THE MOVEMENT OF INTERFACES THROUGH PERMEABLE MEDIA

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INTRODUCTION

The flow of a homogeneous liquid through a porous permeable medium has been considered to be well described by an equation known as Darcy's Law which relates the flow rate of the liquid through the medium to the pressure gradient across the medium, the viscosity of the liquid, and to the single intrinsic flow property of the medium known as permeability. Darcy's Law is in fact the defining equation for permeability. Attempts have been partially successful in extending this relation, through the notion of relative permeability, to account for the flow of multiphase liquid systems through permeable media. See Muskat (1949). The development of a completely satisfactory theory of multiphase liquid flow has been retarded in part by the lack of quantitative information concerning the exchange of energy between the various phases and between the phases and the permeable medium.

An apparatus has been constructed which permits the measurement of the changes in energy involved in the movement of an interface through specimens of permeable media. The extremely small, uniform injection rates obtainable with the apparatus pump which injects the liquid necessary to move the interfaces, allow the investigator to neglect work done against viscous forces and to consider energy changes due only to the alteration of the various surfaces and interfaces present in the specimens. The experiments were primarily concerned with the movement of water-air interfaces through wettable and non-wettable, synthesized permeable specimens containing pore sizes ranging down to 0.001 microliters. The basic data consisted of the pressure required to move the liquid through the specimens at a constant volume flow rate and the pore sizes of the specimen. The derived data
consisted of information obtained by a more detailed analysis of the records obtained with the apparatus.

This thesis presents the following: definitions of terms and descriptions of certain basic phenomena, a description of the apparatus and experiments performed, comparisons of the basic results with existing theory, an analysis of derived experimental data with respect to the possibility of finding more suitable methods of characterizing permeable media and concludes with a discussion of extensions to the previously described experiments. The section entitled "surfaces and capillary phenomena" is included for completeness and may be omitted by the individual familiar with capillary effects in permeable media.
SURFACES AND CAPILLARY PHENOMENA

Surfaces and interfaces are frequently classified by designating the states of the materials which they separate; thus one may speak of liquid-gas, liquid-liquid, liquid-solid, solid-solid, and solid-gas surfaces. This list includes the types of surfaces which are found in a porous medium containing immiscible liquids and gases, therefore a discussion will follow concerning the general characteristics of these types of surfaces.

There are three general ways of describing the capillary phenomena due to surfaces. These methods employ the three physical properties known as surface tension, surface energy, and capillary pressure.

Liquid-gas interfaces or surfaces are characterized by the fact that they tend to contract spontaneously to the smallest possible area consistent with the boundary conditions imposed upon them. Because of this fact, work must be done in order to extend a surface and thus one is able to speak of the surface free energy associated with that surface. Adam (1938) explained that in order to extend a surface molecules must be brought from the interior of the liquid, where the cohesional forces due to the other molecules act in all directions, to the surface where the cohesional forces on the molecules are directed toward the bulk of the liquid. This accounts for the expenditure of energy in extending a surface. The specific surface free energy of a liquid-gas surface, as in all other types of surfaces, is expressed in the units of energy/surface area.

The surface free energy concept is sometimes replaced by a property known as the surface tension. The liquid-gas surface may be considered to be acted upon in all directions parallel to the surface by a hypothetical tension. In order to visualize this tension, one may imagine a line on the liquid surface of length L. The surface tension on the right exerts a force of magnitude F on the line to the right and the surface tension on
the left exerts an equal force \( F \) on the line to the left. The ratio \( F/L \) is known as the surface tension and is given in units of force/length.

The dimensions of specific surface free energy and surface tension are the same and their magnitudes are also the same so that they may be represented by the same symbol which is usually the letter \( \gamma \).

The third way of referring to the capillary phenomena is by the use of capillary pressure. If a liquid-gas surface is curved the pressure on the concave side of the surface is greater than that at a corresponding point on the convex side. The physical interpretation of this fact and the derivation of the fundamental equation of capillarity may be easily accomplished by referring to PLATE I Fig. 1. Adam (1938) considered the displacement of a liquid surface of principal radii \( R_1 \) and \( R_2 \) parallel to its original position. If the displacement is an infinitesimal distance \( \delta L \) then the area of the new surface after the displacement is given by;

\[
(R_1^2 \theta_1 + \delta L \theta_1)(R_2^2 \theta_2 + \delta L \theta_2)
\]

which becomes

\[
R_1^2 \theta_1 R_2^2 \theta_2 + \delta L (R_2^2 \theta_1 \theta_2 + R_1^2 \theta_1 \theta_2)
\]

if second order quantities in \( \delta \) are neglected. The increase in surface area is then

\[
\delta A = \delta L \left[ \frac{R_1^2 \theta_1 \theta_2}{R_1} + \frac{R_1^2 \theta_1 \theta_2}{R_2} \right].
\]

If the surface possesses a specific surface free energy of the magnitude \( \gamma \), then the energy which must be expended in the extension of the surface is

\[
\gamma A \delta L (1/R_1 + 1/R_2).
\]

This value is related to the pressure differential across the surface by the relation

\[
(P_1 - P_2)A \delta L = \gamma A \delta L (1/R_1 + 1/R_2)
\]

or

\[
P_1 - P_2 = \gamma (1/R_1 + 1/R_2).
\]

The latter equation is the fundamental equation of capillarity which states that the pressure differential across a liquid-gas surface is equal to the specific surface free energy multiplied by the sum of the reciprocals of
the principal radii of curvature of the surface.

According to Bikerman (1956) the interfaces between two liquids may be considered to exhibit the same capillary phenomena described for the liquid-gas surfaces and one speaks of interfacial tension and interfacial energy instead of surface tension and surface energy.

Solid-gas and solid-liquid surfaces are not able to contract spontaneously due to the limited mobility of the molecules in a solid, consequently these surfaces have never been observed to exhibit the characteristic of surface tension or interfacial tension. It is, however, still meaningful to speak of the specific surface energy or interfacial energy of the surfaces, and to define either as the energy necessary to produce a unit area of the new surface. One is nearly always correct in applying the surface energy concept but, while the other two methods are helpful in calculations, care must be exercised in their application.

When two immiscible fluid phases are at one point in contact with a solid phase the liquid-liquid interface usually rests at an angle with respect to the solid surface. This angle is known as the contact angle. If only one liquid is present it is designated as the angle in the liquid between the interface and the solid boundary. If the angle is less than 90° the liquid is said to wet the solid while for an angle greater than 90° the solid surface is said to be non-wettable. If two liquids are present the liquid with the smaller contact angle is said to be the wetting phase. The value of the contact angle is not always unique but may depend on the direction of movement of the interface or its previous history of movement. This phenomenon is known as the hysteresis of contact angle.

As an illustration of some of the possible phenomena which may occur, an interface in a uniform cylindrical capillary tube will be considered. Refer to PLATE 1 Fig. 2. The equation of capillarity becomes for this
EXPLANATION OF PLATE I

Fig. 1. The parallel displacement of a surface used in the derivation of the equation of capillarity.

Fig. 2. A hemispherical interface with a single radius of curvature R in a capillary tube of radius r and exhibiting a contact angle θ.

Fig. 3. An illustration of the effect of contact angle hysteresis on a fluid drop moving in the direction of the arrow.
case \( P_a - P_b = \frac{2\gamma}{R} \) where \( R \) is the radius of curvature of the hemispherical interface. In small capillaries the distortion of the interfaces due to the force of gravity is negligible. Now \( r = R \cos \theta \) where \( r \) is the radius of the cylindrical tube and \( \theta \) is the contact angle, so that \( P_a - P_b = 2\gamma \cos \theta / r \). Thus, in order for the interface to exist in a state of equilibrium, a pressure differential of magnitude \( 2\gamma \cos \theta / r \) must exist across the interface. Suppose that the interface is at rest and one wishes to move it to the right. This may be accomplished by injecting an additional amount of liquid \( A \) into the region to the left of the interface. If the injection is at an extremely low rate the pressure differential, \( (P_a - P_b) \), is increased by only an infinitesimal amount beyond the equilibrium value before the interface begins to move. The interface now moves to the right but it is at all times infinitesimally near a state of static equilibrium.

The work done in moving the interface along the capillary tube is proportional to the pressure differential. The pressure differential is in turn proportional to the contact angle and inversely proportional to the tube radius. Thus capillary forces play an important role in the movement of interfaces and surfaces through porous media which may contain pores whose "effective diameters" may be of the order of \( 10^{-5} \) cm or smaller and in which capillary pressures may be of the order of several cm of water and higher.

The hysteresis of contact angle mentioned previously may be easily described with the aid of PLATE I Fig. 3. Consider a column of liquid in a capillary tube in a horizontal position. When the column is at rest, \( \theta_a = \theta_r \). However when the column is moving with a uniform velocity to the right \( \theta_a \) may become larger than \( \theta_r \) and one can see, with the aid of the equation of capillarity, that a pressure differential must exist across the
column in order for it to make such a movement. Some experiments which considered the hysteresis phenomenon and accompanying features will be cited in this report. See page 57.

THE CHARACTERIZATION OF A POROUS MEDIUM

A porous medium generally refers to a solid material containing voids or pores which are capable of containing a fluid. The fraction of the bulk volume of a medium that is capable of containing fluids is known as the porosity of the medium. It is obvious that some of the pores must be interconnected in order for the medium to be able to transmit fluids. The fraction of the bulk volume consisting of interconnected pores capable of transmitting fluids is known as the effective porosity of the medium.

There are many examples of porous media such as bulk sand, lead shot, some rocks, cloth, paper, etc. Because each of these media is different in form it would be advantageous to be able to classify them according to the characteristics of their pores. This, however, is not easily done for it is difficult to give an accurate geometrical description of a pore. Several years ago Manegold divided pore spaces into three classes known as voids, capillaries and force spaces. Voids were designated as pore spaces in which the walls have little effect on the flow of fluids, capillaries as pore spaces in which the walls do have an effect on the flow of fluids in their interior and force spaces as pore spaces in which the flow is influenced by the molecular structure of the fluid. According to Scheidegger (1957) some desirable geometrical properties available for the description of a porous medium are porosity, pore size, specific internal area, grain size, and a property known as tortuosity.

Many different opinions have been expressed as to what should be the
definition of "pore size". Some have suggested that the interconnected pores may be thought of as being tubular in shape and that the pore size should refer to the diameters of such "tubes". This, however, is inconsistent since the cross sectional area of such tubes is not constant and their shape varies. Others have suggested that the diameter of a pore should be defined as the diameter of a bundle of uniform capillary tubes having the same fluid transmitting properties as the system of pores. These and many more proposed definitions are encountered in the literature and can be useful for the description of a given medium, but they are not able to provide a generally workable definition of much use to the experimenter. Scheidegger (1957) indicates that a possible way of defining a pore diameter, \( \delta \), at any one point in the pore space might be to designate it as the diameter of the largest sphere which contains the point and remains wholly within the pore space. According to this definition one might then talk of a cumulative pore size distribution designated by \( f(\delta) \); which is defined to be the fraction of the total pore space which has a pore diameter larger than \( \delta \), where \( \delta \) denotes the pore diameter as defined previously. Then

\[
f(\delta) = \int_{\delta}^{\infty} \alpha(\delta')d\delta'
\]

where \( \alpha(\delta) \) is the fraction of pores having diameters between \( \delta \) and \( \delta + d\delta \). \( f(\delta) \) is normalized so that \( f(0) = 1 \). Scheidegger's definition is an improvement over previous attempts and may be used to good advantage in describing pore size distributions of porous media but it is difficult to use quantitatively.

The method described in a following section of this paper (see page 41) provides a simple, direct means of specifying pore size and of determining the pore size distribution in a permeable medium. The determination is based upon the fluctuations in the injection pressure as an interface is moved through the medium. See PLATE III.
Another property of a porous medium often used in its characterization is known as the **specific internal area** and is defined as the ratio of the internal surface area to the bulk volume. This property can be measured in naturally occurring media by any one of several methods which will not be discussed in this paper. See Scheidegger (1957). This quantity is used by analogy of the actual porous media to the dynamical properties of capillaric models. As an example, the fluid transmitting properties of a bundle of uniform capillary tubes with a given specific internal area can be employed to predict the same properties of a naturally occurring medium by comparing the specific internal areas of the two. Experiments dealing with the effect of the specific internal area of a permeable specimen on the work required to move an interface through the specimen will be discussed in succeeding portions of this paper.

The term **tortuosity** is mentioned merely because of its frequent use in the literature of porous media. It was used, when first introduced, to denote the average length of the flow path of a fluid particle from one side of the medium to the other. It too has come into use to describe similar properties of constructed capillaric models.

It may be realized from the preceding discussion that the concepts discussed leave much to be desired in providing a quantitative characterization of porous permeable media. The author believes that the new approach to the study of the flow of liquids through porous media described in this paper enables one to give more logical and experimentally useful definitions to some of the concepts discussed in the preceding paragraphs. The method employed, the apparatus, and the experimental techniques involved will be explained in subsequent sections of this paper.
EXPERIMENTAL METHOD

The basic experiments consisted of measuring the work done in moving interfaces through synthesized permeable media which were constructed in short lengths of cylindrical pyrex or teflon tubing of approximately 1.0 mm diameter. The flow paths in the tubes were of controlled cross sectional areas. The cross sectional area was controlled either by constrictions in the diameters or by carefully packing glass spheres in the tube. The experiments were of three general types involving the movement of: (1) single air-liquid interfaces through both wettable and nonwettable media, (2) single water-oil interfaces through various media, and (3) multiple interface systems through simple capillary tubes.

The apparatus provided a record of the instantaneous capillary pressure at the injection face of the permeable medium vs the injected volume of liquid. A planimeter was used to measure the area under the resulting curves to determine the work done by the pump on the fluid system. Work done by the pump on the system was designated a positive quantity. The work done for a given amount of liquid injected was equated to the sum of all the terms that might represent energy changes in the system as follows.

\[ \int_{v_i}^{v_f} P \, dv = \sum \gamma_A \Delta A + js + G + K_v + E_e \]  
(1)

where \( P \) is the pressure at the injection face in excess of ambient pressure and may be positive or negative, \( \gamma_A \) is the surface free energy per unit area of any surface whose area is altered by an amount \( \Delta A \) during the flow of the volume of liquid \( (v_f - v_i) \), \( j \) is a constant which when multiplied by the linear speed \( s \) of the interface yields work done against viscous forces, \( K_v \) is the kinetic energy of the water column being moved by the pump, \( G \) is the work done against gravity, and \( E_e \) is the potential energy stored in the elastic elements of the apparatus injection system.

The left hand side of equation (1) was evaluated by the measurement
of the area under the P vs dv curve. Of the terms on the right side, G was eliminated by operating the permeable specimens in a horizontal position, \( K_v \) was computed to be of the order of \( 10^{-5} \) ergs and therefore negligible, and \( j_s \) was demonstrated to be negligible by operating at small fractions of the injection rates at which the injection pressure rose measurably with an increase in interface velocity. \( E_b \) was assumed to be conservative in energy thus contributing nothing to the integral over a complete cycle of expansion and contraction of an interface. The analysis of the experiments concerned primarily the study of the \( \chi A \) terms.

**DESIGN AND OPERATION OF EQUIPMENT**

**Apparatus Operation**

The apparatus and its operation are illustrated by the block diagram on PLATE II. Liquid is driven at a selected volumetric rate by a variable speed(1) pump(2) to a pressure transducer(3) located in the flow line immediately ahead of the injection face of the porous medium specimen(4). The specimen is connected to a reservoir(5) containing \( \Delta V \) or another liquid depending upon the nature of the interface in the specimen. The reservoir serves to reduce "end effects". The electrical signal from the pressure sensitive transducer is fed into an amplifier(6) the output of which is recorded on a strip chart recorder(7). The injected volumetric increments are recorded on the edge of the recorder chart by an event marker which receives its signal from a microswitch(8) on the pump. The final output is a trace of the injection pressure vs the injected volume. See PLATE III.

Photographs of the apparatus appear in PLATES IV and V. The pump consists of a pair of cylinders(1) with screw driven pistons powered by a variable speed, reversible motor(2) through a transmission(3). The screws(4) which drive the pistons are connected through a system of gears (5)
EXPLANATION OF PLATE II

A block diagram of the apparatus. The double lines represent liquid carrying tubes. The single lines represent electrical connections.
EXPLANATION OF PLATE III

Photographs of the injection pressure traces obtained by moving a water-air interface through six specimens of the indicated bead diameter and packing.

Fig. 1. Water-proof spheres in 1.0 mm teflon tube in a single pack.

Fig. 2. " " " " " " a double pack.

Fig. 3. " " " " " " a triple pack.

Fig. 4. Water-wettable spheres in a 1.11 mm pyrex tube in a single pack.

Fig. 5. " " " " " " a double pack.

Fig. 6. " " " " " " a triple pack.

The null pressure in each record is denoted by a heavy line. Each volume increment at the top of each record represents the injection of 1/16 of a microliter of water.
which allow shaft speed ratios of 1:4, 4:1 and 1:1. A pair of reservoirs store the working fluid for each cylinder and are isolated from the system except during the refilling of the cylinders. The cylinders themselves are made of brass. The piston heads are teflon which allows the pistons to slip uniformly along the cylinder walls with no pressure noise to disturb the system. Volumetric injection rates may be selected through adjustments of the motor controller, the transmission, and the size of the cylinder used. The rates range from $2 \times 10^{-2}$ cm$^3$/sec, obtainable with the 3/4 in. diameter cylinder, down to $10^{-7}$ cm$^3$/sec, obtainable with the 3/16 in. diameter cylinder.

The liquid is transmitted to the specimen from the pump in 1.0 mm teflon tubing. The pressure transducer is connected to the injection line immediately preceding the specimen. The system valving is accomplished with teflon lined, gas tight miniature valves made by the Hamilton Company. The transducer is a Dynisco Model PT 25-30 which utilizes a metal diaphragm and an unbonded strain gauge in the form of a four-active-arm wheatstone bridge in the conversion of the pressure signal into an electrical signal. The signal is amplified by means of a Brush Dual Channel Strain Gauge Amplifier, Model RD 4622 00. The output of the amplifier is recorded on a Brush Mark II Recorder.
EXPLANATION OF PLATE IV

A photograph of the pump.

1. cylinders
2. motor
3. transmission
4. driving screws
5. thread speed ratio gears
6. cylinder reservoirs
EXPLANATION OF PLATE V

A photograph of the complete apparatus.

7. motor controller
8. specimen
9. transducer
10. amplifier
11. recorder
Apparatus Calibration

The dual channel apparatus recorder was used for single channel operation by adjustment of the pen bias so that the right pen began to record when the left pen had reached full scale. This accounts for the division between the upper and lower portions of each record. See PLATE III. The pressure scale was calibrated by connecting a 1.0 mm teflon tube to the system in a vertical position at the place normally occupied by the specimens and comparing the recorder pen deflections with the differences in heights of the liquid levels. The desired calibration was obtained through adjustments of the gains of both amplifiers.

The specimens were mounted at a height of approximately 15 cm above the transducer. This provided a static head sufficient in magnitude to prevent the transducer diaphragm from being subjected to pressures less than atmospheric and thereby prevented irregular diaphragm movement. The zero reference point was established by attaching a liquid reservoir, with diameter large enough to eliminate capillary effects, to the system and adjusting the reservoir liquid level to correspond to the level at which the specimen was to be mounted. The strain gauge amplifier was then adjusted to place the zero point at the desired position on the recorder chart.

The experiments were performed with the specimens mounted in a horizontal position. During the execution of the experiments involving air-liquid interfaces, one end of the specimen was left open to the atmosphere and the pressures measured were deviations from atmospheric, while during the execution of experiments involving liquid-liquid interfaces one end of the specimen was placed in a reservoir containing the liquid on the reservoir side of the interface.
Apparatus Performance

Because of the volumetric elasticity of the apparatus injection system, an increase in system pressure was accompanied by a corresponding increase in the system volume. This had the effect of limiting the magnitude of the small pressure changes that could be detected as an interface moved through specimens containing small pores. The system elasticity was measured by injecting liquid into the system when it was closed off at the specimen position and noting the system pressure vs the injected volume. The resulting curves, which appear in PLATE VI, illustrate both the system pressure and the injected volume as functions of time. Liquid was injected at a slow uniform rate until time A when the injection was stopped. During this time the system leakage noticeably reduced the slope of the pressure curve. At time A, when the injection ceased, the pressure dropped rapidly before leveling off as time B was approached. At time B the system was vented, reducing the pressure to ambient. Liquid was again injected from time B to time C until the pressure had increased to about 10 cm of water in order to determine the leak rate in the pressure range in which nearly all of the experimentation was done. The leak rate in that region was such that a reduction in pressure of only 1 mm of water occurred over a period of 90 sec. This corresponded to the loss rate of liquid negligible in comparison to the smallest injection rates employed during the experimentation.

One can define a quantity $K$ which is the ratio of the change in system volume($\Delta V$) to the change in system pressure($\Delta P$) which causes the expansion. The quantity, $K = \Delta V/\Delta P$, is in units of volume/pressure and is a function of the system elasticity and of the system pressure. Appreciable leakage will introduce errors.
EXPLANATION OF PLATE VI

Isolated system pressure and injected volume as functions of time. Injection was stopped at time A, continued at time B, and then stopped again at time C.

--- denotes injection pressure

----- denotes injected volume
In the pressure range of 0 to 10 cm of water $K$ was indicative of only the system elasticity since the leak rate was negligible in that region and its value taken from PLATE VI is,

$$K = 1.25 \times 10^{-6} \text{ cm}^3 \text{ per mm of water pressure}.$$  

This means that an increase of system pressure of 1 mm of water was accompanied by an increase in system volume of $1.25 \times 10^{-6} \text{ cm}^3$ in the pressure range in which the experiments were performed.
EXPERIMENTATION

Water-air Interfaces through Synthesized Permeable Media

Some preliminary experiments involving the simplest porous permeable media were performed mainly to check the validity of the apparatus operation and the various techniques employed. Several measurements were taken by immersing uniform cylindrical capillary tubes both of the non-wettable (teflon) and wettable (pyrex) type in a beaker of distilled water and measuring the capillary depression or rise and then immersing the tubes further and repeating the measurements until enough data were obtained to provide representative values. The specimens were then connected to the calibrated apparatus in a horizontal position and a comparison made of the injection pressure recorded by the apparatus and the height of the average capillary depression or rise. It was found that to within an accuracy of 10% the height of the capillary depression or rise checked with the injection pressure as the interfaces were moved slowly along the tubes. It was also noted that there were no appreciable changes in the injection pressure over a wide range of interface velocities from zero upward verifying that the work done against viscous forces was negligible.

When a water-air interface is moved along a uniform cylindrical teflon tube, water-teflon surface is created at a rate equal to the rate at which air-teflon surface is destroyed. The area of the water-air interface does not change. On the right hand side of Equation (1), page 12, let \( \gamma_1 \Delta A_1 \) represent the effect of the water covering new sections of the tube wall, \( \gamma_2 \Delta A_2 \) the effect of the removal of air from the tube wall and \( \gamma_3 \Delta A_3 \) the effect of the water-air interface. Since the tube is cylindrical, \( \Delta A_3 = 0 \) and because the water replaces the air on the tube wall, \( \Delta A_1 = -\Delta A_2 \) so that \( \gamma_1 - \gamma_2 \Delta A_1 \) represents the right hand side of Equation (1).

The previously described situation is not often encountered in
the movement of interfaces through most permeable media, since the area of
the water-air interface does not remain constant. In order to learn whether
or not the alternate expansion and contraction of a water-air interface
contributes to Equation (1) as this interface is moved through a specimen
with varying cross sectional area, a permeable medium was synthesized by
fitting a series of pinch clamps on a 1.0 mm uniform cylindrical teflon
tube in such a manner that the cross sectional area of the tube changed from
circular to slit-like and then back to circular but the total surface area
per cm of tube length was unchanged. The specimen was 1 cm in length and
was fitted with 5 pinch clamps. The cross sectional area of the tube was
reduced from 0.0079 cm$^2$ to 0.0020 cm$^2$ in the region of each clamp. If it
is assumed that the nature of the tube surface is not altered, the $\int P \, dv$
should be the same for one cm length of the contorted tube as for one cm
length of cylindrical tube if the five alternate expansions and contractions
of a water-air interface are indeed conservative in energy. Since the surface
free energy of a water-air interface is about 70 ergs/ cm$^2$, the work done
in extending such an interface 5 times by 0.0059 cm$^2$ each time is
$5 \times 70 \times 0.0059$ or slightly over 2 ergs. The experimentally determined
work per cm of uniform cylindrical tubing was $14.4 \pm 0.3$ ergs while that
for the contorted tube was $14.9 \pm 0.7$ ergs. The discrepancy is consider-
able less than 2 ergs indicating that energy is returned to the apparatus
when the interface contracts.

Although the previously described experiment did not provide conclu-
sive evidence of the complete conservation of the energy involved in the
expansion and contraction of a water-air interface, it did indicate that
an investigation of additional $\gamma_4 \Delta A_4$ terms could probably be continued
without concern for the $\gamma_3 \Delta A_3$ term.

The interface was visually observed through the transparent teflon
as it moved through the series of constrictions and a discussion of the injection pressure as the interface progressed through a constriction is in order at this point. Since water does not wet teflon, the contact angle is obtuse and the injection pressure must therefore be greater than ambient or to follow the previously suggested convention it must be positive. The movement of the water-air interface through a constriction is depicted in the figures of PLATE VII. The injection pressure remained constant until the interface had progressed into region A. At this point the sharp curvature of the surface wall tended to change the shape of the interface, that is to "flatten" it slightly which caused the injection pressure to drop slightly. This effect was short-lived since the interface area soon began to decrease at a rapid rate as the interface approached region B and the injection pressure rose sharply. This was consistent with the equation of capillarity, \( P = \gamma (1/R_1 + 1/R_2) \), as \( R_1 \) became small causing \( 1/R_1 \) to increase and \( R_2 \) remained nearly the same in magnitude. The peak pressure was attained as the interface reached region B and then began dropping at a rate unequal to the rate with which it had increased. The difference in rates was due to the fact that the interface proceeded from region B to region C in the manner illustrated in PLATE VII Fig. 3; the pinch being not quite symmetrical allowed the interface to proceed first along the side having the wider opening.

**Work vs Internal Surface Area**

In order to study additional \( \gamma_1 \Delta A_1 \) terms, uniform cylindrical tubes were packed with beads (selected glass spheres) and the work required to move a single water-air interface through each of these specimens was measured. The bead surface introduced an additional term, \( \gamma_2 \Delta A_2 \), into Equation (1). The specimens were of three classes: wettable tubes
EXPLANATION OF PLATE VII

Fig. 1. A plot of injection pressure vs injected volume as a water-air interface passes through a teflon capillary tube with a constriction.

Fig. 2. A side view illustrating the progress of the interface through the constriction.

Fig. 3. A top view illustrating the progress of the interface through the constriction.
PLATE VII

FIG. 1

INJECTED VOLUME

FIG. 2

FIG. 3
containing wettable beads, non-wettable tubes containing wettable beads and non-wettable tubes containing non-wettable beads. The total internal surface of each class of specimens was determined by the bead packings employed. See PLATE VIII and Table 1. The beads were matched for size by visual comparison under a microscope and were also selected for sphericity by rolling them down an inclined plane.

When a water-air interface was moved through a 1.11 mm pyrex tube containing wettable beads the injection pressure remained less than ambient and the apparatus pump did negative work in moving the interface. Since the water was injected by the pump at a very small rate, the interface could move only at a rate corresponding to the injection rate and therefore remained in a state of quasistatic equilibrium.

The injection pressure was at all times greater than ambient as the interface progressed through teflon (non-wettable) tubes containing non-wettable beads and the apparatus pump did positive work in moving the interface. The injection pressure of the teflon tube containing the wettable beads was sometimes positive, sometimes negative during the course of the experiments with maximum and minimum values being intermediate in value compared to the previous completely wettable and non-wettable specimens. PLATE III illustrates six individual records taken as a water-air interface passed through the specimens indicated in the explanation of PLATE III.

An upward movement along the vertical axis of each record corresponds to an increase in the injection pressure with each major division representing 1 cm of water pressure. A movement to the left along the horizontal axis corresponds to an increase in the injected volume with the events at the top of each record indicating an injection of a certain volume of liquid.

The work required to move a water-air interface through each of the specimens was measured and compared with the internal surface area of
EXPLANATION OF PLATE VIII

Illustrations of some bead packings possible in cylindrical tubes.

Fig. 1. single pack
Fig. 2. double pack
Fig. 3. triple pack
Fig. 4. hexagonal pack
<table>
<thead>
<tr>
<th>spec.</th>
<th>tube</th>
<th>bead pack</th>
<th>$\Delta A_1$</th>
<th>$\Delta A_4$</th>
<th>$\Delta A_1 + \Delta A_4$</th>
<th>average $\int_{pdv}$ per cm length of tube (ergs)</th>
<th>average $\int_{pdv}$ per pore (ergs)</th>
<th>$\delta_{total}$ (ergs/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>1.11 mm pyrex</td>
<td>none</td>
<td>0.35</td>
<td>0.00</td>
<td>0.35</td>
<td>-9.7</td>
<td>-</td>
<td>-30.0</td>
</tr>
<tr>
<td>2.</td>
<td>&quot; &quot;</td>
<td>single</td>
<td>0.35</td>
<td>0.26</td>
<td>0.61</td>
<td>-12.5</td>
<td>-1.08</td>
<td>-20.1</td>
</tr>
<tr>
<td>3.</td>
<td>&quot; &quot;</td>
<td>double</td>
<td>0.35</td>
<td>0.52</td>
<td>0.87</td>
<td>-14.7</td>
<td>-0.20</td>
<td>-17.5</td>
</tr>
<tr>
<td>4.</td>
<td>&quot; &quot;</td>
<td>triple</td>
<td>0.35</td>
<td>0.55</td>
<td>0.90</td>
<td>-18.3</td>
<td>-0.18</td>
<td>-17.6</td>
</tr>
<tr>
<td>5.</td>
<td>&quot; &quot;</td>
<td>hexagonal</td>
<td>0.35</td>
<td>0.80</td>
<td>1.15</td>
<td>-27.4</td>
<td>-0.06</td>
<td>-23.3</td>
</tr>
<tr>
<td>6.</td>
<td>&quot; &quot;</td>
<td>random</td>
<td>0.35</td>
<td>1.23</td>
<td>1.58</td>
<td>-35.4</td>
<td>-0.06</td>
<td>-22.3</td>
</tr>
<tr>
<td>7.</td>
<td>1.0 mm tef.</td>
<td>none</td>
<td>0.31</td>
<td>0.00</td>
<td>0.31</td>
<td>14.4 ± 0.3</td>
<td>-</td>
<td>46.0</td>
</tr>
<tr>
<td>8.</td>
<td>1.0 mm tef. (contorted)</td>
<td>0.31</td>
<td>0.00</td>
<td>0.31</td>
<td>14.9 ± 0.7</td>
<td>-</td>
<td>47.5</td>
<td></td>
</tr>
<tr>
<td>9.</td>
<td>1.0 mm tef.</td>
<td>single</td>
<td>0.31</td>
<td>0.20</td>
<td>0.51</td>
<td>6.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10.</td>
<td>&quot; &quot;</td>
<td>triple</td>
<td>0.31</td>
<td>0.53</td>
<td>0.83</td>
<td>2.7</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$\Delta A_1$ = tube surface per cm of tube length  
$\Delta A_4$ = bead surface  
$\delta_{total}$ = work per cm tube length/($\Delta A_1 + \Delta A_4$)
the specimens. PLATE IX Fig. 1 illustrates the work per unit length of specimen required to move a water-air interface through the synthetic wettable specimens constructed of wettable beads in pyrex tubes as a function of the internal surface area per unit length. The internal surface area included contributions from the tube wall and from the bead surface. The first pair of points represents the range of values of the work per unit length required to move the interface along a 1.11 mm pyrex tube free of beads. These values were recorded both before and after the experimentation involving the beaded specimens, and the most representative value probably lies in the lower part of the range. The other groups of points were obtained by performing two or more experiments with each of the specimens whose surface per unit length is indicated in Table 1. The uncertainty in the knowledge of the internal surface per unit length of the specimens stemmed primarily from the slight variations in the diameters of the beads. The length of travel of the interface through each specimen was accurately measured with a traveling microscope and the number of beads encountered was accurately known except in the specimen containing beads too small to recognize an ordered packing. This smallest bead packing contained beads with a diameter of about 0.27 mm and was called a "random pack". The vertical variation of the points obtained with a given specimen was most likely due to the inaccurate reproduction of the states of cleanliness of the internal surfaces, since this variation increased with the increase in the internal surface area of the specimens. An attempt was made to maintain reproducible cleanliness rather than absolute cleanlinesses. The specimens were flushed with organic solvents, cleaning solution, and distilled water after each use. They were dried by drawing air at a temperature of about 110°C through them.

PLATE IX Fig. 1 indicates that the magnitude of the work per unit
EXPLANATION OF PLATE IX

Fig. 1. A plot of the work per unit length of specimen required to move a water-air interface through wettable specimens as a function of the internal area per unit length of specimen.

Fig. 2. A plot of the work per unit length of specimen required to move a water-air interface through specimens of wettable beads in teflon tubes versus the total internal area per unit length of specimen.
PLATE IX

FIG. 1

FIG. 2
length of specimen required to move the interface through the specimens was probably a linear function of the internal surface area per unit length of specimen. The fact that the first group of points are situated relatively high on the graph compared to the others might be a consequence of the tube surface being slightly different in nature from the bead surface, a possibility which would have no effect on the linearity of the remainder of the graph.

Figure 2 of PLATE IX illustrates the work per unit length of specimen required to move an interface through specimens constructed of wettable beads in 1.0 mm teflon tubes as a function of the total internal surface area. The first point was obtained using a plain teflon tube void of beads, while the other two were obtained with the same tube containing wettable beads in single and triple packs, respectively. The linear decrease in the work per unit length of specimen required to move the interface as the wettable surface per unit length increased is further evidence that the work done in moving interfaces quasistatically through permeable media is a linear function of the internal surface area of the media, the validity of which has been intuitively assumed in most literature. The fact that the first point is high on the graph in relation to the other points is a consequence of the specific surface free energy of a teflon-water interface being greater in magnitude than that of a pyrex-water interface. See TABLE 1.

Considerable difficulty was encountered in obtaining reliable data involving the experiments with the completely non-wettable specimens since it was impossible to move an interface through even the most elementary bead packing without by-passing some air bubbles which remained in the specimens. The experiments were also performed with the specimens in a vertical position in an attempt to eliminate the air bubbles but were
not successful. Since it was impossible to determine the change in the air-liquid surface due to the formation of the bubbles Equation (1) contained a $\Delta A$ term which could not be evaluated and the effect of increasing the internal surface area on the work required to move the interface through the specimen was not determined. It was observed, however, that more work per unit length of specimen was required to move the interfaces along tubes containing beads than for the tubes void of beads.

**Pore Size Distributions**

It may be noted from PLATE III that the injection pressure behaved in a seemingly discontinuous manner in both the wettable and non-wettable cases. Visual observation of the experiments indicated that the interface progressed through the packed beads in a correspondingly unsteady manner. For the non-wettable case it was noted that the injection pressure increased as the interface moved into the regions of smaller cross sectional area while for the wettable case it decreased as the interface moved into the regions of smaller cross sectional area. The rapid pressure changes occurred as the interface moved suddenly from a region of small cross sectional area into an adjacent region of relatively large cross sectional area in the non-wettable case. In the wettable case they occurred as the interface moved suddenly from regions of large cross sectional area into an adjacent region of smaller cross sectional area. In both cases a small volume of liquid was supplied by the elasticity of the system in order for the rapid movements to take place.

This action provides the physical basis for defining the pore volumes in both the wettable and non-wettable specimens as being the volumes of liquid injected between adjacent pressure surges and enables one to obtain pore size distributions of the specimens. Histograms displaying the pore
size distributions were made by dividing the total pore volumes of each specimen into approximately ten classes and plotting the percent of the total pores whose volumes fell into each of the classes. Two pore size distribution histograms of each individual synthetic porous medium under investigation are illustrated in PLATES X and XI in order to demonstrate the reproducibility of the results obtainable by the method. The limited resolution of the apparatus, due in part to its volumetric elasticity, prevented pores smaller than those in the random pack specimen from being detected. It is also recognized that the system elasticity did affect the delineation of the pores in the specimens studied. Means of improving this situation are under consideration.

Pore by Pore Analysis of Work

The pores formed by the beads in the wettable synthetic specimens vary both in volume and shape from specimen to specimen. A study of the various bead packings depicted in PLATE VIII provides information concerning the pores found in the specimens. First of all, each pore in the double pack specimen appears to be bounded by four convex spherical surfaces due to the beads and by one concave surface due to the tube. All of the pores in the triple pack specimen appear to be formed in the same manner except for the pores in the central region formed only by convex spherical surfaces. It is apparent that the percentage of pores formed only by convex spherical surfaces increases as one progresses specimen to specimen from the double pack to the random pack. The result is that the surface to volume ratio of the pores also increases in going from the double pack to the random pack specimens. This increase is a function of the shapes of the pores and is over and above the increase in the surface to volume ratio due only to a decrease in volume of the pores.
EXPLANATION OF PLATES X AND XI

Porosity distribution histograms of wettable synthetic specimens.

Figures 1 and 2. double pack
Figures 3 and 4. triple pack
Figures 5 and 6. hexagonal pack
Figures 7 and 8. random pack
FIG. 1

FIG. 2

FIG. 3

FIG. 4

FIG. 5

FIG. 6

PORE VOLUME IN $10^{-5}$ CM$^3$
The records enable one to measure the work done in moving an interface through each individual pore in a porous medium. PLATE XII illustrates a graph of the work per pore required to move a water-air interface through pores in the wettable synthetic specimens as a function of pore volume, each point representing one pore. The line drawn through the points obtained from the hexagonal and the random pack specimens has a considerably greater slope than those lines drawn through the points obtained from the double and triple pack specimens. Although the analysis of the differences in the slopes of these lines is incomplete, it is believed that they are indicative of the pore surface to volume ratio in each of the specimens thus giving a graphical method of estimating the differences in pore shapes.

As mentioned previously, the triple pack specimen was the least complex specimen which appeared to have small pores in the central regions of the specimen bounded only by convex spherical surfaces. An analysis of the injection pressure records along with visual observation of the interface movement yielded some unexpected results which should be related at this point.

The interface moved along the cylindrical tube and approached the first bead layer as depicted below.

[Diagram of beads and tube]

When the interface had reached a position very near the first bead layer it suddenly moved into the region between one of the beads and the tube wall causing an abrupt injection pressure drop. It proceeded in a similar manner to move around each of the beads in the layer causing comparable injection
A plot of the work per pore required to move a water-air interface through pores in the synthetic wettable specimens versus specimen pore volume.

denotes pores in double pack specimen

• triple pack specimen

△ hexagonal pack specimen

○ random pack specimen
pressure drops until the entire first bead layer had been wetted. The
procedure was then repeated as it moved over the remaining layers of beads.
A comparison of the number of injection pressure fluctuations with the
number of pores formed by both the bead surface and tube surface indicated
that the movement through the small pores in the central region of the speci-
men was included in the movement through the larger outside pores thus
producing no distinguishable injection pressure fluctuations. An inspection
of Figs. 3 and 4 of PLATE X supports this interpretation since approximately
1/3 of the pores in the triple pack specimens were recorded as being
distinctly larger than the remaining 2/3 of the pores.

The distinct possibility of the magnitude of the specific surface free
energy of the tube-water interface being larger than that of the bead-water
interface might have been responsible for the unexpected manner of movement
of the water-air interface through the triple pack specimen. It was not
possible to observe the pore by pore movement through the smaller pores
bounded only by bead surfaces found in the specimens containing smaller
beads, but the number of pores as recorded by the apparatus and their sizes
indicated that the interface progressed through them in the regular manner.

In light of the previous discussion it appeared advisable to consider
the work per pore/pore volume, a quantity which will be denoted by the
letter M. If it is assumed that the work done in moving an interface
through a pore is proportional to the surface area of the pore then the
work $W_k$ done in moving an interface through the $k^{th}$ pore of a specimen can
be expressed as $W_k = \alpha_k r^2$ and its volume as $V_k = \beta_k r^3$ where $r$ is an
unspecified linear dimension and $\alpha_k$ and $\beta_k$ are proportionality factors
which depend upon the pore shape. Now $M_k$, the work per pore/pore volume of
the $k^{th}$ pore, is given by

$$M_k = \frac{\alpha_k r^2}{\beta_k r^3} = \delta_k r^{-1}$$
where $\delta_k$ is the ratio of the two proportionality factors. The parametric equations of interest are

$$M_k = \delta_k r^{-1}$$

and

$$V_k = \beta_k r^3$$

which become upon elimination of the parameter $r,$

$$M_k = \epsilon_k V_k^{-1/3},$$

with $\epsilon_k = \delta_k \beta_k^{1/3}$. A graph was made of the work per pore/pore volume vs pore volume when a water-air interface is moved through the wettable specimens. This graph appears in PLATE XIII. The solid curve was drawn through the experimental points. The dashed curve is a plot of the equation, $y = 65 x^{-1/3}$. This particular equation was chosen since the curve it defines passes through the middle of the random pack point cluster; the cluster representing pores the most uniform in size and shape. Although the solid curve is similar in form to the dashed curve, it departs from the dashed curve in increasing amounts as one goes from the random pack to single pack points. This is consistent with the previous interpretation concerning the decrease in the surface to volume ratio in going from pores in the random pack to those in the single pack.

**Work per Unit Bulk Volume**

The total pore volume of a porous medium specimen containing 100 pores is given by

$$V_p = \sum R_k V_k$$

where $p_k$ represents the percent of pores in the volume interval $V_k$ as taken from the pore size distribution histograms. The total work $E$ done in moving an interface through the specimen is given by

$$E = \sum p_k W_k,$$

where $W_k$ is the work per pore of volume $V_k$. The substitution of

$$W_k = M_k V_k$$

into the second equation yields,

$$E = \sum p_k V_k M_k.$$
EXPLANATION OF PLATE XIII

A plot of the work per pore/pore volume required to move a water-air interface through synthetic wettable specimens versus specimen pore volume. The dashed curve is a plot of the equation, \( y = 65 x^{-1/3} \). The solid curve was drawn through the experimental points.

Legend:  
1. random pack  
2. hexagonal pack  
3. triple pack  
4. double pack  
5. single pack
Now \[ V_p = \phi V \]
where \( \phi \) is the porosity of the medium and \( V \) is the bulk volume of the portion of medium in question. From these equations
\[
V = V_p / \phi = \sum p_k V_k / \phi,
\]
so that the work per unit volume required to move an interface through the medium is
\[
E/V = (\sum p_k V_k M_k / \sum p_k V_k) \phi
\]
which is a weighted average of \( M_k \), the work per pore/pore volume, illustrated in PLATE XIII times the porosity of the medium. This calculation shows quantitatively that the work expended in the movement of a water-air interface through a wettable specimen with smaller pores is greater than for the movement of the same interface through a specimen with larger pores but with the same porosity. This result and its ramifications could possibly be of considerable value in the field of reservoir mechanics.

Histograms obtained by plotting the products \( p_k V_k \) of the preceding discussion vs the pore volumes appear in PLATE XIV. The right hand scale of each histogram was obtained by setting \( \sum p_k V_k = 1 \). This scale indicates the proportion of the total pore volume represented by each class of pore volume in each indicated specimen. For example in the double pack specimen (Fig. 1 PLATE XIV), approximately 30% of the specimen pore volume was represented by pores with volumes in the interval from 8.5 to \( 9.5 \times 10^{-5} \) cm\(^3\).

The histograms of PLATES X and XI indicate the percent of the total number of pores in each pore volume class interval while those of PLATE XIV indicate the percent of the total pore volume represented by each pore volume class interval. A comparison of the two forms of histograms and the plot of the work per pore/pore volume along with relative permeability data could possibly provide a clearer understanding of relative permeability. It is suggested that this be investigated.
EXPLANATION OF PLATE XIV

Histograms illustrating the percent of pores in each volume interval times the median of the volume interval as a function of the pore volume for wettable synthetic specimens. The right hand scale is normalized to provide the percent of total pore volume versus pore volume.

Fig. 1. double pack
Fig. 2. triple pack
Fig. 3. hexagonal pack
Fig. 4. random pack
PLATE XIV

**Fig. 1**

- **Pore Volume Class Marks**
  - CM^3
  - Bars representing pore volume classes for different CM^3 values.

**Fig. 2**

- **Specimen Volume**
  - Bars indicating specimen volumes per CM^3.

**Fig. 3**

- **Percent of Total Pores**
  - Bars showing the percentage of total pores in units of 10^-5.

**Fig. 4**

- **Percent of Total Pore Volume**
  - Bars illustrating the percentage of total pore volume in 10^-5 CM^3.
Since the movement of water-oil interfaces through permeable media is of considerable practical importance, an attempt was made to repeat the previously described experiments using a water-oil interface instead of a water-air interface. The same specimens were employed as those described previously except that they were modified by placing a side injection tube through the wall of the capillary tube immediately ahead of the bead packs. The side tube permitted the injection of oil into the specimen. The water-oil interface was formed in the capillary tube in a position preceding the bead packs by first injecting water until the water-air interface reached the region where the side injection tube was installed and then by injecting oil until the resulting oil-air interface had progressed through the specimen into the reservoir. It was then possible to move the water-oil interface through the remaining portion of the specimen by injection of water with the apparatus pump.

When the water-oil interface was at rest in the specimen consisting of a uniform cylindrical capillary tube containing no beads the water was the wetting phase. The contact angle in the water was acute resulting in an injection pressure which was less than ambient. However, as water was injected with the apparatus pump the interface was observed to begin to change shape. It became more nearly flat while its perimeter remained stationary during the process. When the interface had completed its change of shape such that the contact angle in the water was obtuse, the interface perimeter began to move along the tube with a speed corresponding to the injection rate. The interface speed was increased from a very slow speed to several cm per min with no accompanying increase in injection pressure.
When the water-oil interface was moved through specimens containing beads the injection pressure behaved in a manner similar to that when a water-air interface moved through the non-wettable specimens; the interface tended to avoid the regions of small cross-sectional area and remain in the regions of larger cross-sectional area. The injection pressure surges were not nearly as sharp and abrupt as those with the water-air interface. In both cases the liquid being displaced was not completely removed from the specimens. Air was left undisplaced in the first case while oil was left undisplaced in the second case. This once again introduced an indeterminate term on the right-hand side of Equation (1) as a result of the unknown oil-water surface area of the undisplaced oil droplets. It was observed, however, that a decrease in the bead size in the specimens required an increase in the injection pressure to move the interfaces through them.

Experiments were performed by moving small oil drops surrounded by water through uniform capillary tubes. PLATE XV illustrates the injection pressure as a function of injected volume as four oil drops were moved through a 1.11 mm pyrex capillary tube and eventually passed out of the tube into the water reservoir. The Plate indicates that the drops moved along the tube with an injection pressure of about 4 cm of water. The rises in injection pressure were due to the increase in curvature of the leading interfaces as they reached the end of the capillary tube and were forced into the water reservoir. The injection pressure required to move the group of drops was proportional to the number of drops present in the tube since it uniformly decreased with the loss of each drop. This result is in agreement with similar results obtained by Jamin who studied the resistance offered by gas bubbles to attempts to force them through capillary tubes. It was also found that the injection pressure was independent of the speed of movement of the drops through a range of speeds from 3 mm per min
A graph of the injection pressure as a function of the injected volume as four oil drops in water were moved through a 1.11 mm pyrex capillary tube.
on up to 100 mm per min. When a single oil drop was moved through a pyrex tube of varying cross section, a considerable increase in injection pressure was required to move the drop through each constriction which was another manifestation of the "Jamin effect".

When four air bubbles were formed in a 1.0 mm teflon tube and water was injected at a slow, uniform rate, the bubbles remained stationary until the injection pressure had increased to approximately 6.5 cm of water whereupon they began to move. See PLATE XVI. It may be noted that the injection pressure was somewhat sensitive to the speed with which the bubbles were moved. This effect was not evident with a single interface but could be a factor when a large number of interfaces are present even when flow rates are not large enough for viscous forces to be a factor. The fact that the dependence of the injection pressure on the injection rate indicated in PLATE XVI was due to the interfaces themselves rather than to viscous effects was verified by noting the independence of the same two factors when the tube contained water free of bubbles.

The experiments performed involving the movement of single water-oil interfaces through synthetic media and the movement of drops through capillary tubes established that the work required to move multiple interface systems is a function of the number of interfaces and can also be a function of the speed with which they are moved. They serve also to indicate the types of experiments that can be performed with the apparatus.
A plot of injection pressure and injected volume versus time as four air bubbles were moved through a 1.0 mm teflon tube containing water.
CONCLUSION

It has been found that the alternate expansion and contraction of a water-air interface is conservative in energy to within experimental error.

It has been shown that the work required to move a single water-air interface through synthetic permeable specimens is, within the limits of experimental error, a linear function of the specific internal area of the specimens.

Methods have been developed for determining the pore volume distributions in porous media and estimating uniformity of pore shapes.

A quantitative measure has been presented of the work per unit volume of specimen required to move a water-air interface through wettable synthetic specimens as a function of pore size.

Some techniques have been described involving liquid-liquid interfaces and it has been found that the work required to move liquid drops through capillary tubes is proportional to the number of interfaces present and in some cases is proportional to the speed of interface movement over and above viscosity effects.

Although most of the above results were obtained by experimentation on synthesized permeable media using water-air interfaces, it is postulated that similar phenomena are present in naturally occurring permeable media containing liquid-liquid interfaces. If this be the case the techniques developed should enable one to determine the work done in moving multiple interface systems through permeable media over and above the work done against viscous forces and could provide the means necessary to obtain a more fundamental understanding of the phenomena related to the concept of relative permeability.
The author takes this opportunity to acknowledge and thank Dr. F. W. Crawford for his guidance and assistance in this work. The author also wishes to thank Dr. A. B. Cardwell, Head of the Department of Physics, and the American Chemical Society Petroleum Research Fund for their financial assistance.
LITERATURE CITED

Adam, N. K.
The Physics and Chemistry of Surfaces, Oxford at the Clarendon Press, 1938

Bikerman, J. J.

Muskat, M.
Physical Principles of Oil Production, McGraw-Hill, 1949

Scheidegger, A. E.
THE MOVEMENT OF INTERFACES
THROUGH PERMEABLE MEDIA

by

GARY M. HOOVER

B. S., University of Nebraska, 1961

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submitted in partial fulfillment of the
requirements for the degree

MASTER OF SCIENCE

Department of Physics

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1965
ABSTRACT

Experiments have been performed to obtain quantitative data on the changes in surface free energy as interfaces are moved quasistatically through synthesized permeable media constructed in short lengths of capillary tubing with controlled cross sectional area from either constriction or carefully packed glass spheres. The apparatus consisted of a pump capable of injecting liquids into the specimens at uniform rates ranging from $10^{-7}$ to $10^{-2}$ cm$^3$/sec along with detecting and recording equipment which provided a record of the injection pressure vs the injected volume. The work done by the pump in moving the interfaces through the specimens was determined by integrating under the measured pressure vs volume curves.

It was found that the work per unit length of specimen required to move a water-air interface along a uniform teflon tube of 1.0 mm diameter was the same, within the probable error, as the work per unit length of tube required to move the same interface along the same tube fitted with a series of clamps which forced the interface to alternately increase and decrease in area. This indicated that the cyclic extension and contraction of the water-air interface conserved energy, to within the experimental error, and could be so considered in later experiments.

The work per unit length of specimen required to move a water-air interface through wettable, synthetic media was found to be proportional, to within the experimental error, to the internal surface per unit length of specimen, which was varied by the type of packing employed. Experiments involving wettable beads in non-wettable tubes of teflon provided additional data to support this linear relationship. Experiments involving the movement of water-air interfaces through non-wettable media and water-oil interfaces
through water wettable media were less successful and provided little quantitative data concerning the work done in moving the interfaces due to the incomplete displacement of the water by the air in the first case and to the incomplete displacement of the oil by the water in the second case. However, it was found that a decrease in the pore volumes in both cases was accompanied by a corresponding increase in the injection pressure required to move the interfaces.

The fluctuations of the injection pressure as the interfaces moved through the synthesized permeable specimens enabled one to measure the specimen pore volumes individually and to thereby obtain pore size distributions of the specimens. The apparatus was able to detect pores as small as 0.001 microliters in volume. The analysis of the work per pore required to move a water-air interface through wettable synthetic specimens as a function of the specimen pore volumes led to a suggested method of distinguishing pore shapes in a porous medium and to calculations exhibiting quantitative information concerning the work per unit volume required to move an interface through a porous medium. This concept along with the other experimental results are discussed with regard to their possible value in providing a more quantitative description of the flow of multiphase liquid systems through porous permeable media.