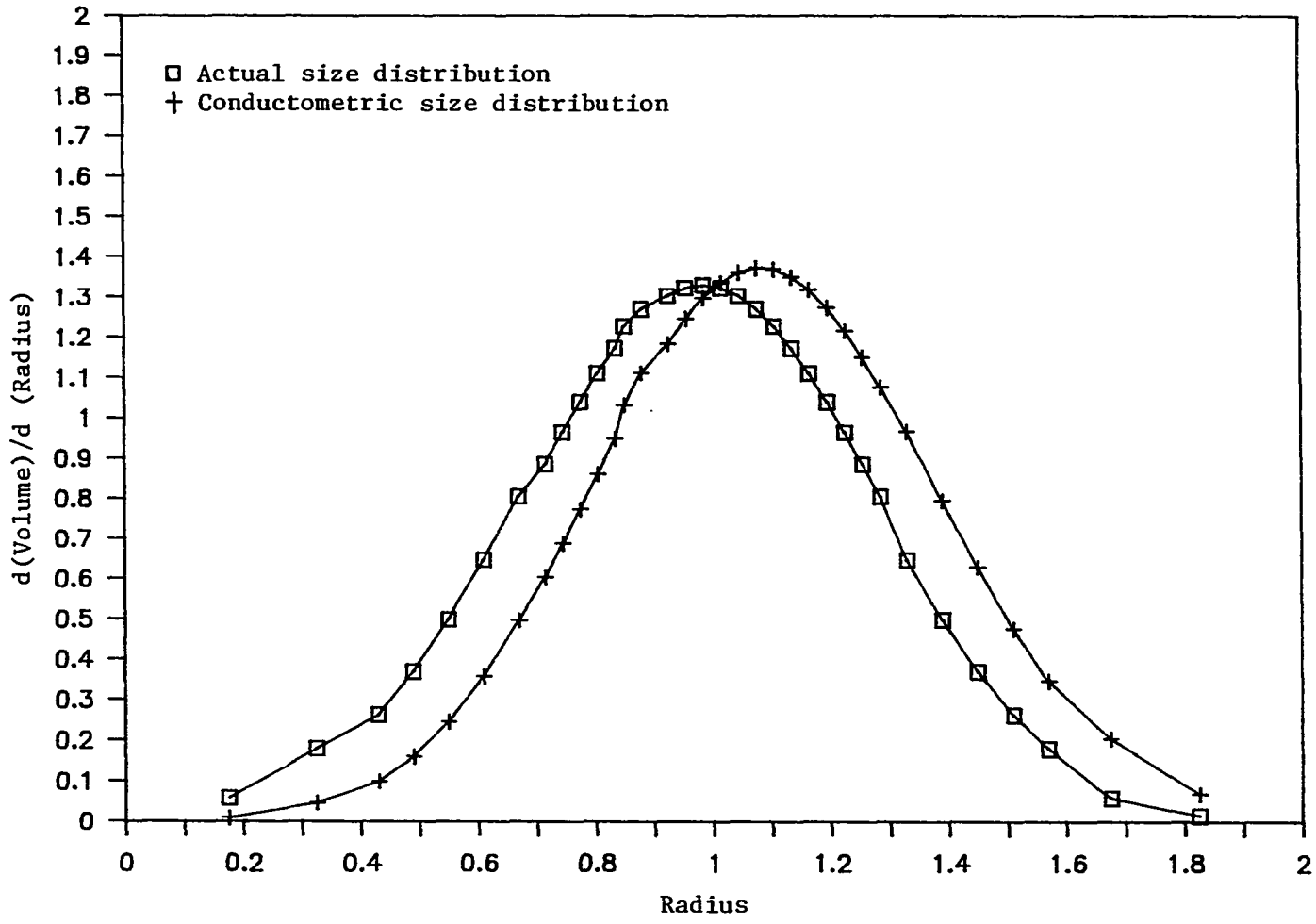


Figure 10. Illustration of error imposed by assuming that pore geometry factor is independent of pore size in CPTP

Table 4. Effect of standard deviation on shift in modal pore size when the pore geometry factor is inversely proportional to the pore radius

Standard deviation	Pore geometry factor ratio[a]	% Error in modal pore radius
0.3 R	19	10.5%
0.2 R	4	5.0%
0.1 R	1.9	0.5%

[a] Pore Geometry Factor Ratio $= \frac{\omega \text{ for pore with radius} = R - 3\sigma}{\omega \text{ for pore with radius} = R + 3\sigma}$.

Table 5. Effect of standard deviation on shift in modal pore size when the pore geometry factor is inversely proportional to the square of the radius

Standard deviation	Pore geometry factor ratio	% Error in modal pore radius
0.3 R	361	16.5%
0.2 R	16	9.0%
0.1 R	3.4	2.5%

were assumed to be proportional to the inverse of the pore radius, the pore geometry factor ratios listed in Table 4 are equal to the ratio of the radius of the largest pore to the radius of the smallest pore for the distribution. Table 5 gives the same information as Table 4 except pore geometry factor is assumed to be inversely proportional to the square of the radius. This results in larger pore geometry factor ratios. Notice that the error in modal pore size is related to both standard deviation and pore geometry factor ratios with the error increasing with increasing standard deviation and increasing pore geometry factor ratios. However, the error is bounded by the maximum pore size for a given size distribution; therefore, the effect of increasing pore geometry factor ratios diminishes as pore geometry factor ratios get larger. It seems conservative to state that errors that result from assuming pore geometry factor to be independent of pore size would be less than 20%. This would result in evaluating the modal size distribution of a pore system with an actual modal size of 100 angstroms as having a modal size distribution for 120 angstroms. For pores with uniform cross-sectional areas, the pore geometry factor of a pore is equal to the tortuosity of the pore; thus, the pore geometry factor ratio is the ratio of the conductive path length of the largest pore to the conductive path length of the smallest pore. From this, it also seems conservative to state that for many materials the error will be much less.

EXPERIMENTAL METHODS AND MATERIALS

Apparatus

The conductometric phase transition porosimeter consists of a conductance meter, a cryostat, a thermistor, the measurement circuitry, a microcomputer, and a plotter.

Conductance measurements are made with a Solomat 2009 conductivity meter. This meter's high frequency alternating current excitation and the use of stainless steel or tungsten electrodes minimize polarization effects. The instrument has a resolution of 0.1 micro-siemens (μS). Digitized conductance output from the meter is relayed to the microcomputer.

A thermistor manufactured by Thermometrics is used to measure the temperature of the sample. The thermistor is used as a variable resistor in a square wave oscillator. The oscillator's output frequency varies with corresponding changes in the resistance of the thermistor. The computer then measures the period of the square wave.

The temperature of the sample is controlled by placing the sample in a suitable container and immersing that container in a Haake cryostat filled with iso-propyl alcohol. The temperature of the cryostat is controlled by the computer through a digital to analog converter.

The computer used is an Apple IIe personal computer equipped with two input/output cards from John Bell Engineering. These cards serve as an interface between the measurement circuitry and the computer. Software was developed to allow the computer to control the temperature

of the cryostat, gather test data, perform necessary data processing, and output the processed data to either the computer's video monitor or a Hewlett-Packard plotter. Cycle starting and ending temperatures, cooling rates, and data collection intervals are all input by the user. In addition, the user can input the total number of cycles for a test sequence and designate different cycle parameters for each cycle within the sequence. These features allow the user to tailor the test sequence to a particular pore system. They also allow periodic determinations of pore size distribution to be made for samples subjected to repeated cycles of freezing and thawing. With this system, a wide range of ambient freezing and thawing conditions can be simulated.

The appendix of this dissertation contains a user's manual for the conductometric phase transition porosimeter. This manual contains instructions for operation of the porosimeter, porosimeter circuitry schematics, computer program descriptions, and computer program listings.

Experimental Procedure

Vycor glass experiment

The conductometric phase transition porosimeter was first used to test a Vycor glass sample obtained from the Corning Glass Company. This porous glass was selected because extensive pore size information is available for it (see Materials section) and thus comparative analysis with either technique is available. A 14-mm diameter and 4-mm thick disk was saturated with a 0.01 molar ammonium nitrate solution. By saturating the sample with this solution, measurable conductance was provided with

negligible freezing point depression.

For many materials, sample preparation necessary for this type of porosimetry will be minimal. It is simply a matter of embedding electrodes in a mass of the material. However, for the brittle Vycor glass, a more complex electrode configuration and containment apparatus was devised (see Figure 11). It consisted of a large glass test tube and two smaller sections of glass tubing. The Vycor disk was press fitted into one end of the larger tubing with a short piece of tygon tubing serving as a gasket. The smaller tubing was located at the opposite end. This tubing provided the inlet for the electrode connections and the thermistor. The upper end of it was filled with a desiccant and cotton to prohibit condensation inside the tube. The electrical contacts with the Vycor disk were provided by mercury placed inside the tube and tubing in contact with the top and bottom surfaces of the Vycor disk. Tungsten wires provided the electrical connections between the mercury contacts and the conductance meter. Finally, a thermistor was placed in the mercury immediately above the Vycor sample to provide necessary temperature measurements.

The assembled apparatus was then placed in the cryostat and the testing cycle was begun. The temperature of the bath was lowered form $7^{o}C$ to $-30^{o}C$ at the rate of $3^{o}C$ per hour. Conductance and temperature measurements were taken at $0.1^{o}C$ intervals and these data composed the cooling portion of the test. The temperature is then raised to $7^{o}C$ at the same rate. Again, conductance and temperature measurements were taken at $0.1^{o}C$ intervals and these data composed the warming portion of

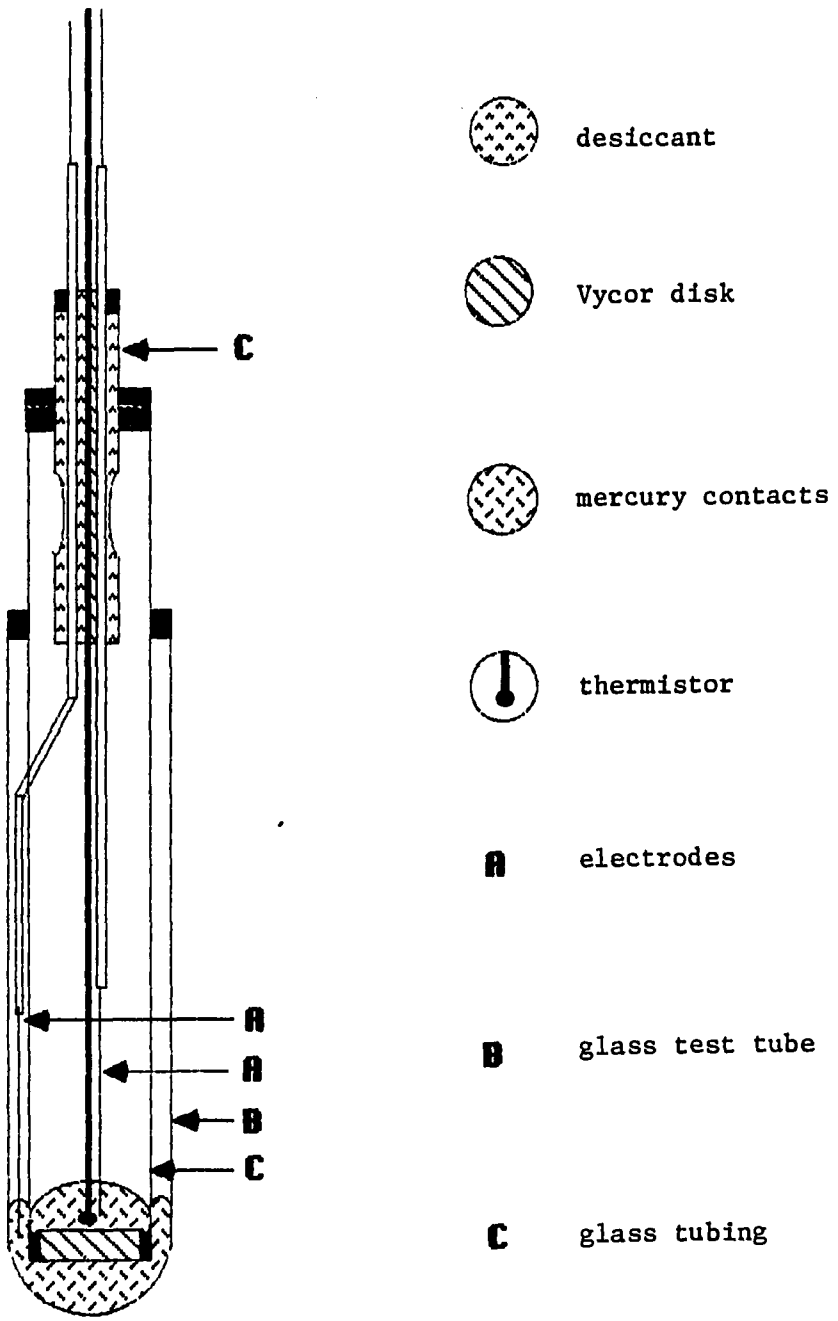


Figure 11. Electrode configuration and containment apparatus for Vycor glass sample

the test.

After some initial experimentation, a test run was made with a 5 kilo-ohm resistor connected in series with the Vycor sample. This allowed the test to be run in the more sensitive conductance range available on the conductance meter (0.1 μS resolution). Experimentally obtained values of conductance were then converted to quantitative conductance values using known relationships for conductors connected in series.

Portland cement mortar and concrete experiments

For the evaluation of pore size distributions of portland cement mortar and concrete, 4-inch diameter by 4-inch high cylinders were molded with an imbedded electrode configuration as shown in Figure 12. The electrodes are fixed in a Plexiglass bottom plate during molding. To prevent surface conductance at the bottom of submersed specimens, the bottom portions of the electrodes were embedded in small plexiglass studs. These studs, when inserted in holes cut in the mold bottom, also held the electrode in place during casting. Also, the upper portion of the electrodes were covered with nonconductive plastic shrink tubing to eliminate conductance between the exposed electrodes. Electrodes were cut from 1/8-inch diameter stainless steel rods. Finally, after curing, a 1 1/2-inch deep hole is drilled in the cylinder to accommodate a plastic thermistor housing. The thermistor is placed in this housing to obtain the necessary temperature measurements.

During testing, the cylinder is placed in a thin-walled plastic

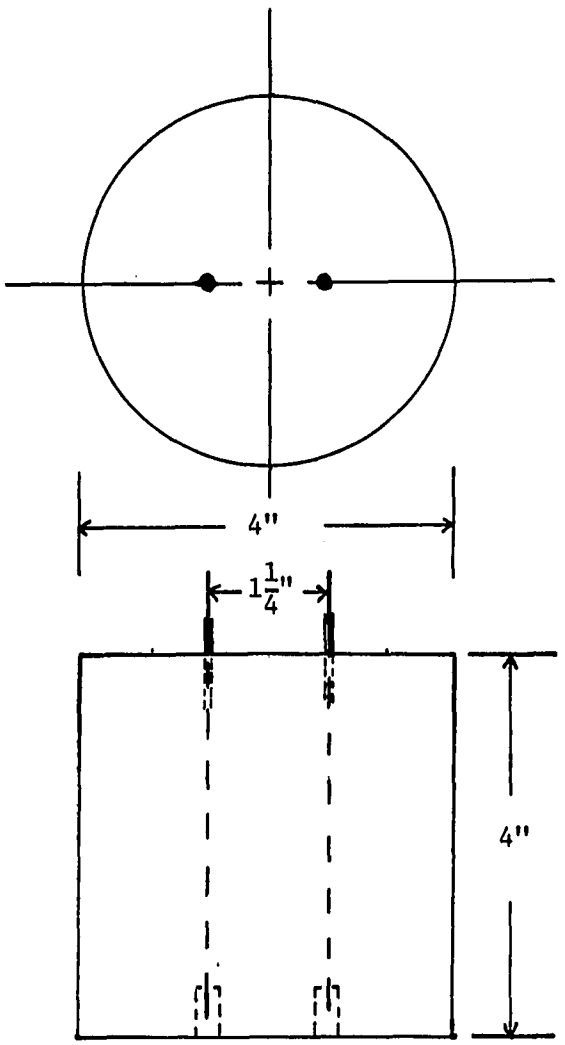


Figure 12. Electrode geometry for mortar and concrete samples

container, and the void between the walls of the cylinder and the container are filled with Ottawa sand. The sand is then saturated with water. Experimentation has shown that the silica crystals in the sand prevent supercooling of the bulk water surrounding the sample. This allows meaningful cooling and warming data to be gathered.

The test cycle for portland cement mortar and concrete cylinders was the same as the test cycle for the Vycor glass sample. For these cylinders, a 7 kilo-ohm resistor was connected in series with the cylinder to allow use of the more sensitive range on the conductance meter. Data processing routines calculated the conductance of the cylinder alone from the measured conductance as was done with the Vycor sample.

Materials

Vycor glass

As stated earlier, the Vycor glass tested was obtained from the Corning glass company. Corning gives this porous glass the designation "Vycor No. 7930." Table 6 (Enüstün et al., 1985a) lists the pore size range, porosity and specific surface of porous Vycor obtained by various researchers using various methods. Values for the conductance method listed in this table were obtained from inflection points of conductance versus temperature data gathered by Enüstün et al. (1978). From these data, these researchers were able to identify minimum, maximum and modal pore sizes. Conductometric phase transition porosimetry builds upon this promising work by calculating a complete pore size distribution from the

Table 6. Pore size range, porosity and specific surface of porous Vycor glass obtained using various methods (Enüstün et al., 1985a)

Method	Range of pore body radius, Å			Range of pore neck radius, Å			Porosity % by vol.	Specific surface, m^2/g
	Min.	Mode	Max.	Min.	Mode	Max.		
Phase trans. poros.	17	42	75-100	12	21	40	27[a]-29[b]	135[c]
Mercury poros.	19	80	--	18	25	35	29[d]	--
Conductance	17	36	60	--	24	26	--	--
TEM	15	38[e]	85	--	--	--	--	--
Manufacturer's specification	10	--	100	--	--	--	28	150-200

[a]From rewarming data.

[b]From cooling data.

[c]Assuming spherical pores.

[d]From intrusion.

[e]After converting number-size distribution to volume-size distribution.

same information. Vycor size distributions presented in this dissertation are slightly larger than those indicated by Table 6 (see Results and Discussion). This is due to the fact that the Vycor sample tested had been stored in deionized water for a period of over three years. This method of storage was suggested by the manufacturer because it would prevent contamination of the glass. It would appear that the storage in deionized water also resulted in some dissolution of silica, resulting in the aforementioned increase in pore sizes. This increase, although observable, is largely insignificant.

Portland cement mortar and concrete

Volumetric proportions for the portland cement mortar and concrete tested are given in Tables 7 and 8, respectively. The portland cement used was Lehigh Type I. The fine aggregate used was sand obtained from the Cordova quarry in eastern Iowa. The coarse aggregate used was an oolitic limestone from the Montour quarry in Iowa. This aggregate had a nominal maximum aggregate size of 3/4 inch. No admixtures were used with either the mortar or concrete mixtures. After mixing and molding, test cylinders were cured in a room temperature water bath until testing was begun. Curing time for mortar samples was 60 days and for concrete samples, 28 days. A replicate cylinder of concrete mortar was cast without electrodes. A sample from the center of this cylinder was used as a test sample for comparative analysis with mercury porosimetry.

Table 7. Volumetric mix proportions for mortar sample

Material	Volume
Cement	.194
Water	.261
Fine aggregate	.545
Total	1.000

Table 8. Volumetric mix proportions for concrete sample

Material	Volume
Cement	.116
Water	.156
Fine aggregate	.327
Coarse aggregate	.401
Total	1.000

RESULTS AND DISCUSSION

Vycor Glass

The conductometric phase transition porosimeter was first used to determine the pore size distribution of porous Vycor glass. In Figure 13, the logarithm of the conductance is plotted against the negative inverse of the absolute temperature (Y versus X) for the Vycor sample tested. The linearity of the curves prior to freezing or after melting of capillary water supports the relationship between electrical conductivity of an electrolyte and temperature as defined in equation 32. The sharp drop in conductance which occurs at approximately $-8^{\circ}C$ on the cooling curve is due to the rapid freezing of supercooled bulk solution.

Figures 14 and 15 illustrate two graphical means of presenting conductometric pore size distributions. To obtain these plots, the Y versus X data illustrated in Figure 13 are processed using equations 35, 36, and 37 and the numerical integration procedure described in Figure 8. Pore geometry factors are assumed to be independent of pore size ($\alpha = 1$ in equation 37). In Figure 14, the cumulative relative conducting pore volume is plotted against pore radius. The relative conducting pore volume at any point on the curves is the fraction of the total pore volume smaller than the corresponding pore radius for that point. The curve labeled neck size is obtained from data gathered during the cooling portion of a test and the curve labeled body size from the warming portion. The first derivative of relative conducting pore volume with respect to pore radius is plotted against pore radius in Figure 15.

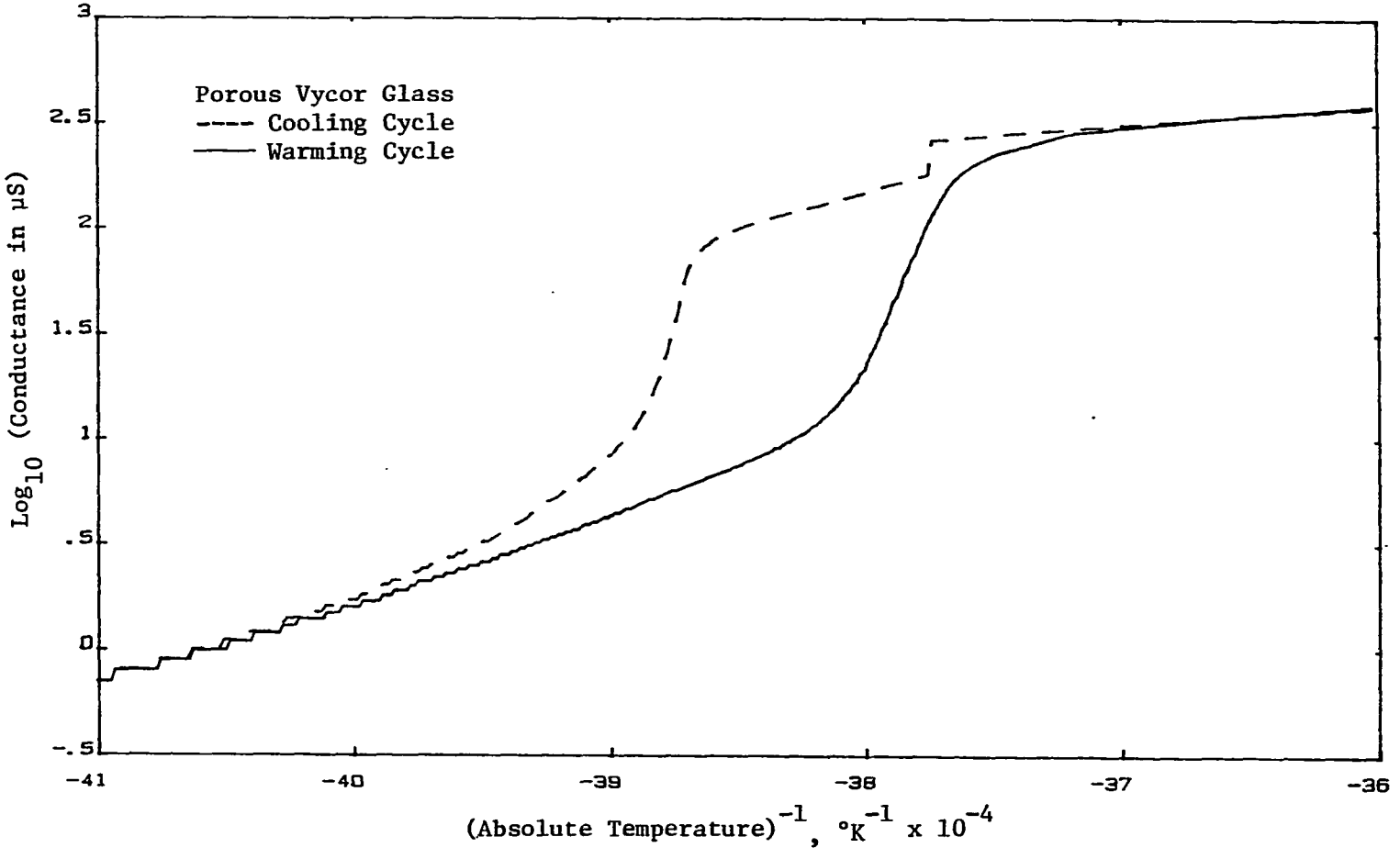


Figure 13. Logarithm of the conductance versus negative inverse of absolute temperature (Y vs. X) for Vycor glass

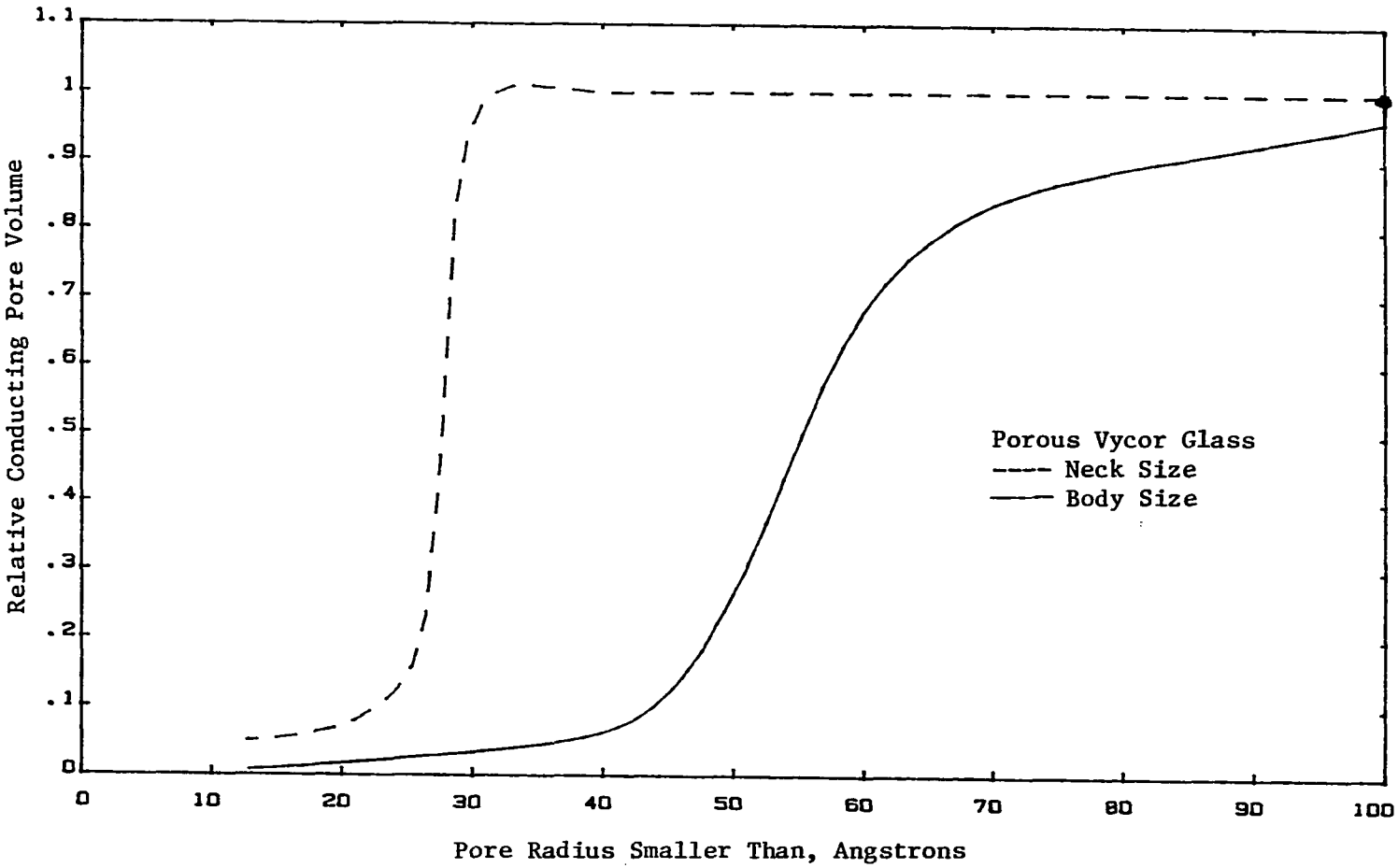


Figure 14. Conductometric pore size distribution of Vycor glass

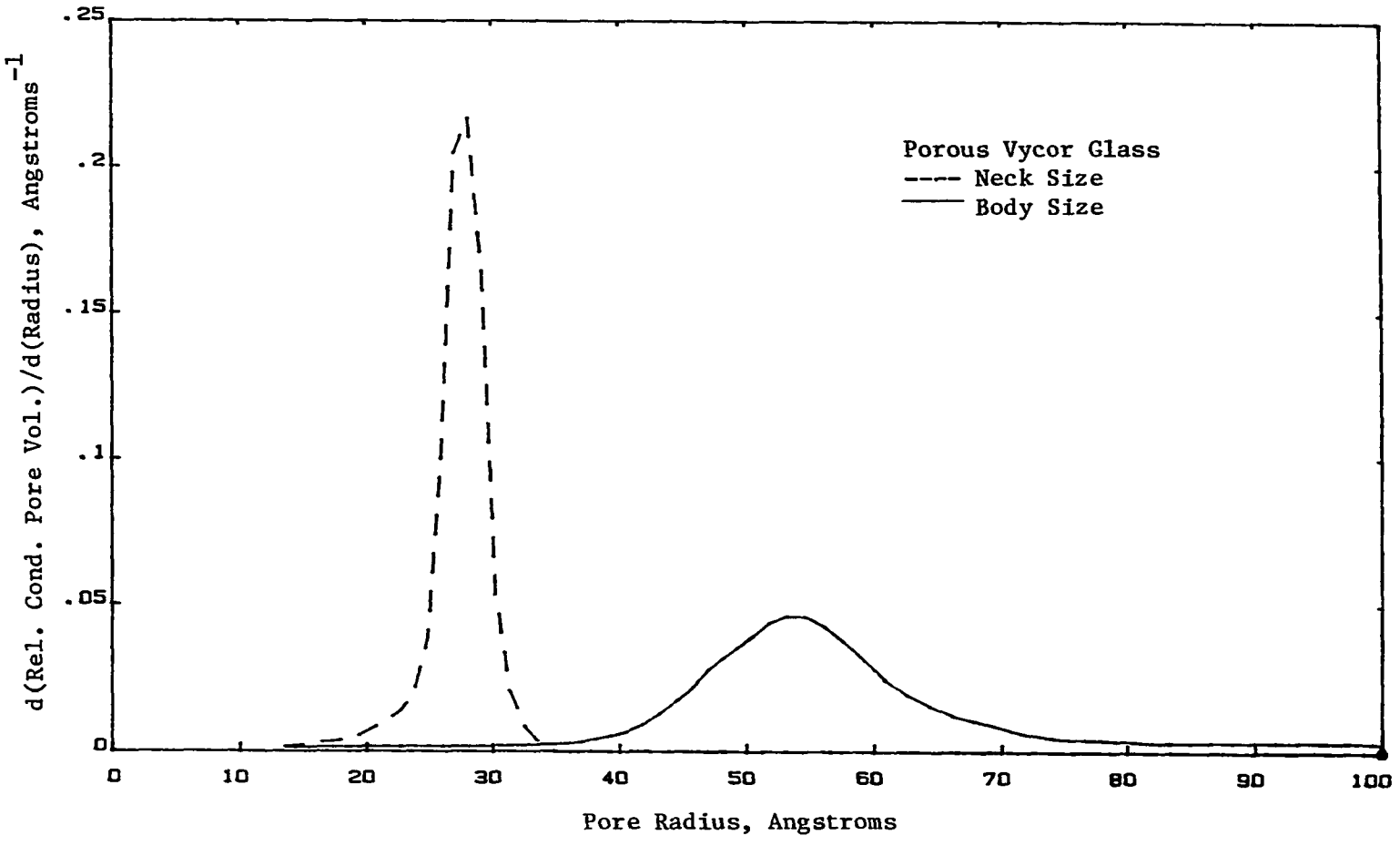


Figure 15. Conductometric pore size distribution of Vycor glass

Table 9 gives the minimum, modal and maximum pore sizes determined from this plot. Extrapolation of maximum and minimum values from distribution curves such as these is somewhat subjective. In spite of this and the aforementioned increase in pore sizes due to dissolution of silica over time, the results presented in Table 9 agree quite well with the results obtained by other researchers presented in Table 6.

Table 9. Minimum, modal and maximum pore radii in angstroms for Vycor glass as determined by conductometric phase transition porosimetry

	Minimum	Modal	Maximum
Neck size	15	29	34
Body size	35	54	75

Evaluations of these results were also made by comparing them with results obtained on the same sample by dilatometric phase transition porosimetry and by mercury porosimetry. Quantitative conductometric pore size distributions were calculated from relative pore size distributions by multiplying relative values by the total pore volume of the sample. The sample's total pore volume was determined gravimetrically to be equal to 0.21 ml. Figures 16 and 17 contrast the pore size distributions obtained from conductometric phase transition porosimetry, dilatometric phase transition porosimetry and mercury porosimetry for neck and body sizes, respectively. It can be seen from these figures that all three methods give comparable results for neck sizes. For body sizes, some

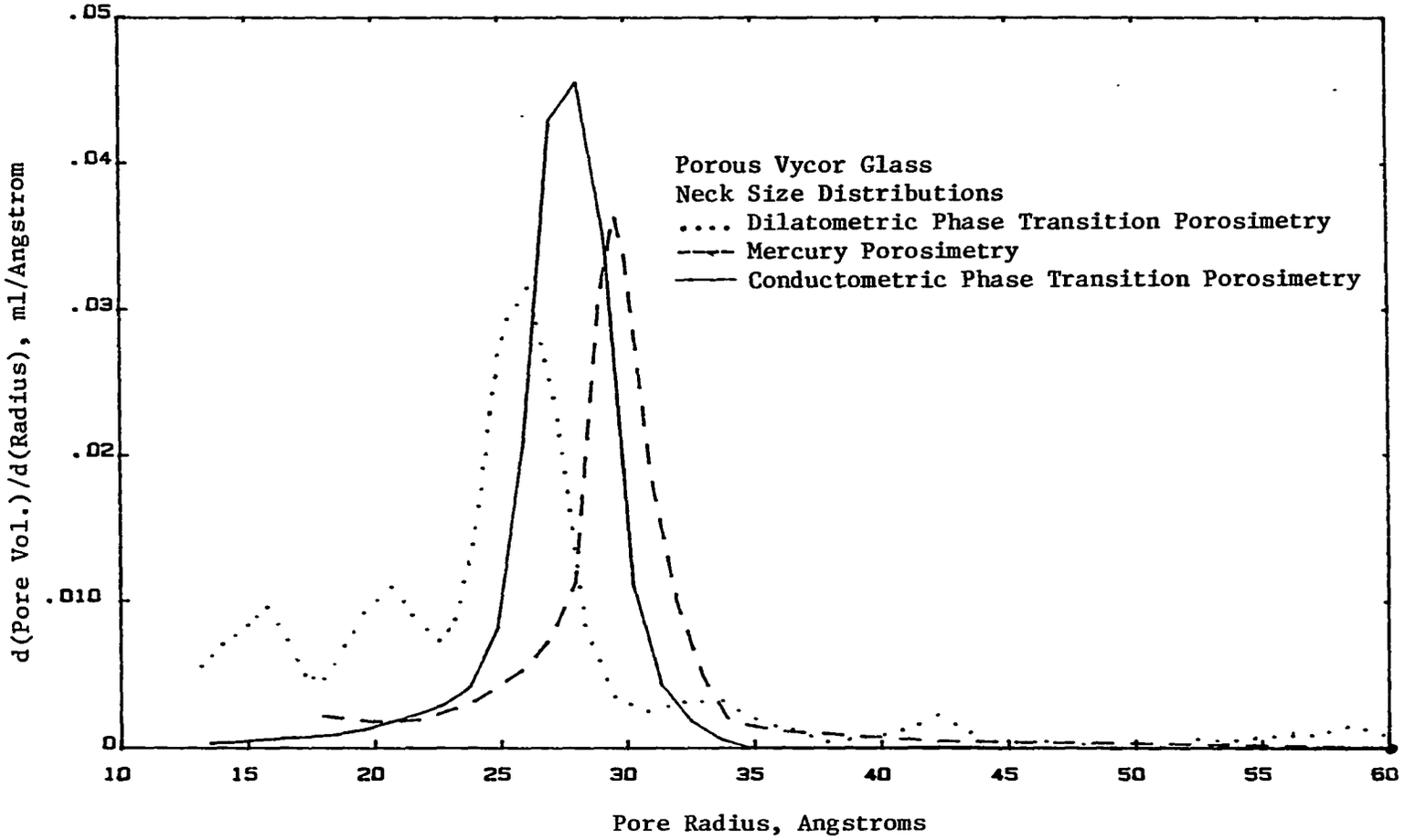


Figure 16. Comparative neck size distributions for Vycor glass

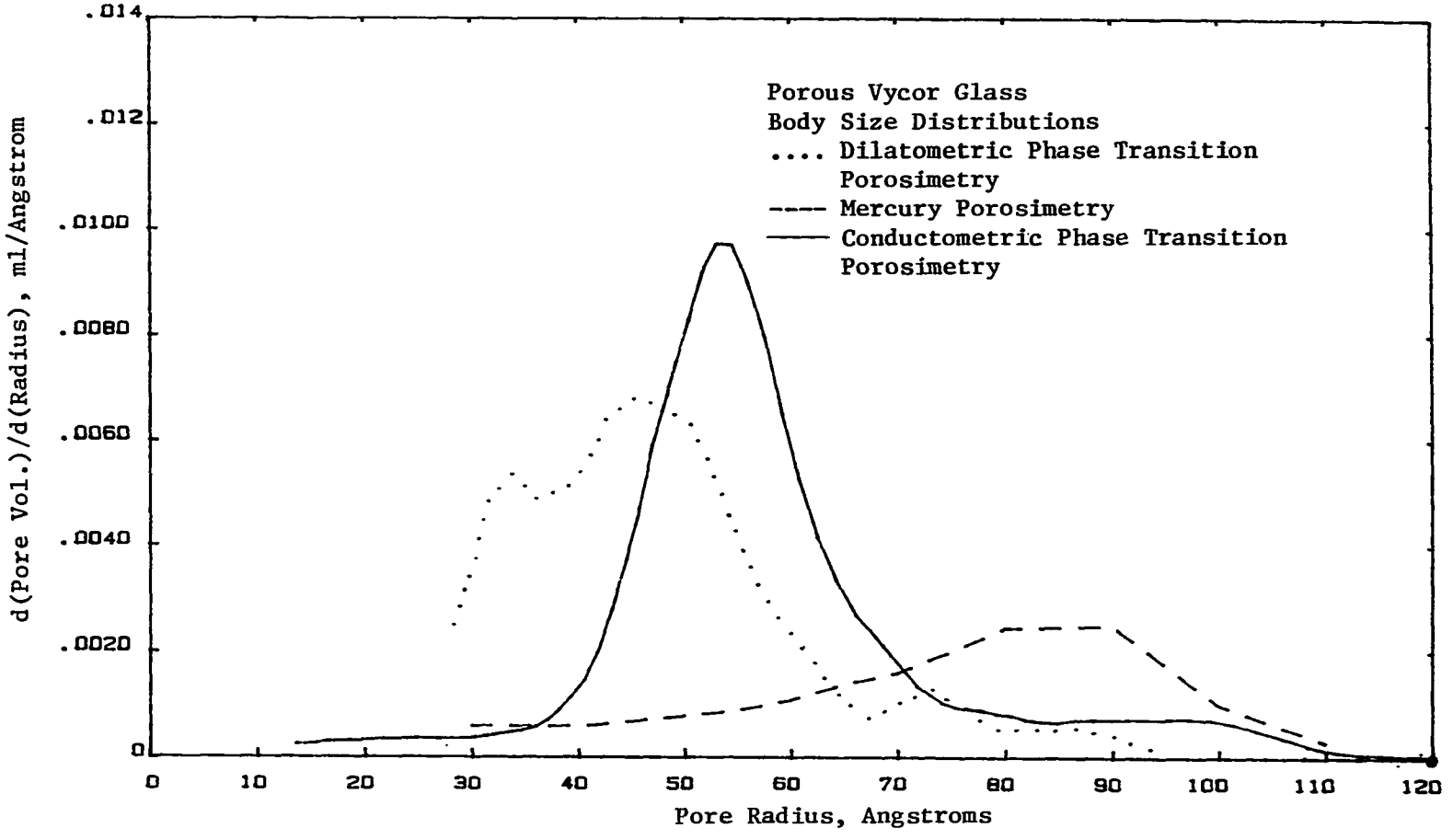


Figure 17. Comparative body size distributions for Vycor glass

differences are observable. It is believed that the differences between the body size distributions as determined by phase transition methods and that determined by mercury porosimetry are due to uncertainties involved with the entrapment of mercury during extrusion as discussed earlier.

Portland Cement Mortar

The conductometric phase transition porosimeter has been used to evaluate the pore size distribution of the 4-inch diameter by 4-inch high portland cement mortar cylinder discussed earlier.

A small portion (approximately 2 gm) was taken from the center of a replicate mortar cylinder. The pore size distribution of this portion of mortar was determined by mercury porosimetry. The mercury porosimeter sample was dried at room temperature, pressure and relative humidity prior to the evacuation process necessary with mercury porosimetry.

Resultant pore size distributions for this concrete mortar are shown in Figure 18. In this figure, percentages of the total pore volume are plotted against the logarithms of the pore radii. The wide range of pore sizes indicated by these size distributions is characteristic of hydrated portland cement (Mikhail et al., 1964). The mean pore neck size as evaluated by mercury porosimetry is nearly three times as large as the mean pore neck size as evaluated by conductometric phase transition porosimetry.

Mikhail et al. (1975), referencing data from Diamond (1971), indicates that mean pore radii of portland cement pastes obtained from water adsorption data range from 21 to 50 angstroms, while mean radii

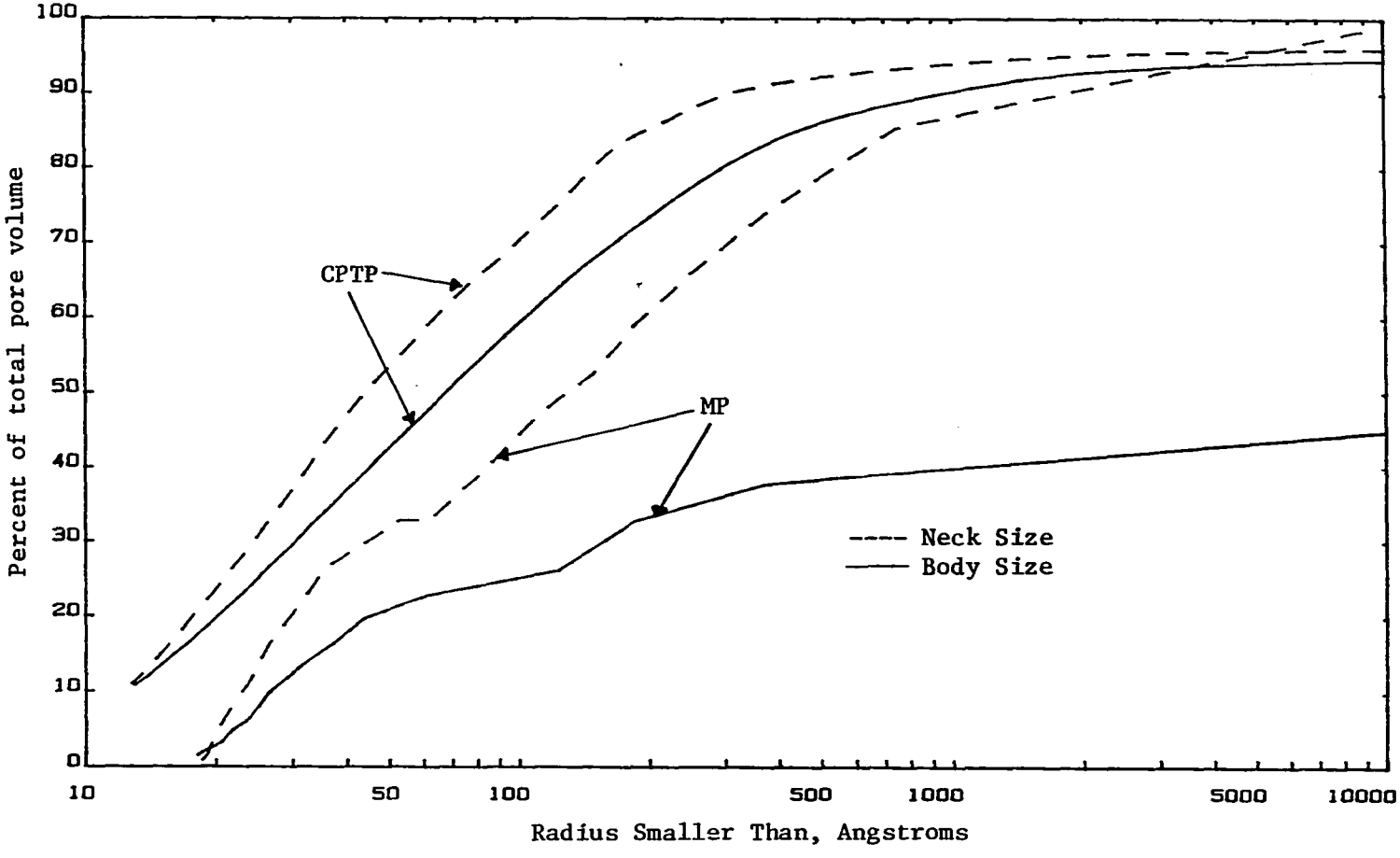


Figure 18. Pore size distribution of portland cement mortar as determined by conductometric phase transition porosimetry (CPTP) and mercury porosimetry (MP)

obtained from mercury intrusion data range from 115 to 385 angstroms. While the material tested in the present study was not portland cement paste but rather portland cement mortar, the mean radii determined for the mortar by mercury porosimetry fall within the expected range for mercury porosimetry. In contrast, the mean radii determined by conductometric phase transition porosimetry fall within the expected range for water adsorption. Mikhail et al. (1975) do not attribute these differences to any fundamental flaw in the theory behind either method, but rather to the inability of mercury porosimetry to determine complete size distributions. They reject the large mean radii and subsequent large surface areas determined by mercury porosimetry because of the presence of pores beyond the range of mercury porosimeters (approximately 18 angstroms). Indeed, they question the validity of results obtained for radii smaller than approximately 50 angstroms due to possible deformation or destruction of pores at the high pressures necessary with mercury porosimetry.

Although direct comparison of results obtained by conductometric phase transition porosimetry with results obtained by adsorption is not possible for the mortar tested, it would appear conductometric phase transition porosimetry would give results more typical of water adsorption than mercury porosimetry. Conductometric phase transition porosimetry results indicate approximately 10% of the total pore volume of the mortar is associated with pores smaller than 12 angstroms. This would be expected because the pressure gradient across the ice/water meniscus in phase transition porosimetry is much less than the gradient

across the mercury meniscus in mercury porosimetry. This, coupled with the ability of phase transition porosimetry to analyze pores down to a size of 12 angstroms, allows a more complete and accurate size distribution to be obtained.

Finally, it would appear from examination of the data presented for Vycor and mortar that the errors introduced by assuming that pore geometry factor is independent of pore size for a given pore system is not significant.

Portland Cement Concrete

Pore size distributions for the portland cement concrete cylinder were determined by conductometric phase transition porosimetry and results are shown in Figures 19 and 20. In Figure 19, relative conducting pore volume is plotted against pore radius; and in Figure 20, the first derivative of pore volume with respect to the logarithm of the radius is plotted against the logarithm of the radius. These distributions illustrate the use of the porosimeter with a material whose pore size distribution is not obtainable by other techniques. Portland cement concrete is a highly heterogeneous material and samples that can be considered to be representative of the material are much too large for analysis by other techniques.

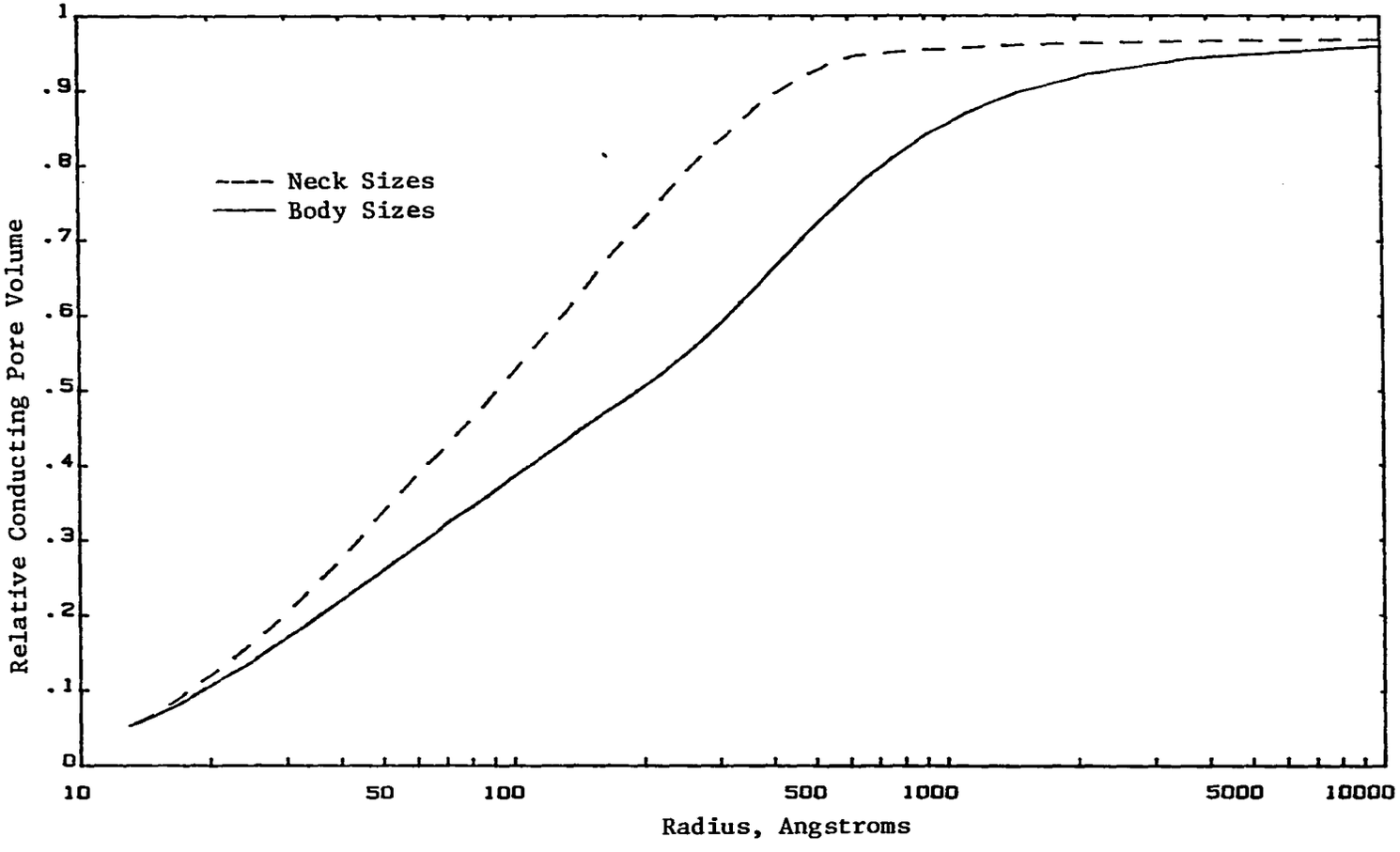


Figure 19. Pore size distribution of portland cement concrete

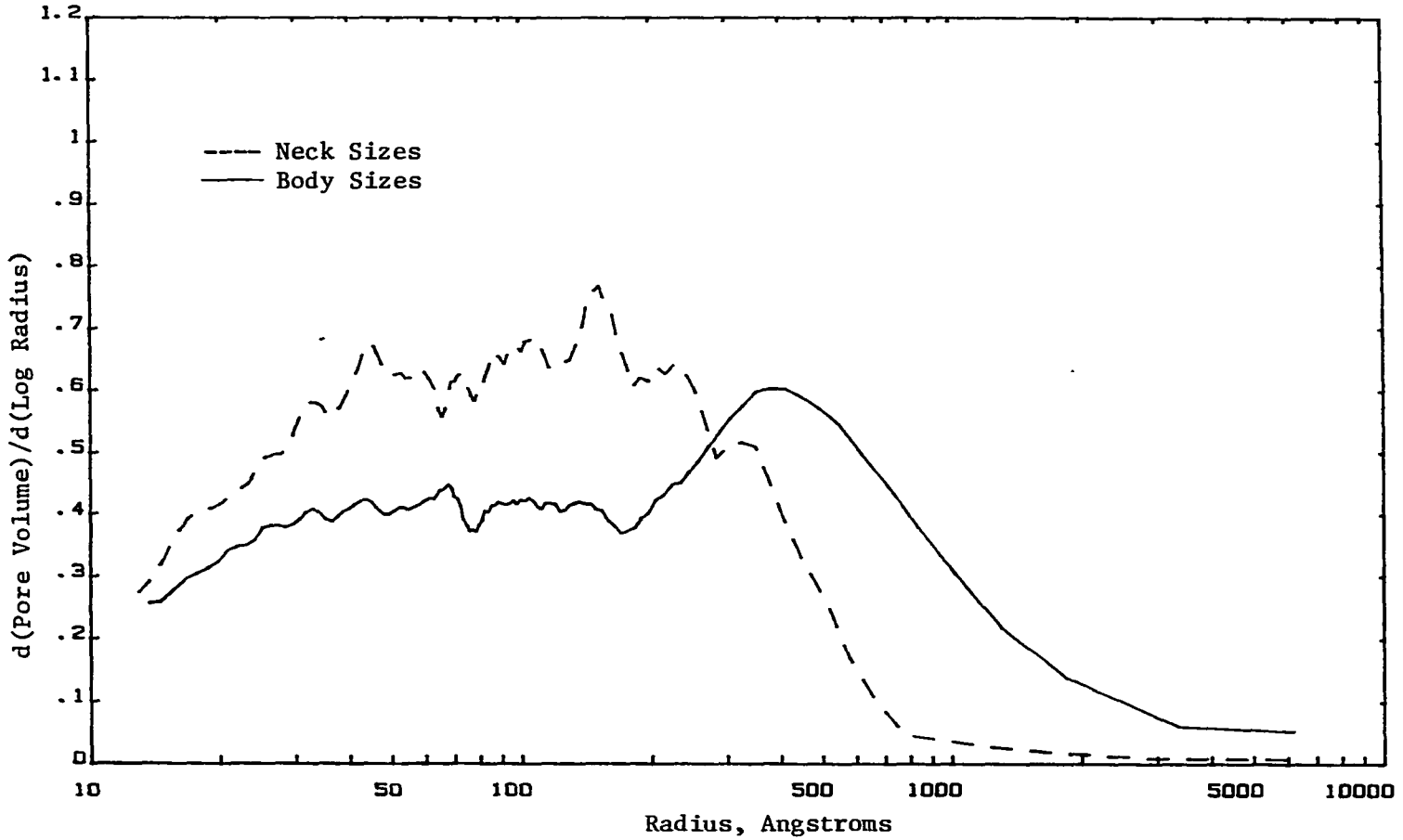


Figure 20. Pore size distribution of portland cement concrete

SUMMARY AND CONCLUSIONS

A new method for determining pore size distributions of saturated porous materials has been developed. This new methodology, referred to as conductometric phase transition porosimetry (CPTP), combines relationships correlating the volume of unfrozen pore solution to electrical conductance, the pore solution freezing temperature to pore radii, and the electrical conductivity of the pore solution to temperature. These relationships are used with measurements of the electrical conductance and temperature to obtain pore size distributions of saturated porous materials subjected to a cycle of capillary freezing and melting.

The plastic ice model of capillary freezing and melting first introduced by Everett is essential to CPTP, and this model is reviewed in this dissertation. This thermodynamically based relationship between pore water freezing temperatures and pore radii has been expanded to include the freezing of pores saturated with solutions containing nonvolatile solutes.

This dissertation also introduces the parameter called pore geometry factor and a relationship which expresses the electrical conductance of a material as a function of pore geometry factor, pore volume, pore solution conductivity, and sample geometry is introduced. This relationship is essential to CPTP and its physical significance is explored.

Based on this newly developed methodology, a conductometric phase

transition porosimeter was constructed. The porosimeter is capable of determining the pore size distributions for a broad range of pore radii ranging from 12 to 5000 angstroms. This porosimeter has been used to accurately determine the pore size distribution of porous Vycor glass. In addition, techniques for determining the pore size distributions of portland cement mortars and concretes have been introduced.

Conductometric phase transition porosimetry is free of the problems of entrapment of mercury inherent to mercury porosimetry. Also, the pressures a sample is subjected to during testing are much less than those necessary with mercury porosimetry. Therefore, deformation or destruction of pores will be significantly less with conductometric phase transition porosimetry for many materials provided the freezing and thawing rate is slow. The slow rate is necessary to prevent viscous forces from damaging the sample.

With conductometric phase transition porosimetry, samples do not have to be dried prior to testing as with mercury porosimetry and adsorption techniques. For materials which have pore structures that vary with moisture content, conductometric phase transition porosimetry provides researchers with a means of investigating these relationships.

In contrast with dilatometric phase transition porosimetry, conductometric phase transition porosimetry can be used to determine the pore size distribution of the saturated pores of a partially saturated pore system.

Conductometric phase transition porosimetry holds an advantage over other available techniques in that it allows much larger samples to be

tested. The porosimeter has been used to evaluate the pore size distributions of 4-inch diameter by 4-inch high portland cement concrete cylinders.

Potential errors associated with the assumption that pore geometry factors are independent of pore sizes for a given pore system have been shown to be insignificant in determining the pore size distributions of Vycor glass and portland cement mortar.

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APPENDIX

CONDUCTOMETRIC PHASE TRANSITION POROSIMETER

USER'S MANUAL
Volume 1
Operation Instructions

CONDUCTOMETRIC PHASE TRANSITION POROSIMETER USER'S MANUAL Volume 1

by
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IOWA STATE UNIVERSITY, 1987

CONDUCTOMETRIC PHASE TRANSITION POROSIMETER
USER'S MANUAL
Volume 1
Operation Instructions

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I. INTRODUCTION

Conductometric phase transition porosimetry is based on the assumption that the electronic conductance through the solid phases of a porous material is negligible when compared to the electrolytic conductance of the pore solution. Thus, when the temperature of a mass of saturated porous material is raised from sub-freezing temperatures the frozen pore solution will melt, and an increase in electrical conductance will be observed. As ice in capillaries melts at temperatures below the normal melting point of ice, the change in electrical conductance of the material with temperature will be a function of the pore structure of that material. The methodology combines the plastic ice model for solid-liquid phase transitions of pore water with relationships between conductance and temperature, and conductance and pore structure. The theory behind conductometric phase transition porosimetry is developed from a few basic relationships.

Assuming that the pore geometry of the sample can be represented by randomly intersecting spheres or cylindrical capillaries with or without constrictions, it can be shown using the plastic ice model, that the solid-liquid phase transition of water in a pore having an effective radius of r takes place at a temperature, t (°C) given by:

$$t = -2\gamma T_o/(\rho\lambda r) \qquad (1)$$

where T_o is the normal melting point of ice in °K, λ is the heat of fusion of ice per unit mass, ρ is the density of water and γ is the ice/water interfacial tension at t. In melting, r is the pore body radius, while in freezing it is the radius of the pore constriction.

A relationship between the ice/water interfacial tension, γ, and temperature is used where

$$\gamma = \gamma_o + kt \qquad (2)$$

where t is the temperature in °C, k is a dimensional constant with a value of 0.25 ergs cm^{-1} K^{-1}, and γ_0 is the value of γ at 0 °C. Also, for conductometric phase transition porosimetry it is helpful to develop a relationship between pore radius, r, and the negative inverse of the absolute temperature, X. With this information equation 1 can be rewritten as

$$r = \frac{-2T_0(k - \gamma_0 X + kT_0 X)}{\rho\lambda(1 + T_0 X)} \qquad (3),$$

where r, T_0, γ_0, k, ρ, and λ are as defined earlier and $X = (-1/T)$, where T is the phase transition temperature in °K.

The numerical values of the various constants used in computations contained in this document were as follows:

$\gamma_0 = 29$ N m^{-1}

$T_0 = 273.16$ °K

$\rho_W = 1.000$ gm cm^{-3}

$\lambda = 333.3$ J gm^{-1}.

These values were obtained from physical and chemical handbooks.

The relationship between conductance of a porous material, C', and pore structure for a cylindrical sample of porous material with cross-sectional area, A, and length, L, is defined as

$$C' = \kappa\,(V_p/(L^2\,\omega)) \qquad (4)$$

where κ is the electrical conductivity of the pore solution, V_p is the pore volume and ω is a dimensionless pore geometry factor.

Also, it is assumed the relationship between the electrical conductivity of an electrolyte and the absolute temperature of the electrolyte is an Arhennius type relationship and can be expressed as

$$\ln \kappa = \frac{a}{T} + b \qquad (5)$$

where

κ = electrical conductivity,

T = absolute temperature,

a = physical constant, and

b = physical constant.

By combining equations 4 and 5 the following equation is derived

$$Y = mX + d + \log_{10}\left(V_p/(L^2\omega)\right) \qquad (6)$$

where L, V_p and ω are as defined earlier,

X = -1/(absolute temperature),

Y = $\log_{10}$ (conductance),

m = physical constant, and

d = physical constant.

A plot of the $\log_{10}$ of the conductance versus the negative inverse of the absolute temperature (Y versus X) for which no phase change occurs will result in a line with a slope equal to m. Below freezing temperatures the phase changes which ocur in a certain range of pores will effectively

decrease the volume of conducting pores. Thus, V_p at below freezing temperatures can be considered to be the volume of conducting pores, V_{cp}.

Taking the first derivative of equation 6 yields

$$\frac{dY}{dX} = m + \frac{d\left(\log_{10}(V_p/(L^2\omega))\right)}{dX} \qquad (7)$$

Integrating equation 7 over the definite interval, X to X_0, yields the following:

$$\log_{10}\left[\frac{\frac{V_{cp}(X_0)}{L^2\omega_{X_0}}}{\frac{V_{cp}(X)}{L^2\omega_X}}\right] = \int_X^{X_0} \frac{dY}{dX}\,dX - \int_X^{X_0} m\,dX \qquad (8)$$

The right half of equation 8 can be calculated numerically from conductance test data and is given the variable name Z. Also, if X_0 is the value of X at the pore solution melting point (273.15 °K for water), then $V_{cp}(X_0)$ is simply the total conducting pore volume, V_p. Rearranging equation 6 and referring to pore radius instead of temperature in light of equation 1 we obtain:

$$\alpha\frac{V_{cp}(r)}{V_p} = 10^{-Z(X,\,X_0)} \qquad (9)$$

where $V_{cp}(r)$ is the volume of the pores with radii smaller than or equal to r containing unfrozen pore solution, V_p is the total pore volume and α is the ratio of the pore geometry factor of the total pore system, ω, to the pore geometry factor of the pores smaller than r, ω_r. If it is assumed that the

shape factor, ω, is independent of pore size, then α is equal to unity and equation 9 can be reduced to

$$\frac{V_{cp(r)}}{V_p} = 10^{-Z(X, X_0)} \qquad (10)$$

Assuming α to be equal to unity implies the pore system has a certain degree of homogeneity. This does not imply that all the conducting pores are exactly the same but rather that the tortuosity and necking inherent to a given pore structure is uniform throughout the pore size distribution or otherwise stated that they are geometrically similar.

These relationship provide the theoretical background for conductometric phase transition porosimetry.

The Apple IIe computerized data acquisition system has been developed. The system consists of the Apple IIe computer (with two disk drives, a monitor, a parallel interface card, and a serial interface card), a cooling bath, a temperature interface box, and a Solomat conductance meter. The computer controls the bath and records the data for a typical experiment.

II. TUTORIAL

This section will take a step by step look at a typical multicycle conductance test. For further information on any step refer to the detailed descriptions in the program or interface sections.

1. Place program disk in drive 1 and raw data disk in drive 2, then reboot the computer by pressing the CTRL, open-Apple, and RESET keys simultaneously. The computer will restart and load the Main Menu program from the program disk. The programs used in this system are menu based. By choosing a number (to change a parameter) or a letter (to choose an action) the program is controlled. While inputting a selection or data, the left and right arrows on the lower right hand corner of the keyboard may be used to correct mistakes. Press the RETURN key to enter your selection.

2. Place the sample in an appropriate container and immerse in the cooling bath. The sample should be saturated with water and surrounded by bulk water. The container should be slightly larger than the sample and able to seperate the cooling fluid from the sample. Connect the leads from the Solomat conductance meter to the probes mounted in the sample. If better resolution is needed at the lower end of the conductance scale place a resistor in series with the sample to lower the overall conductance below 160 µS and set the scale on the Solomat to 160 µS for the 1.0 cell. If a series resistor is used, the sample's conductance will be calculated by the data processing programs when the appropriate data are entered in the Main Menu before processing. If a series resistor is not used set the scale on the conductance meter to 16000 µS for the 1.0 cell. The thermistor should be placed adjacent to the sample. Turn the cooling bath on by using the green main switch first followed by the black compressor switch. Manually set the bath's temperature to the maximum temperature of the first cycle. It will take about 20 to 30 minutes for the temperature of the sample to reach that of the bath.

3. Start the controlling program by entering C for Run Conductance Test. The program will allow some notes to be entered. Then enter the number of cycle types and define each of the types by entering the maximum temperature, minimum temperature, rate of temperature change, and temperature interval between readings for each cycle type. If data collection is not needed for a paticular cycle type enter the number 0 as the

temperature interval. Next enter the total number of cycles for the test sequence and the cycle type for each cycle. Finally, enter the sample's base file name and the starting cycle number for the test sequence. The test sequence will begin. Place the temperature preset switch on the rear of the cooling bath in the ON position. The computer will control the entire test and return to the Main Menu when finished. When the test sequence is completed, turn off the cooling bath and remove the sample.

4. The next step is to process the data. The parameters shown on the Main Menu control the processing. First choose a1 for File Name. If the name of the file you wish to process is unknown, press RETURN and a catalog of the disk in drive 2 will be displayed. Enter the base file name and the cycle number. For example, Mortar.25 would be entered for the 25th cycle of the sample named mortar. If a resistor was connected in series with the sample indicate so and input the CONDUCTANCE of the resistor (μS). The derivative programs use a moving average in their algorithms to smooth the data. Enter the desired moving average for each of the derivative steps. Some of the intermediate steps generate data that may or may not be of interest. Respond with a Y to a Save File option and the data for that file will be saved to a disk. The temperature of T0 is the normal freezing point of the pore solution in degrees Kelvin (usually 273.15 K). Once the parameters are set in the desired manner, enter A and calculations will be performed.

5 About one minute into the processing the program will prompt the user to remove the raw data disk and insert a Caldat disk. The processed information is stored on a different disk than the raw data and the raw data has been loaded and processed at this point. The total process takes roughly 7-8 minutes for a cycle with 350 points per portion (warming and cooling) and the program returns to the Main Menu when finished.

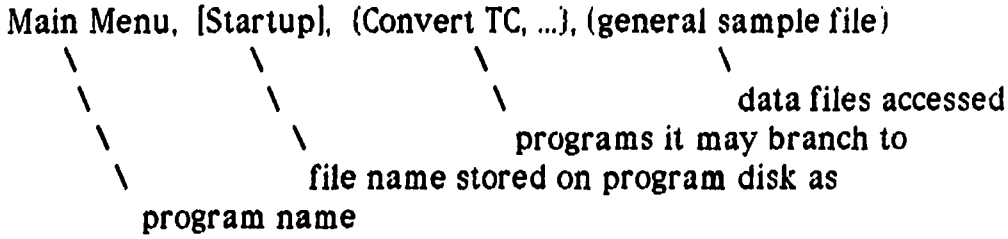
6. To make plots of the data choose B for Plot Curves. The computer will load the Plotting Program and diplay a menu of data file types (from X.Y through R.DVPDLR). If selection 6 or 7 is chosen, the option of plotting the radius on a log scale is available. The plotting menu will then be displayed. Both the warming and the cooling data, may be plotted simultaneously. Enter the file name(s) of the data (base filename, cycle number, and W for warming or C for cooling, i.e., Mortar .25C for the cooling portion of the 25 cycle of a sample named mortar). Plotting parameters may be adjusted to the user's preference and the range of the data. It is advisable to make a

plot on the computer screen to ensure the parameters are set up correctly before making a plot on the plotter. The computer may be stopped while plotting to the screen at any time by pressing the ESC key. The plot is finished when the computer beeps several times. Pressing any key will return the computer to the menu.

7. When all of the necessary plots have been made, enter E to Exit Program and return to the Main Menu. When finished, return the disks to the cases and turn off the computer monitor. The computer itself is left on to maintain the stability of the amplifier circuits.

III. PROGRAMS

In this section the purpose, operation, and the structure of each program will be discussed. The structure will be given to help understand the program and solve possible problems. Each program will be listed with the following information



Most programs are menu based, the user options are listed on the screen by number or letter. Choosing a number allows you to edit the data or a parameter and selecting a letter chooses a particular action. While inputting a selection or data, the left and right arrows on the lower right hand corner of the keyboard may be used to correct mistakes. Press the RETURN key to enter the selection.

There are three types of disks in this system. One of the disks contains the programs to control the tests, process the data and output the results. The other two types are data disks. The raw data disk contains the temperature vs. conductance information for all cycles and the general sample file. The CALDAT disk contains the processed data for the directories listed in the introduction section. Due to disk space limitations, only about two fully processed cycles (all directories saved) or 3 partially processed cycles (only saving X.Y, R.VP, and X.DYDX) may be saved on one CALDAT disk (assuming 340 points per portion of the cycle or 680 points per cycle). More cycles may be stored on a disk if the number of points per cycle is decreased.

DIRECTORY	CONTENT
X.Y	Converted temperature and Conductance
X.DYDX	d(Y)/d(X)
X.Z	Integral of Y
X.VP	Pore Volume
R.VP	Pore Volume vs. Radius
R.DVPDR	d(Pore Volume)/d(Radius)
R.DVPDLR	d(Pore Volume)/d(Radius)

The control program will be discussed first, followed by the data processing and output programs. Program listings can be found in volume 2 of this manual.

MAIN MENU, [Startup], (Plotter, Controller, Convert XY, Derivative XY, Integrate, Convert VP, Convert R, Derivative VP), (raw data file)

PURPOSE : Main Menu is the central program of the entire system. From Main Menu a new test sequence may be started, data plotted, or data calculations initiated.

OPERATION : Main Menu is the first program that will appear upon starting the system. From Main Menu a test may be started, data calculations initiated, or plots of data made. To start a new test press "C" and you will proceed directly to Controller. To make a plot press "B" and Plotter will be run. The format of the test may be printed on the plotter by entering "D" to run the Test Format program.

The items that appear on the screen initially are only used to control the calculation process. This data is only used for current control purposes and is not stored for each file. To load a file input a "1" for File Name and enter a file name consisting of a base file name and the cycle number. If the name or cycle number of the file is unknown, press RETURN and a catalog of the data disk will be shown. If a resistor was placed in series with the sample enter a "Y", if not a "N". If there was a resistor in series enter the conductance (not the resistance) of the resistor in uS. This data will be used to calculate the conductance of the sample. Both derivative programs use an algorithm that averages the data over a specified interval which may be adjusted. Several of the intermediate programs offer the option of saving the file. If the data from these programs is not important enter a "N" in the appropriate spaces. Not saving the intermediate data will speed the calculations and save disk space. When the temperature data is converted to radius the file may be thinned out so that there is at least one Angstrom between each of the data points. Thinning the file will cut the plotting time and also save disk space. The temperature T0 is the pore solution melting point in degrees Kelvin. A sample menu is shown on the next page.

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CONDUCTANCE MENU

1.	File Name		: Mortar.25
2.	T.C to X.Y	Series Resistor	: Y
		Cond of Resistor	: 144.3
3.	X.Y to X.DYDX	Moving Average	: 3
		Save File	: N
4.	X.DYDX to X.Z	Save File	: N
5.	X.Z to X.VP	Save File	: N
6.	X.VP to R.VP	Thin File Out	: Y
		Temp of T0	: 273.15
7.	R.VP to R.DVPDR	Moving Average	: 3
8.	R.VP to R.DVPDLR	Moving Average	: 3

A. Calculate the data
B. Plot data
C. Run Conductance test
D. Print Test Format
E. Exit to system

Enter your menu choice :

CONTROLLER, [Cond2], (Main Menu, Clock, Temp Timer), (raw data, general sample file, CAL)

PURPOSE : Controller controls the cooling bath and records data during a conductance test of the sample.

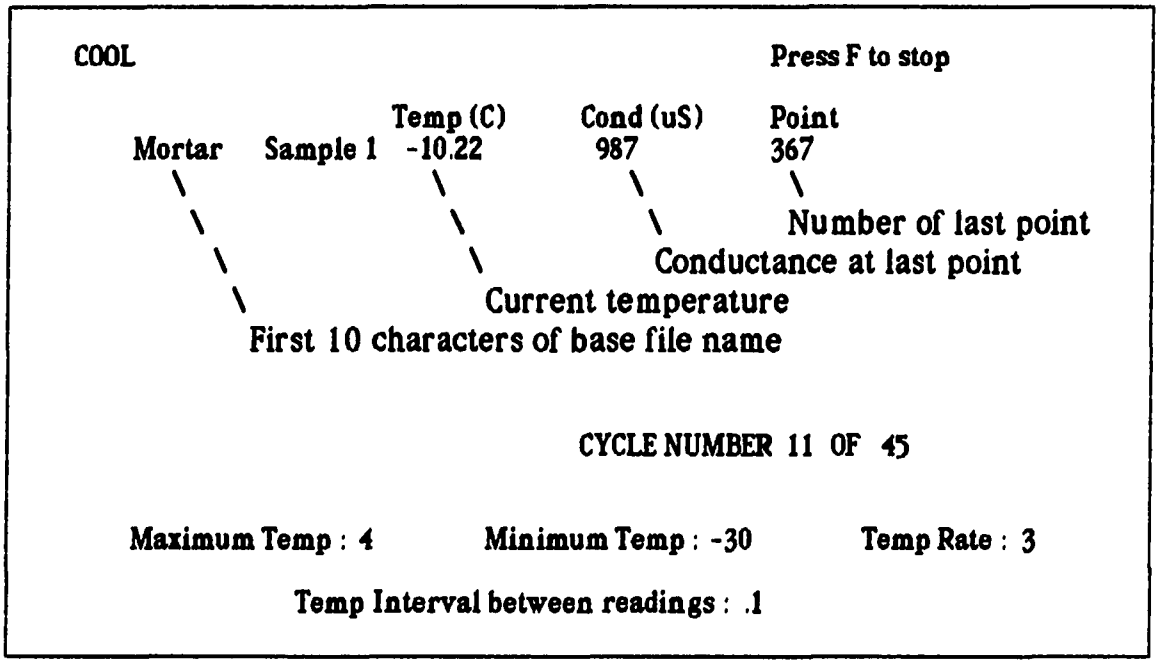
OPERATION : At the beginning of the program will prompt the user to enter some information about the sample and specify the testing parameters. The computer will first prompt the user to enter some notes on the sample. Typical information would be the date and sample material. Don't put any commas into the information or the computer will ignore the rest of the line after the comma. At the end of each line press RETURN.

Now the program prompts the user to enter the number of cycle types. Any number of cycle types may be specified. For each cycle type enter the maximum temperature, minimum temperature, rate of temperature change, and the temperature interval between data readings. The computer will check the input values to insure the minimum temperature is above the maximum, a negative rate of temperature change is not entered, a rate greater than 30 C/hr is not entered, and that the temperature interval for data readings isn't greater than the difference between the maximum and minimum temperature or negative. If a temperature interval of zero is entered the program will not record any data on that cycle. This feature is useful for multiple cycle runs when only data at certain cycle intervals is needed. All of the maximum temperatures must be the same so that when the computer switches from one cycle type to another there is a smooth transition. If the current cycle has a maximum lower than the next cycle's the computer will begin taking data as soon as the current cycle is over and continue until the temperature is above the level of the next reading.

Once the data for all of the cycle types has been entered the program will prompt the user to input a test profile consisting of a sequence of the cycle types. Input the total number of cycles in the test profile and the cycle type for each cycle. The cycle types are described by number, the first one entered being number one.

Now that the test profile is completed, input the base file name for the sample and the cycle number the test is starting on. For example if a previous test of 45 cycles was run on the sample, input the same base file name and then enter the starting cycle as 46 and the cycle number of the data will now be correct.

The test will now start and a status screen will be displayed. A sample status screen is shown below.



The display shows the current temperature of the sample, the conductance of the last data point taken, and the number of that point. The screen also displays the cycle parameters, the current portion of the cycle (heat or cool), and the progress of the overall test (in this case on the 11th of 45 cycles).

To discontinue the experiment at any time press F and the computer will stop at the end of the cycle. The computer must stop at the end of a cycle to save the data for that cycle.

The data is saved at the end of each cycle and when the test is complete the program returns to the Main Menu.

STRUCTURE : Controller allows the user to input notes on the sample, the parameters each cycle type, and the cycle types that make up the test profile. This information is stored on the raw data disk as the CT file.

The cycle type parameters are stored in the arrays TP, BTTM, INVL,, and RA for maximum temperature, minimum temperature, temperature interval and the rate of temperature change respectively. The TD$ array is used to tell the program whether data should be taken during the cycle. If the temperature interval is set at 0 then TD$ is set to tell the computer not to take data during the cycle, otherwise TD$ is always set for taking data.

The test profile is stored in the array TC. Each element contains the cycle type corresponding to the cycle number.

The sample descriptions are used for the base file name. The starting cycle number will be one unless previous tests were run on the sample. If previous tests were run the starting cycle number is added to the current cycle number to get the cycle number the file is saved under (see the introduction for an explanation of the file names). For example if the starting cycle number is 10 the first cycle will be stored under cycle 10 and the second under 11 and so on.

When all of the data are entered the computer begins the test. There are two parts to each cycle, cooling and warming. During both portions of a cycle the same type of control cycle is performed. The temperature interval of the next reading is set and the temperature is continuously monitored. When the temperature passes the interval a conductance reading is taken and both the temperature and conductance are stored in the array SDT. The temperature of the interval is checked to see if it is past the end temperature for the current portion of the cycle. If the interval is past the end temperature then that portion of the cycle is completed. If the interval is not past the end temperature, then the next interval is set and the control cycle is repeated. While cooling a reading is taken when the temperature is lower than the temperature interval set and the cycle ends when the interval is less than the minimum temperature for the cycle. While warming, the temperature must be greater than the interval and the interval must be greater than the maximum temperature for the cycle.

The temperature of the cooling bath is controlled throughout the cycle. The bath is either cooled or warmed at the rate of temperature change specified. The temperature is controlled by sending a number between 0 and 255 to the temperature controller card. The card then converts the digital input to a voltage output that is sent to the cooling bath (for more information see the hardware section). A 0 represents 7 °C and 255 represents -35 °C. The temperature can be controlled in integer steps between these two values for a resolution of .164 °C/integer. For example 0 °C would be set by sending a 42.6 but really either a 42 or 43 would be sent for .112 or -.052 °C respectively. At the beginning of either portion of the cycle the starting and ending temperature points are set and and the time (in seconds) between integer steps is calculated. If a cycle has end points, for example, of 4 and -16 °C, the corresponding integers would be 18 and 141. If the rate of temperature change was 20 °C/hr then the time between integer steps would be

(4 - (-16)) °C / 20 °C/hr = 1 hr * 3600 sec/hr = 3600 sec

3600 sec/ (141 - 18) steps = 29 sec / step.

Each time the sample temperature is read the time is checked to see if it is time for the next temperature step. The bath temperature will continue to change until the end of the cycle even if it passes one of the end points. The bath would only stop if one of the limiting end points (7 or -35 °C) is reached.

The clock for controlling the rate of temperature change is produced by the temperature controller card. An machine language program, Clock, is loaded from the program disk converts one of the timers on the temperature controller card to a clock.

The temperature of the sample is measured by a thermistor. The variable resistance of the thermistor is converted to variable frequency by an square wave oscillator. The period of the square wave is then measured by the interface card using a machine language program, Temp Timer, loaded from the program disk. The length of the period is then read by the program. The period is converted back to a temperature by linear interpolation of a temperature table read from the CAL file on the program disk.

The conductance is measured by the Solomat conductance meter. The meter's reading is transmitted in parallel to the interface card. The conductance may then be read directly from the interface card by the program.

When the cooling portion of a test cycle is completed the data are saved to the disk, the temperature controller parameters are set for the warming portion, and the controlling loop is started. At the end of a warming portion there is one extra thing tis checked. The data is saved, but then the cycle number is checked to see if the test is completed. If there are still cycles left to complete, the next cycle type is loaded, the temperature controller parameters for the cooling portion are set, and the controlling loop is started.

At the end of a test the program returns to the Main Menu.

PLOTTER, [Plot], (Main Menu, HP Plotter), (general sample file, V, PCV, DVDP, DVR, DSR, S)

PURPOSE : Plotter allows the user to load a sample's data files from any of the directories and plot the data on the computer screen. The plotting parameters may be changed. Plotter may also pass the data to HP Plotter to make a plot of the data on a Hewlett Packard plotter.

OPERATION : Plotter first prompts the user to enter the directory to plot from. The menu below will appear.

```
MENU OF SUBDIRECTORIES

1. X.Y
2. X.DYDX
3. X.Z
4. X.VP
5. R.VP
6. R.DVPDR
7. R.DVPDLR
8. EXIT TO MAIN MENU
ENTER NUMBER OF YOU CHOICE
```

Choose a type of data. If 6 or 7 is selected the user has the option of plotting the radius on a log scale. The plotting menu will then be displayed (a sample is shown).

```
Enter the letter of any value that you wish to change
and press RETURN.
    1.  Title ..... Concrete Mortar  27 March 87
    2.  Filename ..... Mortar.25W
    3.    Label ..... Warming
    4.    Linetype ..... 7
    5.  Filename ..... Mortar.25C
    6.    Label ..... Cooling
    7.    Linetype ..... 0
    8.   Minimum X ..... 10
    9.   Maximum X ..... 10000
   10.  X-Interval Size ..... 10
   11.  Minimum Y ..... 0
   12.  Maximum Y ..... 1
   13.  Y-Interval Size ..... .1
   14.  Paper Length ..... 8.5

-------------------------------------------------------------------

    A - Onscreen Plotting          D - Clear Graphics Screen  False
    B - HP722 Plotting             E - Exit Program
    C - View Graphics Screen       F - Find New Data Points

    Enter your choice and press RETURN.
```

Choices from this menu may either load data files, change plotting parameters, or choose an action. Two files may be plotted at the same.time, usually the warming and cooling data from the same sample and cycle. To load a file enter 2 or 5, and enter the complete file name for the data. When a file name is entered, the computer does not load the file into an array but instead loads it during plotting. The label and the type of line associated with each file may be changed by choosing 3,and 4 or 6,and 7.

The other parameters are for adjusting the X and Y axis. The minimum and maximum value for each axis scale and also the spacing between scale markings may be adjusted. If the X axis is radius and a log scale is chosen, the interval for the X axis is not used so changes to the interval will have no effect on the plot. The paper size is normally set for the smaller plotters and 8.5 X 11 paper. If a larger plotter is used the paper length may be changed to 14 for 11 X14 paper.

Now that the plotting parameters and file names have been entered, the data may be plotted. It is recommended to first plot the data on the computer screen to insure the parameters are set correctly before starting a more time consuming plot on a plotter. If a "TRUE" appears after "D - Clear Graphics Screen", the graphics screen will be cleared before the new data is plotted. To plot a second set of data on top of the previous plot, make sure

it says "FALSE". At any time after the axis are drawn pressing the ESC key will discontinue the plot. The computer will stop plotting and by pressing another key, the plotting menu will reappear. This escape feature only works while plotting on the computer screen.

To make the plot on paper, choose B to transfer the data to HP Plotter. HP Plotter will plot the data on the plotter and then return the data to Plotter.

To load a different sample or a different directory of files from the same sample, choose F. The program will start over by prompting the user to select a file directory.

Select E to return to the Main Menu.

STRUCTURE : The user is first prompted to select the directory of the files to plot. When the file name is entered (must include sample name, cycle number, and portion of the curve) data isn't loaded but it is ready to be loaded during plotting. Two files may be loaded and plotted at the same time. The top file is plotted first followed by the lower.

The plotting parameters set the X and Y axis. If a plot with a log scale X axis is selected the X interval is not used by the computer. The computer automatically sets up a log scale plot from the minimum X to the maximum X, but if either of these values are not a power of ten the computer rounds down to the next lowest power of ten. For example if the minimum X is set at 15 and the maximum is set at 15000 the computer will plot from 10 to 10000 with a log scale.

Line types for each of the files may be chosen from the following list.

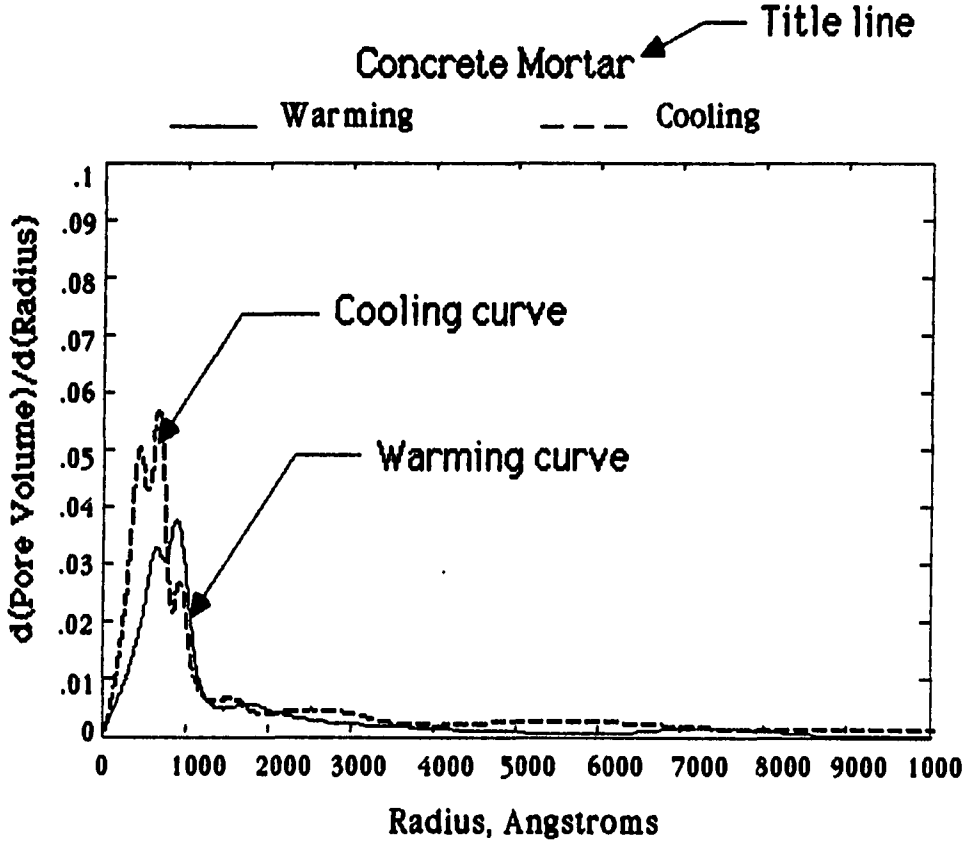
Pattern #	Line Pattern
0	only the data points are plotted
1	. . . . .
2	— — — — —
3	—— —— —— —— ——
4	—— . —— . —— . —— . —— .
5	—— — —— — —— — —— — —— —
6	—— — — —— — — —— — — —— — —
7	————————————
	→| |← one pattern length

The arrays are passes to HP Plotter when a hard plot is desired.

HP PLOTTER, [Hpplot], (Plotter), (none)

PURPOSE : HP Plotter receives the parameters passed from Plotter and makes a plot on a plotter.
OPERATION : HP Plotter requires no user input.

STRUCTURE : The file names and parameters are passed to HP Plotter by Plotter. HP Plotter then initializes the Plotter and begins to draw the plot. A sample plot is shown below.



CONVERT XY, [T.C.to.X.Y], (Main Menu), (raw data file, X.Y)

PURPOSE : Convert XY reads in the raw temperature vs. conductance data from the disk and converts it to the X vs. Y format for further processing.

OPERATION : Convert XY requires no user input.

STRUCURE : Convert XY is the first in a string of data processing programs. Therefore Convert XY is responsible for loading the data from the disk and converting it into the format required for the rest of the processing programs. The Main Menu sends the file name to Convert XY. Convert XY loads the raw data from the warming and cooling files into the two-dimensional arrays A and B for the temperature and the conductance respectively. The first dimension of the array indicates whether the data are from the warming (0) or cooling (1) portion of a cycle. The second element is the numerical value of the data.

The raw data are converted to the X vs. Y format where

$$X = (-1 / T) * 10000$$

and T is the temperature in degrees Kelvin. During the conductance test you a resistor may be connected in series with the sample to narrow the conductance range of the test. This allows a lower scale on the conductance meter to be used and thus resolution is better at lower temperatures where low conductances occur. During the calculation of Y values the effect of the conductance of the series resistor is compensated for and the conductance of the sample alone is determined. The following relationships apply.

$$Y = \log (CT), \text{ and}$$

$$CT = (C * R) / (C - R),$$

where R is the conductance of the resistor in μS, and C is the conductance of the resistor and sample in μS. With the effect of the resistor is removed, CT is the conductance of the sample.

The new X vs. Y data are stored in the X.Y directory and the data are passed back to the Main Menu for further processing.

DERIVATIVE XY, [Der.X.Y], (Main Menu), (X.DYDX)

PURPOSE : Derivative XY calculates the derivative of Y with respect to X, dY/dX, for both the warming and the cooling data. The derivative algorithm also smooths the data using the moving average set in the Main Menu. The relationship between the derivative, dY/dX, and the samples pore volume is expressed in equations 7 and 8 in the Introduction.

OPERATION : Derivative XY requires no input by the user.

STRUCTURE : The data are passed from Main Menu through arrays A and B for X and Y respectively. The derivatives, dY/dX, are calculated and stored in the conductance array, therefore the conductance data in the array are lost, but the data are still in the disk file. The derivative is found with an algorithm that uses a moving average to smooth the data somewhat. The moving average (MA) is set in the Main Menu. If the user has chosen to save the data, they are stored in the X.DYDX directory. When the program is finished the data are passed back to the Main Menu for further processing.

INTEGRATE XDYDX, [Int], (Main Menu), (X,Z)

PURPOSE : Integrate XDYDX perform 2 integrations on the X, DYDX data, resulting with the calculation of the parameter Z expressed in equation 8 of the Introduction.

OPERATION : Integrate XDYDX requires no user input.

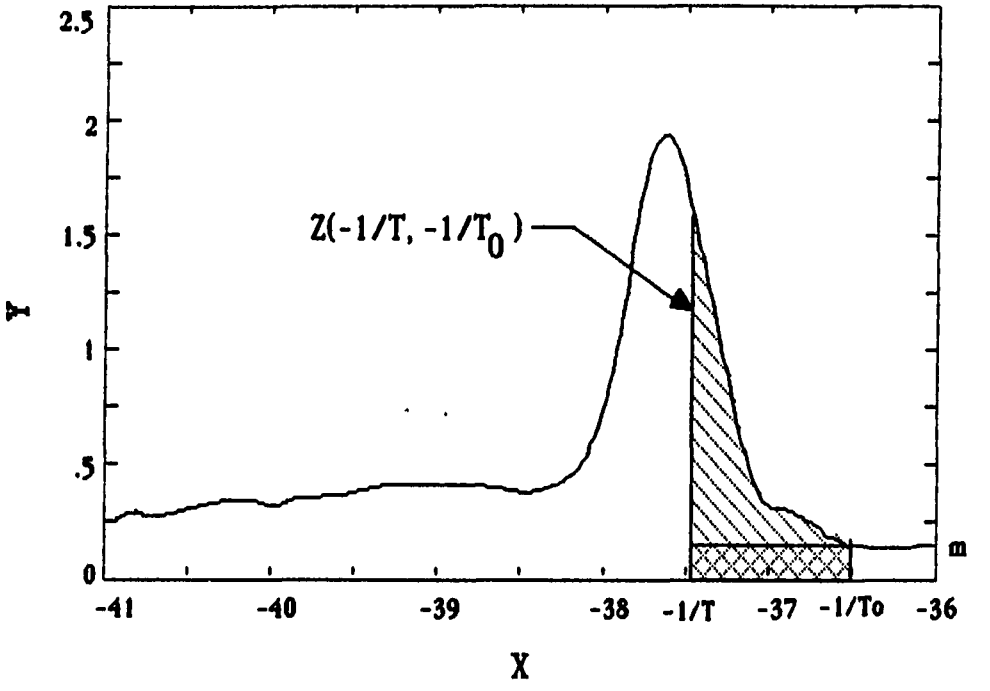
STRUCTURE : The arrays A and B are passed from the Main Menu containing the information X and dY/dXrespectively. The Z values are cumulative totals of the integral and replace the dY/dX values in the array B.

The warming file is processed first with the data pairs processed sequentially from right to left on a X vs. dY/dX plot (the larger X value pairs first). The Z value for all pairs with an X greater than -36.5 are set equal to 0. The average value of Y on the dY/DX interval from -36 to -36.5 is found and stored in Y1 as the slope m. For the rest of the file the Z value is calculated using the following formula:

$$Z\left(\frac{-1}{T},\frac{-1}{T_0}\right) = \int_{\frac{-1}{T}}^{\frac{-1}{T_0}} \frac{d(\log C)}{d\left(\frac{-1}{T}\right)}\, d\left(\frac{-1}{T}\right) - \int_{\frac{-1}{T}}^{\frac{-1}{T_0}} m\, d\left(\frac{-1}{T}\right)$$

where

The calculations are graphically shown on the graph below.



The cooling portion is processed next, in a left to right manner. The same base m is used on the cooling curve. The data pairs with a dY/dX value greater than -36.5 receive the Z value of the last pair less than -36.5. When the cooling curve is complete the data are passed back to the Main Menu and stored in the directory X.Z if the user has directed the computer to save the X.Z File in the Main Menu.

CONVERT VP, [X.VP.from.X.Z], (Main Menu), (X.VP)

PURPOSE : Convert VP calculates the total conducting pore volume from the X vs. Z data. The total conducting pore volume is the ratio of Vcp / Vp as shown in equation 10 in the Introduction.

OPERATION : Convert VP requires no user input.

STRUCTURE : The data are passed into Convert VP via the arrays A and B for X and Z respectively. The pore volume is found using the equation,

$$V_p = 1 / 10^Z$$

and replaces Z in the B array. If the user chooses to save the data, they are stored in the X.VP directory. The data are passed back to the Main Menu when the program has completed the calculations.

CONVERT R, [R.VP.from.X.VP], (Main Menu), (R.VP)

PURPOSE : Convert R changes the X variable to a pore radius. Relative conducting pore volume is now expressed as a function of radius, as shown on the left hand sides of equations 9 and 10 in the Introduction.

OPERATION : Convert R requires no user input.

STRUCTURE : The data are passed to Convert R via two arrays, A and B containing X and VP respectively. The X data are converted from a temperature to radius using the equation

$$R = \frac{-2 * T_0 * (.25 - (29 * X) + (.25 * T_0 * X))}{(.9998 * 3.335 \text{ X } 10^9) * (1 + T_0 * X)} * 10^8$$

where T_0 is the pore solution melting point (273.15 °K for water) which is entered in the Main Menu and X is the X variable. All data points with an original temperature greater than 0 °C are meaningless and removed from the arrays. If you have chosen to "thin" the file, the program only saves points that are spaced at least one Angstrom apart. The data are saved in the R.VP directory on the data disk and then passed back to the Main Menu for further processing.

DERIVATIVE VP, [Der.R.VP], (Main Menu), (R.DVPDR)

PURPOSE : Derivative VP calculates the derivative of Vp with respect to R, dVp/dR, for both the warming and the cooling data. The derivative algorithm also smooths the data using the moving average entered in the Main Menu.

OPERATION : Derivative VP requires no input by the user.

STRUCTURE : The data are passed from Main Menu through arrays A and B for R and Vp respectively. The derivative, dVp/dR, is calculated but not stored in the conductance array. The arrays are passed back to the Main Menu without any changes so that the derivative with respect to the log(R) can be computed. The derivative is found with an algorithm that uses a moving average to smooth the data somewhat. The moving average (MA) is set in the Main Menu. The data are stored in the R.DVPDR directory. When the program is finished the R and Vp data are passed back to the Main Menu for further processing.

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DERIVATIVE LVP, [Der.LR.VP], (Main Menu), (R.DVPDLR)

PURPOSE : Derivative LVP calculates the derivative Vp with respect to log (R), dVp/dLR, for both the warming and the cooling data. The derivative algorithm also smooths the data using the moving average entered in the Main Menu.

OPERATION : Derivative LVP requires no input by the user.

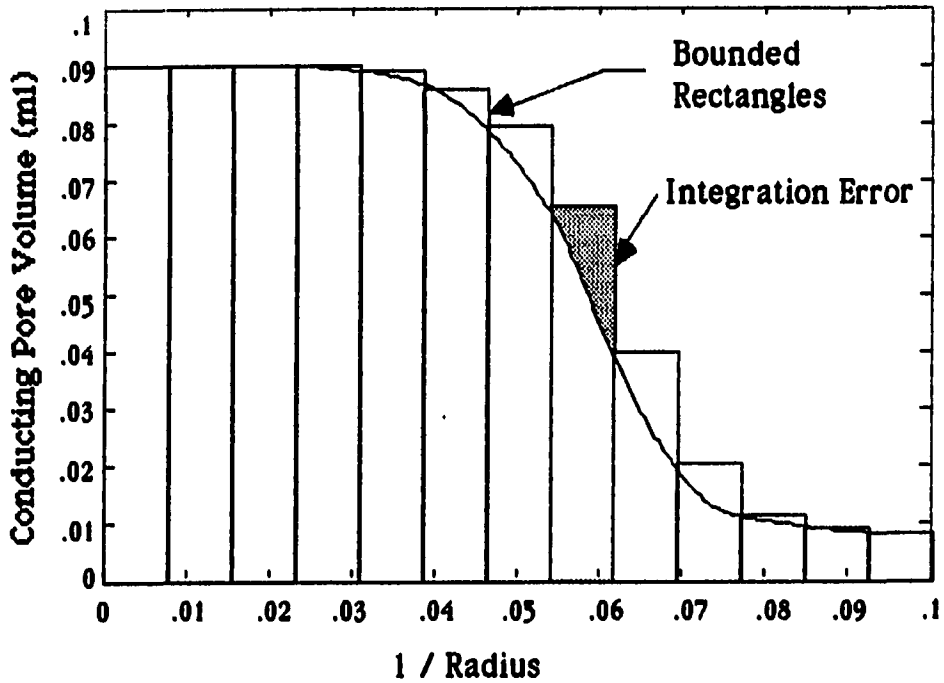
STRUCTURE : The data are passed from Main Menu through arrays A and B for R and Vp respectively. The radius is converted to the log (R) before any of the calculations and then the derivative of Vp is computed with respect to the $\log_{10}$ (R). The derivative, dVp/dLR, is calculated and stored in the conductance array. The derivative is found with an algorithm that uses a moving average to smooth the data somewhat. The moving average (MA) is set in the Main Menu. The data are stored in the R.DVPDLR directory. This is the last step in the data processing cycle and the program returns to the Main Menu when finished.

SURFACE AREA, [Int.Sa], (none), (R.VP)

PURPOSE : Surface Area loads the radius vs. relative pore volume data and after the actual sample pore volume is entered calculates the surface area of the sample.

OPERATION : Surface Area is not offered as an option on the Main Menu, therefore to load and run the program, first exit the menu and type "RUN INT.SA,D1". Once the program is started, input a file name consisting of the base file name for the sample and the cycle number. After the R.VP file for the sample is loaded for the warming portion, enter the pore volume of the sample. The relative pore volume is multiplied by the actual total pore volume to get the pore volume at any given point. The computations will be performed and the surface area printed on the screen.

STRUCTURE : Surface area computations are only performed on the warming portion of the curve. Once the file name is entered, the pore volume data from the warming portion is loaded into an array for processing. Then a modified version of the data, changed to pore volume vs. 1/radius, is integrated from 0 to 1/12 using a method of rectangles. The change in 1/radius between points is multiplied by the height of the larger pore volume to get the area of a rectangle. The total integral is the sum of all of the rectangles. The area will be over estimated using this method but as the number of points increases and therefore the width of the rectangle decreases, the error becomes negligible. The integration method is illustrated on the next page. The width of the rectangles is exaggerated for clarity.



The surface area of the sample (excluding pores less than 12 Angstroms) is found to be the area under the curve multiplied by 2.5. The surface area is graphically represented on the next page.

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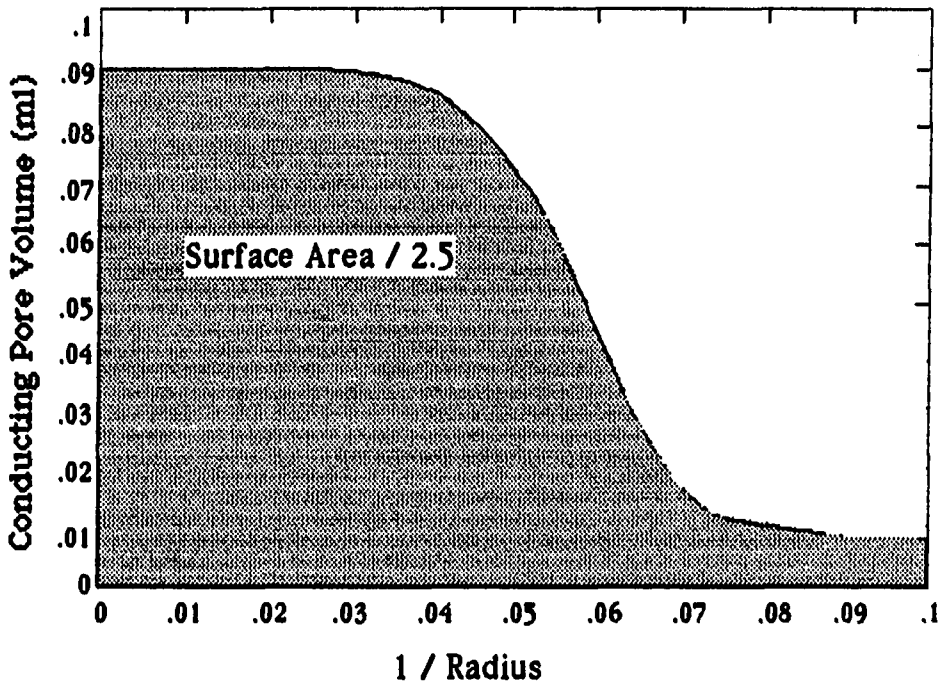


The surface area is then printed to the screen and the program ended. To return to the Main Menu type "RUN STARTUP,D1"

TEST FORMAT, [Sample.Data], (Main Menu), (general sample file)

PURPOSE : Test Format prints out the test format, the cycle types and the cycles, for a test sequence.

OPERATION : To run Test Format enter a "D" in the Main Menu. Test Format will be loaded and the computer will prompt the user to insert the appropriate raw data disk. Enter the test format file name including the sample name, staring cycle number, and CT (for example Mortar.25.CT). The file will be loaded into memory and displayed on the computer screen. The user may choose to either quit and return to Main Menu or print the information on the plotter.

STRUCTURE : The data is loaded into an array and displayed on the screen. Due to limitations of screen size only 48 cycles may be displayed, the cycles over 48 will be loaded from the disk but not be shown on the screen. The program sends the data to the plotter.

CLOCK, [IO.Clock.Slot1], (Controller), (none)

PURPOSE : Clock generates a system clock that is accessed by Controller to maintain the rate of temperature change.

OPERATION : Clock requires no user input.

STRUCTURE : The operation of Clock is described in detail in Byte, March 1982 in an article by Ned Rhodes, the author of the program. The clock uses one of the 16-bit timers on the parallel interface card located in slot 1. The timer generates an interrupt every 1/60 of a second and calls Clock. Clock then displays the time on the screen and maintains a register which can be read by the program. The number in the register represents the number of interrupts since the clock was reset. Controller then divides the number in the register by 60 to get the number of seconds.

TEMP MEASUREMENT, [Cap.Res.2], (Controller), (none)

PURPOSE : Temp Measurement determines the period of the square wave generated by the thermistor's oscillator. The period is used to determine the temperature of the sample.

OPERATION : Temp Measurement requires no user input.

STRUCTURE : Temp Measurement uses one of the 16-bit timers from the parallel interface card located in slot 1. The progam turns the timer on when it senses a rising edge on the signal. The timer then counts down until a falling edge is detected. The computer can then access the counter and subtract the initial value to get the half period of the wave.

CALIBRATE, [Calibrate], (none), (Cal)

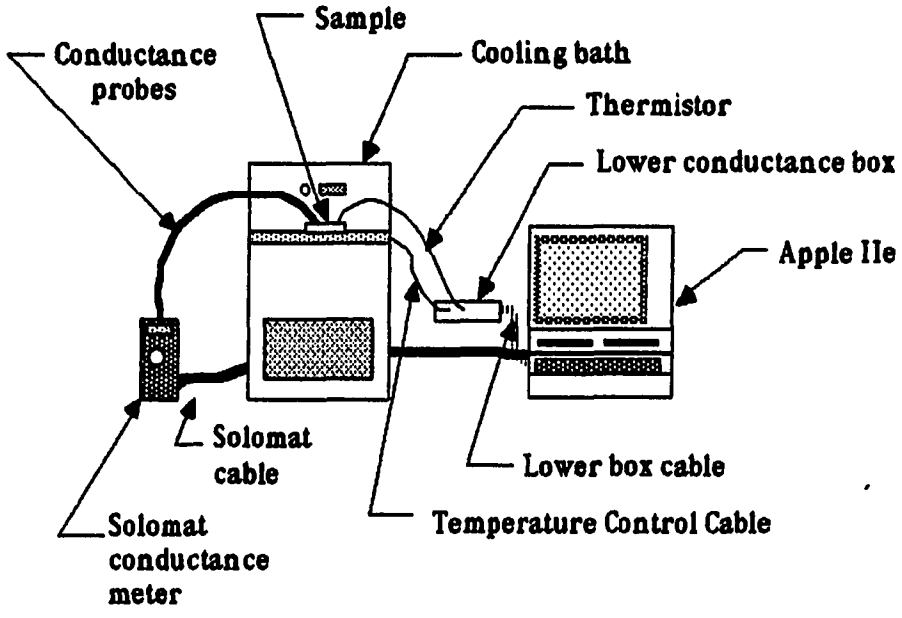
PURPOSE : Calibrate is a data editing program to allow the user to change the temperature calibration data for the thermistor.

OPERATION : Calibrate is not an option on the Main Menu. To load and run the program exit the Main Menu and type "RUN CALIBRATE,D1". The program will automatically load the Cal file and display it on the screen. The method of determining the calibration data is described in the Appendix. By using the arrows the cursor can be moved around the screen. When the cursor is at the desired location, type in the new data and press RETURN. The new data will then replace the old in the file located in the computer. When editing is completed the new version of the file in the computer may be saved to the disk, by pressing CTRL and S. If the user doesn't want the changes made to the data to be save pressing CTRL and Q will exit the program without saving the changes (NOTE : the data in the disk file is NOT changed in this case). In both cases you are returned to the Main Menu when finished.

STRUCTURE : The Cal file is automatically loaded into an array when the program is started. The user is then allowed to change the data in the array by moving the cursor on the screen to the data to be changed and entering the new data. The number of data points in the file is set at 22 and may not be changed using this program. When editing is finished the data is either written back to the file on the disk or discarded. The program returns to the Main Menu when completed.

IV. INTERFACE

The Conductance Porosimeter system consists of a Solomat conductance meter, an Apple IIe (with 2 disk drives, a monitor, and 2 parallel interface cards), an interface box, and a cooling bath. This section will mainly discuss the interface box but will also look at some of the aspects of the rest of the system. The main components are shown below.



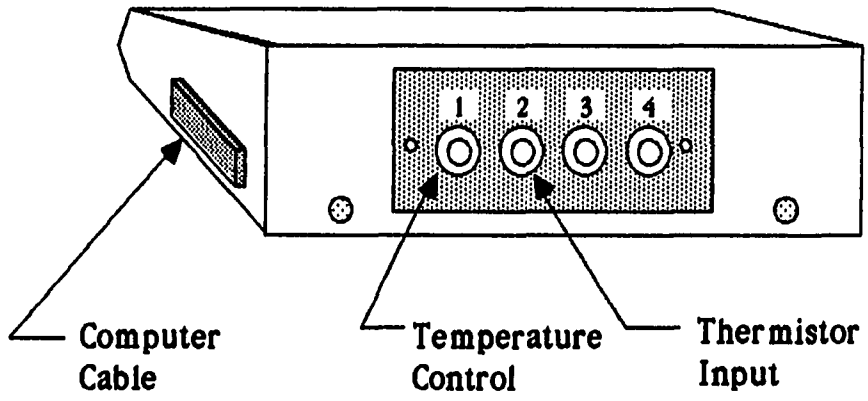
The Solomat measures the conductance of the sample and sends the digital data to the parallel interface card located in slot 4 of the Apple IIe. The temperature is converted from the variable resistance of the thermistor to a variable frequency square wave. The period of the square wave is found by a timer on the parallel interface card located in slot 1 of the Apple. Control of the cooling bath is accomplished by the parallel interface card in slot 1 sending a digital number to the temperature control circuit in the interface box. The temperature control circuit converts the digital data to a voltage level which is sent to the cooling bath. The voltage level represents the temperature level of the bath.

The following sections will take a closer look at each of these main functions of the interface.

INTERFACE BOX

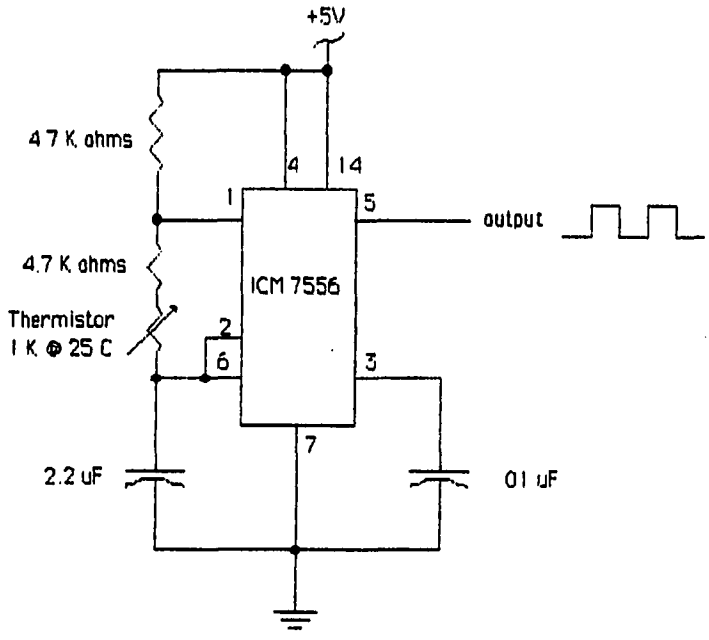
PURPOSE : The interface box provides the circuitry to control the cooling bath and record temperature readings.

OPERATION : The interface circuits are housed in a low profile box with connections for the computer cable, the thermistor, and the temperature control cable. The cables should be connected as shown.



STRUCTURE : There are two main components of the interface box, the thermistor and temperature control circuits. The thermistor circuit converts the variable resistance of the thermistor to a variable frequency square wave. The temperature control circuit converts the digital output from the computer to a voltage level that is sent to the cooling bath.

The main component of the thermistor circuit is a 556 timer chip. The chip is wired as a square wave oscillator with its frequency dependent on the capacitance and resistance on pins 6,1 and 4. Since the resistance of the thermistor is dependent on temperature, and the frequency of the oscillator is dependent on resistance, the frequency is a function of the temperature of the thermistor. The square wave is sent to the parallel interface card in slot 1. The thermistor circuit is shown on the next page.

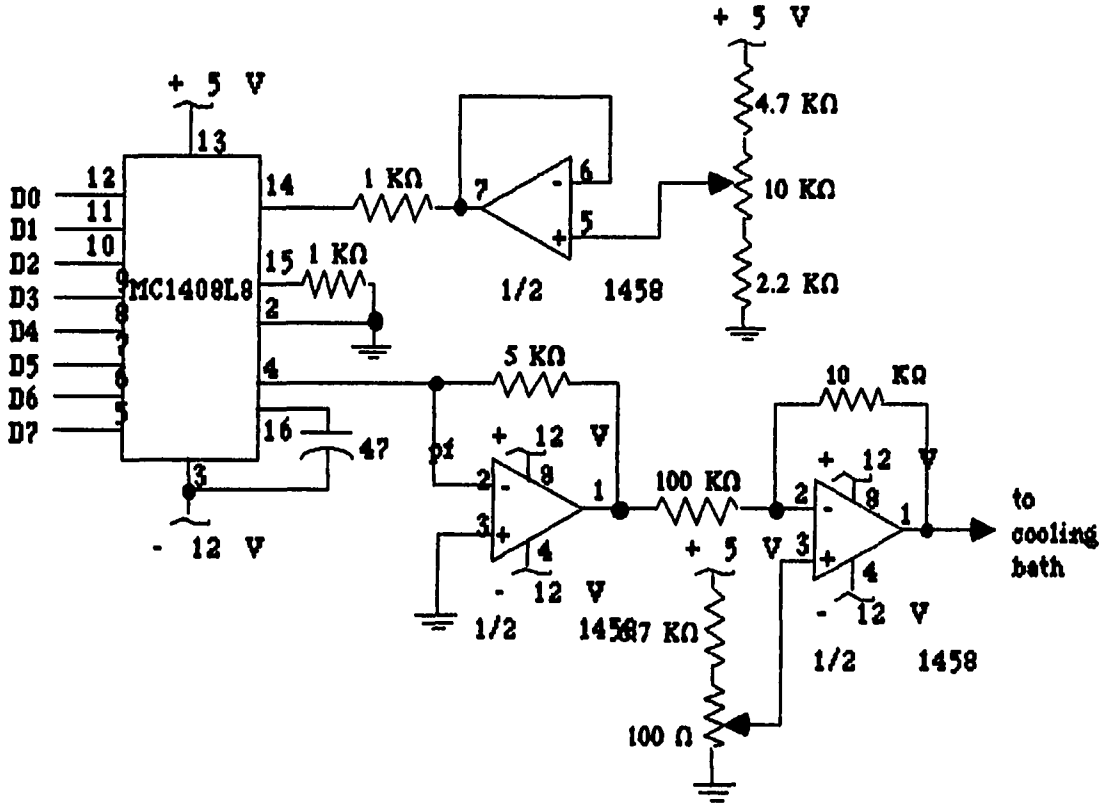


The temperature control circuit consists of a Digital-to-Analog (D/A) converter and three operational amplifiers (op amps). The temperature control output from the computer is in the form of a number from 0 to 255 corresponding to 7 and -33 °C respectively. The 8-bit number is transferred through the parallel interface card in slot 1 of the Apple. Lines PA0-7 are used to represent the 8 bits (see the parallel interface card section). The 8-bit number is converted to an analog voltage output by the D/A converter (MC1408L8).

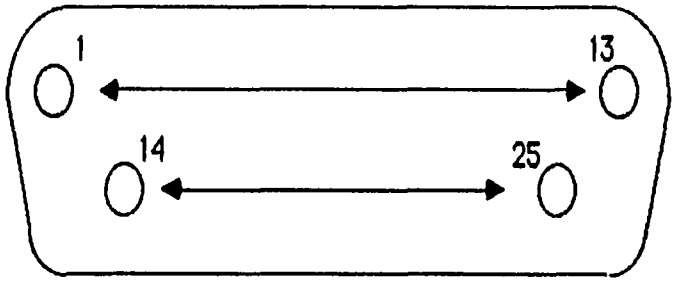
Adjusting the voltage on pin 14 of the D/A converter controls the range of voltage from the maximum to minimum inputs. The voltage on pin 14 is controlled a the voltage divider and op amp. Adjusting the 10 KΩ trim pot changes the voltage sent to the op amp. The op amp is configured as a voltage follower (just maintains the voltage input) and is connected to pin 14.

The D/A converter outputs a voltage on pin 4. The output is then amplified by the first op amp and reduced by the second one in line. The 100 Ω trim pot controls the offset voltage of the second op amp. The offset voltage is used to move the output voltage range to the proper level. The output should be .07 to -.33 V corresponding to 7 and -33 °C respectively. In practice, the 10 KΩ trim pot is used to set the low voltage and the 100 Ω for the high voltage (see the Appendix for calibrating the circuit).

The output is then connected by cable to a socket on the back of the cooling bath. The format of the socket may be found in the cooling bath's manual. The schematics of the temperature circuit are shown on the next page.



The cable connecting the interface box to the computer is a DB 25 connector configured as follows. The cable is connected to the other DB 25 connector on the back of the Apple.



Pin #	Name	Description
1	+ 5 V	Power supply
2	+ 12 V	Power
3	- 12 V	Power
4	GND	Common or Ground
5	PA0	Data line 0 for temperature control
6	PA1	" "1 " "
7	PA2	" "2 " "
8	PA3	" "3 " "
9	PA4	" "4 " "
10	PA5	" "5 " "
11	PA6	" "6 " "
12	PA7	" "7 " "
13-21	Unused	
22	CA1	Square wave output of temp oscillator
23-25	Unused	

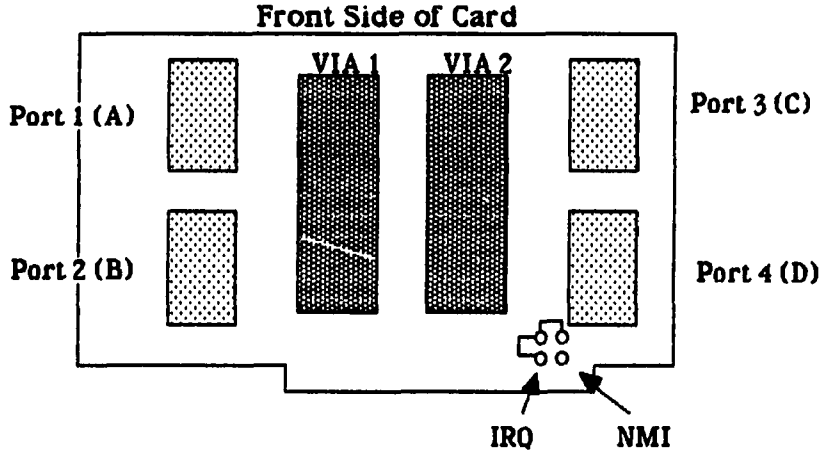
PARALLEL INTERFACE CARD

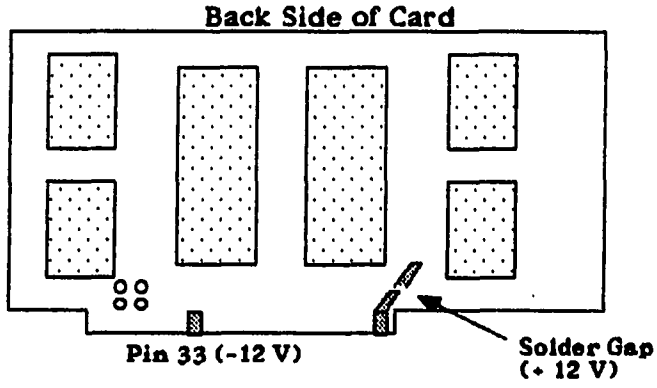
PURPOSE : The parallel interface card is used to input and output data in a parallel fashion (simultaneously on many lines rather than serially one bit at a time on one line), provide the system clock, and measure the period of the temperature signal square wave.

OPERATION : The parallel interface cards require no user intervention other than attachment of cables.

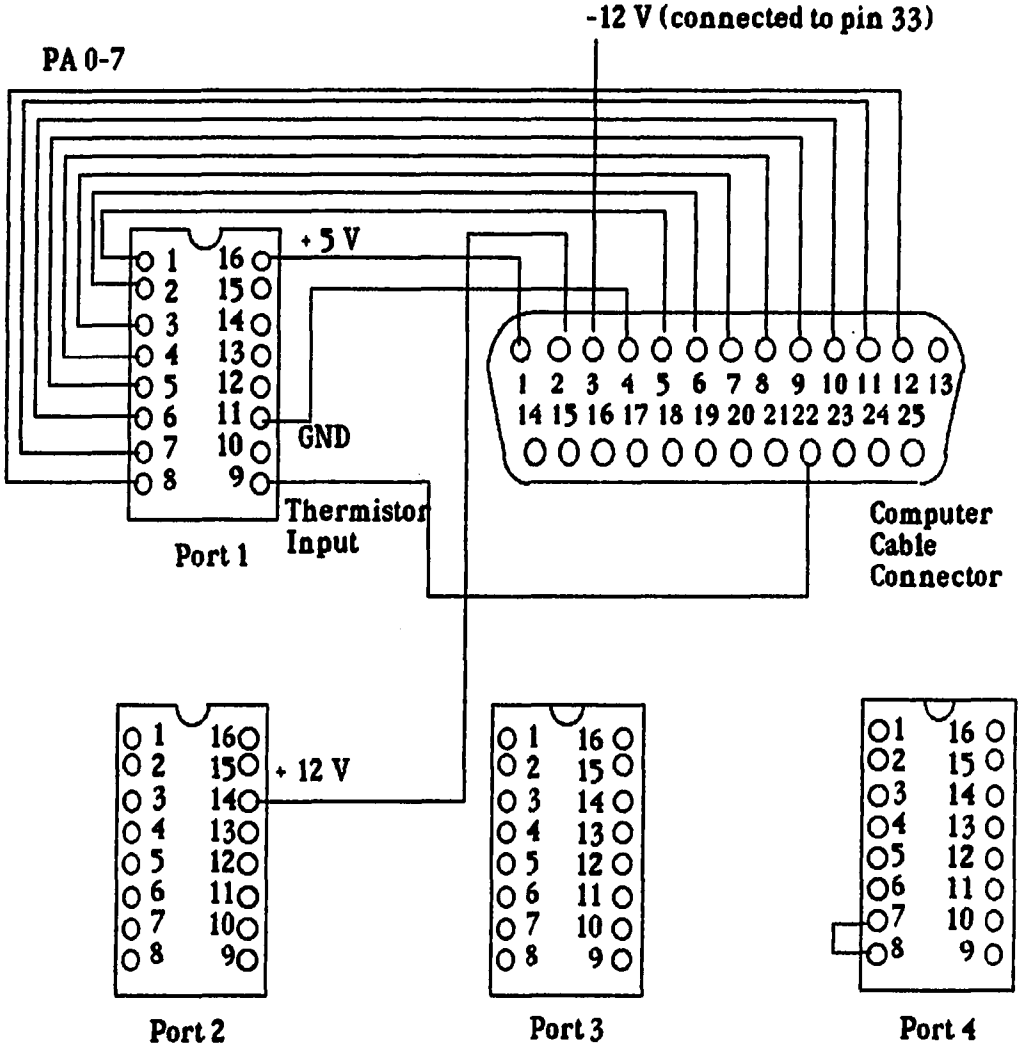
STRUCTURE : The parallel interface card used in this system is supplied by John Bell Engineering, 1014 Center St, San Carlos, CA 94070 (Tel: 415-592-8411). The card consists mainly of two 6522 Versatile Interface Adapters (VIA) with a total of four 8-bit bidirectional I/O ports and four independent 16-bit timers. More information may be found in the manuals supplied by the manufacturer.

Two parallel interface cards are used in the system. One of the cards in slot 1 of the Apple, controls the cooling bath, supplies the system clock, and measures the period of the thermistor's square wave. The other is located in slot 4 and is used to interface the Solomat conductance meter.



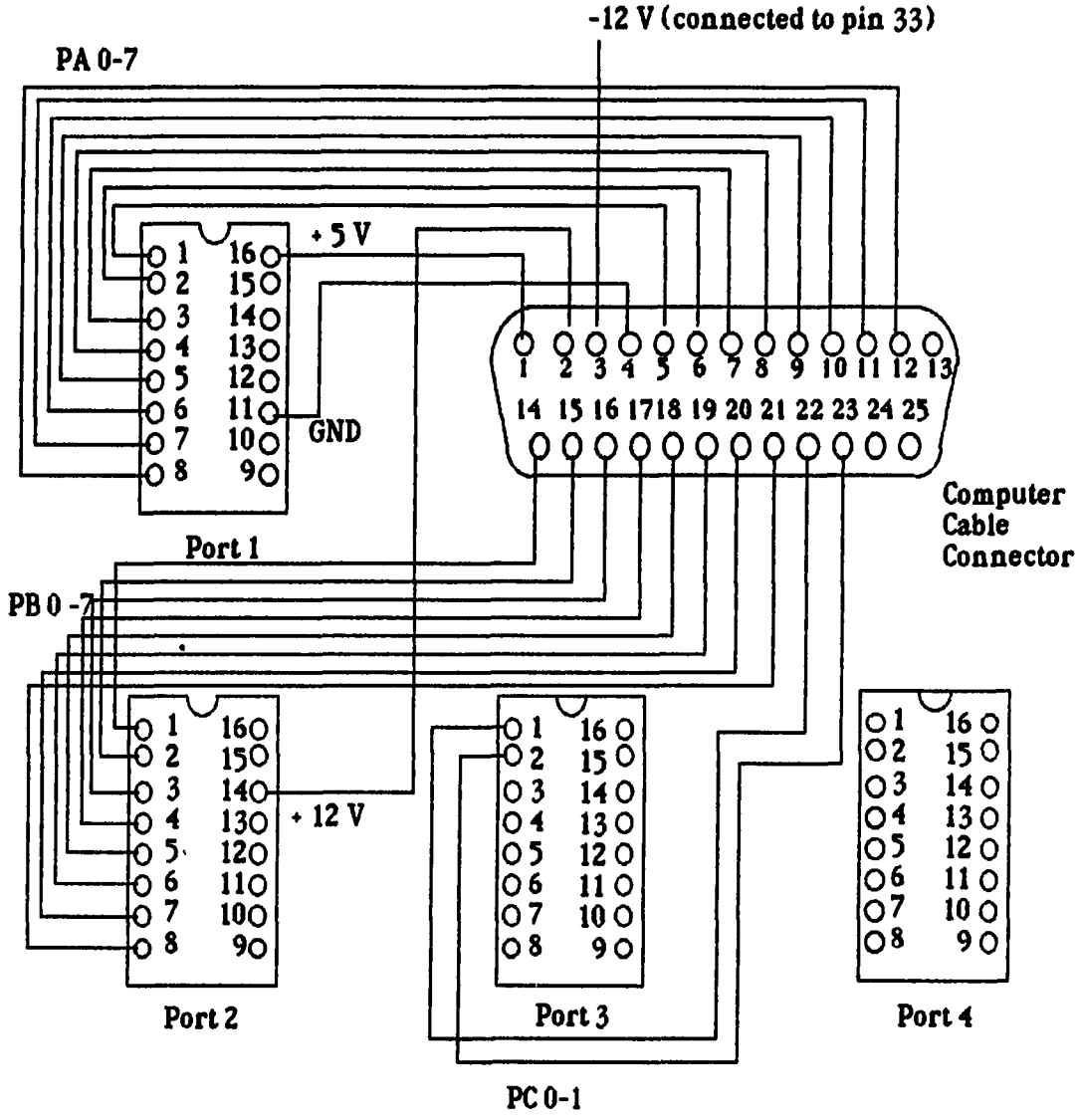


The card located in slot 1 generates the system clock through a program published in Byte, March 1982 by Ned W. Rhodes (Clock). Using the Apple's interrupts one of the 16-bit timers is triggered every 1/60 of a second. The program then reads the time from the timer. This is why the IRQ and NMI must be configured correctly. The period measurement for the thermistor is accomplished by triggering a timer on the rising edge and stopping on the falling edge. The timer counts down while operating and the program reads the timer. The temperature control data is simply passed in parallel through port 1. The connections are as shown, note the connector on port 4 and the fact that the -12 V line must be directly connected to pin 33.



Parallel Interface in Slot 1

The parallel interface card in slot 4 is used exclusively for interfacing with the Solomat. The Solomat is powered by the 5 volt line from the parallel interface card. The data is then sent back in parallel through ports 1, 2, and 3. The connections should be made as shown.



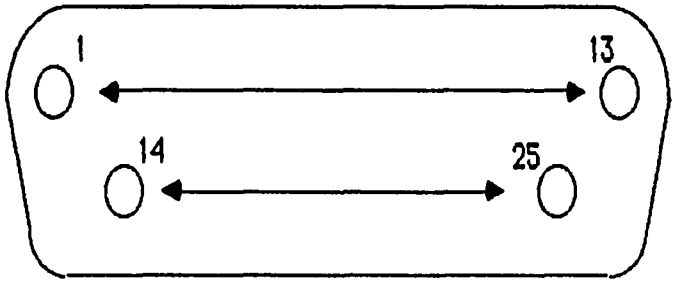
Parallel Interface Card in Slot 4

SOLOMAT CONDUCTANCE METER

PURPOSE : The Solomat conductance meter measures the conductance of the sample and sends the digital data to the Apple.

OPERATION : The conductance cables should be attached to the probes in the sample and the cable from the computer plugged into the socket on the side of the meter. The conductivity scale should be set to 16000 µS for the 1.0 cell unless a series resistor is used. A resistor is sometimes put in series with the sample to give better resolution at the lower end of the conductance cell. If a series resistor is used set the scale to 160 µS again for the 1.0 cell. The meter is powered by the computer and doesn't need to be switched on.

STRUCTURE : The Solomat is described in detail in the manufacturer's manual. The configuration of the socket is described in the section 6. All five digits are passed through the parallel interface. Power is supplied through pin 19. The configuration of the DB 25 connector on the back of the Apple is shown below. The digits are sent in Binary Coded Decimal (BCD) requiring 4 bits per digit except for digit 5 (digit 1 being the least significant) which only requires 1 bit as it can only be a one or a zero.

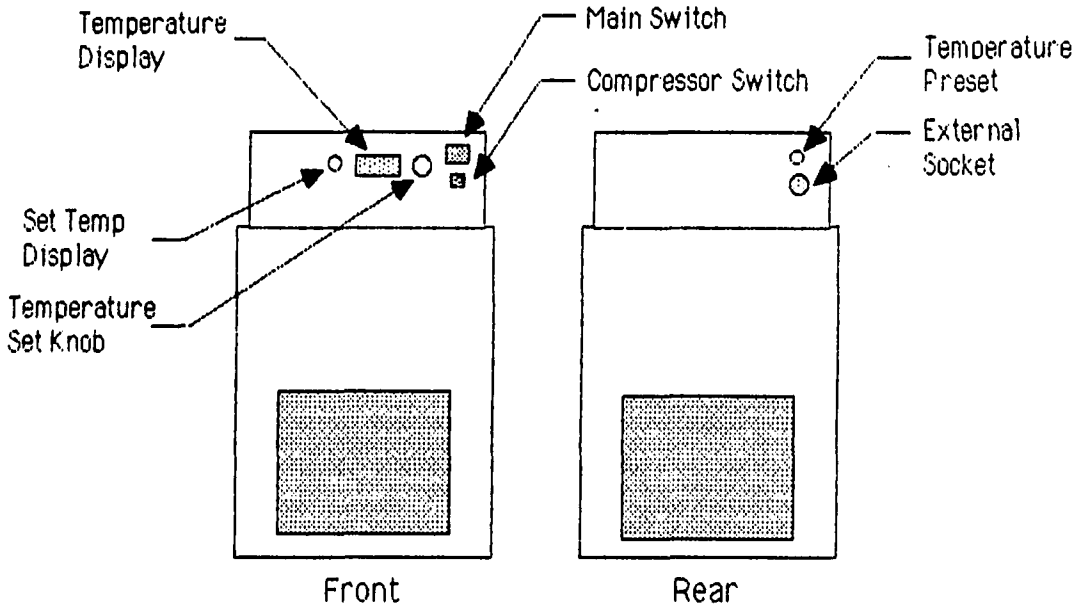


Pin #	Name	Description
1	+ 5 V	Power supply
2	+ 12 V	Power
3	- 12 V	Power
4	GND	Common or Ground
5	PA0	Digit 1 Bit 0
6	PA1	Digit 1 Bit 1
7	PA2	Digit 1 Bit 2
8	PA3	Digit 1 Bit 3
9	PA4	Digit 2 Bit 0
10	PA5	Digit 2 Bit 1
11	PA6	Digit 2 Bit 2
12	PA7	Digit 2 Bit 3
13	GND	Common or Ground
14	PB0	Digit 3 Bit 0
15	PB1	Digit 3 Bit 1
16	PB2	Digit 3 Bit 2
17	PB3	Digit 3 Bit 3
18	PB4	Digit 4 Bit 0
19	PB5	Digit 4 Bit 1
20	PB6	Digit 4 Bit 2
21	PB7	Digit 4 Bit 3
22	PC0	Digit 5 Bit 0
23-25	Unused	

COOLING BATH

PURPOSE : The cooling bath controls the temperature of the sample and allows the computer to cycle the sample through a freeze-thaw cycle while monitoring the conductance of the sample.

OPERATION : The controls of the cooling bath are shown below.



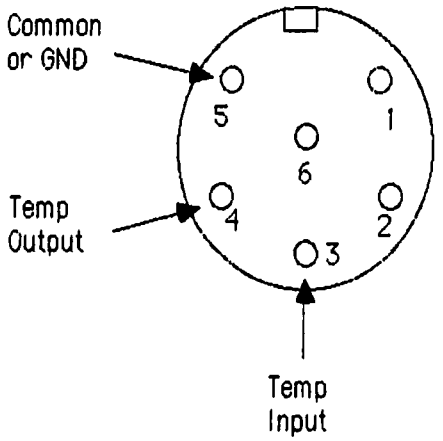
To turn on the bath, first place the main switch in the on position and then turn the compressor on. Turning them both on at the same time causes a large power surge on the power line. When turning the bath off turn off the compressor before turning the main power off.

The bath's display serves two purposes. It usually displays the current temperature of the bath, but when the set temp display button is pressed the display shows the temperature the bath has been set at. To set the bath temperature press the set temp display button and adjust the temperature set knob until the desired temperature is shown.

The external control socket is located on the rear of the bath. The cable from the temperature control circuit should be connected to the external socket. To place the bath under external control place the temperature preset switch in the ON position. The temperature of the bath will now be set by an external device, in this case the computer. A small mark will appear in the upper left hand corner of the bath's display indicating external

control. The temperature the external device is setting may be shown on the bath's display by pressing the set temp display button.

STRUCTURE : The cooling bath contains a refrigerating unit and a circulator for the bath's fluid. The bath currently contains isopropyl alcohol. The bath is a Haake model A 82 supplied by Haake Inc., 244 Saddle River Road, Saddle Brook, NJ 07662. For further information of the bath see the manufacturer's manual. The format of the external socket is as shown below.



The temperature voltage is sent into the bath using pin 3. The output pin is not used but could be used to externally monitor the bath's temperature. Both the output and the input represent temperature with voltages, 0.00 volts corresponding to 0 °C and 1.00 volts for 100 °C. Therefore for our range of 7 and -33 °C, we use .07 and -.33 volts respectively.

THERMISTOR

PURPOSE : The thermistor is a temperature dependent variable resistor used to measure the temperature of the sample.

OPERATION : The thermistor requires no intervention.

STRUCTURE : The thermistor used in model SP85DA102FA1 supplied by Thermometrics, 808 U.S. Highway 1, Edison N. J. 08817. It is .085" in diameter and 1/2" long with a nominal resistance of 1 kΩ at 25 °C and stable to ± .02% per year.

V. APPENDIX

INITIALIZING DISKS

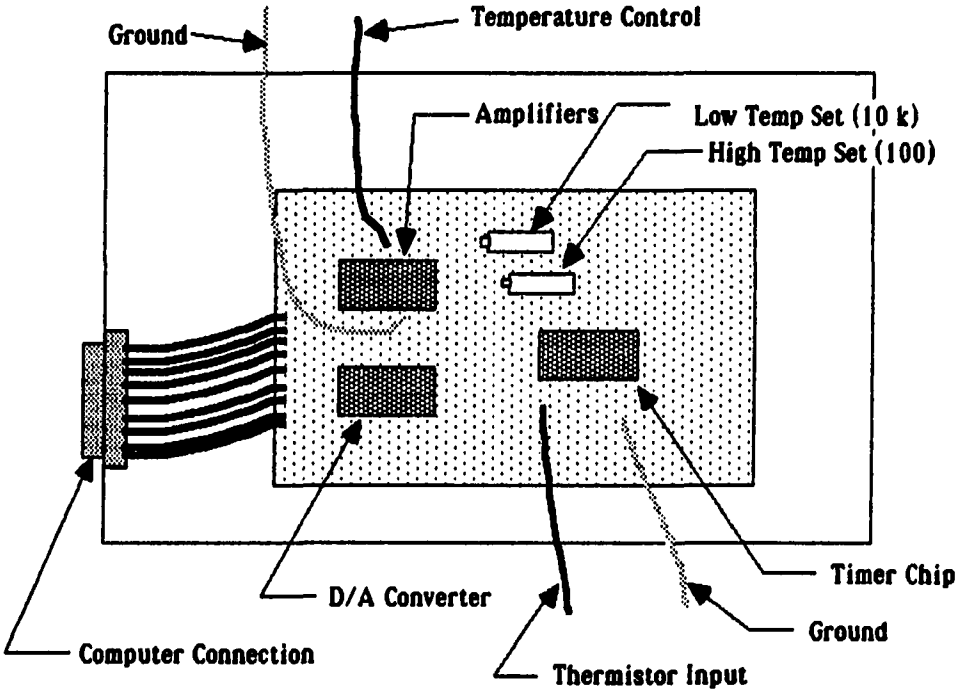
The data disks used by this system need to be initialized and directories established before data may be stored on them. To initialize a disk the user needs the ProDOS User's Disk and the /Caldat master disk. Insert the ProDOS User's Disk in drive one and press the CTRL and open-Apple, and RESET keys to reboot the system. The main menu for the ProDOS User's Disk will be displayed on the screen. Select F for ProDOS Filer (Utilities). This is a set of programs to allow the manipulation of disks. The next menu will be the ProDOS Filer menu. This time select V for Volume commands. This will further define the programs to those that manipulate entire disks rather than single files. When the Volume Commands menu is displayed select C for Copy a Volume. This program will copy the contents of an entire disk to another. This program will be used to copy the contents of the /Caldat master disk to the blank disk. The Copy a Volume screen will be displayed next. The program prompt the user to enter "THE VOLUME IN SLOT : " with a "6" being displayed. The program is asking what slot the disk drive controller card is in which in this case is the default value, slot 6. The copying will be done from drive 1 to drive 2 so answer the prompts respectively. Place the /Caldat master disk in drive 1, the blank disk in drive 2 and press RETURN. The volume name "/Caldat" will appear for the new volume name. Press RETURN to accept this as the new volume name for the blank disk. The program will format the blank disk and proceed to copy the contents from the /Caldat master disk to the blank disk. When the program is finished remove the disks and reboot the system with the porosimeter programs disk or initialize more disks. It is a wise idea to have a number of initialized data disks available.

CALIBRATING TEMPERATURE CONTROL

As described in the interface box section, the temperature of the bath is controlled by sending a number from 0 to 255 representing 7 and -33 °C respectively. The interface converts the number to a voltage level that is sent to the bath. To set the proper voltage levels the adjustment of two trim pots in the interface box will be necessary to send the appropriate maximum and minimum numbers.

The program used to calibrate the temperature control circuit isn't an option on the Main Menu. To run the program exit the menu and type "RUN I.O.CARD.TEST,D1". This program will allow the user to send a number from the parallel interface card to the interface box. The program will prompt the user to enter the port, enter 1 for port 1. Then enter the letter O for output on port 1. Only port 1 needs to be addressed as this is the port used to send the data to the interface box, so type a number 0 to begin the calibration.

The user will now need to remove the cover of the interface box to expose the trim pots that will be adjusted.



Turn the cooling bath on (the compressor doesn't need to be running) and place the external temperature preset switch (see cooling bath section)

to the ON position. By pressing the temperature set button on the front of the bath (and holding it in), the temperature the control circuit is sending in will be shown on the bath's display.

To set the trim pots, alternate between sending a 0 and a 255 to the temperature control circuit and adjusting the appropriate trim pot so that the correct temperature will be displayed on the bath. Enter 1/0 into the computer for port 1 with a 0 output. Then adjust the 100 Ω trim pot (High Temp Set) until 7 °C is shown on the display. Now enter 1/255 and adjust the 10 kΩ trim pot (Low Temp Set) until -35 °C is displayed. Repeat these steps until no adjustments to the trim pots need to be made.

Replace the cover on the interface box. To return to the Main Menu type "RUN STARTUP,D1" and the calibration is completed.

CALIBRATION OF THERMISTOR

New thermistors do not have the same temperature-resistance charateristices and individual thermistors themselves change over time. Therefore the calibration file may need to be updated occasionally. The thermistor circuit converts the variable resistance of the thermistor to a variable frequency square wave. The period of the square wave is then measured by the parallel interface card so that the program may read the period. The program converts the period back to temperature using the table of values in the Cal file.

The Cal file contains 22 period - temperature pairs. The controlling program reads a period and then searches the table. If the period is within the range of the table, the program linearly interpolates between the two closest points of the table to calculate the temperature of the sample. If the period is outside of the boundaries of the table, either the maximum temperature or minimum is assumed accordingly.

To find the 22 data points needed place a thermocouple and the thermistor in a test tube and immerse the tube in the cooling bath. The thermocouple is used to determine the temperature of the thermistor. Exit the Main Menu and type "RUN TEMP.PERIOD,D1" to load a program that will display the square wave's period. Two numbers will be shown on the screen, the top number is the current reading of the thermistor and the lower a moving average of 30 readings.

Turn the bath on and set the temperature at 7 °C. When the temperature of the thermocouple stabilizes record the temperature and the period of the thermistor's square wave shown on the screen. This is the first data pair. Continue changing the bath's temperature and making readings until you have taken 22 pairs. The readings should be spread over the range of 7 and -33°C with a higher concentration near zero where the temperature is critical in the data processing. Press the ESC key to exit the program.

The program Calibrate will automatically be loaded. As described in the software section, Calibrate allows you to view and edit the Cal file. Enter the new data points into the Cal file. Make sure to keep the order straight and put the highest temperature pair at the beginning of the file (point 1). The algorithms in the controlling program assume this order. When finished save the file and return to the Main Menu. The calibration is now completed.

SIMPLIFICATIONS

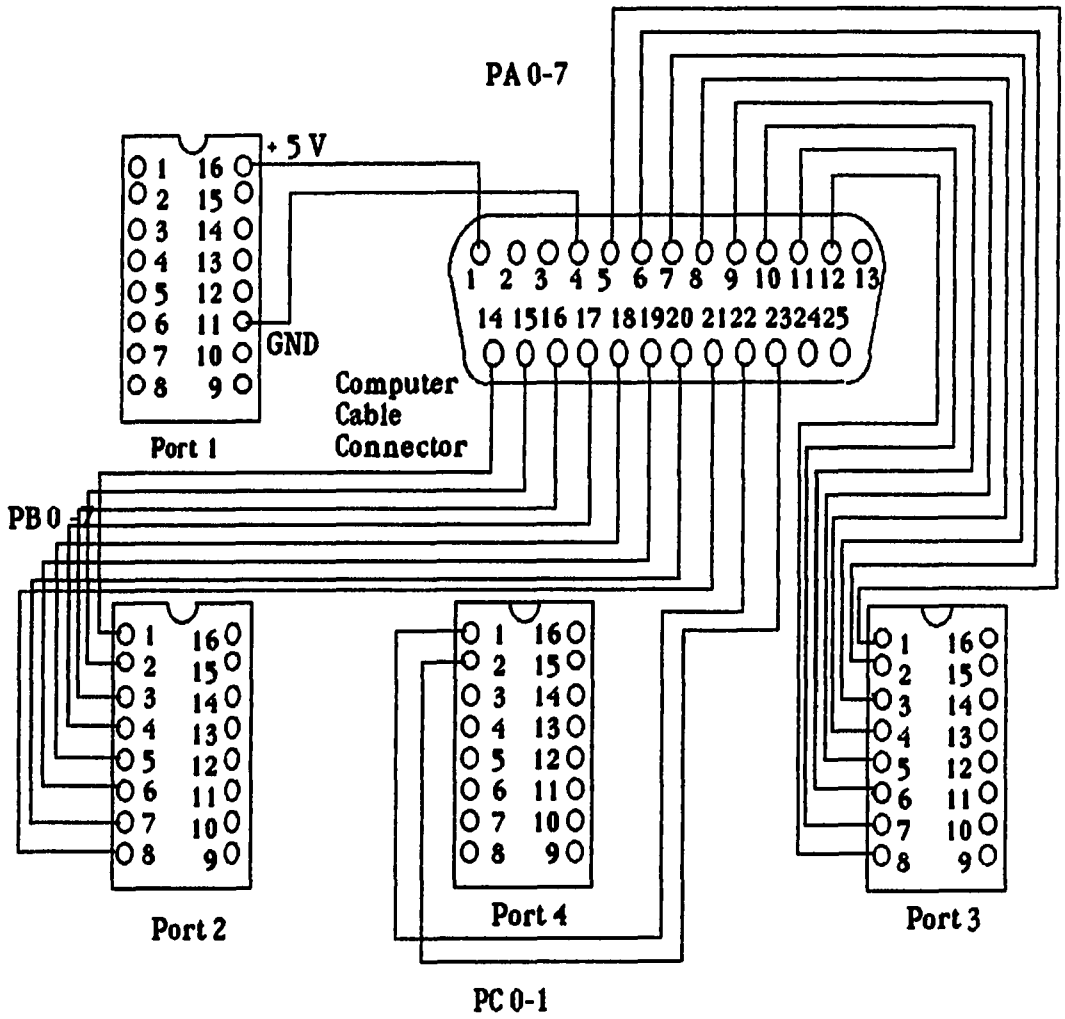
The conductance porosimeter system uses two parallel interface cards because the original system was designed to handle both conductance PTP and phase transition porosimetry. In phase transition porosimetry the height of mercury in a capillary tube is monitored using capacitance. The variable capacitance was converted to a variable frequency square wave by a circuit similar to the one used for the thermistor. Because the amount of capacitance is so small, the noise from the temperature circuit necessitated two separate interface boxes and separate parallel interface cards. Therefore the conductance system can be set up so that only one parallel interface is used.

There are some changes to the programs and to the wiring to convert to only one interface card. The Solomat data must now be channelled through the card in slot 1 along with the thermistor input and the temperature control output. In the controlling program, Controller, change A1, B1 and C1 in lines 2040-2057 to these new values:

```
2040  A1 = -16256 + ISLOT * 256 + 1: B1 = -16384 + ISLOT * 256
2050  A3 = A1 + 2 :  B3 = B1 + 2
2057  C1 = -16256 + ISLOT * 256  : C3 = C1 + 2
```

This changes the addresses the computer reads from the location in slot 4 to the card in slot 1. A1 is the location of port 1 and lines PA 0 - 7. It is used to send the digits 1 and 2 from the Solomat. Since the temperature control circuit uses port 1 of the card in slot 1 to send the control data to the temperature control circuit, A1 is also changed to port 3 and C1 (PC 0 or digit 5) is moved to port 4. The power line (+ 5V) remains with port 1. The +12 V line is not used and therefore eliminated. The computer connector for the interface box doesn't change but the new connector for the Solomat is as shown on the next page.

55


PA 0-7
+ 5 V
GND
Computer
Cable
Connector
Port 1
PB 0-7
Port 2
Port 4
Port 3
PC 0-1

VI. INDEX

CONDUCTOMETRIC PHASE TRANSITION POROSIMETER

USER'S MANUAL
Volume 2
Program Listings

CONDUCTOMETRIC PHASE TRANSITION POROSIMETER USER'S MANUAL Volume 2

by
Todd Millard
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IOWA STATE UNIVERSITY, 1987

CONDUCTOMETRIC PHASE TRANSITION POROSIMETER
USER'S MANUAL
Volume 2
Program Listings

LIST OF PROGRAMS

MAIN MENU
CONTROLLER
PLOTTERHP PLOTTER
CONVERT XY
DERIVATIVE XY
INTEGRATE XDYDX
CONVERT VP
CONVERT R
DERIVATIVE VP
DERIVATIVE LVP
SURFACE AREA
TEST FORMAT
TEMP MEASUREMENT
CALIBRATE

MAIN MENU

```
100  REM   ******************************************************
110  REM   *  MAIN MENU FOR COND CALC                           *
120  REM   *  DOES ALL OF THE CALCULATIONS IN ORDER             *
130  REM   *  BASED ON THE INPUT PARAMETERS SET HERE            *
140  REM   ******************************************************
150 D$ =  CHR$ (4): SPEED= 255: PRINT D$"PR#3"
160 SR$ = "Y":CR$ = "144.3":M1$ = "7":S1$ = "N"
170 S2$ = "N":S3$ = "N":K$ = "Y":M2$ = "3":C$(1) = "C":C$(0) = "W"
172 M3$ = "3"
175 TO$ = "273.15"
180  GOSUB 3000: REM  PRINT MENU OUT
190  VTAB 21: INPUT "Enter your menu choice :";MN$
200  IF MN$ = "" THEN 190
210  IF  LEN (MN$) > 1 THEN 190
220  IF  ASC (MN$) > 56 OR  ASC (MN$) < 49 THEN 250
230  ON  ASC (MN$) - 48 GOSUB 400,700,850,1000,1100,1200,1300,1362
240  GOTO 190
250  IF  ASC (MN$) < 65 OR  ASC (MN$) > 68 THEN 190
260  ON  ASC (MN$) - 64 GOTO 1400,1700,1800,270
270  END
400  REM   ************************************************
410  REM   *  ENTER THE FILENAME                            *
420  REM   ************************************************
430  VTAB 4: POKE 36,40
440  INPUT "";FIL$
450  IF FIL$ <  > "" THEN 520
460  POKE 34,4
470  HOME
480  ONERR  GOTO 600
490  PRINT D$"CATALOG /RAWDAT"
495  POKE 216,0
500  TEXT
510  GOTO 430
520  ONERR  GOTO 650
530  PRINT D$"OPEN "FIL$;"C,D2"
535  PRINT D$"READ "FIL$;"C"
537  INPUT Z
540  PRINT D$"CLOSE"
545  POKE 216,0
550  GOSUB 3000
560  RETURN
600  REM  NOT RAWDAT DISK
610  PRINT "Please insert the RAWDAT disk and press any key ...."
620  GET KB$
630  GOSUB 490
640  GOTO 190
650  REM  FILE NOT FOUND
655  PRINT D$"CLOSE"
```

MAIN MENU

```
660  VTAB 23
670  PRINT "File not found on drive 2..."
675  PRINT D$"DELETE "FIL$;"C"
680  GOSUB 430
690  GOTO 190
700  REM   ************************************************
710  REM   *  SET X.Y PARAMS                              *
720  REM   ************************************************
730  VTAB 5: POKE 36,40
740  INPUT "";SR$
750  IF SR$ < > "Y" AND SR$ < > "N" THEN 730
760  IF SR$ = "N" THEN CR$ = "": GOSUB 3000: GOTO 800
770  VTAB 6: POKE 36,40
780  INPUT "";CR$
790  IF  VAL (CR$) < = 0 THEN 770
800  RETURN
850  REM   ************************************************
860  REM   *  SET DERIVATIVE PARAMS                       *
870  REM   ************************************************
880  VTAB 7: POKE 36,40
890  INPUT "";M1$
900  IF  VAL (M1$) < 3 THEN 880
910  VTAB 8: POKE 36,40
920  INPUT "";S1$
930  IF S1$ < > "Y" AND S1$ < > "N" THEN 910
940  RETURN
1000  REM   ************************************************
1010  REM   *  SET X.Z PARAMS                              *
1020  REM   ************************************************
1030  VTAB 9: POKE 36,40
1040  INPUT "";S2$
1050  IF S2$ < > "Y" AND S2$ < > "N" THEN 1030
1060  RETURN
1100  REM   ************************************************
1110  REM   *  SET X.VP PARAMS                             *
1120  REM   ************************************************
1130  VTAB 10: POKE 36,40
1140  INPUT "";S3$
1150  IF S3$ < > "Y" AND S3$ < > "N" THEN 1130
1160  RETURN
1200  REM   ************************************************
1210  REM   *  SET R.VP PARAMS                             *
1220  REM   ************************************************
1230  VTAB 11: POKE 36,40
1240  INPUT "";K$
1250  IF K$ < > "Y" AND K$ < > "N" THEN 1230
1260  VTAB 12: POKE 36,40
1270  INPUT "";T0$
```

MAIN MENU

```
1280  RETURN
1300  REM   ************************************************
1310  REM   *  SET R.DVPDR  PARAMS                         *
1320  REM   ************************************************
1330  VTAB 13: POKE 36,40
1340  INPUT "";M2$
1350  IF  VAL (M2$) < 3 THEN 1330
1360  RETURN
1362  REM   ************************************************
1365  REM   *  SET R.DVPDLR PARAMS                         *
1370  REM   ************************************************
1375  VTAB 14: POKE 36,40
1380  INPUT "";M3$
1385  IF  VAL (M3$) < 3 THEN 1375
1390  RETURN
1400  REM   ************************************************
1410  REM   *  RUN CALCULATIONS                            *
1420  REM   ************************************************
1422  IF FIL$ = "" THEN 190
1424  HOME
1428  PRINT "Performing the calculations..."
1430  REM  CALL T.C.TO.X.Y
1440 CR =  VAL (CR$)
1450  PRINT D$"CHAIN /CONPROG1/PROGRAMS/T.C.TO.X.Y"
1460  REM  CALL DER.X.Y
1470 MA =  VAL (M1$):SA = 1
1480  IF S1$ = "Y" THEN SA = 0
1490  PRINT D$"CHAIN /CONPROG1/PROGRAMS/DER.X.Y"
1500  REM  CALL INT
1510 SA = 1
1520  IF S2$ = "Y" THEN SA = 0
1530  PRINT D$"CHAIN /CONPROG1/PROGRAMS/INT"
1540  REM  CALL X.VP.FROM.X.Z
1550 SA = 1
1560  IF S3$ = "Y" THEN SA = 0
1570  PRINT D$"CHAIN /CONPROG1/PROGRAMS/X.VP.FROM.X.Z"
1580  REM  CALL R.VP.FROM.X.VP
1590  PRINT D$"CHAIN /CONPROG1/PROGRAMS/R.VP.FROM.X.VP"
1600  REM  CALL DER.R.VP
1610 MA =  VAL (M2$)
1620  PRINT D$"CHAIN /CONPROG1/PROGRAMS/DER.R.VP"
1625 MA =  VAL (M3$)
1630  PRINT D$"CHAIN /CONPROG1/PROGRAMS/DER.LR.VP"
1700  REM   ************************************************
1710  REM   *   CALL PLOT                                  *
1720  REM   ************************************************
1730  PRINT D$"RUN /CONPROG1/PROGRAMS/P"
1800  REM  ************************************
```

MAIN MENU

```
1810  REM  *  RUN CONDUCTANCE TEST              *
1820  REM  ************************************
1830  PRINT D$"RUN COND2,D1"
3000  REM   ******************************************
3010  REM   *   PRINT OUT THE MENU                    *
3020  REM   ******************************************
3030  HOME : PRINT
3040  HTAB 32: PRINT "CONDUCTANCE MENU"
3050  PRINT
3060  PRINT "1. Base Filename                        : ";FIL$
3070  PRINT "2. T.C to X.Y        Series Resistor    : ";SR$
3080  PRINT "                     Cond of Resistor   : ";CR$
3090  PRINT "3. X.Y to X.DYDX     Moving Average     : ";M1$
3100  PRINT "                     Save File          : ";S1$
3110  PRINT "4. X.DYDX to X.Z     Save File          : ";S2$
3120  PRINT "5. X.Z to X.VP       Save File          : ";S3$
3130  PRINT "6. X.VP to R.VP      Thin File Out      : ";K$
3135  PRINT "                     Temp of T0         : ";T0$
3140  PRINT "7. R.VP to R.DVPDR   Moving Average     : ";M2$
3150  PRINT "8. R.VP to R.DVPDLR  Moving Average     : ";M3$
3155  PRINT : PRINT
3160  PRINT "  A.  Calculate the data"
3170  PRINT "  B.  Plot data"
3180  PRINT "  C.  Run Conductance test"
3185  PRINT "  D.  Exit to system"
3190  RETURN
```

CONTROLLER

```
10  REM   CONDUCTANCE CONTROLLER FOR ONE SAMPLE
11  REM    MODIFIED TO ONE SAMPLE ON 2 OCT 86
12  HOME
15 D$ =  CHR$ (4)
18  HIMEM: 256 *  PEEK (116) +  PEEK (115) - 1024
20  PRINT D$"BLOAD CAP.RES.2,A$340,D1"
30  PRINT D$"BLOAD IO.CLOCK.SLOT1,A$9800"
45  POKE 1535,0
50  POKE 1407,0
55  POKE 1279,0
60  CALL  - 26624
65  POKE 1919,1: REM    DISPLAYTIME
70  GOTO 2000
100  POKE 824,0: CALL 832
110  IF  PEEK (822) > 3 THEN 140
120 TV =  PEEK (823): IF TV <  > 255 THEN  POKE 823,TV + 1: GOTO 140
130  POKE 823,0
140 R = 65536 - ( PEEK (823) * 256 +  PEEK (822))
150 R = R - 25000: IF R < 0 THEN R = R + 40536
160 RR = RR + R - AR(SR):AR(SR) = R: IF MR > SR THEN SR = SR + 1: GOTO 180
170 SR = 1
180 TEMP =  INT (RR / MR + .5)
182  IF TEMP > P(NMPT) THEN TEMP = P(NMPT)
184  IF TEMP < P(1) THEN TEMP = P(1)
186  IF (TEMP < P(TI)) AND (TI > 1) THEN TI = TI - 1: GOTO 186
188  IF (TEMP > P(TI + 1)) AND (TI < NMPT - 1) THEN TI = TI + 1: GOTO 188
190 TEMP =  INT (((TEMP - P(TI)) * (T(TI + 1) - T(TI)) / (P(TI + 1) -
    P(TI)) + T(TI)) * 1E3 + .5) / 1E3
192  VTAB 6: HTAB 30
194  PRINT "          ";: HTAB 30
196  PRINT TEMP;
200 OSEC =  PEEK (1279) + 60 *  PEEK (1407) + 3600 *  PEEK (1535)
210  RETURN
300  REM  SWITCH LEADS AND READS CONDUCTANCE
310 PO = (PO -  INT (PO / 2) * 2) +  INT (PO / 4) * 4
320  POKE C1,PO
340 CX =  PEEK (C1):CY =  PEEK (B1):CZ =  PEEK (A1)
350 CX = (CX -  INT (CX / 2) * 2) * 10000
360 CY = (CY -  INT (CY / 16) * 6) * 100
370 CZ = CZ -  INT (CZ / 16) * 6
380 CND = CX + CY + CZ
390  RETURN
400  REM  CALCULATE TEMP CONTROL INFO
410 OT =  INT ((M1 * S9 + B) + .5)
420 PT =  INT ((M1 * F9 + B) + .5)
430 TS = 60 * ( ABS (F9 - S9) / (RA(TC(CCYCLE)) / 60)) /  ABS (OT - PT)
440 SD =  SGN (S9 - F9)
450 U6 = OSEC
```

CONTROLLER

```
460  RETURN
500  REM  TURN 'FF HEATER
510  POKE D1,0
530  VTAB 2: POKE 36,10: PRINT "Off      "
540  RETURN
550  REM  TURN ON COMPRESSOR, HEATER OFF
555 CCYCLE = CCYCLE + 1
560 S9 = TP(TC(CCYCLE)):F9 = BTTM(TC(CCYCLE))
570  GOSUB 400: POKE D1,OT
585  VTAB 14: HTAB 40: PRINT "CYCLE NUMBER ";CCYCLE;" OF ";MCYCLE
590  VTAB 2: POKE 36,10: PRINT "Cool    "
595  RETURN
600  REM  TURN ON HEATER, COMPRESSOR OFF
610 S9 = BTTM(TC(CCYCLE)):F9 = TP(TC(CCYCLE))
620  GOSUB 400: POKE D1,OT
630  VTAB 2: POKE 36,10: PRINT "Heat    "
640  RETURN
700  REM  INITIALIZE DATABASE AND FLAGS
710  REM  SAMPLE DATA
730  FOR Y = 1 TO 300
740 SDT(Y,0) = 0
750 SDT(Y,1) = 0
760  NEXT Y
790 PNT = 1
800 FDNE = 0
840 INVL(TC(CCYCLE)) =  - INVL(TC(CCYCLE))
850 COOL =  NOT COOL
860  RETURN
1000  REM  SAVE OFF DATA ON TEMPORARY DISK
1001 D$ =  CHR$ (4)
1002  IF COOL THEN W1$ = "C": GOTO 1010
1005 W1$ = "W"
1010  IF TD$(TC(CCYCLE)) = "N" THEN 1110
1020  PRINT D$;"OPEN   ";DIS$;".";CCYCLE + SCYCLE - 1;W1$;",D2"
1030  PRINT D$;"WRITE  ";DIS$;".";CCYCLE + SCYCLE - 1;W1$
1040  PRINT PNT
1050  FOR N = 1 TO PNT
1060  PRINT SDT(N,0)
1070  PRINT SDT(N,1)
1080  NEXT N
1090  PRINT D$;"CLOSE  ";DIS$;".";CCYCLE + SCYCLE - 1;W1$
1110  RETURN
1900  REM   READ IN NUMBERS
1910 TMP$ = ""
1920  GET K$
1930  IF K$ = "." OR  ASC (K$) =  > 48 AND  ASC (K$) <  = 57 OR K$ = "-"
      THEN 960
1940  IF  ASC (K$) = 13 THEN 1980
```

CONTROLLER

```
1950  IF  ASC (K$) = 8 AND  LEN (TMP$) = 1 THEN TMP$ = "": PRINT  CHR$ (8);
      " "; CHR$ (8);
1952  IF  ASC (K$) = 8 AND  LEN (TMP$) > 1 THEN TMP$ =  LEFT$ (TMP$, LEN
      (TMP$) - 1): PRINT  CHR$ (8);" "; CHR$ (8);
1955  GOTO 1920
1960 TMP$ = TMP$ + K$
1965  PRINT K$;
1970  GOTO 1920
1980 TMP =  VAL (TMP$)
1990  RETURN
2000  REM  PRE MAIN PROGRAM
2005  GOSUB 4000
2020 PSLOT = 4:ISLOT = 1:COOL = 0:LCYCLE = 0:D$ =  CHR$ (4):INVL = 0
2030 FSTP = 0:CCYCLE = 0
2035 M1 = 255 / ( - 35 - 7):B = 7 *  - M1:D1 =  - 16384 + ISLOT * 256 + 1:
OKE D1 + 2,255
2040 A1 =  - 16384 + PSLOT * 256 + 1:B1 =  - 16384 + PSLOT * 256
2050 A3 = A1 + 2:B3 = B1 + 2
2057 C1 =  - 16256 + PSLOT * 256 + 1:C3 = C1 + 2
2058  POKE A3,0: POKE B3,0: POKE C3,254
2059  GOSUB 3500: REM  GET NOTES
2060  HOME
2062  VTAB 16: HTAB 2: PRINT "# of Cycle Types : ";
2064  GOSUB 1900
2066  IF TMP =  > 1 THEN 2072
2068  HTAB 21: PRINT "     ";: HTAB 21
2070  GOTO 2064
2072 CT =  INT (TMP)
2074  DIM TP(CT),BTTM(CT),INVL(CT),RA(CT),TD$(CT)
2076  FOR X = 1 TO CT
2080  HOME : VTAB 16: HTAB 2: PRINT "Cycle Type : ";X
2085  VTAB 18: HTAB 4
2087  PRINT "Maximum Temp : ";
2090  GOSUB 1900
2092  IF TMP <  = 7 THEN 2100
2094  POKE 36,18: PRINT "    ";: POKE 36,18
2096  GOTO 2090
2100 TP(X) = TMP
2110  HTAB 30
2120  PRINT "Minimum Temp : ";
2130  GOSUB 1900
2140  IF TMP < TP(X) THEN 2170
2150  POKE 36,44: PRINT "      ";: POKE 36,44
2160  GOTO 2130
2170 BTTM(X) = TMP
2171  VTAB 18: POKE 36,58: PRINT "Temp Rate : ";
2172  GOSUB 1900
2173  IF TMP > 0 AND TMP <  = 30 THEN 2178
```

CONTROLLER

```
2174  POKE 36,70: PRINT "    ";: POKE 36,70
2175  GOTO 2172
2178 RA(X) = TMP
2250  VTAB 20: HTAB 10
2260  PRINT "Temp Interval Between Readings : ";
2270  GOSUB 1900
2280  IF TMP <  = (TP(X) - BTTM(X)) AND TMP >  = 0 THEN 2302
2290  POKE 36,42: PRINT "      ";: POKE 36,42
2300  GOTO 2270
2302  IF TMP = 0 THEN TD$(X) = "N":INVL(X) = .1: GOTO 2440
2304 TD$(X) = "Y"
2305 INVL(X) = TMP
2440  VTAB 24: HTAB 5
2450  PRINT "Is all information correct?";
2460  GET TMP$
2470  IF TMP$ = "Y" OR TMP$ = "y" THEN  HTAB 5: CALL  - 868: GOTO 2492
2480  IF TMP$ = "N" OR TMP$ = "n" THEN 2080
2490  GOTO 2460
2492  NEXT X
2493  GOSUB 6000: HOME
2496 CCYCLE = 0
2500  POKE 35,15: HOME : TEXT : VTAB 5: HTAB 30
2510  PRINT "Sample Description      Starting Cycle"
2515  VTAB 6: HTAB 18: CALL  - 868: PRINT "Sample  1";: INPUT DIS$
2516  VTAB 6: POKE 36,55: GOSUB 1900:SCYCLE = TMP
2520  VTAB 15: HTAB 5:.PRINT "Is This name correct? ";: GET TMP$
2522  IF TMP$ = "Y" OR TMP$ = "y" THEN 2528
2525  IF TMP$ = "N" OR TMP$ = "n" THEN 2500
2527  GOTO 2520
2528  POKE 35,15: HOME : TEXT : GOSUB 7000
2530  VTAB 5: HTAB 30
2532  PRINT "Temp (C)  Cond (uS)  Point"
2534  VTAB 6: HTAB 5: PRINT  LEFT$ (DIS$,1)
2535  VTAB 6: HTAB 18: CALL  - 868: PRINT "Sample  1"
2545  VTAB 3: POKE 36,50: PRINT "Press F to stop at cycle"
2550  DIM SDT(400,1)
2562 MR = 30
2565  DIM AR(MR)
2580 RTEMP = TP(TC(1))
2600  GOSUB 550: REM  START COMPRESSOR
2610  GOSUB 6500
2620  GOSUB 700: REM  INITIALIZE
2630  GOSUB 100: REM  READ TEMP
2631  IF  ABS (OSEC - U6) >  = TS THEN U6 = OSEC:OT = OT + SD: IF OT >  = 0
      AND OT <  = 255 THEN  POKE D1,OT
2632  IF  PEEK ( - 16384) = 195 THEN 2637
2633  IF  PEEK ( - 16384) <  > 198 THEN 2639
2634 FSTP = 1: VTAB 3: POKE 36,50
```

CONTROLLER

```
2635  CALL  - 868: INVERSE : PRINT " Press 'C' to not halt ": NORMAL
2636  GOTO 2639
2637 FSTP = 0: VTAB 3: POKE 36,50
2638  PRINT "Press F to stop at cycle"
2639  POKE  - 16368,0
2640  IF COOL AND TEMP <  = RTEMP OR  NOT COOL AND TEMP >  = RTEMP THEN
      GOTO 2655
2650  GOTO 2630: REM   NEXT TEMP
2655  IF TD$(TC(CCYCLE)) = "N" THEN 2730
2660  GOSUB 300: REM  TAKE CND READING
2670 SDT(PNT,0) = TEMP
2680 SDT(PNT,1) = CND
2705  HTAB 40: PRINT "       ";
2710  HTAB 40: PRINT CND;
2715  POKE 36,51: PRINT "      ";
2720  POKE 36,51: PRINT PNT
2730  IF RTEMP <  = BTTM(TC(CCYCLE)) AND COOL OR RTEMP =  > TP(TC(CCYCLE))
      AND  NOT COOL THEN 3000: REM  AT END OF CYCLE FOR SAMPLE
2740 RTEMP =  INT ((RTEMP + INVL(TC(CCYCLE))) * 100) / 100
2750 PNT = PNT + 1
2760  GOTO 2630
3000  REM  SAVE OFF DATA
3010  GOSUB 1000: REM  SAVE TO TEMPORARY DISK
3020  IF  NOT FSTP OR COOL AND FSTP THEN 3130
3030  GOSUB 500: REM  SHUT OFF HEATER
3040  VTAB 15: HTAB 5
3050  PRINT "Program halted, do you wish to continue?";
3060  GET TMP$
3070  IF TMP$ = "Y" OR TMP$ = "y" THEN 3100
3080  IF TMP$ = "N" OR TMP$ = "n" THEN  CALL  - 868: GOTO 3140
3090  GOTO 3060
3100  HTAB 5: CALL  - 868: REM  ERASE LINE
3110  VTAB 3: POKE 36,50: PRINT "Press F to stop at cycle"
3120 FSTP = 0
3130  IF (CCYCLE - LCYCLE = NCYCLE OR CCYCLE = MCYCLE) AND  NOT COOL THEN
      3140
3135  GOTO 3180
3140  REM   NO NEED TO TRANSFER DATA TO PERMANENT DISKS
3165 LCYCLE = CCYCLE
3170  IF (CCYCLE = MCYCLE) OR FSTP THEN 3210
3180  IF COOL THEN  GOSUB 600: GOTO 3200: REM  TURN ON HEATER
3190  GOSUB 550: REM  TURN ON COMPRESSOR
3200  GOTO 2610: REM  START NEXT CYCLE
3210  GOSUB 500: REM  TURN OFF HEATER AND QUIT
3220  VTAB 24: HTAB 5
3230  PRINT "Program finished   "
3240  PRINT : PRINT
3250  PRINT D$"RUN STARTUP,D1"
```

CONTROLLER

```
3500  REM  NOTES ON SAMPLE
3510  HOME : VTAB 3: HTAB 29
3520  PRINT "Conductance Controller"
3530  VTAB 8: PRINT "Notes on Sample (press 'Return' at end of line) :"
3540  INPUT ">";N1$
3550  INPUT ">";N2$
3560  INPUT ">";N3$
3570  INPUT ">";N4$
3580  RETURN
4000  PRINT D$"OPEN CAL,D1"
4005  PRINT D$"READ CAL"
4010  INPUT NMPT
4020  DIM P(NMPT),T(NMPT)
4025  FOR TI = 1 TO NMPT
4030  INPUT P(TI),T(TI)
4040  NEXT TI
4042 TI = 1
4045  PRINT D$"CLOSE"
4050  RETURN
6000  REM  NOW SPECIFY EACH CYCLE
6010  HOME : VTAB 16: HTAB 10
6020  PRINT "Number of Cycles : ";
6030  GOSUB 1900
6040  IF TMP =  > 1 THEN 6070
6050  HTAB 29: PRINT "     ";: HTAB 29
6060  GOTO 6030
6070 MCYCLE =  INT (TMP)
6075  DIM TC(MCYCLE)
6080  FOR CCYCLE = 1 TO MCYCLE
6090  HOME : VTAB 16: HTAB 10
6100  PRINT "Cycle Number : ";CCYCLE;
6110  POKE 36,40
6120  PRINT "Cycle Type : ";
6130  GOSUB 1900
6140  IF TMP =  > 1 AND TMP <  = CT THEN 6160
6150  POKE 36,53: PRINT "     ";: POKE 36,53
6155  GOTO 6130
6160 TC(CCYCLE) =  INT (TMP)
6170  GOSUB 6500: REM  PRINT OUT PARAMETERS
6180  VTAB 24: HTAB 5
6190  PRINT "Is this the correct cycle type ?";
6200  GET TMP$
6210  IF TMP$ = "Y" OR TMP$ = "y" THEN 6250
6220  IF TMP$ = "N" OR TMP$ = "n" THEN 6090
6230  GOTO 6200
6250  VTAB 24: HTAB 1: CALL  - 868
6255  NEXT CCYCLE
6330  VTAB 16: HTAB 1: CALL  - 868
```

CONTROLLER

```
6340  RETURN
6500  REM  DISPLAY ITEMS
6510  VTAB 18: HTAB 4
6520  PRINT "Maximum Temp : ";TP(TC(CCYCLE));"    ";
6530  HTAB 30
6540  PRINT "Minimum Temp : ";BTTM(TC(CCYCLE));"    ";
6550  POKE 36,58
6560  PRINT "Temp Rate : ";RA(TC(CCYCLE));"    ";
6570  VTAB 20: HTAB 10
6580  PRINT "Temp Interval between readings : ";
6590  IF TD$(TC(CCYCLE)) = "N" THEN  PRINT "0": GOTO 6610
6600  PRINT INVL(TC(CCYCLE))
6610  RETURN
7000  REM    SAVE OFF CYCLE TYPE DESCRIPTIONS ON DISK
7010 D$ =  CHR$ (4)
7030  PRINT D$;"OPEN  ";DIS$;".";SCYCLE;".CT,D2"
7040  PRINT D$;"WRITE ";DIS$;".";SCYCLE;".CT"
7045  PRINT SCYCLE
7050  PRINT CT
7060  FOR N = 1 TO CT
7070  PRINT TP(N)
7072  PRINT BTTM(N)
7074  PRINT RA(N)
7076  PRINT INVL(N)
7078  PRINT TD$(N)
7080  NEXT N
7081  PRINT MCYCLE
7082  FOR N = 1 TO MCYCLE
7083  PRINT TC(N)
7084  NEXT N
7085  PRINT N1$: PRINT N2$: PRINT N3$: PRINT N4$
7090  PRINT D$;"CLOSE ";DIS$;".";SCYCLE;".CT"
7110  RETURN
9999  POKE  - 15986,64: HIMEM: 38400: END
```

PLOTTER

```
100  REM ************************************************
110  REM * THIS PROGRAM PLOTS ONSCREEN PLOTS OR SAVES THE*
120  REM * VARIABLES IN A VARIABLE FILE AND PLOTS ON THE *
130  REM * HP7220 PLOTTER.                               *
140  REM ************************************************
150  TEXT :CS$(1) = "TRUE":CS$(0) = "FALSE"
155  DIM AS%(30)
160  HOME :D$ =  CHR$ (4)
170 DR$ = "CALDAT"
180 L(1) = 7:L(2) = 2
200 CS = 1
235  REM ********************************************
236  REM * CHECKING TO SEE IF DISK IN DRIVE TWO IS   *
237  REM * CALDAT OR NOT.                            *
238  REM ********************************************
240 K = 10: PRINT "MENU OF SUBDIRECTORIES"
250  PRINT : PRINT
260  HTAB (K): PRINT "1.  X.Y"
270  HTAB (K): PRINT "2.  X.DYDX"
275  HTAB (K): PRINT "3.  X.Z"
280  HTAB (K): PRINT "4.  X.VP"
290  HTAB (K): PRINT "5.  R.VP"
300  HTAB (K): PRINT "6.  R.DVPDR"
302  HTAB (K): PRINT "7.  R.DVPDLR"
305  HTAB (K): PRINT "8.  EXIT TO MAIN MENU"
310  INPUT "          ENTER NUMBER OF YOUR CHOICE  ";A$
320  IF (A$ < "1") AND (A$ > "8") THEN  GOTO 240
330 A =  VAL (A$)
332  IF A$ = "8" THEN 1040
333  IF A >  = 2 AND A <  = 4 THEN  PRINT : INPUT "DO YOU WISH PORE RADIUS
     MARKS ON TOP (Y/N  DEFAULT = N)  ";PZ$
334 K1$ = "Y": IF A$ = "6" THEN K1$ = "N"
335  IF A$ <  > "6" AND A$ <  > "7" AND A$ <  > "5" THEN 338
336  PRINT : PRINT "DO YOU WISH TO PLOT THE RADIUS ON A LOG SCALE (Y/N
     DEFAULT = ";K1$;")  ";: INPUT TEMP$
337 KB$ = TEMP$: IF TEMP$ = "" THEN KB$ = K1$
338  IF A$ < "5" THEN L$(1) = "WARMING":L$(2) = "COOLING": GOTO 340
339 L$(2) = "NECK SIZES":L$(1) = "BODY SIZES"
340  ON A GOSUB 1180,1230,1330,1270,1320,1361,1361
390  HOME : PRINT "ENTER THE LETTER OF ANY VALUE THAT YOU WISH TO CHANGE."
391 L = 3:K = 2
400  PRINT "AND PRESS RETURN"
401  HTAB (K): PRINT "1.  TITLE .....  "TI$
402  HTAB (K): PRINT "2.  FILENAME .....  "F$(1)
403  HTAB (K): PRINT "3.    LABEL .....  "L$(1)
404  HTAB (K): PRINT "4.    LINETYPE .....  "L(1)
405  HTAB (K): PRINT "5.  FILENAME .....  "F$(2)
406  HTAB (K): PRINT "6.    LABEL .....  "L$(2)
```

PLOTTER

```
407  HTAB (K): PRINT "7.    LINETYPE ..................  "L(2)
410  HTAB (K): PRINT "8.  MINIMUM X ..................  "X1
420  HTAB (K): PRINT "9.  MAXIMUM X ..................  "X2
430  HTAB (K): PRINT "10. X-INTERVAL SIZE ............  "XINC
440  HTAB (K): PRINT "11. MINIMUM Y ..................  "Y1
450  HTAB (K): PRINT "12. MAXIMUM Y ..................  "Y2
460  HTAB (K): PRINT "13. Y-INTERVAL SIZE ............  "YINC
480  HTAB (K): PRINT "14. PAPER LENGTH ...............  "PL
495  PRINT "----------------------------------------"
500  PRINT "A-ONSCREEN PLOTTING";: HTAB 30: PRINT "D-CLEAR GRAPHICS
     SCREEN";CS$(CS)
502  PRINT "B-HP722 PLOTTING ";: HTAB 30: PRINT "E-EXIT PROGRAM"
504  PRINT "C-VIEW GRAPHICS SCREEN";: HTAB 30: PRINT "F-FIND NEW DATA
     POINTS"
510  PRINT
520  VTAB (23): INPUT "ENTER YOUR CHOICE AND PRESS RETURN.";SE$
525  IF SE$ = "" THEN 520
530  IF ( VAL (SE$) < 1 OR  VAL (SE$) > 13) AND (SE$ < "A" OR SE$ > "F")
     THEN 520
540 M =  VAL (SE$)
550  ON M GOTO 3000,3050,3150,3200,3250,3350,3400,3450,3500,3550,3600,3650,
     3700,3750
560  IF  ASC ( LEFT$ (SE$,1)) = 65 THEN 720: REM  A
570  IF  ASC ( LEFT$ (SE$,1)) = 66 THEN  PRINT D$"CHAIN
     /CONPROG1/PROGRAMS/PLOT": REM  B
580  IF  ASC ( LEFT$ (SE$,1)) = 67 THEN  GOTO 1200: REM  C
590  IF  ASC ( LEFT$ (SE$,1)) = 68 THEN CS =  NOT CS: GOTO 390: REM  D
600  IF  ASC ( LEFT$ (SE$,1)) = 69 THEN  PRINT D$"RUN STARTUP,D1": REM  E
610  IF  ASC ( LEFT$ (SE$,1)) = 70 THEN 160: REM  F
720  PRINT  CHR$ (17)
730  IF  NOT CS THEN  POKE  - 16304,0: POKE  - 16302,0: POKE  - 16299,0:
     POKE  - 16297,0: GOTO 755
740  HGR2
750  POKE  - 16368,0
755 YA = 159:YB = 0:XA = 1:XB = 279
760  HCOLOR= 3: IF  NOT CS THEN  GOTO 862
770  HPLOT 0,0 TO 279,0 TO 279,159 TO 1,159 TO 1,0
790 VARSCAL = (YA - YB) * YINC / (Y2 - Y1)
800  FOR K = 1 + VARSCAL TO YA STEP VARSCAL
810  HPLOT 1,K TO 5,K: HPLOT 279,K TO 274,K: NEXT K
815  IF A = 5 THEN 2100: REM  PLOT X ON LOG SCALE
820 HARSCAL = (XB - XA) * XINC / (X2 - X1)
825  IF HARSCAL < 1 THEN HARSCAL = 1
830  FOR K = 1 TO XB - HARSCAL STEP HARSCAL
840  HPLOT K,159 TO K,154
850 K =  INT (K)
860  NEXT K
862  FOR I = 1 TO 2
```

PLOTTER

```
865  IF F$(I) = "" THEN 1021
870  PRINT  CHR$ (4)"OPEN /"DR$"/"FIL$"/"F$(I)
880  ONERR  GOTO 1090
890  PRINT  CHR$ (4)"READ/"DR$"/"FIL$"/"F$(I)
900  INPUT NMPTS
920  POKE 216,0
930  FOR T = 1 TO NMPTS
935  IF  PEEK ( - 16384) = 27 THEN T = NMPTS: GOTO 1010
936  POKE  - 16368,0
940  INPUT X,Y
950  IF (X <  = X2) AND (X >  = X1) THEN J =  FN CN(X)
960  IF (Y <  = Y2) AND (Y >  = Y1) THEN K =  FN MOH(Y)
970  IF (X > X2) OR (X < X1) THEN J = 0
980  IF (Y > Y2) OR (Y < Y1) THEN K = 1
990  IF (J = 0) OR (K = 1) THEN J = 0:K = 1
1000  HPLOT J,K
1010  NEXT T
1020  PRINT  CHR$ (4)"CLOSE/"DR$"/"FIL$"/"F$(I)
1021  NEXT I
1022  PRINT  CHR$ (7); CHR$ (7); CHR$ (7)
1030  GET A$: PRINT  CHR$ (18): TEXT : PRINT D$"PR#3":K = 10: HOME :
      GOTO 390
1040  PRINT  CHR$ (4)"RUN STARTUP,D1"
1050  REM  ****************************************************
1060  REM  *THIS IS AN ERROR HANDLING ROUTINE WRITTEN TO CLEAR*
1070  REM  *ERRORS IN INPUTING FILE NAMES.                     *
1080  REM  ****************************************************
1090  TEXT : PRINT  CHR$ (4)"CLOSE/"DR$"/"FIL$"/"SUB$
1100  PRINT  CHR$ (4)"DELETE /"DR$"/"FIL$"/"SUB$: POKE 216,0
1110  GET A$: PRINT D$"PR#3": GOTO 150
1130  END
1140  REM  ******************************************************
1150  REM  *THIS IS A LOOKUP TABLE FOR VARIABLE DEFAULTS AND    *
1160  REM  *EQUATIONS.                                          *
1170  REM  ******************************************************
1180 LAB$ = "Degrees Celcius":PL = 8.5:X1 =  - 41:X2 =  - 36:Y1 =  - 1:
     Y2 = 4:XNUM = .15:YNUM = .185:EL$ = "Log (Conductance in micro Mho)":
     BT$ = "(-1/T), K  x 10"
1190 SL = 2:XIN = 1:YIN = .5:LIN = 7:PEN = 1:FIL$ = "X.Y"
1200  DEF  FN MOH(T) = 159 - (T - Y1) * (YA - YB) / (Y2 - Y1)
1210  DEF  FN CN(R) = ((R - X1) * XB / (X2 - X1)) + 1
1220  RETURN
1230 LAB$ = "":PL = 8.5:YINC = .5:XIN = 1:PEN = 1:X1 =  - 41:X2 =  - 36:
     Y1 = 0:LIN = 7:Y2 = 3:XNUM = .15:YNUM = .185:BT$ = "(-1/T), K  x 10":
     EL$ = "d(log(Conductance))/d(-1/T)"
1231 FIL$ = "X.DYDX"
1240  DEF  FN MOH(T) = 159 - (T - Y1) * (YA - YB) / (Y2 - Y1)
1250  DEF  FN CN(R) = ((R - X1) * XB / (X2 - X1)) + 1
```

PLOTTER

```
1260  RETURN
1270 LAB$ = "":PL = 8.5:LIN = 7:PEN = 1:X1 =  - 41:X2 =  - 36:Y1 = 0:
     Y2 = 1:YIN =  1:XNUM = .15:YNUM = .185:XINC = 1
1280 EL$ = "Relative Conducting Pore Volume":BT$ = "(-1/T), K  x 10":
     FIL$ = "X.VP"
1290  DEF  FN MOH(T) = 159 - (T) * YA / (Y2 - Y1)
1300  DEF  FN CN(R) = ((R - X1) * XB / (X2 - X1)) + 1
1310  RETURN
1320 LAB$ = "":PL = 8.5:X1 = 10:X2 = 10000:Y1 = 0:Y2 = 1.1:YIN = .1:
     XNUM = .15:YNUM = .185:XINC = 10:BT$ = "Radius, Angstroms":
     EL$ = "Relative Conducting Pore Volume":FIL$ = "R.VP"
1321  DEF  FN MOH(T) = 159 - (T - Y1) * (YA - YB) / (Y2 - Y1)
1322  DEF  FN CN(R) = ( LOG (R) /  LOG (10) -  LOG (X1) /  LOG (10)) /
     ( LOG (X2) /  LOG (10) -  LOG (X1) /  LOG (10)) * XB + 1
1324  IF KB$ = "N" THEN  DEF  FN CN(R) = ((R - X1) * XB / (X2 - X1)) + 1:
     A = 6:X1 = 0:XINC = 1000
1325 PEN = 1:LIN = 7
1326  RETURN
1330 LAB$ = "":PL = 8.5:YIN = 1:XIN = 1:X1 =  - 41:X2 =  - 36:Y1 = 0:
     Y2 = 5:PEN = 1:LIN = 2:XNUM = .15:YNUM = .185:BT$ = "(-1/T) K  x 10":
     EL$ = "      Z          "
1333 PEN = 1:LIN = 7:FIL$ = "X.Z"
1340  DEF  FN MOH(T) = 159 - (T - Y1) * (YA - YB) / (Y2 - Y1)
1350  DEF  FN CN(R) = ((R - X1) * XB / (X2 - X1)) + 1
1360  RETURN
1361 LAB$ = "":PL = 8.5:X1 = 10:X2 = 10000:Y1 = 0:Y2 = 2:YIN = .2:
     XNUM = .15:YNUM = .185:XINC = 10:BT$ = "Radius, Angstroms "
1362 EL$ = "d(Pore Volume)/d(log Radius) ":PEN = 1:LIN = 7:
     FIL$ = "R.DVPDLR"
1363  IF A = 6 THEN EL$ = "d(Pore Volume)/d(Radius)":FIL$ = "R.DVPDR":
     Y2 = .1:YIN = .01
1364  IF KB$ = "N" THEN X1 = 0:XINC = 1000
1365  DEF  FN MOH(T) = 159 - (T - Y1) * (YA - YB) / (Y2 - Y1)
1366  IF KB$ = "Y" THEN  DEF  FN CN(R) = ( LOG (R) /  LOG (10) -  LOG (X1)
     / LOG (10)) / (LOG (X2) / LOG (10) -  LOG (X1) / LOG (10)) * XB + 1:
     A = 5: GOTO 1368
1367  DEF  FN CN(R) = ((R - X1) * XB / (X2 - X1)) + 1
1368  RETURN
1370  HOME
1380  PRINT D$"CATALOG /"DR$"/"FIL$
1390  INPUT "ENTER NEW FILE NAME     ";SUB$
1400  IF SUB$ = "" THEN  GOTO 1370
1410  RETURN
1420  ONERR  GOTO 1510
1430  PRINT D$"OPEN /CALDAT, TDIR"
1440  PRINT D$"CLOSE /CALDAT"
1450  POKE 216,0: GOTO 240
1470  REM  ************************************
```

PLOTTER

```
1480  REM  * CHECKING THE DISK IN DRIVE 2 FOR*
1490  REM  * THE PREFIX OF /CALDAT.          *
1500  REM  ************************************
1510  PRINT "THE DISK IN DRIVE 2 IS NOT CALDAT.  PLEASE REPLACE THE DISK IN
      DRIVE 2 WITH CALDAT."
1520  INPUT "AND PRESS RETURN TO CONTINUE.";X$
1530  POKE 216,0: GOTO 100
2000  PRINT  CHR$ (17): POKE  - 16304,0: POKE  - 16302,0: POKE  - 16299,0:
      POKE  - 16297,0
2001  GET A$
2010  POKE  - 16303,0: POKE  - 16300,0
2020  PRINT D$"PR#3": PRINT : GOTO 390
2100  REM  SETS UP X AXIS ON A LOG SCALE
2105  IF X1 = 0 THEN X1 = 1
2110  FOR K =  LOG (X1) /  LOG (10) TO  LOG (X2) /  LOG (10) - 1
2120  FOR K1 = 1 TO 10
2130 XP =  FN CN(K1 * 10 © K)
2135  IF XP = 280 THEN 2150
2140  HPLOT XP,159 TO XP,154
2150  NEXT K1
2160  NEXT K
2180  GOTO 862
2300  REM  ROUNDS DOWN TO THE NEXT CYCLE
2310  VTAB (L): HTAB (MM)
2320  INPUT "";X1
2330 X1 = 10 © ( INT ( LOG (X1) /  LOG (10)))
2340  VTAB (L): HTAB (MM)
2350  PRINT X1;"  "
2360  GOTO 520
2400  REM  ROUNDS TO NEAREST CYCLE
2410  VTAB (L + 1): HTAB (MM)
2420  INPUT "";X2
2430 X2 = 10 © ( INT ( LOG (X2) /  LOG (10) + .5))
2440  VTAB (L + 1): HTAB (MM)
2450  PRINT X2;"  "
2460  GOTO 520
3000  REM  TITLE
3010  VTAB 3: HTAB 40
3020  INPUT "";TI$
3030  GOTO 520
3050  REM  FILENAME
3060  VTAB 4: HTAB 40
3070  INPUT "";F$(1)
3080  IF F$(1) <  > "" THEN 390
3090  POKE 34,9
3100  HOME
3110  PRINT D$"CATALOG /"DR$"/"FIL$
3120  TEXT
```

PLOTTER

```
3130  GOTO 3060
3150  REM  LABEL
3160  VTAB 5: HTAB 40
3170  INPUT "";L$(1)
3180  GOTO 520
3200  REM  LINETYPE
3210  VTAB 6: HTAB 40
3220  INPUT "";L(1)
3230  GOTO 520
3250  REM  FILENAME 2
3260  VTAB 7: HTAB 40
3270  INPUT "";F$(2)
3280  IF F$(2) <  > "" THEN 390
3290  POKE 34,9
3300  HOME
3310  PRINT D$"CATALOG /"DR$"/"FIL$
3320  TEXT
3330  GOTO 3260
3350  REM  LABEL
3360  VTAB 8: HTAB 40
3370  INPUT "";L$(2)
3380  GOTO 520
3400  REM  LINETYPE
3410  VTAB 9: HTAB 40
3420  INPUT "";L(2)
3430  GOTO 520
3450  REM  MIN X
3460  VTAB 10: HTAB 40
3470  INPUT "";X1
3475  IF X1 = 0 AND KB$ = "Y" THEN X1 = 1
3477  VTAB 10: HTAB 40: PRINT X1
3480  GOTO 520
3500  REM  MAX X
3510  VTAB 11: HTAB 40
3520  INPUT "";X2
3530  GOTO 520
3550  REM  X INT
3560  VTAB 12: HTAB 40
3570  INPUT "";XIN
3580  GOTO 520
3600  REM  MIN Y
3610  VTAB 13: HTAB 40
3620  INPUT "";Y1
3630  GOTO 520
3650  REM  MAX Y
3660  VTAB 14: HTAB 40
3670  INPUT "";Y2
3680  GOTO 520
```

PLOTTER

```
3700  REM  Y INT
3710  VTAB 15: HTAB 40
3720  INPUT "";YIN
3730  GOTO 520
3750  REM  PAPER LENGTH
3760  VTAB 16: HTAB 40
3770  INPUT "";PL
3780  GOTO 520
```

HP PLOTTER

```
100  REM   ******************************************
110  REM   *  HARD PLOTS TO THE HP FROM PLOT PROGRAM *
120  REM   ******************************************
130 D$ =  CHR$ (4):LT =  LOG (10):C$ =  CHR$ (3)
135 XNUM = .15:YNUM = .185
140 SP$ = "      .00000":SN$ = "     -.00000":BL$ = "          "
150  GOSUB 1000: REM  INITIALIZE HP
160  GOSUB 1200: REM  DEFINE FUNCTIONS
170  PRINT "PA"XA","YA";"
180  PRINT "PD;PA"XA","YA","XB","YA","XB","YB","XA","YB","XA","YA",
     "XB","YA","XB","YB","XA","YB","XA","YA";PU;"
190  GOSUB 2000: REM  PLOTS SCALES
200  GOSUB 4500: REM  PLOTS LABELS
210  GOSUB 4000: REM  PLOTS POINTS
220  GOTO 5000: REM  GRAPH TITLES
1000  REM   ***************************************
1010  REM   *  INIT FOR THE HP                     *
1020  REM   ***************************************
1030  PRINT D$"PR#2"
1040  PRINT  CHR$ (27)".("
1050  PRINT " IN;"
1060  PRINT  CHR$ (27)".I40;0;17:"
1070  PRINT "SP1;SI"XNUM","YNUM";"
1080  PRINT "DI1,0;VS20;"
1090  IF PL = 14 THEN XA = 900:XB = 9470:YA = 900:YB = 6400: GOTO 1110
1100 XA = 900:XB = 9470:YA = 900:YB = 6400
1110  RETURN
1200  REM   ***************************************
1210  REM   * DEFINE FUNCTIONS                     *
1220  REM   ***************************************
1230  IF A <  > 5 THEN 1290
1240  REM  LOG FUNCTION
1250 HARSCAL = ( LOG ( ABS (X2 / X1)) / LT) / (XB - XA)
1260 XT =  LOG ( ABS (X1)) / LT
1270  DEF  FN XL(R) = ( LOG ( ABS (R)) / LT - XT) / HARSCAL + XA
1280  GOTO 1380
1290  REM  LINEAR FUNCTION
1300 HARSCAL = (X2 - X1) / (XB - XA)
1310  DEF  FN XL(R) = (R - X1) / HARSCAL + XA
1380  REM  LINEAR FUNCTION
1390 VERSCAL = (Y2 - Y1) / (YB - YA)
1400  DEF  FN YL(T) = (T - Y1) / VERSCAL + YA
1410  RETURN
2000  REM   ******************************************
2010  REM   *  PLOTS SCALES                          *
2020  REM   ******************************************
2030  IF A <  > 5 THEN  GOSUB 2100: GOTO 2060
2040  GOSUB 2300: REM  LOG X
```

HP PLOTTER

```
2060  GOSUB 2500: REM   LINEAR Y
2070  RETURN
2100  REM   ****************************************
2110  REM   *   LINEAR X PLOT                       *
2120  REM   ****************************************
2130  FOR XS = X1 TO X2 STEP XIN
2140 XN =  FN XL(XS)
2150  GOSUB 3000: REM  X LABEL
2160  PRINT "PA"XN - 550","YA - 200";LB"XS$;C$
2170  PRINT "PA"XN","YA";PD; PA"XN","YA + 50";PU;"
2180  NEXT XS
2190  FOR XS = X1 TO X2 STEP XIN
2200 XN =  FN XL(XS)
2210  PRINT "PA"XN","YB";PD;PA"XN","YB - 25";PU;"
2220  NEXT XS
2230  RETURN
2300  REM   ****************************************
2310  REM   *  LOG X PLOT                           *
2320  REM   ****************************************
2330  FOR K =  LOG ( ABS (X1)) / LT TO  LOG ( ABS (X2)) / LT - 1
2340  FOR K1 = 1 TO 10
2345 XS = K1 * 10 © K
2350 XN = ( LOG (XS) / LT - XT) / HARSCAL + XA
2360  PRINT "PA"XN","YA";PD;PA"XN","YA + 50";PU;"
2370  IF (K1 <  > 1) AND (K1 <  > 5) AND ((K1 <  > 10) OR
     (K <  > ( LOG ( ABS (X2)) / LT - 1))) THEN 2400
2375 XIN = 10 © K
2380  GOSUB 3000: REM  X LABEL
2390  PRINT "PA"XN - 550","YA - 200";LB"XS$;C$
2400  NEXT K1
2410  NEXT K
2420  FOR K =  LOG ( ABS (X1)) / LT TO  LOG ( ABS (X2)) / LT - 1
2430  FOR K1 = 1 TO 10
2435 XS = K1 * 10 © K
2440 XN =  FN XL(XS)
2450  PRINT "PA"XN","YB";PD;PA"XN","YB - 25";PU;"
2460  NEXT K1
2470  NEXT K
2480  RETURN
2500  REM   ****************************************
2510  REM   *  LINEAR Y PLOT                        *
2520  REM   ****************************************
2530  FOR YS = Y1 TO Y2 STEP YIN
2540 YN =  FN YL(YS)
2550  GOSUB 3200: REM  Y LABEL
2560  PRINT "PA"XA - 640","YN";LB"YS$;C$
2570  PRINT "PA"XA","YN";PD;PA"XA + 50","YN";PU;"
2580  NEXT YS
```

HP PLOTTER

```
2590  FOR YS = Y1 TO Y2 STEP YIN
2600 YN =  FN YL(YS)
2610  PRINT "PA"XB","YN";PD;PA"XB - 25","YN";PU;"
2620  NEXT YS
2630  RETURN
3000  REM   ******************************************
3010  REM   *    X LABELS                             *
3020  REM   ******************************************
3030 RF = 0
3040  IF XIN <  > 0 THEN RF =  -  INT ( LOG ( ABS (XIN)) / LT)
3050 XS =  INT (XS * 10 © RF + .5) / 10 © RF
3060  IF XS = 0 OR  ABS (XS) >  = .01 THEN XS$ =  LEFT$
      (BL$,7 -  LEN ( STR$ (XS))) +  STR$ (XS): GOTO 3100
3065 XS$ =  STR$ ( INT ( ABS (XS) * 10 © RF + .5))
3070  IF XS < 0 THEN XS$ =  MID$ (SN$,1 + RF,7 -  LEN (XS$)) + XS$: GOTO
3100
3080 XS$ =  MID$ (SP$,1 + RF,7 -  LEN (XS$)) + XS$
3090 XS$ =  RIGHT$ (XS$, LEN (XS$) - 1)
3100  RETURN
3200  REM   ******************************************
3210  REM    *    Y LABELS                             *
3220  REM   ******************************************
3230 RF = 0
3240  IF YIN <  > 0 THEN RF =  -  INT ( LOG (YIN) / LT)
3250 YS =  INT (YS * 10 © RF + .5) / 10 © RF
3260  IF YS = 0 OR  ABS (YS) >  = .01 THEN YS$ =  LEFT$ (BL$,7 -  LEN
      ( STR$ (YS))) +  STR$ (YS): GOTO 3300
3265 YS$ =  STR$ ( INT ( ABS (YS) * 10 © RF + .5))
3270  IF YS < 0 THEN YS$ =  MID$ (SN$,1 + RF,7 -  LEN (YS$)) + YS$:
      GOTO 3300
3280 YS$ =  MID$ (SP$,1 + RF,7 -  LEN (YS$)) + YS$
3290 YS$ =  RIGHT$ (YS$, LEN (YS$) - 1)
3300  RETURN
4000  REM   ******************************************
4010  REM   *   PLOT FUNCTION                         *
4020  REM   ******************************************
4040  FOR K = 1 TO 2
4041  IF F$(K) = "" THEN 4225
4042  PRINT "SP1;LT"L(K)",2;"
4045  PRINT D$"OPEN /"DR$"/"FIL$"/"F$(K)
4047  PRINT D$"READ /"DR$"/"FIL$"/"F$(K)
4048  INPUT NMPTS
4050 I = 1
4055  INPUT X,Y
4060 XP =  FN XL(X)
4070 YP =  FN YL(Y)
4080  IF XP > XB THEN XP = XB
4090  IF (XP < XA) THEN XP = XA
```

HP PLOTTER

```
4095  IF YP > YB THEN YP = YB
4100  IF (YP < YA) THEN YP = YA
4120  PRINT "PA"XP","YP";PD;PA"
4130  FOR I = 2 TO NMPTS
4135  INPUT X,Y
4140 XP =  FN XL(X)
4150 YP =  FN YL(Y)
4160  IF XP > XB THEN XP = XB
4170  IF (XP < XA) THEN XP = XA
4180  IF YP > YB THEN 4210
4190  IF (YP < YA) THEN 4210
4200  PRINT XP","YP","
4210  NEXT I
4215  PRINT D$"CLOSE"
4220  PRINT XP","YP";PU;"
4225  NEXT K
4230  RETURN
4500  REM   ****************************************
4510  REM   *   PLOT AXIS LABELS                    *
4520  REM   ****************************************
4530  PRINT "SP1;SI.24,.38;"
4540 XP = (XB + XA) / 2 -  LEN (BT$) / 2 * 150
4560 YP = YA - 600
4570  PRINT "PA"XP","YP";LB"BT$;C$
4575  IF A > 4 THEN 4580
4577  PRINT "SI.1,.12;PA"(XB + XA) / 2 - 50 +  LEN (BT$) / 2 * 150",
      "YA - 500";LB - 1"C$
4578  PRINT "SI.24,.38;"
4580 YP = (YB + YA) / 2 -  LEN (EL$) / 2 * 150
4590  PRINT "DI0,1;PA"XA - 700","YP";LB"EL$;C$
4595  PRINT "DI1,0;"
4600  RETURN
5000  REM   ****************************************
5010  REM   *  TITLES                               *
5020  REM   ****************************************
5025  PRINT "SI.30,.50;"
5030 XP = (XB + XA) / 2 -  LEN (TI$) / 2 * 160
5040 YP = YB + 700
5050  PRINT "PA"XP","YP";LB"TI$;C$
5055  FOR K = 1 TO 2
5057  IF F$(K) = "" THEN 5120
5060 LIN = L(K)
5070  IF LIN = 0 THEN LIN = 2
5080  PRINT "SI.22,.30;LT"LIN",2;"
5085  IF LIN = 7 THEN  PRINT "LT;"
5090  PRINT "PA"XA + 600","YB + 170";PD;PA"XA + 1275","YB + 170";PU;"
5100  PRINT "PA"XA + 1475","YB + 170";LB"L$(K);C$
5110 XA = (XA + XB) / 2
```

HP PLOTTER

```
5120  NEXT K
5130  PRINT "SPO;"
5200  PRINT D$"PR#3": PRINT D$"CHAIN  /CONPROG1/PROGRAMS/P,@390,D1"
```

CONVERT XY

```
100  REM ************************************************
110  REM * THIS PROGRAM CONVERTS RAW DATA OF TEMP AND     *
120  REM * CONDUCTANCE INTO X,Y DATA PAIRS                *
130  REM ************************************************
140 SU = 1
142  IF SR$ = "Y" THEN SU = 10
145  DEF  FN CN(X) =  LOG (X / SU) /  LOG (10)
170  PRINT "Converting Raw Data to X.Y"
180  DEF  FN CN(X) =  LOG ((X * CR / SU) / (CR - X / SU)) /  LOG (10)
190  IF SR$ = "N" THEN 240
200  PRINT D$"OPEN  "FIL$;C$(0)",D2"
210  PRINT D$"OPEN  "FIL$;C$(1)
220  PRINT D$"READ "FIL$;C$(0)
230  INPUT NMPTS(0)
240  PRINT D$"READ "FIL$;C$(1)
250  INPUT NMPTS(1)
260 N = NMPTS(0)
270  IF NMPTS(1) > NMPTS(0) THEN N = NMPTS(1)
280  DIM A(1,N),B(1,N)
285  PRINT D$"READ "FIL$;C$(0)
287  FOR K = NMPTS(0) TO 1 STEP  - 1
290  INPUT A(0,K),B(0,K)
295  NEXT K
300  PRINT D$"READ "FIL$;C$(1)
305  FOR K = 1 TO NMPTS(1)
307  INPUT A(1,K),B(1,K)
310  NEXT K
320  PRINT D$"CLOSE"
325  INPUT "Please insert the CALDAT disk in drive 2 and press
     RETURN...";KB$
327  IF KB$ <  > "" THEN 325
328  ONERR  GOTO 1000
329  FOR L = 0 TO 1
330  PRINT D$"OPEN/CALDAT/X.Y/"FIL$;C$(L)
340  PRINT D$"WRITE/CALDAT/X.Y/"FIL$;C$(L)
344  PRINT NMPTS(L)
350  FOR K = 1 TO NMPTS(L)
360 A(L,K) =  - 1 / (A(L,K) + 273.6) * 1E4
370 B(L,K) =  FN CN(B(L,K))
380  PRINT A(L,K): PRINT B(L,K)
390  NEXT K
400  PRINT D$"CLOSE /CALDAT/X.Y/"FIL$;C$(L)
410  NEXT L
495  POKE 216,0
500  PRINT D$"CHAIN STARTUP,@1460,D1"
1000  PRINT "Check disk in drive 2"
1010  GOTO 325
```

DERIVATIVE XY

```
100  REM  ***********************************************
110  REM  * THIS PROGRAM FINDS THE DERIVATIVE           *
120  REM  * OF X W/RESPECT TO Y, DY/DX                  *
140  REM  ***********************************************
160  PRINT "Converting X.Y to X.DYDX"
360  DIM TE(MA),VO(MA),TZ(MA),VZ(MA)
440  FOR K = 0 TO 1
445 FL = 0
446  FOR S = 1 TO MA:TE(S) = 0:VO(S) = 0: NEXT S
450  FOR S = 1 TO MA - 1:TE(S) = A(K,S):VO(S) = B(K,S)
460  NEXT S
465 PO = 0:PI = MA - 1
470  FOR I =  INT (MA / 2 + 1) TO MA - 1:T = 0:V = 0
480  FOR J = 1 TO I:T = T + TE(J):V = V + VO(J): NEXT J
490 TS = T / I
500 VS = V / I
510  IF  NOT FL THEN FL = 1: GOTO 570
520 DVDT =  INT ((VS - OV) / (TS - OT) * 1E5 + .5) / 1E5
530 WT =  INT ((TS + OT) / 2 * 1E3 + .5) / 1E3
540 FL = FL + 1
550 PO = PO + 1
560 A(K,PO) = WT:B(K,PO) = DVDT: IF FL = 2 THEN PO = PO + 1:
    A(K,PO) = WT:B(K,PO) = DVDT
570 OT = TS:OV = VS
580  NEXT I
590  FOR I = 1 TO NMPTS(K) - MA + 1
600 PI = PI + 1:TE = A(K,PI):VO = B(K,PI)
610  IF I > NMPTS(K) - 2 * MA + 2 THEN Z = I - NMPTS(K) + 2 * MA - 1:
     TZ(Z) = TE:VZ(Z) = VO
620 T = T + TE - TE(S):TE(S) = TE
630 V = V + VO - VO(S):VO(S) = VO
640 S = S + 1: IF MA < S THEN S = 1
650 TS = T / MA
660 VS = V / MA
680  IF TS = OT THEN DVDT = 00: GOTO 700
690 DVDT =  INT ((VS - OV) / (TS - OT) * 1E5 + .5) / 1E5:00 = DVDT
700 WT =  INT ((TS + OT) / 2 * 1E3 + .5) / 1E3
710 PO = PO + 1:A(K,PO) = WT:B(K,PO) = DVDT
720 OT = TS:OV = VS
730  NEXT I
740  FOR I = 2 TO  INT (MA / 2 + 1):T = 0:V = 0
750  FOR J = I TO MA:T = T + TZ(J):V = V + VZ(J): NEXT J
760 TS = T / (J - I)
770 VS = V / (J - I)
790 DVDT =  INT ((VS - OV) / (TS - OT) * 1E5 + .5) / 1E5
800 WT =  INT ((TS + OT) / 2 * 1E3 + .5) / 1E3
810 PO = PO + 1:A(K,PO) = WT:B(K,PO) = DVDT
820 OT = TS:OV = VS
```

DERIVATIVE XY

```
830  NEXT I
835 NMPTS(K) = NMPTS(K) - 1
840  IF (SA) THEN 920
850  PRINT D$"OPEN /CALDAT/X.DYDX/"FIL$;C$(K)
860  PRINT D$"WRITE /CALDAT/X.DYDX/"FIL$;C$(K)
870  PRINT NMPTS(K)
880  FOR L = 1 TO NMPTS(K)
890  PRINT A(K,L): PRINT B(K,L)
900  NEXT L
910  PRINT D$"CLOSE"
920  NEXT K
930  PRINT D$"CHAIN STARTUP,@1500,D1"
```

INTEGRATE XDYDX

```
100  REM ******************************************************
110  REM * THIS PROGRAM INTEGRATES X, DY/DX DATA              *
120  REM * TO CALCULATE THE PARAMETER Z                       *
130  REM ******************************************************
150 D$ =  CHR$ (4): SPEED= 255: PRINT D$"PR#3"
160  PRINT "Converting X.DYDX to X.Z"
260  REM  PROCESS DATA
305 I = 1:Z = 0:TS = 0:TN = 0
330  IF A(1,I) <  =  - 36 THEN 370
340 B(1,I) = 0
350 I = I + 1
360  GOTO 330
370  IF A(1,I) <  =  - 36.5 THEN 420
380 TS = TS + B(1,I)
390 TN = TN + 1
400 I = I + 1
405 B(1,I) = 0
410  GOTO 370
420 Y1 = TS / TN:X1 = A(1,I - 1)
440  FOR K = I TO NMPTS(1)
450 Z = Z + (X1 - A(1,K)) * (B(1,K) - Y1)
460 B(1,K) = Z
475 X1 = A(1,K)
490  NEXT K
520 Z = 0:X1 = A(0,1)
540  FOR K = 1 TO NMPTS(0)
550  IF A(0,K) >  - 36.5 THEN 570
560 Z = Z + (X1 - A(0,K)) * (B(0,K) - Y1)
570 B(0,K) = Z
580 X1 = A(0,K)
590  NEXT K
600  IF (SA) THEN 700
610  FOR K = 0 TO 1
620  PRINT D$"OPEN /CALDAT/X.Z/"FIL$;C$(K)
630  PRINT D$"WRITE /CALDAT/X.Z/"FIL$;C$(K)
640  PRINT NMPTS(K)
650  FOR L = 1 TO NMPTS(K)
660  PRINT A(K,L): PRINT B(K,L)
670  NEXT L
680  PRINT D$"CLOSE"
690  NEXT K
700  PRINT D$"CHAIN STARTUP, @1540,D1"
```

CONVERT VP

```
100  REM   ****************************************
110  REM   *  CONVERTS THE.X.Z FILE TO X.VP        *
120  REM   *  BASES THE LOW POINT ON THE AVERAGE OF *
130  REM   *  COOLING DATA FROM -36 TO -36.5       *
140  REM   ****************************************
150  PRINT "Converting X.Z to X.VP"
330  FOR K = 0 TO 1
340  FOR L = 1 TO NMPTS(K)
360 VP = 1 / 10 © B(K,L)
370 B(K,L) = VP
380  NEXT L
390  NEXT K
400  IF (SA) THEN 500
410  FOR K = 0 TO 1
420  PRINT D$"OPEN /CALDAT/X.VP/"FIL$;C$(K)
430  PRINT D$"WRITE /CALDAT/X.VP/"FIL$;C$(K)
440  PRINT NMPTS(K)
450  FOR L = 1 TO NMPTS(K)
460  PRINT A(K,L): PRINT B(K,L)
470  NEXT L
490  NEXT K
500  PRINT D$"CHAIN STARTUP,@1580,D1"
```

CONVERT R

```
100  REM ************************************************
110  REM *THIS PROGRAM CONVERTS THE X VS PORE VOLUME FILE *
120  REM * TO RADIUS VS PORE VOLUME.                     *
130  REM ************************************************
135 TO =  VAL (TO$)
140  PRINT "Converting X.VP to R.VP"
320  FOR K = 0 TO 1
325 PO = 0:R1 = 0
330  FOR L = 1 TO NMPTS(K)
422 XO = A(K,L) * 1E - 4
425 R = (( - 2 * TO * (.25 - (29 * XO) + (.25 * TO * XO))) /
    ((.9998 * 3.335E9) * (1 + TO * XO))) * 1E8
427  IF R < 0 THEN 490
428  IF ( ABS (R - R1) < 1) AND (K$ = "Y") THEN 490
450 PO = PO + 1:R1 = R
460 A(K,PO) = R:B(K,PO) = B(K,L)
490  NEXT L
500 NMPTS(K) = PO
510  NEXT K
520  FOR K = 0 TO 1
530  PRINT D$"OPEN /CALDAT/R.VP/"FIL$;C$(K)
540  PRINT D$"WRITE /CALDAT/R.VP/"FIL$;C$(K)
550  PRINT NMPTS(K)
560  FOR L = 1 TO NMPTS(K)
570  PRINT A(K,L): PRINT B(K,L)
580  NEXT L
590  PRINT D$"CLOSE"
600  NEXT K
610  PRINT D$"CHAIN STARTUP,@1600,D1"
```

DERIVATIVE VP

```
100  REM  ***********************************************
110  REM  * THIS PROGRAM CALCULATES THE DERIVATIVE OF   *
120  REM  * OF THE PORE VOLUME WITH RESPECT TO          *
130  REM  * PORE RADIUS                                *
140  REM  ***********************************************
160  PRINT "Converting R.VP to R.DVPDR"
360  DIM T1(MA),V1(MA),T2(MA),V2(MA)
440  FOR K = 0 TO 1
442  PRINT D$"OPEN /CALDAT/R.DVPDR/"FIL$;C$(K)
443  PRINT D$"WRITE /CALDAT/R.DVPDR/"FIL$;C$(K)
444  PRINT NMPTS(K) - 1
445 FL = 0
446  FOR S = 1 TO MA:T1(S) = 0:V1(S) = 0: NEXT S
450  FOR S = 1 TO MA - 1:T1(S) = A(K,S):V1(S) = B(K,S)
460  NEXT S
465 PI = MA - 1
470  FOR I =  INT (MA / 2 + 1) TO MA - 1:T = 0:V = 0
480  FOR J = 1 TO I:T = T + T1(J):V = V + V1(J): NEXT J
490 TS = T / I
500 VS = V / I
510  IF  NOT FL THEN FL = 1: GOTO 570
520 DVDT =  INT ((VS - OV) / (TS - OT) * 1E5 + .5) / 1E5
530 WT =  INT ((TS + OT) / 2 * 1E3 + .5) / 1E3
540 FL = FL + 1
560  PRINT WT: PRINT DVDT: IF FL = 2 THEN  PRINT WT: PRINT DVDT
570 OT = TS:OV = VS
580  NEXT I
590  FOR I = 1 TO NMPTS(K) - MA + 1
600 PI = PI + 1:TE = A(K,PI):VO = B(K,PI)
610  IF I > NMPTS(K) - 2 * MA + 2 THEN Z = I - NMPTS(K) + 2 * MA - 1:
     T2(Z) = TE:V2(Z) = VO
620 T = T + TE - T1(S):T1(S) = TE
630 V = V + VO - V1(S):V1(S) = VO
640 S = S + 1: IF MA < S THEN S = 1
650 TS = T / MA
660 VS = V / MA
680  IF TS = OT THEN DVDT = 00: GOTO 700
690 DVDT =  INT ((VS - OV) / (TS - OT) * 1E5 + .5) / 1E5:00 = DVDT
700 WT =  INT ((TS + OT) / 2 * 1E3 + .5) / 1E3
710  PRINT WT: PRINT DVDT
720 OT = TS:OV = VS
730  NEXT I
740  FOR I = 2 TO  INT (MA / 2 + 1):T = 0:V = 0
750  FOR J = I TO MA:T = T + T2(J):V = V + V2(J): NEXT J
760 TS = T / (J - I)
770 VS = V / (J - I)
790 DVDT =  INT ((VS - OV) / (TS - OT) * 1E5 + .5) / 1E5
800 WT =  INT ((TS + OT) / 2 * 1E3 + .5) / 1E3
```

DERIVATIVE VP

```
810  PRINT WT: PRINT DVDT
820 OT = TS:OV = VS
830  NEXT I
910  PRINT D$"CLOSE"
920  NEXT K
930  PRINT D$"CHAIN STARTUP,@1630,D1"
```

DERIVATIVE LVP

```
100  REM  ************************************************
110  REM  * THIS PROGRAM CALCULATES THE DERIVATIVE OF   *
120  REM  * THE PORE VOLUME W/RESPECT THE LOG OF THE    *
130  REM  * PORE RADIUS                                 *
140  REM  ************************************************
150  GOSUB 1000
160  PRINT "Converting R.VP to R.DVPDLR"
440  FOR K = 0 TO 1
445 FL = 0
446  FOR S = 1 TO MA:T1(S) = 0:V1(S) = 0: NEXT S
450  FOR S = 1 TO MA - 1:T1(S) = A(K,S):V1(S) = B(K,S)
460  NEXT S
465 PO = 0:PI = MA - 1
470  FOR I =  INT (MA / 2 + 1) TO MA - 1:T = 0:V = 0
480  FOR J = 1 TO I:T = T + T1(J):V = V + V1(J): NEXT J
490 TS = T / I
500 VS = V / I
510  IF  NOT FL THEN FL = 1: GOTO 570
520 DVDT =  INT ((VS - OV) / (TS - OT) * 1E5 + .5) / 1E5
530 WT =  INT ((TS + OT) / 2 * 1E3 + .5) / 1E3
540 FL = FL + 1
550 PO = PO + 1
560 A(K,PO) = WT:B(K,PO) = DVDT: IF FL = 2 THEN PO = PO + 1:A(K,PO) =
    WT:B(K,PO) = DVDT
570 OT = TS:OV = VS
580  NEXT I
590  FOR I = 1 TO NMPTS(K) - MA + 1
600 PI = PI + 1:TE = A(K,PI):VO = B(K,PI)
610  IF I > NMPTS(K) - 2 * MA + 2 THEN Z = I - NMPTS(K) + 2 * MA - 1:T2(Z)
     = TE:V2(Z) = VO
620 T = T + TE - T1(S):T1(S) = TE
630 V = V + VO - V1(S):V1(S) = VO
640 S = S + 1: IF MA < S THEN S = 1
650 TS = T / MA
660 VS = V / MA
680  IF TS = OT THEN DVDT = 00: GOTO 700
690 DVDT =  INT ((VS - OV) / (TS - OT) * 1E5 + .5) / 1E5:00 = DVDT
700 WT =  INT ((TS + OT) / 2 * 1E3 + .5) / 1E3
710 PO = PO + 1:A(K,PO) = WT:B(K,PO) = DVDT
720 OT = TS:OV = VS
730  NEXT I
740  FOR I = 2 TO  INT (MA / 2 + 1):T = 0:V = 0
750  FOR J = I TO MA:T = T + T2(J):V = V + V2(J): NEXT J
760 TS = T / (J - I)
770 VS = V / (J - I)
790 DVDT =  INT ((VS - OV) / (TS - OT) * 1E5 + .5) / 1E5
800 WT =  INT ((TS + OT) / 2 * 1E3 + .5) / 1E3
810 PO = PO + 1:A(K,PO) = WT:B(K,PO) = DVDT
```

DERIVATIVE LVP

```
820 OT = TS:OV = VS
830  NEXT I
835 NMPTS(K) = NMPTS(K) - 1
850  PRINT D$"OPEN /CALDAT/R.DVPDLR/"FIL$;C$(K)
860  PRINT D$"WRITE /CALDAT/R.DVPDLR/"FIL$;C$(K)
870  PRINT NMPTS(K)
880  FOR L = 1 TO NMPTS(K)
885 A(K,L) = 10 © A(K,L)
890  PRINT A(K,L): PRINT B(K,L)
900  NEXT L
910  PRINT D$"CLOSE"
920  NEXT K
925  FOR T = 1 TO 5: PRINT  CHR$ (7): NEXT T
930  PRINT D$"CHAIN STARTUP,@180 ,D1"
1000  REM   *************************
1010  REM   * TO LOG R              *
1020  REM   *************************
1025 LT =  LOG (10)
1030  FOR K = 0 TO 1
1040  FOR L = 1 TO NMPTS(K)
1050 A(K,L) =  LOG (A(K,L)) / LT
1060  NEXT L
1070  NEXT K
1080  RETURN
```

SURFACE AREA

```
100  REM   ****************************************
110  REM   * PROGRAM TO CALCULATE SURFACE AREA      *
120  REM   ****************************************
125 D$ =  CHR$ (4)
130  PRINT "Calculating the surface area..."
135  IF DT = 0 THEN  GOSUB 2000
140 A = 0
150  FOR L = 2 TO NMPTS(0)
155  IF A(0,L) <  = 12 THEN 170
160 A = A + (1 / A(0,L - 1) - 1 / A(0,L)) * (PV * B(0,L - 1)) *  - 1E4
170  NEXT L
210 A =  INT (A * 2.5 * 1E4) / 1E4
220  PRINT "Surface Area = ";A
230  PRINT : PRINT
260  END
2000  REM   ****************************************
2010  REM   *   FILE LOADER                          *
2020  REM   ****************************************
2030  INPUT "Base Filename : ";FIL$
2040  IF FIL$ = "" THEN  PRINT D$"CATALOG /CALDAT/R.VP/": GOTO 2000
2050  PRINT D$"OPEN /CALDAT/R.VP/";FIL$;",D2"
2060  PRINT D$"READ /CALDAT/R.VP/";FIL$
2070  INPUT NMPTS(0)
2080  DIM A(1,NMPTS(0)),B(1,NMPTS(0))
2090  FOR I = 1 TO NMPTS(0)
2100  INPUT A(0,I),B(0,I)
2110  NEXT I
2120  PRINT D$"CLOSE"
2130  INPUT "Pore volume of Sample : ";PV$
2140 PV =  VAL (PV$)
2150  RETURN
2160  INPUT DIL$,CO$,DT$
2165  INPUT MA$,N1$,N2$
2170  PRINT D$"CLOSE"
2180  RETURN
```

TEST FORMAT

```
10  REM   READ DATA ON SAMPLE AND PLOT OUT
15 D$ =  CHR$ (4)
20  HOME : VTAB 5
30  PRINT "Insert a /RAWDAT disk in drive 2 and hit a key...";
40  GET TMP$
50  PRINT D$"CATALOG,D2"
60  PRINT : INPUT "Enter new file name : ";F$
70  IF F$ = "" THEN 60
80  GOSUB 200: REM  READ IN DATA
90  GOSUB 500: REM  PRINT TO SCREEN
100  GOSUB 1000: REM  PLOT OUT
110  GOTO 90
200  PRINT D$"OPEN ";F$;",D2"
210  PRINT D$"READ ";F$
215  INPUT SCYCLE
220  INPUT CT
230  FOR X = 1 TO CT
240  INPUT TP(X),BTTM(X),RTE(X),IT(X),TD$(X)
245  IF TD$(X) = "N" THEN IT(X) = 0
250  NEXT X
251  INPUT MCYCLE
253  DIM TC(MCYCLE)
254  FOR X = 1 TO MCYCLE
256  INPUT TC(X)
258  NEXT X
260  INPUT N1$,N2$,N3$,N4$
270  PRINT D$"CLOSE ";F$
280  RETURN
500  REM  PRINT TO SCREEN
510  HOME : VTAB 2
520  HTAB  INT ( LEN (F$) / 2)
530  PRINT F$
540  VTAB 4
550  PRINT "Cycle Type";: POKE 36,15: PRINT "Top Temp";: POKE 36,30:
     PRINT "Bottom Temp";: POKE 36,45: PRINT "Rate";: POKE 36,55:
     PRINT "Sample Interval"
560  FOR X = 1 TO CT
570  PRINT  TAB( 5);X;: POKE 36,20: PRINT TP(X);: POKE 36,34:
     PRINT BTTM(X);: POKE 36,46: PRINT RTE(X);: POKE 36,62: PRINT IT(X)
572  NEXT X
574  VTAB 9: PRINT "Cycle Type  Cycle Type  Cycle Type  Cycle Type  Cycle
     Type  Cycle Type"
576  FOR Y = 0 TO MCYCLE - 1
578 X = 2 +  INT (Y / 8) * 11
580  VTAB 10 + (Y -  INT (Y / 8) * 8): POKE 36,X
582  PRINT Y + SCYCLE;: POKE 36,X + 6: PRINT TC(Y + 1)
584  NEXT Y
590  VTAB 18: PRINT "NOTES : "
```

TEST FORMAT

```
600  PRINT N1$
610  PRINT N2$
620  PRINT N3$
630  PRINT N4$
640  VTAB 23: HTAB 10
650  PRINT "  1.  Plot Out to HP"
655  VTAB 23: POKE 36,40
660  PRINT "  2.  Quit"
670  INPUT "Enter menu choice (1-2) : ";TMP$
680  IF TMP$ > "2" OR TMP$ < "1" THEN 510
700  IF TMP$ = "1" THEN  RETURN
710  PRINT "DONE"
720  END
1000  REM ****************************************************
1010  REM   *  PLOT OUT TO PLOTTER                            *
1020  REM   ****************************************************
1030  REM  INIT HP
1035 C$ =  CHR$ (3)
1040  PRINT D$"PR#2"
1050  PRINT  CHR$ (27)".("
1060  PRINT "IN;"
1070  PRINT  CHR$ (27)".I40;0;17:"
1075  PRINT  CHR$ (27)".N;19:"
1080  PRINT "SP1;SI.4,.6;"
1090  PRINT "DI1,0;VS20;"
1095  PRINT "PA"5150 -  LEN (F$) / 2 * 240;",6500;LB";F$;C$
1096  PRINT "SI.2,.3;"
1100  PRINT "PA1000,5650;"
1110  PRINT "LBCycle Type    Top Temp       Bottom Temp    Rate       Sample
      Interval";C$
1120  PRINT "PA1000,5450;PD;PA9280,5450;PU;"
1130  FOR X = 1 TO CT
1140  PRINT "PA1600,";5450 - 200 * X;";LB";X;C$
1150  PRINT "PA3400,";5450 - 200 * X;";LB";TP(X);C$
1160  PRINT "PA5080,";5450 - 200 * X;";LB";BTTM(X);C$
1170  PRINT "PA6520,";5450 - 200 * X;";LB";RTE(X);C$
1180  PRINT "PA8440,";5450 - 200 * X;";LB";IT(X);C$
1182  NEXT X
1183  PRINT "PA1000,4250;PD;PA9280,4250;PU;"
1184  PRINT "PA1000,4050;"
1185  PRINT "LBCycle Type  Cycle Type  Cycle Type  Cycle Type  Cycle Type
      Cycle Type";C$
1186  PRINT "PA1000,3850;PD;PA9280,3850;PU;"
1187  FOR Y = 0 TO MCYCLE - 1
1188 X = 2 +  INT (Y / 8) * 12
1190  PRINT "PA"1000 + X * 120","3650 - 200 * (Y -  INT (Y / 8) * 8)";"
1192  PRINT "LB"Y + SCYCLE;C$;"PA"1720 + X * 120","3650 - 200 *
      (Y -  INT (Y / 8) * 8)";"
```

TEST FORMAT

```
1194  PRINT "LB"TC(Y + 1);C$
1198  NEXT Y
1200  PRINT "PA1000,1750;LBNotes :";C$
1210  PRINT "PA1250,1550;LB";N1$;C$
1220  PRINT "PA1250,1350;LB";N2$;C$
1230  PRINT "PA1250,1150;LB";N3$;C$
1240  PRINT "PA1250,950 ;LB";N4$;C$
1250  PRINT D$"PR#3"
1260  RETURN
```

TEMP MEASUREMENT

VARIABLES

```
C100      BASE ADDRESS FOR I/O CARD
C100      OUTPUT REGISTER B
C101      OUTPUT REGISTER A
C104      TIMER 1, LATCH LOW
C105      TIMER 1, COUNTER HIGH
C108      TIMER 2, LATCH LOW
C109      TIMER 2, COUNTER HIGH
C10B      AUXILLIARY CONTROL REGISTER
C10C      PERIPHERAL CONTROL REGISTER
C10D      INTERRUPT FLAG REGISTER
```

PROGRAM

```
0340   A2 70       LDX #$70
0342   8E A2 70    STX $70A2      CA1 POSITIVE ACTIVE EDGE
0345   8E 0C C1    STX $C10C      CB1 NEGATIVE ACTIVE EDGE
0348   A0 00       LDY #$00
034A   8C 0B C1    STY #C10B      T2 TIMED INTERRUPTS
034D   A9 02       LDA #$02       SWITCHING MASK
034F   AC 38 03    LDY $0338
0352   F0 02       BEQ $0356      IF EQUAL THEN DON'T SWITCH
0354   A9 10       LDA #$10       MASK
0356   A0 FF       LDY #$FF
0358   8C 0D C1    STY $C10D      CLEAR INTERRUPT FLAGS
035B   2C 0D C1    BIT $C10D      FIRST ACTIVE EDGE?
035E   F0 FB       BEQ $0358      NO, THEN CONTINUE POLLING
0360   8C 08 C1    STY $C108
0363   8C 09 C1    STY $C109      START COUNTING PERIOD
0366   8C 0D C1    STY $C10D      CLEAR INTERRUPT FLAGS
0369   2C 0D C1    BIT $C10D      SECOND ACTIVE EDGE?
036C   F0 FB       BEQ $0369      NO, THEN CONTINUE POLLING
036E   AC 08 C1    LDY $C108      GET LOW BYTE OF PERIOD
0371   AE 09 C1    LDX $C109      GET MID BYTE OF PERIOD
0374   8C 36 03    STY $0336      STORE PERIOD
0377   8E 37 03    STX $0337      STORE PERIOD
037A   60          RTS            RETURN TO PROGRAM
```

CALIBRATE

```
100  REM   ************************************************
110  REM   *  DATA ENTRY PROGRAM                          *
120  REM   ************************************************
125 D$ =  CHR$ (4)
235 CO = 1
240  REM  RETRIEVE AND DISPLAY FILE
250  HOME : GOSUB 1000
260  POKE 34,0
270  VTAB 1: HTAB 12
280 FIL$ = "CAL": PRINT "CAL"
285  VTAB 1: HTAB 40: PRINT "# of points : ";
290  GOSUB 2000
295 N = 1
300  VTAB 1: POKE 36,55: PRINT NMPT
310  VTAB 2: HTAB 16: PRINT XA$
320  VTAB 3: HTAB 16: PRINT YA$
330  GOSUB 1300
340 N = 1
350  GOSUB 1500
360 X = 1:Y = 5
370  GOSUB 1900
380  GOTO 500
400  REM  INPUT NEW FILE
410  HOME : GOSUB 1000
415  POKE 34,0
420  VTAB 1: POKE 36,55
430  INPUT "";NMPT
440  DIM X(NMPT),Y(NMPT)
445  POKE 34,4
450 N = 1
460  GOSUB 1500
480  GOSUB 1300
485 X = 1:Y = 5
490  GOSUB 1900
500  REM   ****************************************************
510  REM   *  MAIN CONTROLLER FOR EDITING AND ENTRY           *
520  REM   ****************************************************
530  GET KB$
540  IF (KB$ >  = "0" AND KB$ <  = "9") OR KB$ = "." OR KB$ = "-" THEN 3000
550  IF  ASC (KB$) = 8 THEN 3200: REM  LEFT ARROW
560  IF  ASC (KB$) = 21 OR  ASC (KB$) = 32 THEN 3300: REM   RIGHT ARROW
570  IF  ASC (KB$) = 10 THEN 3400: REM  DOWN ARROW
580  IF  ASC (KB$) = 11 THEN 3500: REM  UP ARROW
590  IF  ASC (KB$) = 19 THEN 3600: REM  CONTROL S
610  IF  ASC (KB$) = 17 THEN 4200: REM   CONTROL Q
620  GOTO 530
1000  REM   ************************************************
1010  REM   *   DISPLAY HEADINGS                            *
```

CALIBRATE

```
1020  REM   ************************************************
1030  POKE 34,0: REM  SET TOP TO LINE 0
1040  POKE 35,4: REM  SET BOTTO TO LINE 3
1050  HOME
1060  PRINT "Filename : ";: HTAB 40: PRINT "# of points : "
1070  PRINT "X-Axis Label : "
1080  PRINT "Y-Axis Label : "
1090  PRINT "Point #"; TAB( 30);"X";: POKE 36,50: PRINT "Y";
1100  POKE 34,4: POKE 35,23
1110  RETURN
1300  REM   ************************************************
1310  REM   *  PRINTS BOTTOM LINE                          *
1320  REM   ************************************************
1330  POKE 34,23: POKE 35,24
1340  HOME
1350  PRINT "Control-S to Save     Control-Q to Exit";
1360  POKE 34,4: POKE 35,23
1370  RETURN
1500  REM   ************************************************
1510  REM   *  DISPLAY A PAGE OF DATA (19 LINES)           *
1520  REM   *  N = THE DATA NUMBER TO START FROM           *
1530  REM   ************************************************
1540  HOME
1550  FOR I = N TO N + 18
1560  IF I > NMPT THEN 1590
1570  PRINT  TAB( 3);I; TAB( 25);X(I);: POKE 36,45: PRINT Y(I);
1580  IF I <  > N + 18 THEN  PRINT
1590  NEXT I
1600 X = 1:Y = 5
1610  GOSUB 1900
1620  RETURN
1700  REM   ************************************************
1710  REM   *  SCROLL UP ONE LINE                          *
1720  REM   ************************************************
1725  IF N + 18 > NMPT THEN 1800
1730  VTAB 23: POKE 36,78
1735  PRINT
1740 I = N + 18
1750  IF I > NMPT THEN 1780
1760  PRINT  TAB( 3);I; TAB( 25);X(I);: POKE 36,45: PRINT Y(I);
1780 X = 1:Y = 23
1790  GOSUB 1900
1800  RETURN
1900  REM   ************************************************
1910  REM   *  MOVE CURSOR TO APPROPRIATE X,Y POSITION     *
1920  REM   ************************************************
1930  VTAB Y
1940  IF X = 1 THEN  HTAB 25
```

CALIBRATE

```
1950  IF X = 2 THEN  POKE 36,45
1960  RETURN
2000  REM   ****************************************************
2010  REM   *  RETRIEVE FILE                                    *
2020  REM   ****************************************************
2030  PRINT D$"OPEN "FIL$",D1"
2040  PRINT D$"READ "FILE$
2050  INPUT NMPT
2060  DIM X(NMPT),Y(NMPT)
2065  IF CO = 1 THEN 2080
2070  INPUT XA$
2072  IF XA$ = "" THEN  INPUT XA$
2075  INPUT YA$
2077  IF YA$ = "" THEN  INPUT YA$
2080  FOR I = 1 TO NMPT
2090  INPUT X(I),Y(I)
2100  NEXT I
2110  PRINT D$"CLOSE"
2120  RETURN
2300  REM   ****************************************************
2310  REM   *  SAVE FILE                                        *
2320  REM   ****************************************************
2330  PRINT D$"OPEN "FIL$",D1"
2340  PRINT D$"WRITE"FIL$
2350  PRINT NMPT
2352  IF CO = 1 THEN 2370
2355  IF XA$ = "" THEN XA$ = "none"
2357  IF YA$ = "" THEN YA$ = "none"
2360  PRINT XA$: PRINT YA$
2370  FOR I = 1 TO NMPT
2380  PRINT X(I): PRINT Y(I)
2390  NEXT I
2400  PRINT D$"CLOSE"
2410  RETURN
3000  REM   ****************************************************
3010  REM   *   ENTER THE DATA INTO ARRAY                       *
3020  REM   ****************************************************
3025  PRINT KB$;
3030  GET IN$
3040  IF (IN$ >  = "0" AND IN$ <  = "9") OR IN$ = "." OR IN$ = "-" OR IN$ =
      "E" THEN KB$ = KB$ + IN$: PRINT IN$;: GOTO 3030
3042  IF  ASC (IN$) = 8 AND  LEN (KB$) = 1 THEN KB$ = "": PRINT  CHR$ (8);"
       "; CHR$ (8);
3044  IF  ASC (IN$) = 8 AND  LEN (KB$) > 1 THEN KB$ =  LEFT$ (KB$, LEN
      (KB$) -1): PRINT  CHR$ (8);" "; CHR$ (8);
3050  IF  ASC (IN$) = 13 THEN 3070
3060  GOTO 3030
3070  IF X = 1 THEN X(N + Y - 5) =  VAL (KB$)
```

CALIBRATE

```
3080  IF X = 2 THEN Y(N + Y - 5) =  VAL (KB$)
3090  GOSUB 1900: REM  RESET CURSOR
3100  PRINT  VAL (KB$);"     ";
3110  IF X = 1 THEN X = 2: GOTO 3140
3120  IF (Y - 5) + N <  > NMPT THEN Y = Y + 1:X = 1
3130  IF Y > 23 THEN N = N + 1: GOSUB 1700
3140  GOSUB 1900
3150  GOTO 530
3200  REM   ************************************************
3210  REM   *  LEFT ARROW                                   *
3220  REM   ************************************************
3230  IF X = 2 THEN X = 1: GOSUB 1900
3240  GOTO 530
3300  REM   ************************************************
3310  REM   *  RIGHT ARROW                                  *
3320  REM   ************************************************
3330  IF X = 1 THEN X = 2: GOSUB 1900
3340  GOTO 530
3400  REM   ************************************************
3410  REM   *  DOWN ARROW                                   *
3420  REM   ************************************************
3430  IF (Y - 5) + N <  > NMPT THEN Y = Y + 1
3440  IF Y > 23 THEN N = N + 1:Y = 23: GOSUB 1700
3450  GOSUB 1900
3460  GOTO 530
3500  REM   ************************************************
3510  REM   *  UP ARROW                                     *
3520  REM   ************************************************
3530  IF Y = 5 AND N <  > 1 THEN N = N - 1: GOSUB 1500: GOTO 3560
3540  IF Y <  > 5 THEN Y = Y - 1
3550  GOSUB 1900
3560  GOTO 530
3600  REM   ************************************************
3610  REM   * CONTROL-S  SAVE DATA                         *
3620  REM   ************************************************
3625  IF FIL$ = "" THEN 4000
3630  POKE 34,23: POKE 35,24
3640  HOME
3650  PRINT "Saving ";FIL$;" ...";
3660  GOSUB 2300
3670  POKE 34,0
3680  CLEAR
3690  GOTO 9000
4000  REM   ********************************************
4010  REM   *  TRIED TO SAVE WITHOUT A FILE NAME        *
4020  REM   ********************************************
4030  POKE 34,23: POKE 35,24
4040  HOME
```

CALIBRATE

```
4050  PRINT "You must have a filename to save data.";
4060  GET KB$
4070  GOSUB 1300
4080  GOSUB 1900
4090  GOTO 530
4200  REM   ******************************************
4210  REM   *  ESCAPE SO EXIT OR NOT                 *
4220  REM   ******************************************
4230  POKE 34,23: POKE 35,24
4240  HOME
4250  PRINT "This will leave the data unchanged.  Continue (Y/N  Default =
      N).";
4260  GET KB$
4270  IF KB$ = "Y" THEN 9000
4280  GOSUB 1300
4290  GOSUB 1900
4300  GOTO 530
9000  REM  WE GONE BYE BYE
9010  PRINT D$"RUN STARTUP,D1"
```