Mines Branch Technical Bulletin TB45

POROSIMETRY BY MERCURY INJECTION

by

G.T. Shaw*, B.I. Parsons* and D.S. Montgomery**

SYNOPSIS

Apparatus and techniques are described for quick routine determinations of the pore size distribution by mercury injection. In porosimetry by mercury injection, the amount of mercury that can be forced into a porous solid is measured as a function of the applied pressure. Details of apparatus for measurements at low pressures (1 to 15 psia) and high pressures (up to 60,000 psi) are given. The range of pore radii measurable with the equipment is 100 microns to 17A in materials, such as alumina, silica and activated clays, which have a low compressibility. Pore size distributions determined by the mercury method are compared with pore size distributions calculated from nitrogen desorption isotherms. A discussion is also given on the application of mercury porosimetry to porous bodies containing non-cylindrical pores.

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Direction des mines

POROSOMÉTRIE PAR VOIE D'INJECTION DE MERCURE

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RÉSUMÉ

Le présent bulletin technique décrit des appareils et des procédés qui permettent de déterminer rapidement et facilement la répartition des pores de diverses dimensions par voie d'injection de mercure. Dans le cas de la porosimétrie par injection de mercure, la quantité de mercure qui peut être introduite de force au sein d'un solide poreux se mesure en fonction de la pression appliquée. Les auteurs fournissent des détails sur les appareils utilisés pour procéder aux mesures à basse pression (de 1 à 15 livres au pouce carré, pression absolue) ainsi qu'à haute pression (jusqu'à 60,000 livres au pouce carré). La gamme des rayons des pores mesurables à l'aide des appareils varie de 100 microns à 17Å, dans le cas de matières telles que l'alumine, la silice et les argiles activées, qu'il est plutôt difficile de comprimer. Les répartitions des dimensions des pores telles que déterminées à l'aide du procédé au mercure sont comparées à celles qui sont calculées à partir des isothermes de désorption de l'azote. Les auteurs étudient également la possibilité d'appliquer la porosimétrie au mercure aux corps poreux qui comprennent des pores non cylindriques.

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CONTENTS

TABLE

FIGURES

INTRODUCTION

Measurement of pore volume and pore size distribution in porous inorganic catalysts and catalytic supports has been the subject of research at the Mines Branch for many years. In a previous Technical Bulletin (1) the calculation of the pore size distribution from the results of nitrogen desorption measurements was described. This nitrogen method is very reliable for porous materials, such as alumina or silica gels, where the average size is in the region of 50 A diameter or less and the range of pore sizes involved is usually quite small. However, where large pores are present and form a reasonable proportion of the total pore volume, calculations based upon the desorption isotherms are subject to large possible errors. Further, the nitrogen desorption method is slow; with many substances, four to five days are required to determine the complete adsorption-desorption isotherm. The technique is thus not suitable for any investigation entailing a large number of determinations over widely varying pore size ranges.

Porosimetry by high-pressure mercury injection (2), the subject of the present report, offered advantages of speed and simplicity, and seemed to be applicable to a wide range of pore sizes. However, the method had apparently never been set up as a routine determination. The principal purposes of the present investigation were, therefore: (a) to develop the equipment and techniques required for reliable, routine measurements of the pore volume distribution in the pore size range 100 microns to 17A radius, and (b) to compare the results of porosimetry by mercury injection and by nitrogen desorption measurements.

HISTORICAL BACKGROUND

In the technique of porosimetry by mercury injection, the amount of mercury that can be forced into a porous solid is measured as a function of the applied pressure. The contact angle which mercury makes with many solids is of the order of 140°. Because of this large angle of contact the resolved component of the surface tension tends to expel the mercury from the pore. When a pressure is applied to the mercury a certain volume enters the pores until equilibrium is achieved. At this point the mercury that has entered fills all the cylindrical pores with a radius greater than r given by the following expression:

$$r = \frac{-2S \cos a}{P} \times 1.45 \times 10^3,$$

where P is the pressure (psia),

r is the pore radius (A),

S is the surface tension of mercury at the
temperature of the experiments
(480 dynes per cm),

a is the contact angle, and

1.45×10^3 is the conversion to consistent
units.

This relation between the pore size and the pressure required to
force mercury to enter was first pointed out by Washburn (3)
in 1922. Chiefly because of the high pressures involved, it
was not until 1945 that the first application of this equation
was made to porosimetry. In 1945, Ritter and Drake (2) published
results of measurements made from 25 to 10,000 pounds per square
inch (10,000 psi, corresponding to approximately 100 A radius).
Later, in 1949, the measurements were extended to 60,000 psi,
or 17A radius, by Drake (4).

Inherent in the Washburn equation is the assumption
that all pores are circular (or nearly circular) in cross section.
The application of mercury porosimetry to structures containing
both cylindrical and non-cylindrical pores is discussed in detail
on page 24. Other assumptions implied in the Washburn equation
are that the surface tension of mercury in small pores is the
same as that of mercury in the bulk phase, and that the surface
tension and the contact angle are not affected by pressure. For
the present investigation the distribution data were calculated
using the bulk phase values of S and a. If, at a later date,
improved values are reported, the results can be corrected in an
appropriate manner.

Ritter and Drake (2) measured the contact angle of
mercury with many inorganic oxides at atmospheric pressure and
found values ranging from 135° and 142°; small differences in the
contact angle did not change the results of the calculation to a
large extent, and they selected 140° as a good average value for
all common oxides. The effects of widely differing values of
contact angle on the calculations are listed in their paper (2).
Another comment made by Ritter and Drake, in connection with the

calculation of the results, is also of interest:

> "The pore radius calculated by this method
> is the radius of the opening to the pore.
> If there exist in the material pores which
> are considerably larger than the largest
> entrances to them, these pores will be
> measured as of the size of the largest
> opening. Inasmuch as availability of
> internal surface is determined by the
> size of opening to a pore, however,
> this is an advantage in that it gives
> the total volume of pores available to
> penetrants of any given size."

A number of mercury porosimeters have been constructed
and used for the investigation and measurement of large pores.
The pressure limit of such equipment was usually 10,000 psi,
corresponding to a minimum pore size of approximately 100 A radius.
As mentioned previously, high-pressure porosimetry for the
measurement of small pores was not begun until after World War II.
Drake in 1949 (4) described equipment designed for pressures up
to 60,000 psi. Later, Cochran and Cosgrove (5), in an investigation
of the pore structure in alumina gel, described equipment with a similar
pressure range. Ingles (6), in Australia, reported a porosimeter
for use up to 45,000 psi. Plachenov (7), in Russia, referred to
a porosimeter having a maximum pressure rating of 75,000 psi.
The Russian equipment has the highest pressure rating of any
porosimeter reported to date. The smallest pore that could be
penetrated at 75,000 psi would be approximately 15A radius.

At about the same time that various laboratories were
endeavouring to build equipment with higher and higher pressure
ratings (to measure smaller and smaller pores), others were
experimenting at very low pressures to measure pores of 10 to 100
microns diameter. The main problem experimentally at pressures
below one atmosphere is the tendency of mercury to stick to
surfaces, small pressure differences frequently being insufficient
to force the mercury to penetrate around the particles of the
sample. Dubinin, Sarakhov and Ryabikov (8) designed a low-pressure
porosimeter for the measurement of macro-pores in activated
charcoal. Later, Cameron and Stacy (9) combined low-pressure
and high-pressure on a single sample to measure both large and
small pore sizes.

THE MERCURY POROSIMETER - APPARATUS AND PROCEDURE

The apparatus for mercury porosimetry was made up of three units:

1. A dilatometer for containing the sample and measuring the volume of mercury that has been forced into the pore structure.

2. A glass apparatus for degassing the sample, filling the dilatometer with mercury, and determining the amount of mercury forced into the sample at low pressures (1 to 15 psia).

3. A steel high-pressure apparatus for containing the dilatometer, and pumps for stepwise increasing the pressure from 15 psia up to 60,000 psi.

A diagram of a typical dilatometer is shown in Figure 1 and simplified diagrams of the low-pressure and high-pressure, apparatus are shown in Figure 2.

Dilatometer Preparation and Calibration

Each dilatometer was made from a length of precision-bore pyrex capillary tubing. The sample to be examined is sealed into a standard 10-mm diameter tube fused to the bottom of the capillary. The amount of mercury that is forced into the pore structure of the sample at low pressures (1 to 15 psia) is determined visually in the glass apparatus by following the level of the mercury in the capillary with a cathetometer. In the steel high-pressure apparatus the level of the mercury in the dilatometer is determined by means of the electrical resistance of a fine platinum-iridium wire loop threaded in the capillary. As mercury is forced into the sample, the level drops in the precision-bore tube, exposing more wire and thereby increasing the electrical resistance.

The first step in the manufacture of a dilatometer is to determine the internal diameter of the precision-bore capillary tubing. This is done by weighing a slug of pure mercury of known length that has been sucked into the bore and calculating the diameter from the length and density. The capillary tube is then fused to a short length of 10-12 mm diameter pyrex tubing containing

PLATINUM LEADS

WIRES HELD TO GLASS WITH GLYPTAL CEMENT

SOFT IRON ROD

15 CM

PRECISION BORE TUBE 0.225 CM I.D.

Pt-Ir RESISTANCE WIRE LOOP

GLASS BRIDGE

SCREEN 40 MESH

SAMPLE

Figure 1 - Diagram of the dilatometer.

LOW PRESSURE POROSIMETER (1-15 P.S.I.A.)

HIGH PRESSURE POROSIMETER (15-60,000 P.S.I.A.)
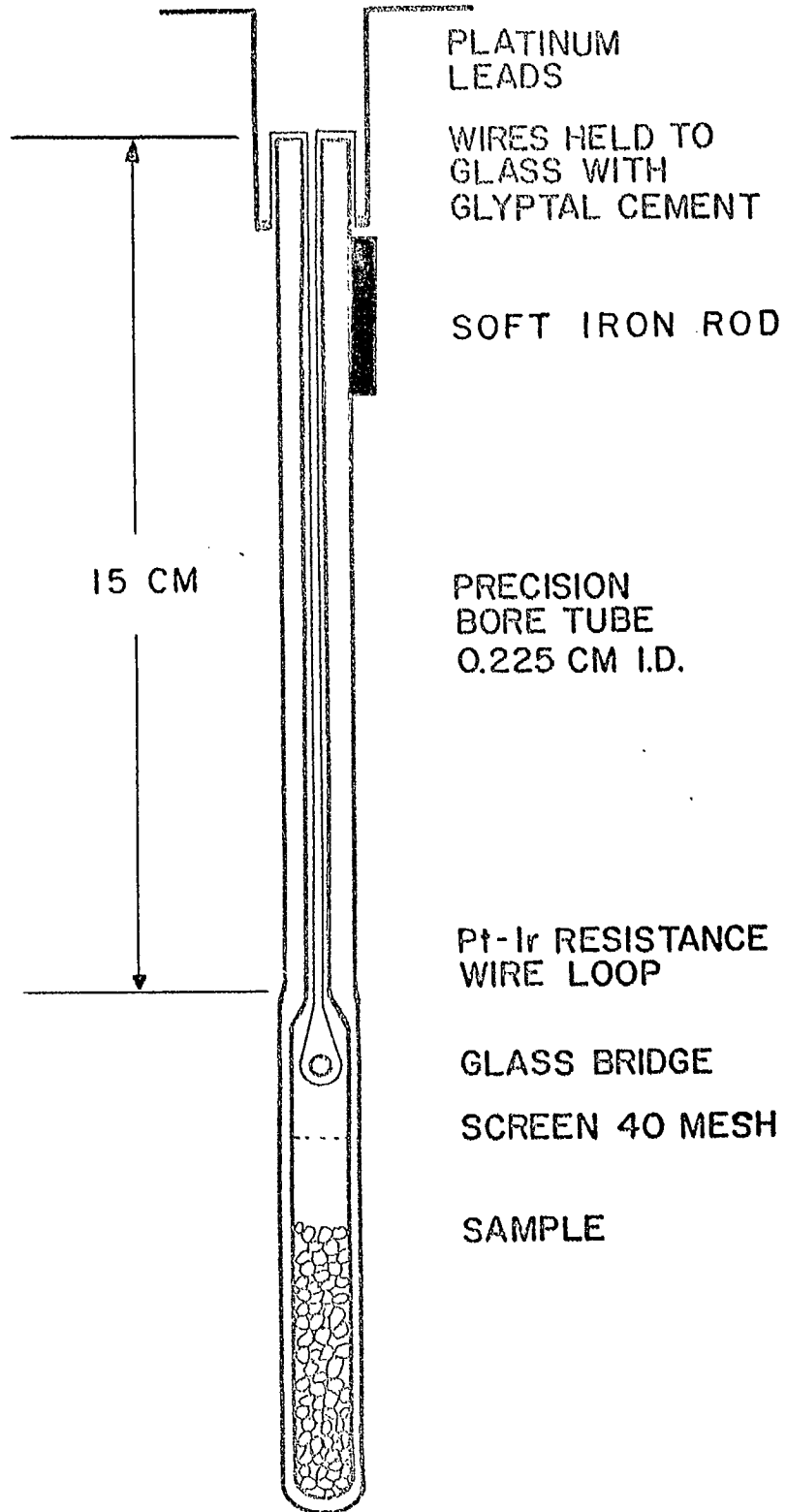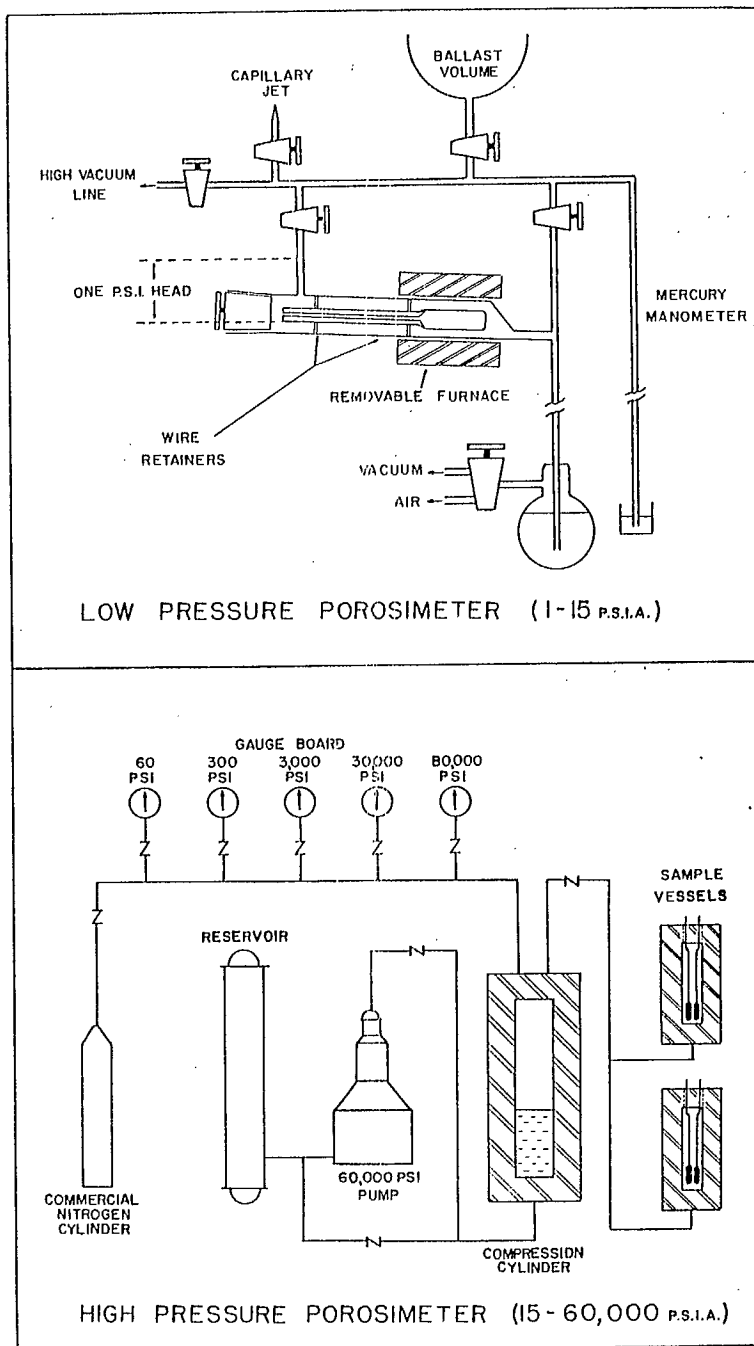
Figure 2 — Diagram of the low- and high-pressure
mercury porosimeters.

a glass bridge set about 2 cm from the junction. Considerable care must be taken to anneal the bridge connections. Platinum-iridium (25% Ir) resistance wire, 0.003 in. diameter, is threaded along the inside of the tube and looped around the bridge. The two ends of the resistance wire loop are brought out of the top of the dilatometer for a distance of about 2 cm and each is fused to a 4-cm length of heavier gauge platinum wire to act as electrical leads (copper wire is not satisfactory, because copper forms an amalgam with mercury). The two ends of the resistance wire are folded back along opposite sides of the outside of the capillary tube for a short distance, and then the heavier gauge wires are reversed to project beyond the tube to serve as leads. The wires are held in place by narrow strips of masking tape. A thin layer of "glyptal"* cement is spread over the tape, the wires, and the surrounding glass. This cement is allowed to harden and then a second layer is applied. When the wires are firmly cemented into place, the glass near the junction of the capillary and the sample tube is softened slightly with a small flame and then pulled to stretch the wire loop taut.
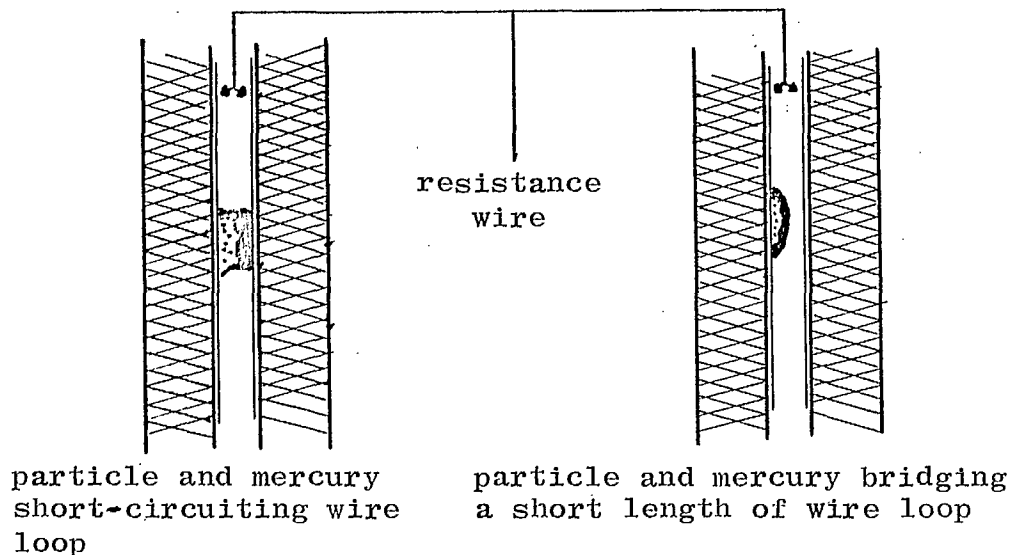
This method of mounting the resistance wire was found to be relatively simple and effective. It supplanted the customary use of a threaded type of stretching head (2) on the dilatometer. Glyptal cement was found to be superior to other adhesives, such as epoxy resin, varnish or lacquer, for anchoring the wires in place, primarily because it retains a certain amount of plasticity when set. When the dilatometers are subjected to pressure in the high-pressure vessels, a degree of compression does occur. A substance such as epoxy resin tends to crack under pressure, and the fine resistance wire is frequently broken in the process. The best technique for threading the wire loop around the bridge and up the capillary was found to be to solder the ends of the required length of fine wire to long, stiff copper wires (ordinary copper hook-up wire that had been work-hardened by stretching), to push these ends through the dilatometer on either side of the bridge, and then to pull the fine resistance wire into place. The best results are obtained when no kinks are allowed to form in the wire loop — the entire threading operation is better carried out manually by two people, rather than to attempt some mechanical means to keep the wires from twisting or snarling.

*An electrical insulating cement manufactured by the Canadian General Electric Co. Ltd., Toronto, Ontario.

The resistance of the platinum-iridium wire loop was measured with a Mueller Bridge, manufactured by the Rubicon Co., of Philadelphia. The dilatometer is calibrated by filling the capillary tube with mercury and determining the value of the resistance with the mercury at various levels. In the calibration experiments the level of the mercury is lowered systematically from the top of the dilatometer to the bottom, to simulate the shape of the mercury surface in contact with the glass wall and the wire during actual operation. From these measurements and the known diameter of the precision-bore tube, the calibration factor, "volume of mercury/ohm resistance", is calculated. The volume occupied by the resistance wire itself is negligible. Our experience has been that the calibration factor is essentially constant over the working length of the capillary.

As mentioned previously, the measurements at pressures less than one atmosphere are made visually with a cathetometer. To secure the dilatometer in one place in the glass apparatus, a soft iron rod (part of a nail) was cemented to the side of the capillary and held against the wall of the apparatus with an external magnet. By means of the magnet the dilatometer could also be rolled or raised to reveal reference marks, etc. To be able to control the position of the dilatometer in the glass apparatus was found to be of considerable advantage.

Where samples of small granular size were being examined it was found best to force a small disc of 40-mesh stainless steel screening into the sample tube just below the bridge, to keep the particles from floating up into the capillary. Small pieces of sample in the capillary tube frequently acted as points for mercury to stick - resulting in either a short circuit across the wire loop or a bridge across one or two mm of the loop on one side. A sketch indicating the difficulties arising because of the presence of solid particles in the capillary is shown below:

resistance wire

particle and mercury   particle and mercury bridging
short-circuiting wire   a short length of wire loop
loop

Low Pressure Porosimetry

A schematic diagram of the low-pressure apparatus is shown in the top section of Figure 2. To simplify the drawing, facilities for handling only one dilatometer are shown. In the actual apparatus, four dilatometers were treated at a time. The low-pressure equipment was made up from standard pyrex tubing, flasks, stopcocks, and ground glass joints. High vacuum was attained with a two-stage mercury diffusion pump backed by a Welch Duo-Seal mechanical oil pump. Low vacuum (for controlling the level of the mercury in the reservoirs) was obtained with a second mechanical oil pump. The removable furnace was made by winding Chromel A heating element wire on two halves of a tube. When required, the two halves were clamped together around the tube. For quick cooling the two halves were removed completely. The power to each furnace was controlled with a variable transformer. Very briefly, the procedure used was as follows:

The sample to be examined is weighed and placed in a dilatometer. The dilatometer is then placed in the low-pressure apparatus and the sample degassed overnight under vacuum at 250°C. The dilatometer is held nearly horizontal to minimize the hydrostatic head of mercury over the sample in the filling operation*. The sample tube containing the dilatometer is inclined slightly away from the stoppered end to allow the mercury to drain from the apparatus. The pressure over the sample after approximately 16 hours' evacuation is usually 10^{-3} mm or less. On completion of the degassing operation the dilatometer is filled with mercury at 1 psia. This is done by raising the mercury above the mouth of the dilatometer until the head is equivalent to 1 psia. The stopcock to the diffusion pump is then closed and air is allowed to bleed slowly into the system through the capillary jet (and the mercury allowed to return to the reservoir) until the dilatometer is in view. The air bleed is then shut off and the mercury drawn down into the reservoir with the vacuum pump. At

*5.17 cm head of mercury corresponds to 1 psia.

this point the pressure on the sample in the dilatometer is very nearly 1 psia (1 psia air pressure plus head of mercury in capillary due to slight slope of the dilatometer*). The pressure on the sample is then increased stepwise up to atmospheric pressure and the volume of mercury forced into the sample is measured by noting the change in level in the dilatometer with a cathetometer.

Almost always, the sample requires degassing before submerging in mercury. Large amounts of any absorbed material affect the contact angle of the mercury with the solid and, in an extreme case, would fill small pores completely and lead to an incorrect result. Most inorganic oxides, such as alumina or silica, can withstand a vigorous degassing procedure. Certain materials, however, cannot be treated at either high temperatures or high vacuum without serious effects on crystal structure, surface roughness, or pore size. With an untried substance the best procedure is to try various degassing temperatures and durations, and to compare the results in conjunction with microscopic examination.

High Pressure Porosimetry

A block diagram of the high-pressure porosimeter is shown in the lower section of Figure 2. Details of the sample vessels and electrical leads are shown in Figures 3 and 4. The high-pressure pumps and vessels were designed and constructed by Autoclave Engineers, of Erie, Pa.

Pressures up to 2000 psi are obtained by bleeding nitrogen gas from a commercial cylinder into the system. Pressures greater than 2000 psi are obtained by isolating the

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*It is not possible to fill the dilatometers under vacuum conditions, because of the inertia of the mercury. The pressure, or head, required to cause the mercury to flow around the granules of a sample is governed to a large extent by the particle size. For most of our experiments the particle size was a -14 to 30 mesh U.S. Standard Screen fraction or larger. A smaller particle size requires higher pressures, - up to 15 to 25 psia for fine powders.
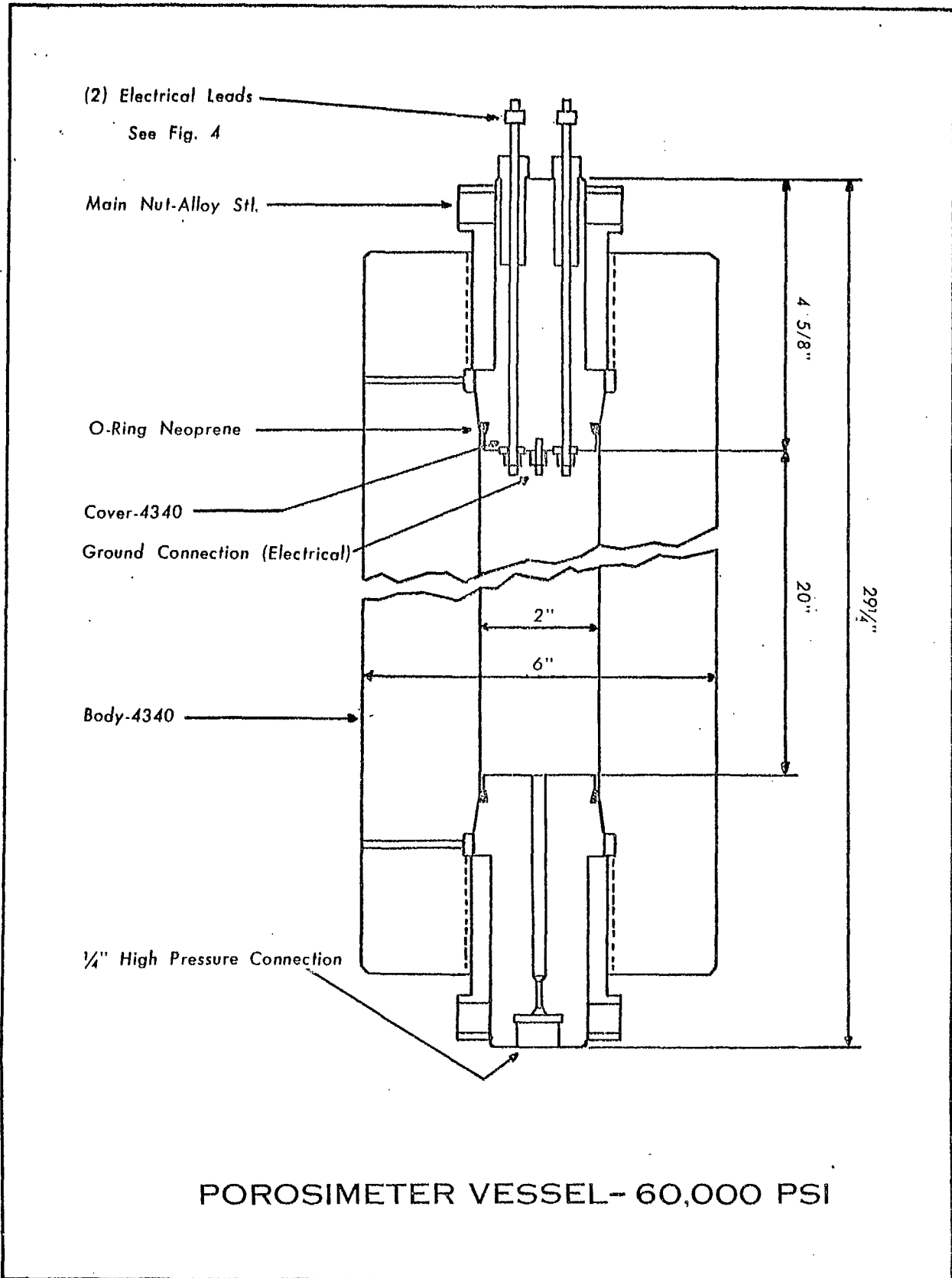
(2) Electrical Leads —
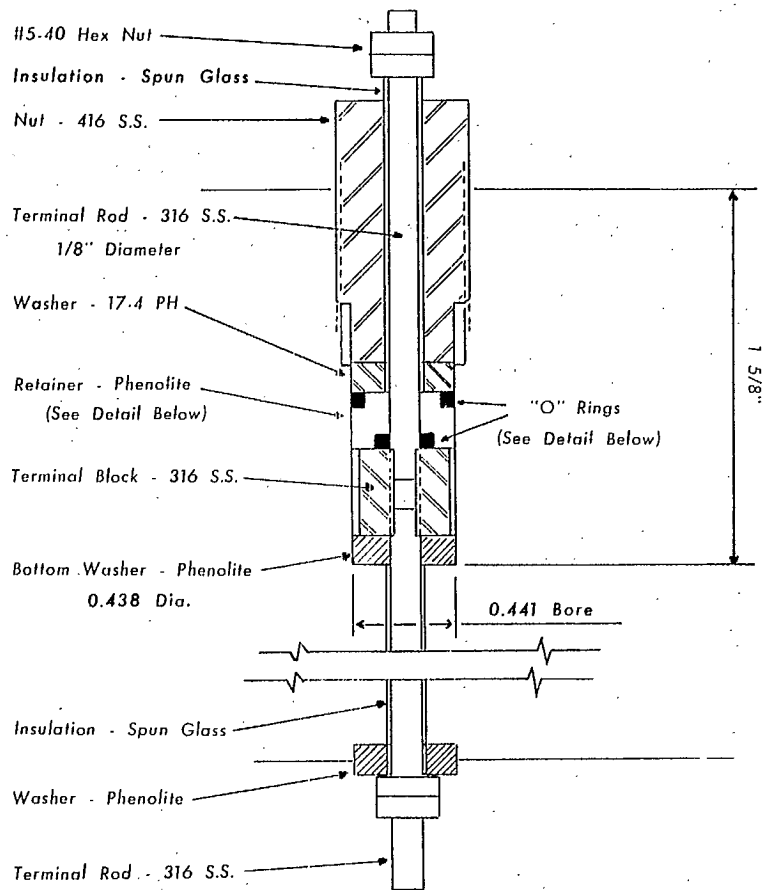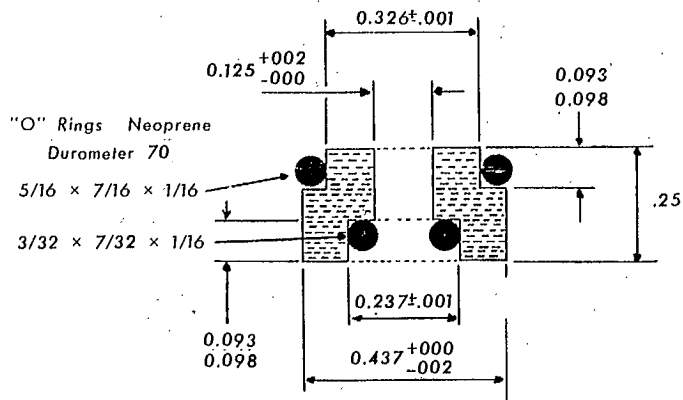See Fig. 4

Main Nut-Alloy Stl.

O-Ring Neoprene

Cover-4340

Ground Connection (Electrical)

Body-4340

¼" High Pressure Connection

4 5/8"

20"

29¼"

2"

6"

POROSIMETER VESSEL- 60,000 PSI

Figure 3 - Diagram of the high-pressure sample vessel.

ELECTRICAL LEAD - 60,000 PSI

#5-40 Hex Nut

Insulation - Spun Glass

Nut - 416 S.S.

Terminal Rod - 316 S.S.
   1/8" Diameter

Washer - 17-4 PH

Retainer - Phenolite
   (See Detail Below)

Terminal Block - 316 S.S.

Bottom Washer - Phenolite
   0.438 Dia.

"O" Rings
(See Detail Below)

0.441 Bore

Insulation - Spun Glass

Washer - Phenolite

Terminal Rod - 316 S.S.

1 5/8"

PHENOLITE "O" RING RETAINER

0.326^{+}.001

0.125$^{+002}_{-000}$

0.093
0.098

"O" Rings   Neoprene
   Durometer 70

5/16 × 7/16 × 1/16

3/32 × 7/32 × 1/16

.25

0.237^{+}.001

0.093
0.098

0.437$^{+000}_{-002}$

Dimensions in Inches

Figure 4 - Diagram of the electrical leads in the high-
          pressure sample vessel.

the commercial cylinder and pumping water into the compression cylinder to reduce the volume of the system. The volume of the compression cylinder is approximately 10 times greater than that of the sample vessels, so that with an initial pressure of approximately 2000 psi, pressures of up to 20,000 psi can be obtained by this displacement technique. When the compression cylinder is full, the valve leading to the sample vessels is closed, the water is returned to the reservoir, and the compression vessel is refilled with nitrogen to a pressure equal to that in the commercial cylinder; the process is then repeated until the desired pressure is attained. After the first cycle the valve connecting the compression cylinder and the sample vessels is not opened until the pressure in the compression vessel is equal to or greater than the pressure in the sample vessels. The apparatus contains various additional valves and by-pass lines, not shown in the diagram, for conserving pressure and/or connecting or disconnecting vessels separately in the event of difficulties. Also, each gauge, except the 80,000-psi gauge, is equipped with a rupture disc as a protective measure. The vessels, pumps, and high-pressure gauges are contained in a room approximately 6 ft by 8 ft, with 12-in. reinforced concrete walls and a steel blasting mat ceiling. At 60,000 psi, considerable energy is stored in the system, and care was taken to anchor securely all lines, tees, valves, etc., to prevent components from lashing about in the event of a failure. Gauges with blow-out safety backs were also used.*

The electrical leads (Figures 3 and 4) in the sample vessels are each made up of two lengths of insulated steel rod threaded into a terminal block. The pressure seal is made with two "O" rings held in position on a phenolite retainer. Care must be taken to machine the phenolite (a bakelite plastic strengthened with cloth) retainer in such a way that the laminations run at right angles to the direction of thrust; otherwise, gas will diffuse through the laminations. The best results were obtained when the leads were assembled in SAE-30 lubricating oil so that the "O" ring was made to seal against a liquid rather than against a gas. The procedure for assembling

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*On this point of gauges with blow-out backs, the authors recommend that the thin brass or fibre sheets usually used by manufacturers to cover the back of the gauge be removed and the gauge be covered-in with thin plastic film. A brass disc blown off the back of a gauge at high pressure is almost as dangerous as a failure of the gauge towards the front.

the leads was briefly as follows: the various components of each lead are first put on the terminal rod, then both the head and the lead assembly are saturated with oil and threaded together in an oil bath. The main retaining nut is tightened by hand as much as possible in the oil bath, the head is removed from the oil bath and clamped in a vice, and the nut is tightened with a 6 in. wrench. Seals made in this way have been in service, cycling up to 60,000 psi and back to atmospheric pressure, daily for over a year.

In general, the "O" ring type of closure for all vessels and leads is recommended, because of the simplicity of construction and the ease and speed with which the actual closure can be made. Closures made with gaskets tightened in place with a series of head bolts are not too reliable at high pressures and require considerable physical effort. Seals made with Bridgeman-type steel rings are easier to make than gasket closures, but if any of the surfaces become scratched much re-machining is required. "O" ring closures were found to be successful even where small scratches are present at the point of sealing; the high pressures involved appear to force the rubber compound into all the surface imperfections and thus effect a good seal. Before assembly, care was always taken to coat all surfaces, and the "O" ring itself, with SAE-30 lubricating oil.

The sample vessels used for high-pressure porosimetry were mounted in a plywood box "oven" thermostatted at $27 \pm 0.5°C$. to minimize errors due to the expansion and contraction of the mercury and to changes in the electrical resistance of the wire loop with fluctuations in room temperature.

The procedure used for high-pressure porosimetry is generally as follows:

At atmospheric pressure the dilatometers are removed from the low-pressure apparatus and attached in pairs to the head of the sample vessels. The physical weight of the dilatometers is held by a plastic thimble tied with a short length of string to the ground terminal in the head. One platinum lead of each dilatometer is connected to one of the insulated electrical connections, and the other is grounded to the head. Small Fahnestock spring clips were found to be the best method for connecting the leads of the dilatometer to the ends of the terminals (a good solder contact is difficult to obtain because of the presence of small amounts of mercury and oil which are inevitably scattered on the

head).

Once the dilatometers are attached to the head, the assembly is placed in the sample vessel, the "O" ring closure is tightened into place, and the electrical connections are made to the Mueller Bridge. The resistance of each dilatometer is measured with the Mueller Bridge connected in turn to the appropriate insulated terminal and ground. A short interval of time, approximately 30 minutes, is usually allowed for the head and dilatometers to reach a steady temperature before the first resistance measurements are made at atmospheric pressure. The pressure is then increased stepwise up to 60,000 psi and the volume of mercury forced into the sample is determined after each additional increase in pressure. At pressures less than 15,000 psi the mercury is allowed to penetrate into the sample for approximately 10 to 20 minutes before the resistance measurements are made. At higher pressures than 15,000 psi the system is generally allowed to stand for 30 minutes before the readings* are taken.

Most of the experimental results shown in the next section are presented as cumulative pore volume distribution curves, i.e., the total amount of mercury per gram of sample forced into the pore structure is plotted as a function of the applied pressure. In each figure the smallest pore radius penetrated, as calculated from the equation, corresponding to the applied pressure is shown across the top of the plate. The pore volume distribution (dV/dr versus r) is calculated from the cumulative plot by taking increments of pore volume ($\triangle$ V) and pore size ($\triangle$ r) at various values of r.

Where the total pore volume is small, a larger amount of sample must be loaded into the dilatometer to maintain the same degree of reading accuracy in the measurements. If one is dealing with a series of porous substances of similar type and

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*Drake (4) reported a very low rate of penetration of mercury into small pores at 60,000 psi and recommended a long waiting period at high-pressures. Our own experience has been that the rate of penetration with most substances is remarkably fast, and that a steady resistance value can usually be obtained after 20 minutes at all pressures.

particle size, the apparent bulk density can generally be used as a guide in the selection of the best sample size. A typical relationship between apparent bulk density and total pore volume for alumina is shown in Table 1 (10). A similar type of relationship exists between the apparent density and the total pore volume for pelleted materials. The best sample size, in the case of a completely unknown material, can usually only be determined by trial and error. With the type of dilatometer shown in Figure 1 it was found that a sample size of one gram was sufficient for accurate measurements, provided the total pore volume did not exceed 0.5 ml/g. For those samples where the pore volume was 5 to 10 ml/g (or greater), special dilatometers were made with capillary tubes of larger internal diameter to increase the capacity of the measuring system. Using a dilatometer with a larger capillary was found to be a better practice than using the standard dilatometer with a very small amount of sample. To increase the capacity of the dilatometer still further, it is also possible to lengthen the capillary; such a change, however, requires modification of the sample vessels, degassing tubes, etc.

TABLE 1

The Apparent Bulk Density and the Total Pore Volume in Alumina Gel

Apparent Bulk Density* (g/ml)	Total Pore Volume** (ml/g)	Apparent Bulk Density* (g/ml)	Total Pore Volume** (ml/g)
0.07	5.32	0.33	0.99
0.13	2.72	0.41	0.81
0.15	2.07	0.47	0.55
0.19	1.57	0.59	0.51
0.26	1.29	0.67	0.28

*-14 + 30 mesh U.S. Standard Screen fraction.
**Cumulative pore volume in all pores larger than
  20 A radius.

TYPICAL EXPERIMENTAL RESULTS

Typical results of low- and high-pressure porosimetry measurements on several samples of alumina are shown in Figure 5. The highly porous forms of alumina shown in this figure were prepared by the addition of water-soluble organic polymers to the hydrous gels prior to dehydration and calcination (10). As described in the procedure, the usual way of presenting the results of the measurements is as a cumulative pore volume distribution, i.e., the total amount of mercury per gram of sample forced into the pore structure is plotted as a function of the applied pressure. The range of pressures involved (and the corresponding pore sizes penetrated by the mercury) is quite large, and for this reason the distribution is generally shown as a plot of the cumulative pore volume vs the logarithm of the applied pressure (or pore radius).

The versatility of the mercury injection technique is clearly demonstrated in Figure 5. The range of pore sizes measurable with the apparatus is 100 microns to 17A radius. Many catalytic materials contain both large and small pores, and the wide range of applicability reduces the number of measurements required to cover all pore sizes. Also, the mercury injection method is comparatively simple and quick to carry out. With the present apparatus, four individual samples can be run every 24 hours. The dilatometers are usually loaded and put into the degassing apparatus overnight, the porosimetry measurements being made in the course of the next day.

The chief disadvantage of mercury porosimetry is the high pressure required to penetrate small pores. At 60,000 psi no safety precaution can be regarded as too extreme. Several improved types of high-pressure barricades have been proposed recently (11), notably laminated steel and wood sheeting. We used concrete barricading primarily because the walls were there from another project, not because we considered it to be the best type.

The amount of energy stored in the steel vessels at high pressure can be reduced considerably if the pressure to the mercury in the dilatometers is applied directly via the hydraulic fluid, i.e., with no gas layer between the hydraulic fluid and the dilatometers. The extent of compression that occurs in a hydraulic fluid at 60,000 psi (and the corresponding amount of energy required to bring about this compression) is small as compared with a gaseous system. Typical pore volume distribution
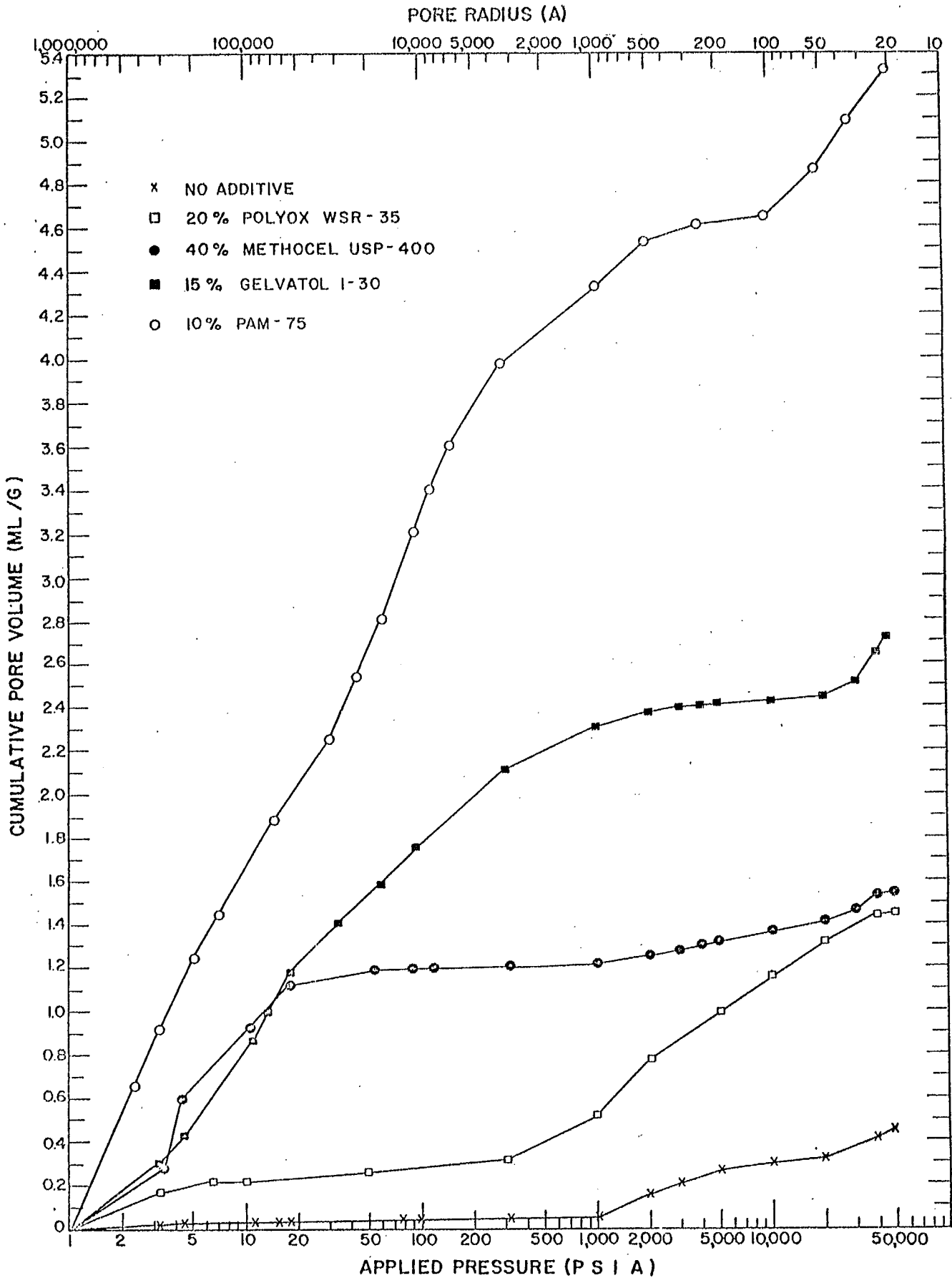
Figure 5 — Typical results of pore volume distribution
measurements made on samples of alumina
gel prepared using organic addition agents

curves obtained with a sample of pelleted alumina, using a) an all-hydraulic system and b) a nitrogen gas layer between the hydraulic fluid and the dilatometer are shown in Figure 6. Within experimental error the results are the same.

At the Mines Branch we generally use a nitrogen gas layer between the hydraulic fluid and the sample, because it greatly simplifies the problem of cleaning and maintaining the dilatometers. In experiments made using an all-hydraulic system, it was found that a film of fluid frequently adhered to the resistance wire loop, and that the vigorous cleaning treatment required to remove this film shortened the life of the dilatometers considerably. Also, in recent years vast improvements have been made in the type of steels used for high-pressure vessels, and the danger of vessel failure is thus much reduced from ten years ago.

The weakest parts in any modern high-pressure apparatus are usually the gauges: the bourdon tube must bend to record each pressure change, and the safety factor incorporated in the design of a gauge must, of necessity, be much lower than for a vessel or a valve. A solution to the gauge problem might be to use a strain-gauge type of pressure cell.

A COMPARISON OF THE PORE SIZE DISTRIBUTIONS CALCULATED FROM MERCURY INJECTION MEASUREMENTS AND FROM NITROGEN DESORPTION MEASUREMENTS

The sample of porous material selected as a basis for the comparison of the nitrogen and mercury injection methods was an alumina-base, cobalt-molybdate catalyst manufactured by the Union Oil Co. of California. The catalyst was designated as type N-H760 by the manufacturers and was in the form of 1/8 in. diameter pellets. This particular material had been intensively investigated at the Mines Branch during past years; hence the nitrogen adsorption-desorption isotherms were known with considerable accuracy (1). Moreover, the pore size distribution in the Union Oil pellets was of a type ideally suited to the nitrogen technique of measurement. The average pore size in the pellets was between 25A and 30A radius, and there were virtually no pores present greater than 100A radius. The nitrogen method is generally regarded as highly accurate with a sample of this type, and the catalyst was therefore felt to be an excellent material on which to base a comparison of the two methods.
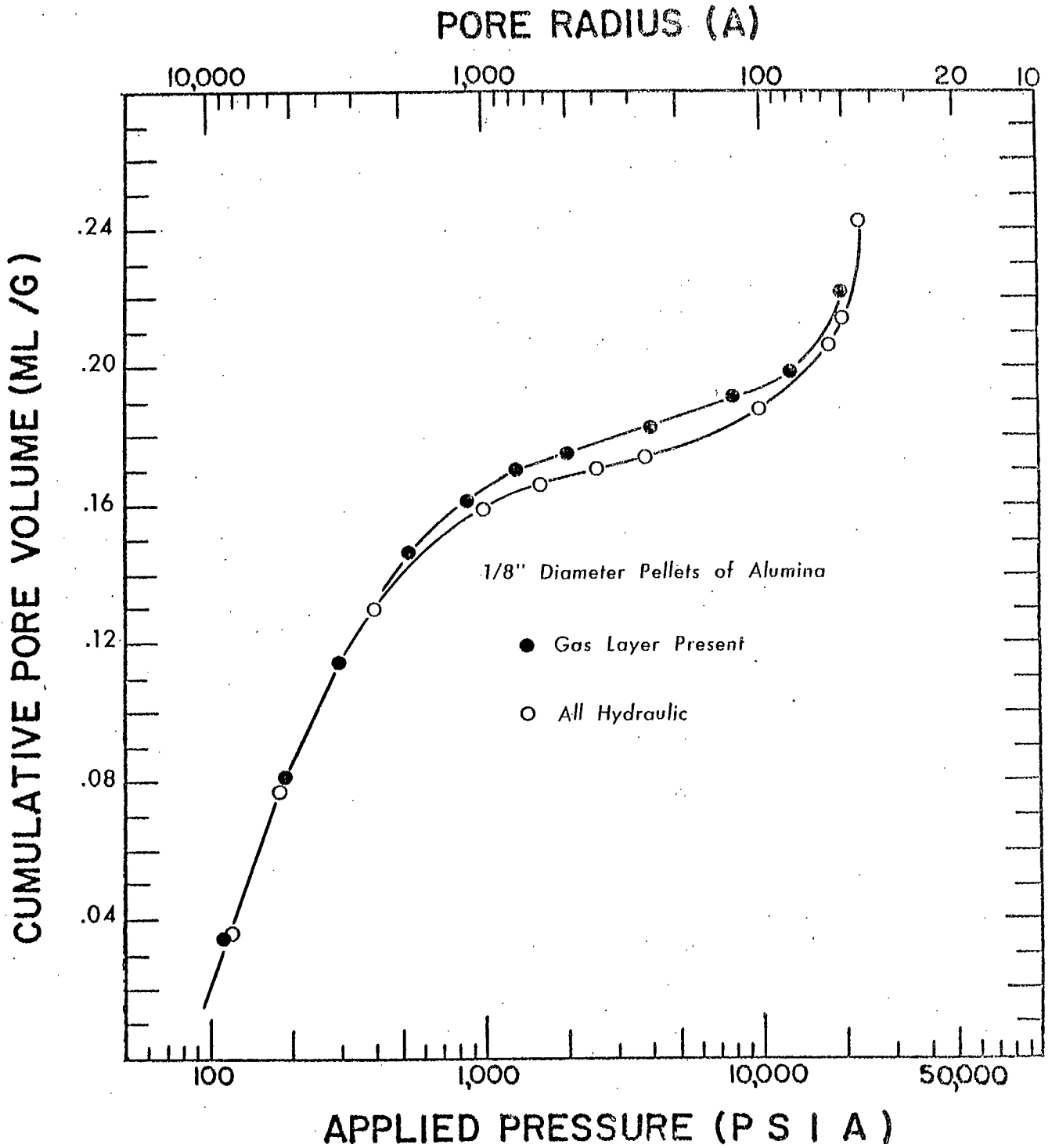
Figure 6 — Cumulative pore volume distribution curves
determined using a) an all-hydraulic system
and b) a nitrogen gas layer.

The cumulative pore volume distribution in the Union Oil pellets is shown in Figure 7, and a comparison of the pore size distributions calculated from the cumulative plot and from nitrogen desorption measurements is given in Figure 8. The results obtained by the two methods agree very closely. The peak in the distribution calculated from the nitrogen desorption measurements occurs at 25A, and the peak in the distribution calculated from the mercury measurements occurs at 30A. Both distribution curves were determined from the experimental measurements by simple graphical differentiation techniques. The curves shown in Figure 8 are the results obtained by selecting equal increments of volume. The height of the peak in either distribution could be raised or lowered by selecting larger or smaller increments of volume in the critical region. The important facts are that the areas under the curves are very nearly equal and that both distributions have their peak at essentially the same value. All matters being considered, the agreement between the two methods is very good.

As mentioned in the discussion of "Typical Results", one of the chief advantages of the mercury injection technique is the wide range of pore sizes over which it can be used. The nitrogen method is seriously restricted in this respect and cannot be used for many types of porous substances containing a high proportion of their pore volume in pores greater than 100-200A radius. Frequently, however, there are borderline cases of substances where investigators attempt to use the nitrogen technique to obtain qualitative information. Such a case was described by the authors in a previous Bulletin (1). The sample in question was a clay-base hydrogenation catalyst manufactured in Germany during World War II and designated as K-536. The catalyst was in the form of 1-cm extrusions. The nitrogen isotherms for this particular material approached the saturation pressure asymptotically, and it was not possible to obtain a clearly defined pressure at which the desorption isotherm began to differ from the adsorptive branch. Simply for the record we would like to illustrate just how incorrect the results of the nitrogen method can be for these borderline cases.

The cumulative pore volume distribution curve determined by mercury porosimetry for the K-536 extrusions is shown in Figure 7. A comparison of the pore size distribution as calculated by the two methods is given in Figure 9. The pore size distribution in the K-536 catalyst extended over a very wide range, and the results of the calculations for this sample are shown as a plot of log dV/dr vs log r. It was known that the distribution
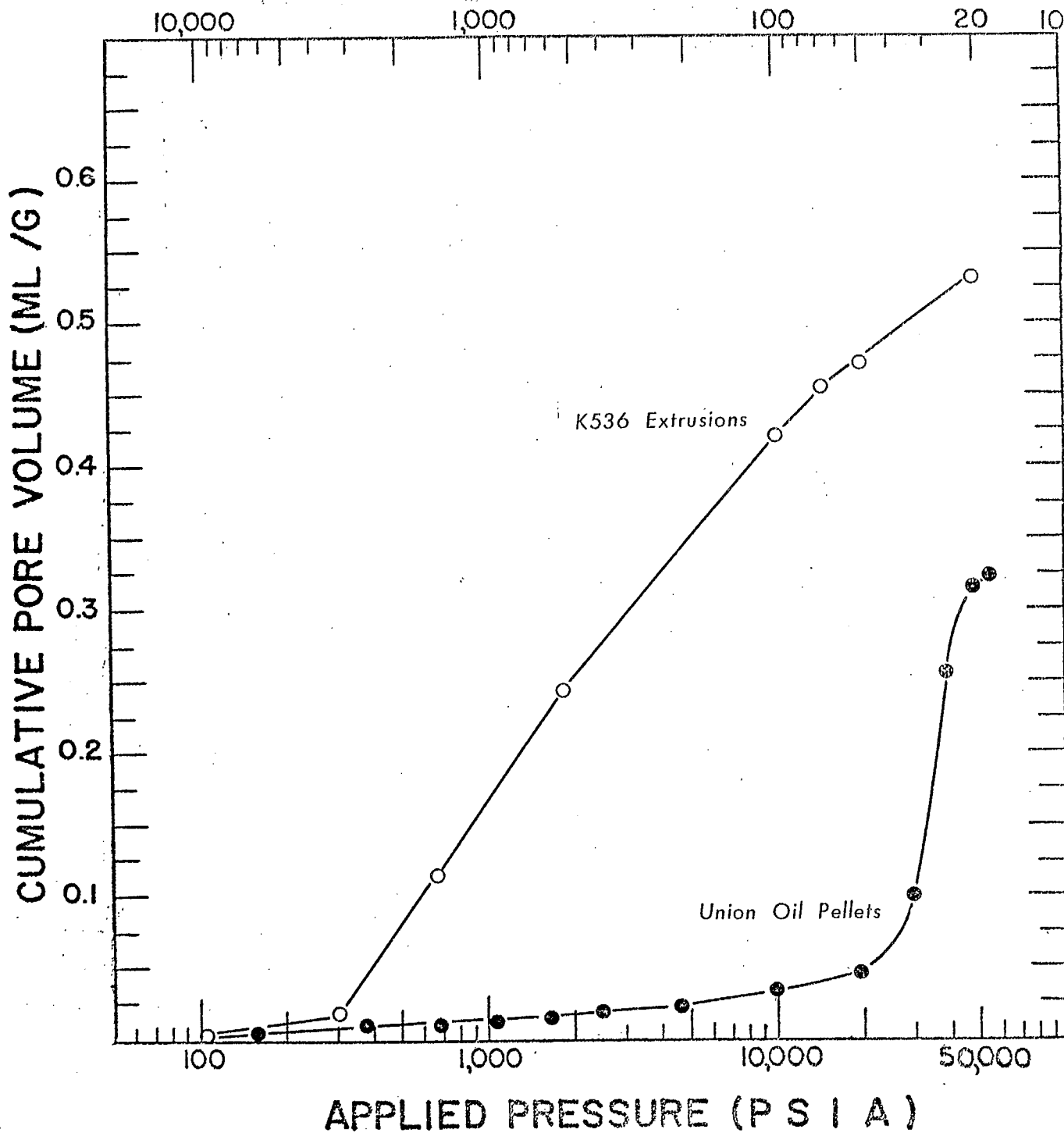
Figure 7 – Cumulative pore volume distribution in the
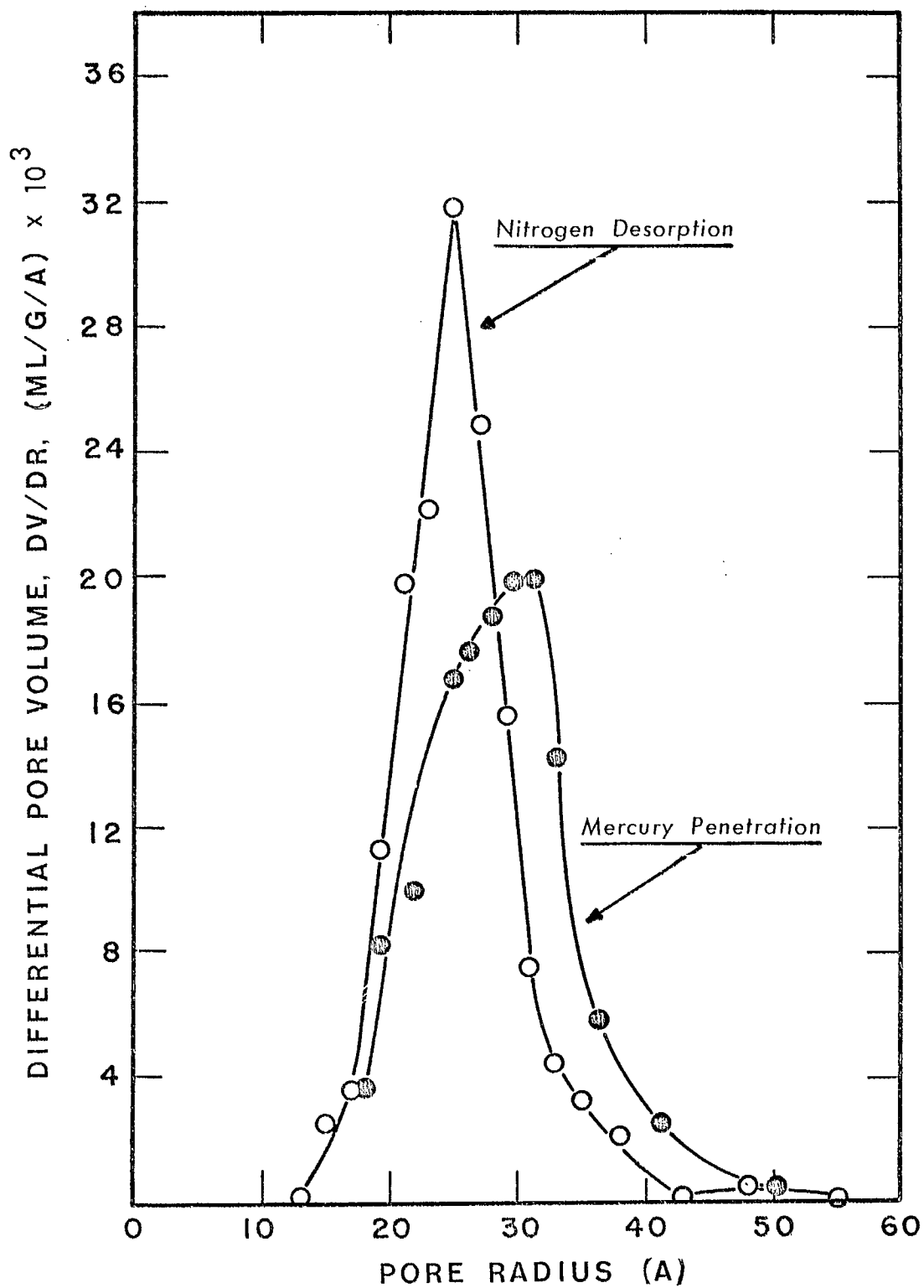K-536 extrusions and the Union Oil cobalt-
molybdate catalyst.

Figure 8 – The pore size distribution in the Union Oil
cobalt-molybdate catalyst.

calculated from the nitrogen desorption measurements was probably incorrect, but it was not suspected that there was such a large pore volume present in the region 3000 to 500A radius. As the results shown in Figure 9 clearly indicate, the distribution calculated from the nitrogen measurements does not even approximate the correct order of magnitude. Our experience with this type of sample has been that, where the total pore volume (estimated from the difference between the reciprocals of the particle density and the true solid density) is 20 to 30% greater than that determined by the nitrogen method, the pore size distribution calculated from the desorption isotherm is completely misleading.

MERCURY POROSIMETRY AND NON-CIRCULAR PORES

One of the basic assumptions embodied in the Washburn equation, $r = -2S(\cos a)/P$, is that the pores are circular in cross section. For routine measurements of the pore size distribution in various types of porous materials, the "cylindrical pore" concept is a very good practical basis from which to work. It should be pointed out, however, that the equation can be modified to take into account shapes of pores other than cylindrical, provided an independent method (optical or electron microscope) is available to establish what the particular shape is. Mercury porosimetry cannot be used to determine the shape of the pore, but where the shape is known the equation can be modified to calculate the pore size distribution corresponding to a particular geometry.

In Ritter and Drake's derivation of the equation, the mercury surface is regarded as moving parallel to itself into a cylindrical pore (2). The difference in interfacial forces across the surface of the mercury is equated to the externally applied force, thus:

$$-2 \pi r S \cos a = \pi r^2 P,$$

where all the symbols are as before. A negative sign is added to the left-hand term because "a" is greater than $90°$ (-cos a is therefore positive) and the forces must be regarded as intrinsically positive. However, it was shown by Laplace, as long ago as 1880 (12), that the pressure difference across any curved surface having r_1 and r_2 as principal radii of curvature is given by:
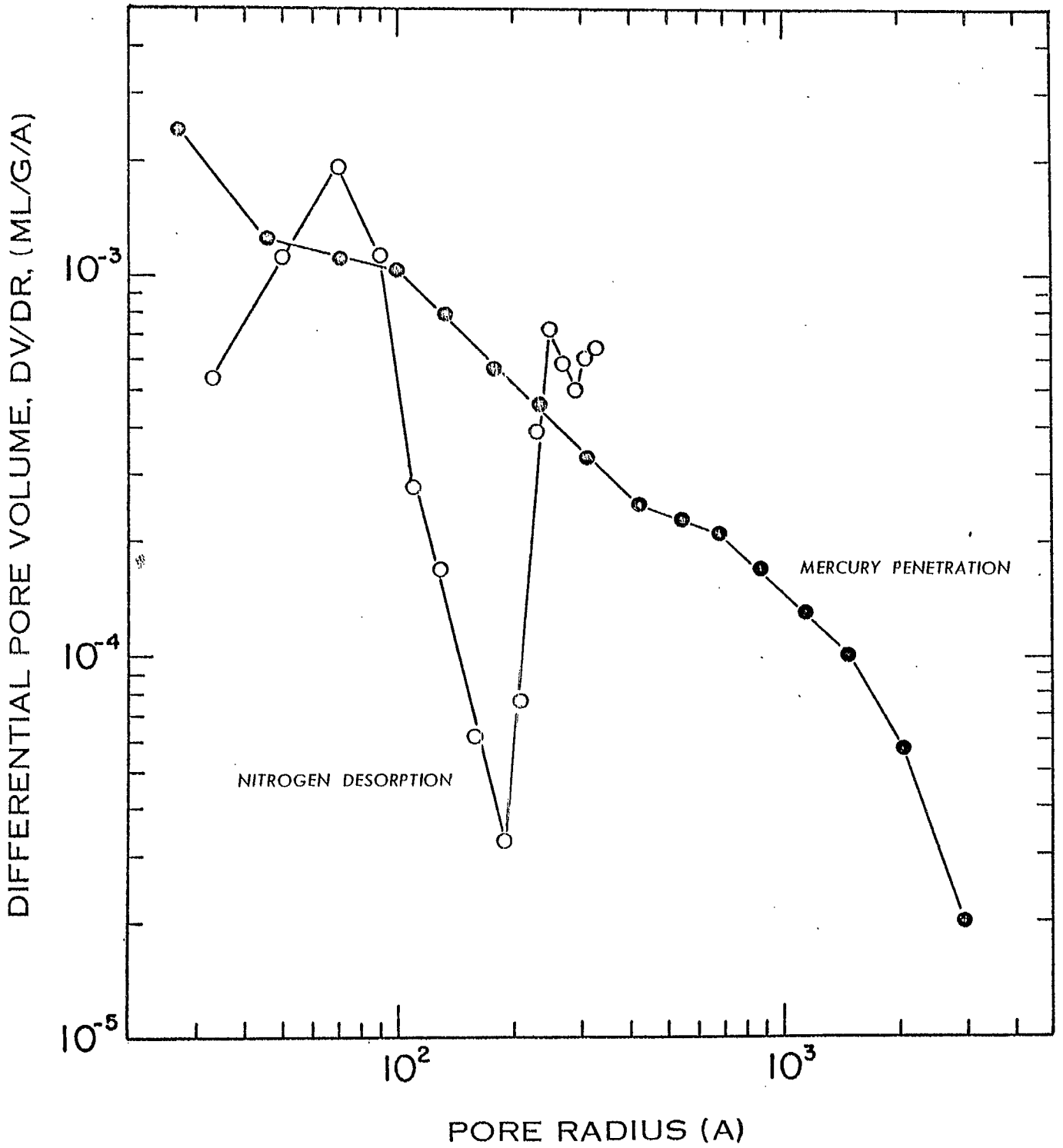
Figure 9 – The pore size distribution in the K–536 extrusions.

$$P = S\left(\frac{1}{r_1} + \frac{1}{r_2}\right).$$

Taking the contact angle into account, a more general form of the equation for the purpose of porosimetry would be:

$$P = -S\left(\frac{1}{r_1} + \frac{1}{r_2}\right)\cos a.$$

For a spherical surface $r_1 = r_2$, and the usual form of the equation, $P = -2S(\cos a)/r$, is obtained.

The general form of the equation is also of considerable interest, because it allows an estimate to be made of the magnitude and direction of the possible error attributable to non-circular pores. An extreme deviation from the assumption of circular pores is the case of a crack between parallel plates.
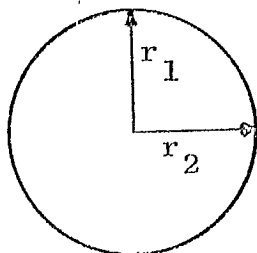
Circular
Pore
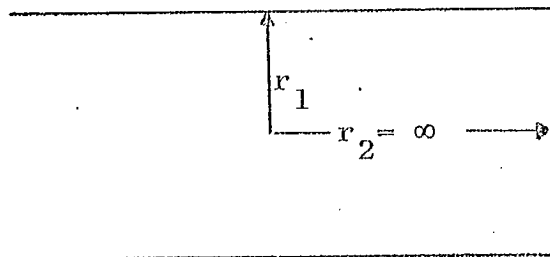
Crack

For the crack, $r_2 = \infty$, and the Washburn equation would be in error by a factor of 2 (i.e. mercury will penetrate a crack of width 50A at the same pressure as it would penetrate a circular pore of 100A diameter). In any porous material, such as alumina or silica gel, the shape of the pores must be between these two extremes. The general form of the equation would indicate that the error in the Washburn equation, attributable to non-circular pores, would result in the calculation of an average pore size somewhat larger than the true value. To a certain extent the results of the present investigation support this indication. In the case of the Union Oil catalyst, the peak in the pore size distribution, calculated from the mercury measurements, occurred at a radius approximately 20% greater than the peak radius

calculated from the nitrogen desorption isotherm. It is difficult
to decide just how far to extend any reasoning along these lines.
Both the contact angle of the mercury with the solid and the value
of the surface tension are probably affected by pressure and
pore size.

ACKNOWLEDGEMENT

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