Capillary Behavior in Porous Solids

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Knowledge of the theory underlying the behavior of mixtures of fluids in reservoir rocks is essential to the proper solution of certain types of problems in petroleum production, but is as yet incompletely developed. The object of this paper is to show the application of well established thermodynamic and physical principles to these problems, and thus to assist in the development of the basic theory. For convenience the problems to be considered here may be divided into two groups:

1. Static problems, involving only the static balance between capillary forces and those due to the difference in densities of the fluids; i.e., gravitational forces.

2. Dynamic problems, involving analysis of the motion of mixtures of immiscible fluids in porous media under the influence of forces due to gravity, capillarity, and an impressed external pressure differential.

Capillary Equilibrium in Sands

Under this heading the static type of problem will be discussed and the results of experimental investigations on the capillary properties of unconsolidated sands will be presented. Although the discussion of this section is, in a sense, prefatory to the treatment of problems of mixture flow, the concepts developed here have considerable intrinsic importance apart from their application to flow problems. For, it is reasonable to postulate that the reservoir fluids are, owing to their long existence in undisturbed mutual contact prior to exploitation, in substantial equilibrium. It follows that their distribution in the reservoir at the time of tapping should be entirely predictable from the theory of capillary equilibrium, provided certain experimentally measurable properties of the reservoir rock are known. Knowledge of the distribution of the several fluids in the reservoir is, of course, helpful in the estimation of reserves and in other problems.

It is to be emphasized that throughout the discussion of capillary statics it is assumed that the fluids are in equilibrium from the capillary standpoint. Thus, water, where it is referred to as being in a reservoir, will be understood to be interstitial water, present at the time of drilling the reservoir, commonly termed "connate" water.

The theory developed here is perfectly general for any porous solid, whether a carefully prepared unconsolidated sand or a natural sandstone from an oil reservoir. At present, however, only problems involving clean, unconsolidated sands can be made to yield numerical solutions, since only such sands have been adequately investigated experimentally. Experimental evaluation of the pertinent properties of natural reservoir rocks will permit the extension of the numerical treatment to problems involving these materials. We shall now consider in some detail the static equilibrium of fluid mixtures in porous solids; that is, the manner in which the reservoir fluids are distributed vertically when the forces due to capillarity are just balanced by those due to gravitation.

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Interfacial Curvature and Capillary Pressure

Although it is not infrequently assumed that sands may be represented as behaving like a bundle of straight, cylindrical capillary tubes, this analogy is in many respects an unwarrantable and misleading simplification. It is necessary for the purpose of this discussion to discard this concept and substitute a more realistic one.

Simple visual examination of a porous material, in the pore space of which a mixture of two fluids exists, shows that the *interfacial boundary between the fluids is curved*, and that the sharpness of the curvature depends on the size of the intergrain spaces and the proportions of the fluids present. It is well established that the cause of this curvature is the interfacial tension between the fluids; the physical law determining the shape of the interfacial surface is that the interfacial-surface free energy shall be the minimum compatible with the volumes of fluids present and the shapes of the restraining solid surfaces. The view here taken is that this *interfacial curvature is the most significant property of the system from the standpoint of capillary behavior.*

The curvature of the interfacial surface gives rise to a pressure differential across the interface, which here will be termed the "capillary pressure." When fluids flow under the action of capillarity, the driving force causing flow is this capillary pressure; it is thus of the first importance in problems of capillary flow. The capillary pressure is related to the curvature of the interface by the well-known expression[1] due to Plateau:

$$P_c = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \qquad [1]$$

where P_c is the capillary pressure, γ is the interfacial tension or unit free surface energy, and R_1 and R_2 are the principal radii of curvature of the surface. The expression $\left(\frac{1}{R_1} + \frac{1}{R_2} \right)$ is defined as the *mean curvature* of the surface and will be represented by C. Fig. 1 shows the approximate shape of the oil-water interface when only a small amount of water is present between two spherical grains. The radii of curvature, R_1 and R_2, are vector quantities and hence have direction as well as magnitude. If both radii have their centers of rotation on the same side of the interface in question, both radii have the same sign. But if the centers of rotation are on opposite sides of the interface, one radius is positive and the other negative in sign. The latter situation prevails in Fig. 1. It makes no difference which of the two radii R_1 and R_2 is called positive or negative as long as the same con-

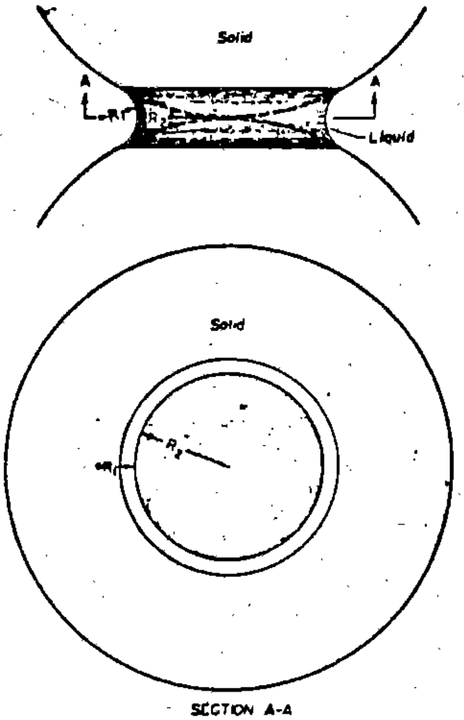

FIG. 1.—ACCUMULATION OF LIQUID AT CONTACT POINT BETWEEN SPHERICAL GRAINS.
R_1 rotates in plane of paper in upper view, R_2 rotates in plane of paper in lower view.

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[1] References are at the end of the paper.

vention is used throughout. In order to be consistent with our later definition of P_c, we shall say here, arbitrarily, that in Fig. 1 R_1 is positive but R_2 is negative. That is, in general if the center of rotation of a radius of curvature lies on the side of the interface occupied by the fluid which preferentially wets the solid, that radius will be given a negative sign. If the center of rotation lies on the side of the non-wetting fluid, the radius will be given a positive sign. As drawn in Fig. 1, R_2 is numerically greater than R_1, so that the mean curvature of the interface, $\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$, is positive even though $\frac{1}{R_2}$ is a negative number. In general, the water-oil, or water-gas, interface will have a positive curvature whenever the water tends to be imbibed by capillarity.

Interfacial Curvature and Height

In a petroleum reservoir rock, interstitial water coexists with the oil at all levels throughout the entire reservoir and, as stated above, we shall assume that these fluids are initially in substantial capillary equilibrium. Where the interfacial tension is constant throughout the reservoir, a well-known relation exists among the capillary pressure across a given interface, its mean curvature, and its vertical position in the reservoir.

In order to derive this relation, let us consider a large porous mass, preferentially wetted by water, in which two fluids, such as oil and water, are distributed in the manner required for capillary equilibrium. Let us suppose that a very small volume of water, ΔV, is to be transferred from the level h in the sand to the level $h + dh$. Since, by assumption, capillary equilibrium exists in the sand the free energy change dF (i.e., the isothermal reversible work possible to get out of the transfer) is zero; $dF = 0$. However, the total change in free energy, dF, accompanying this transfer is the sum of two parts:

1. The partial change of free energy of the water element in rising a distance dh in a gravitational field, which is given by

$$\left(\frac{\delta F}{\delta h}\right) = \rho_w g \Delta V$$

where the element has the volume ΔV.

2. The partial change of free energy of the water element in passing from a level h where the pressure in the water is P_w to a level $(h + dh)$ where the pressure in the water is $(P_w + dP_w)$. This is given by

$$\left(\frac{\delta F}{\delta P_w}\right) = \Delta V$$

The total change in free energy is the sum of these two, whence we may write immediately

$$dF = \left(\frac{\delta F}{\delta h}\right) dh + \left(\frac{\delta F}{\delta P_w}\right) dP_w = \rho_w g \Delta dh + \Delta V dP_w = 0 \quad [2]$$

or

$$-dP_w = \rho_w g dh \quad [2a]$$

in which ρ_w is the density of the water, and g is the acceleration due to gravity.

A similar derivation may be made for any other fluid present at equilibrium, with an exactly similar result regardless of the nature of the fluid. If, in the case under discussion, the second fluid is oil, the equation corresponding to eq. *2a* is

$$-dP_o = \rho_o g dh \quad [2b]$$

(The subscripts *o* and *w* will be used to indicate oil and water respectively.)

In accordance with our convention regarding the sign of the mean interfacial curvature, P_c, the capillary pressure across the water-oil interface is, by definition, $P_c = P_o - P_w$, whence, differentiating,

$$dP_c = dP_o - dP_w$$

Combination of this expression with eqs. *2a* and *2b* yields

$$dP_c = \Delta\rho_{wo} g dh \quad [2c]$$

where $\Delta\rho_{wo}$ represents the difference in densities between the water and oil.

When the capillary pressure P_c is zero, the interface has zero curvature, and hence is in equilibrium with a flat interface (a "free liquid surface") at its own level and external pressure. However, as will be observed below, there is a limit to the smallness of the interfacial curvature that may possibly exist in a column of sand of definite properties. For this reason there is no interface in the system across which the pressure differential is zero. We may, however, calculate for any equilibrium surface of known curvature how far below that surface the hypothetical free liquid surface is, and it will be convenient to call $h = 0$ at this level, since at this level the capillary pressure is likewise zero. In an oil-water-sand system, the hypothetical free liquid surface is always below the lowest level at which oil is found if the oil is less dense than the water. Therefore, calling $h = 0$ at the level at which the surface, if it actually existed, would have zero curvature, eq. *2c* becomes, on integrating between limits and recalling eq. 1,

$$P_c = \Delta\rho_{av}gh = \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) = \gamma C \quad [2d]$$

where h is the vertical distance of the interface in question above the free liquid surface. As indicated in eq. *2d*, the average value of the density difference $\Delta\rho_{av}$ must be used in the integrated form if this difference varies significantly with height.

It should be remarked that the free liquid surface is not always hypothetical. For example, where water is being imbibed from an open dish into a sand column standing in an air-filled room, the free liquid surface is real, and is the water-air interface in the dish.

It is to be emphasized that eq. *2d* was derived without any assumptions regarding the fluids or system, except that they are isothermal and in capillary equilibrium. It applies equally well to water-air, water-oil, or oil-gas systems, and the solid phase may have any properties whatever. A corollary of eq. *2d* is that all interfaces in any particular two-fluid system have the same curvature and capillary pressure at the same horizontal level.

Approximate Magnitude of Capillary Pressures in Oil Sands

Eq. *2d* is a direct means of estimating the maximum differences in capillary pressure that may exist in a virgin reservoir. For example, in an oil sand 100 ft. thick, in which the average difference in specific gravities of oil and water is 0.3, the capillary pressure at the top of the sand is about 13 lb. per sq. in. greater than at the bottom of the oil zone. The capillary pressure at the bottom of the oil zone depends on the minimum curvature that may exist in the sand, and hence varies widely depending on the texture of the sand. Nevertheless, it seems unlikely that original capillary pressures greater than a few times the value in the above illustration will be encountered frequently. Although, as in this example, the pressures due to capillarity may be of fairly large size, it must be realized that at equilibrium they are exactly balanced by the differences in gravitational forces on the two fluids. It is only when this balance is disturbed that part of the capillary pressure becomes available to cause flow of fluids.

Eq. *2d* likewise permits estimation of the mean curvature of the capillary surface at any height if the interfacial tension is known. In the example above the mean curvature at the top of the oil zone is (assuming it to be comparatively small at the bottom of the oil zone) about 65,000 in.$^{-1}$ (25,000 cm.$^{-1}$) if the interfacial tension is 35 dynes per centimeter.

Relation between Interfacial Curvature and Saturation

Since eq. *2d* relates curvature and height, a relation between curvature and saturation (fraction of voids occupied by a given fluid) would suffice to determine, for given values of the density difference and interfacial tension, the height-saturation diagram; i.e., the vertical distribution of the fluids. It is apparent from this that the *curvature-saturation function is the fundamental relation* necessary for solution of problems of static capillarity in sands.

Quite apart from its thermodynamic relation to capillary pressure and height, the curvature of the oil-water interface is a geometric quantity determined by the dimensions of the interstice in which it exists and by the proportions of the fluid phases present. There is thus the theoretical possibility of determining mathematically the mean curvature corresponding to a given water saturation in an interstice of given dimensions. However, analytical attempts to evaluate the curvature-saturation function have failed in all except highly oversimplified cases. For example, the problem has been attacked by Smith and others[2-7] for regularly packed spheres. In actual sands or sandstones the extreme irregularity of the intergrain spaces prohibits analytical treatment. Some characteristics of the saturation-curvature function, however, may be determined without recourse to extensive experiments, and these will be discussed briefly before proceeding to the experimental evaluation of the function.

It is evident from Fig. 1 that changes in water saturation in a pore of any shape whatever result, in general, in curvature changes at the water-oil interface. It is likewise true that there is a lower limit, greater than zero, to the curvature that may exist in a column of sand of definite properties, although this fact is not readily deducible from purely geometric considerations. Rather, it is demonstrable by the simple experimental observation that in sand columns containing two fluids in equilibrium it is well known that substantially complete water saturation prevails up to a definite distance above the free water surface. Again, the simple fact that a solid imbibes a liquid to near-saturation shows that there is no interfacial configuration of zero curvature typical of any saturation (less than unity) in the sand.

Smith,[5,6] Keen,[7] Versluys[8] and others have pointed out that there are three general types of occurrence of water, or regions of water saturation in a porous solid:

1. Saturation region. Complete water saturation.

2. Pendular region. Lowest water-saturation range. Water occurs as pendular rings around grain-to-grain contacts. The solid, where not covered by water in the pendular rings, is covered with a very thin film of water if the contact angle[9] is zero,[*] or by oil if not. Fig. 2*a* illustrates this saturation region.

3. Funicular region. Intermediate water saturation. Addition of water to the pendular rings of Fig. 2*a* causes them to grow and soon they become so large that they touch each other at their edges and merge. This state of coalesced rings is indicated in Fig. 2*b*. Addition of still more water causes complete coalescence of the funicular rings, the result being a web of water across the interspace between three or more grains. Both of these configurations are included in the funicular saturation region, since in either case it is possible to pass from any position in one fluid to any other in the same fluid by a tortuous, cordlike (funicular) path through that fluid.

The nomenclature is that used by Versluys.[8]

Saturation Hysteresis

Previous work in this field[2-7] has shown also that the curvature-saturation function is not single valued over its entire range;

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[*] It is believed that the contact angle in natural petroleum reservoirs is substantially zero, with few exceptions; this view is based on a considerable amount of evidence which, if not rigorously conclusive, is strongly presumptive. It may be pointed out that the thermodynamic discussion presented here is valid regardless of the magnitude or existence of the contact angle; if the contact angle is not zero some changes in the numerical values of the curvature-saturation relation and permeability-saturation curves must be made, but these changes are in predictable directions. In the experimental work described in the following pages undoubtedly the contact angle was zero.

there is a considerable hysteresis loop in the function. The reasons for this behavior are derivable from the geometry of the system, and have been discussed in detail by Smith,[9] who shows that there is a large variety of configurations that may stably correspond to a given average water saturation. This is particularly true of the funicular region of saturations.

Aside from this ambiguity in the curvature-saturation relation, which is probably often unimportant, we may regard the curvature-saturation function as characterizing the sand to which it applies. This view obviates any necessity for inventing fictions about the sand, such as a suppositious distribution of "pore sizes" of "equivalent circular section." The latter concept in particular is likely to be misleading, since the same intergrain space is capable of behaving as though possessed of many different such sizes. It is sufficient to state, first, that the intergrain spaces, the pores, are in fact of various dimensions, and, second, that any such space may contain in it a capillary surface having a curvature larger than a definite minimum. Thus the sand has a characteristic distribution of interfacial curvatures with respect to saturation.

Displacement Pressure

It may be noted in passing that the capillary pressure existing at the maximum position of the top of the saturation zone in a vertical sand column is numerically the "displacement pressure,"[10] since it is the minimum pressure differential that suffices to displace water from the water-saturated sand.

Experimental Evaluation of Curvature-saturation Function

The attempts of Smith and others to evaluate analytically the curvature-saturation function have been mentioned previously. The results of this work give curvature-saturation plots that undoubtedly are of the proper form and hence are of value but which cannot be applied quantitatively to real sands or sandstones. Therefore this function has been investigated experimentally in the present research.

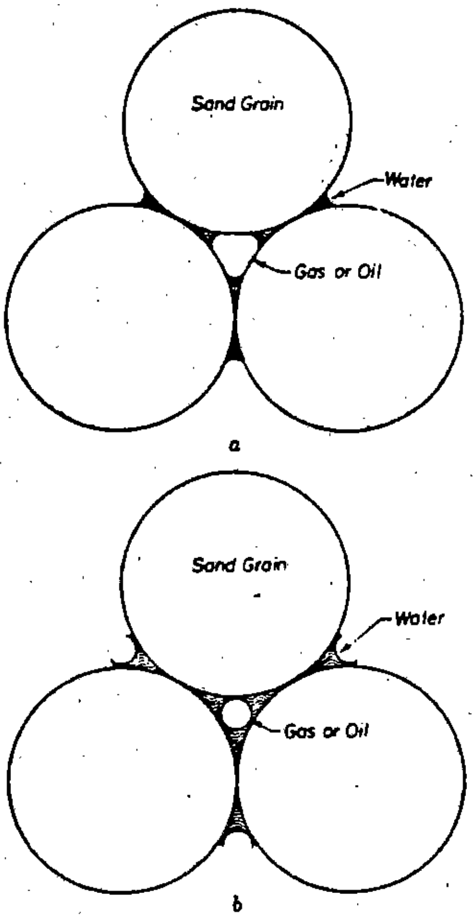

FIG. 2.—SATURATION RINGS.
a. Pendular saturation rings.
b. Funicular saturation region, water existing as coalesced rings.

Of the various theoretically possible techniques for evaluating this function, the height-saturation method was chosen. Essentially, this comprises letting water and air come to capillary equilibrium in a vertical sand column, and measuring the resultant water saturations at a number of heights. Similar work by King,[11] Haynes and Keen[7] and Smith[4-6] has been reported, but these experiments were incomplete because the permeabilities, and in some cases other properties of the system, were not measured.

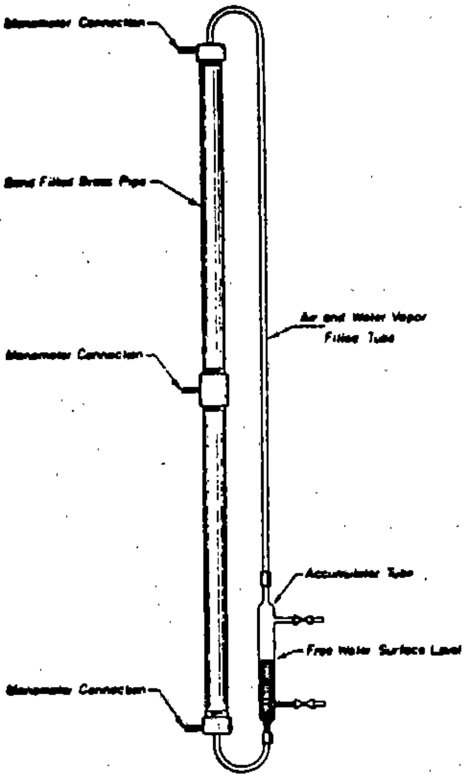

FIG. 3.—BRASS APPARATUS FOR DETERMINING CAPILLARY EQUILIBRIUM OF WATER DISTRIBUTION IN UNCONSOLIDATED SAND.

Two very similar procedures were used in the present study. The first comprised packing sand in vertical glass tubes and measuring its porosity and permeability to both water and air where possible. (The manometer taps, used during permeability measurements, were closed while the system came to equilibrium.) The tubes were about ¾ in. in diameter and up to 10 ft. long. Two such tubes were packed with each sand used. One tube of each pair was saturated with water, which was then allowed to drain from the sand into the accumulator tube (Fig. 3). The water level in the accumulator tube was kept constant by removing water as it drained. The other tube of each pair was initially dry; water was fed to the accumulator tube as fast as the sand imbibed it. Equilibrium was thus approached from both directions and the maximum extent of the hysteresis zone defined. The saturation changes in the sands were followed by means of the conductometric technique previously described,[12,13] metallic screens at top and bottom of the columns serving as electrodes by which to introduce the alternating current. The electrical potential drop along the sand column was measured at 6-in. intervals by means of stiff wires sealed through the side of the glass column. Because of its fragility, this apparatus was later replaced by the one sketched in Fig. 3, where a brass tube replaces the glass one. At the end of the run the brass tubing was cut into 10-cm. sections and the water content of the sand in each section determined gravimetrically. With either apparatus it was found that very little change in distribution of water took place after about two weeks (imbibition and drainage rates were followed, for the brass apparatus, to gauge the progress of the experiment); however, the experiments usually ran several times that length of time.

In all, four previously sized and ignited sands and two that contained clayey material were thus studied. Of the clayey sands, one was a clean ignited sand to which 5 per cent by weight of Drilloid (a bentonitic drilling-mud addition agent) was added, and the other was a naturally occurring surface sand (Queen City, Texas, formation). Table 1 summarizes the properties of the systems investigated by both techniques.

Results of Height-saturation Experiments

When the results of these experiments were plotted (Fig. 4) in dimensionless form as

$$\frac{\Delta\rho g h}{\gamma}\sqrt{\frac{K}{\phi}} \text{ against } S_w$$

it was found that the data for the four clean sands fell satisfactorily near two curves, one for imbibition of water and the other for drainage. K is the permeability of the sand to a homogeneous fluid, expressed in units consistent with the other variables in the group, and ϕ is the fractional porosity of the sand. The form of this correlation may be derived from either of two assumptions:

1. That the height at which a definite water saturation is found at equilibrium is inversely proportional to an "equivalent circular diameter" of the voids in the sand[13] calculated from its porosity and permeability, inversely proportional to the density difference and directly proportional to the interfacial tension.

2. That the interfacial surface area between the two fluids is, at a given water saturation, a definite fraction of the total surface of the sand itself.[14]

It is believed that the nearly vertical trend of the drainage data at low water saturations in Fig. 4 represents a relatively poor approach to equilibrium, caused by the low permeability to water in this saturation region. This view is substantiated by the results of an experiment on the capillary depression of mercury in an "air-wetted" sand (the mercury-air-sand contact angle was probably near 140°). Because of the low viscosity of air compared to that of water, a much accelerated approach to equilibrium was attained. The broken portions of the curves of Fig. 4 represent a reasonable estimate of water distribution in the low-saturation region, based on Smith's theoretical work and the mercury-sand-air experiment.

The ordinate of Figs. 4 and 5 is, referring to eq. *2d*,

TABLE 1.—*Properties of Systems Used in Height-saturation Experiments*

Sand No.	I		II		III		IV		V		VI	
Screen analysis	100–200 Mesh Plus 5 Per Cent by Wt. Drilloid		200–325 Mesh		80–100 Mesh		50 Per Cent 100–200 Mesh 50 Per Cent 200–325 Mesh		100–200 Mesh		Queen City Sand*	
Type experiment	Drainage	Imbibition	Drainage	Imbibition	Drainage	Imbibition	Drainage	Imbibition	Drainage	Imbibition	Drainage	Imbibition
Permeability to air, darcys:												
Top half column	1.80	2.43	3.17	3.29	17.1	17.5	2.20	2.72	3.50	3.27	0.650	0.731
Bottom half column	2.14	2.30	3.19	3.77	17.3	17.5	2.52	2.72	3.76	3.76	0.750	0.830
Average	1.97	2.37	3.18	3.53	17.2	17.5	2.36	2.72	3.63	3.52	0.700	0.781
Permeability to water, darcys:												
Top half column	0.328						2.48		3.60		0.119	
Bottom half column	0.234						2.48		3.60		0.025	
Average	0.282						2.48		3.60		0.072	
Average porosity, per cent	40.8	41.5	46.1	46.4	39.1	39.0	48.2	49.1	39.5	39.4	38.2	39.4
Interfacial tension, dynes per cm.	70	53	70	73	70	69	70	60	70	49	70	62
Duration of experiment, days	75	76	30	30	30	30	83	43	78	79	70	74

* Screen analysis:

	PER CENT BY WT.
−100 mesh	>0.1
100–200	5.9
200–325	85.6
325+	8.5
	100.0
Porosity in situ	43.8

$$\frac{\Delta\rho g h}{\gamma}\sqrt{\frac{K}{\phi}} = C\sqrt{\frac{K}{\phi}}$$

Evidently the group

$$\frac{\Delta\rho g h}{\gamma}\sqrt{\frac{K}{\phi}}$$

is interfacial curvature multiplied by a factor that is a property of the sand alone. Hence the curves of Fig. 4 may be regarded as generalized curvature-saturation plots, applicable to all clean unconsolidated sands.

Where, as in the imbibition experiments, water advances into the sand, displacing, for example, air, it is invariably found that the water does not completely displace the air from the sand. Part of the air remains apparently trapped in what would otherwise be a region of 100 per cent water saturation. Microscopic examination shows this residual air to exist as globules surrounded by water. It is thus unable to escape by ordinary flow. From Smith's work,[8] it appears highly probable that such residual globules are thermodynamically unstable; it is believed that they tend to disappear by solution in the water and subsequent diffusion to more stable positions. This behavior has been observed experimentally in one case in the present research, and is believed to have been typical of all the cases studied, although perhaps too slow to attract notice in any but the one instance mentioned. The lower curve of Fig. 4 has been drawn in accordance with this view.

The experimental results (Fig. 4) demonstrate that clean sands of low permeability retain more water at a given height than more permeable ones. The hysteresis zone is clearly evident in Fig. 4, but it is seen to be of limited vertical extent. Hence, although it is difficult to state from the results obtained the saturation corresponding to a curvature falling in the hysteresis zone, the curvature corresponding to a given water saturation can be estimated with relatively small error.

Clayey Sands

The data for clayey sand do not correlate on the basis of Fig. 4. The results, plotted in Fig. 5, show that more water was retained at large values of h, the height, and less at small ones than the clean-sand correlation predicts. Use of the permeability of the water-saturated sand to water for K in the ordinate did not improve the correlation.

These results are explainable by the fact that clays and shales sorb water, the water so taken up being held more tightly than the same amount of water would be held by capillarity. The amount of so-called "hydratable" material in natural sandstones is thus important, since, as these data show, it affects strongly the curvature-saturation function. The large "connate" water saturations of some reservoir rocks therefore may be attributable to the presence of "hydratable" solids mixed with the sands. The lower permeability of clayey or shaly sands to water than to dry air is probably explained by the swelling of these "hydratable" materials in water, which reduces the effective size of the flow passages.

CAPILLARY THERMODYNAMICS IN TWO-FLUID SYSTEMS

Some of the thermodynamic properties of two-fluid mixtures in porous solids are of particular interest, among them the free surface energy.

Let us consider an element of sand containing, for example, only water and oil, and suppose that there is, at the same horizontal level, a water reservoir, which has a surface of zero curvature, and that both sand and water reservoir are enclosed in an otherwise oil-filled space. Evidently, the pressure in the water in the sand (because it is bounded by a curved surface) is less than that in the water reservoir (the two are not assumed to be in equilibrium), and it is readily shown that this pressure deficiency is P_c, the capillary pressure, in the sand. For the water, the partial change of free energy with pressure is

$$\left(\frac{\delta F}{\delta P}\right) = V$$

or, since water is substantially incompressible

$$F_2 - F_1 = V(P_2 - P_1) \qquad [3]$$

whence the difference in free energy per unit volume of water in the external reservoir, F_2, and in the sand, F_1, is

$$F_2 - F_1 = P_2 - P_1 = P_c \qquad [4]$$

Since P_c is the free energy increase (the isothermal, reversible, work necessary) accompanying the transfer of unit volume of

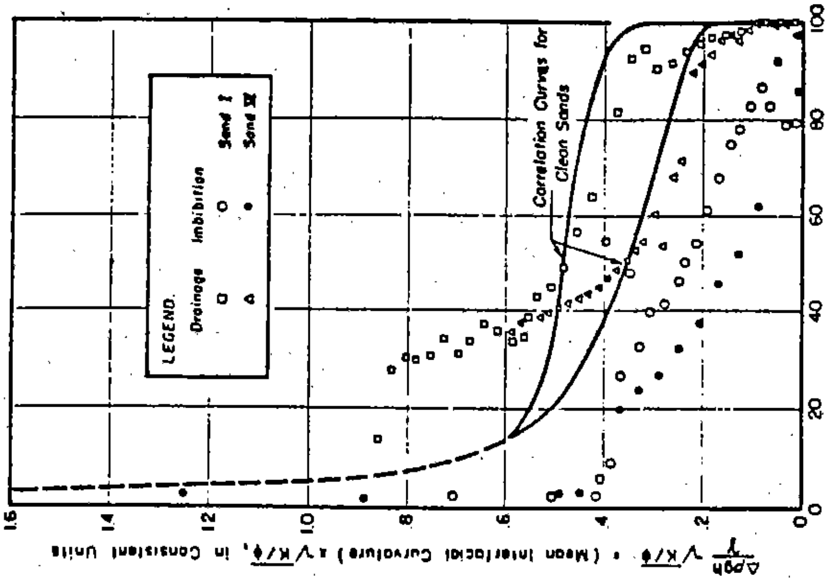

FIG. 5.—DATA FROM HEIGHT-SATURATION EXPERIMENTS ON CLAYEY SANDS, SHOWING DEVIATION FROM CLEAN SANDS.

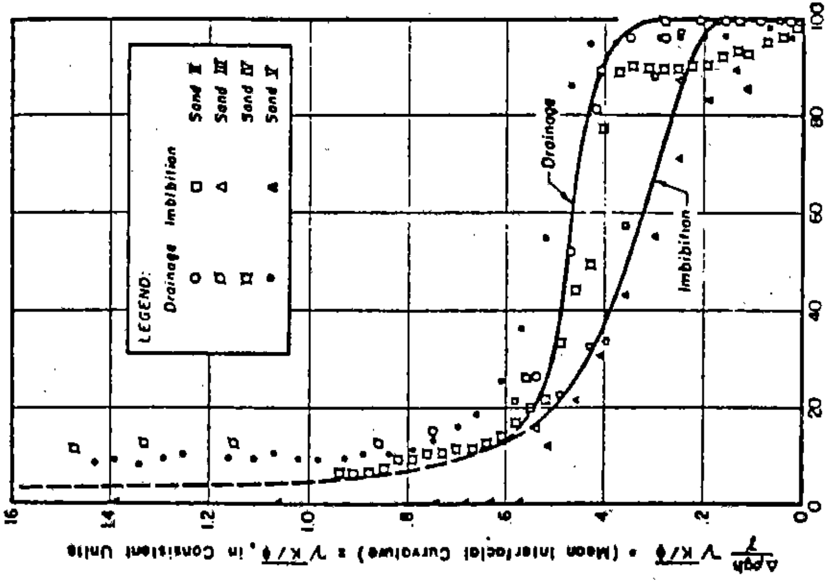

FIG. 4.—CORRELATION OF DATA FROM HEIGHT-SATURATION EXPERIMENTS ON CLEAN UNCONSOLIDATED SANDS.

water from the sand to the zero curvature reservoir at the same level, we may consider that

$$P_c = \left(\frac{\delta F}{\delta V}\right) \qquad [5]$$

where V represents the volume of water transferred out of the sand. It is evident from this that the negative capillary pressure, $-P_c$, is the partial free energy per unit volume of water in the sand with respect to that of water at the same level and external pressure, but bounded by a zero curvature interface. Thus viewed, the capillary pressure is clearly a close analog to the "partial free energy" of Lewis and Randall[15] and to the "chemical potential" of Gibbs.[16] For this reason some authors have called P_c the "capillary potential."[17,18]

If, arbitrarily, the element of sand is so chosen that it has unit volume of pore space, it is evident that the volume of water in it and its fractional water saturation are numerically equal, and $dV = -dS_w$, since V represents water transferred *out* of the sand. Substitution in eq. 5 and rearrangement gives

$$dF = -P_c dS_w \qquad [6]$$

where dF is now the increase in free energy of the water per unit of pore space when the water saturation is changed by the amount dS_w. The reversible work necessary to decrease the water saturation by a differential amount is quantitatively converted into free surface energy, whence dF must also be the increase in free surface energy.

The difference in free surface energies between two saturation states in the same sand, therefore, is, per unit of pore volume,

$$\Delta F = -\int_{S_{w_1}}^{S_{w_2}} P_c dS_w \qquad [7]$$

This integral is the area under the capillary pressure-saturation curve and may be determined graphically.

Although, in the foregoing derivation, it has been assumed that only water and oil were present, a completely similar result is obtained for water-gas or oil-gas systems.

Eq. 7 is rigorous as derived, but its numerical evaluation necessarily assumes that P_c, capillary pressure, and S_w, water saturation, are uniquely related. Inasmuch as saturation hysteresis exists, this is only approximately true, and some uncertainty is thus inherent in this manner of evaluating the free surface energy.

Extent of Interfacial Fluid: Fluid Surface

The surface tension γ is by definition the unit free surface energy

$$\left(\frac{\delta F}{\delta \sigma}\right) = \gamma \qquad \text{or} \qquad \frac{dF}{\gamma} = d\sigma$$

where σ will be defined as the two-fluid interfacial surface area per unit of pore volume. If all the change in free surface energy is due to areal changes in the fluid:fluid interface, it is evident that the difference in interfacial surface areas between two saturation states results from dividing eq. 7 by γ, the interfacial tension:

$$\sigma_2 - \sigma_1 = \frac{F_2 - F_1}{\gamma} = -\frac{1}{\gamma}\int_{S_{w_1}}^{S_{w_2}} P_c dS_w \qquad [8]$$

It is important to note, however, that two kinds of interfacial surface exist in the sand:

1. Water-oil (or water-gas). The unit free surface energy of this surface is γ, the interfacial tension.

2. Solid-liquid; either sand-water or sand-oil. The unit free surface energy of these surfaces is not known, and undoubtedly is different for the sand-water and the sand-oil interfaces.

Eq. 8, therefore, is valid only if the amounts of sand-oil and sand-water interfaces are constant over the range of saturations S_{w_1} to S_{w_2}. This condition definitely does not prevail in the pendular region of saturations, and possibly does not obtain in certain parts of the funicular region. Eq. 8 therefore is inapplicable for relatively low water saturations, but probably may be applied where water saturations of 25 per cent or more are involved.

If, in the integration of eq. 8, S_{w_1} is chosen equal to unity (100 per cent water saturation), the integral gives the total two-fluid interfacial surface at S_{w_2}, since at 100 per cent water saturation there is obviously no two-fluid interface in the sand. Fig. 7 shows, as an example, the results of the graphical integration of the capillary pressure-saturation curves of Fig. 6. Although, because of the existence of saturation hysteresis, significantly different results for the extent of the two-fluid inter-

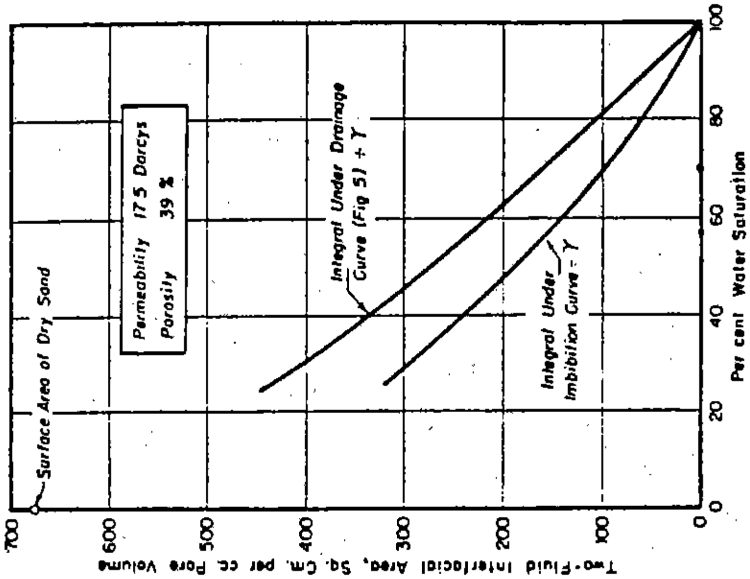

FIG. 7.—TWO-FLUID INTERFACIAL SURFACE AS FUNCTION OF WATER SATURATION IN UNCONSOLIDATED SAND.

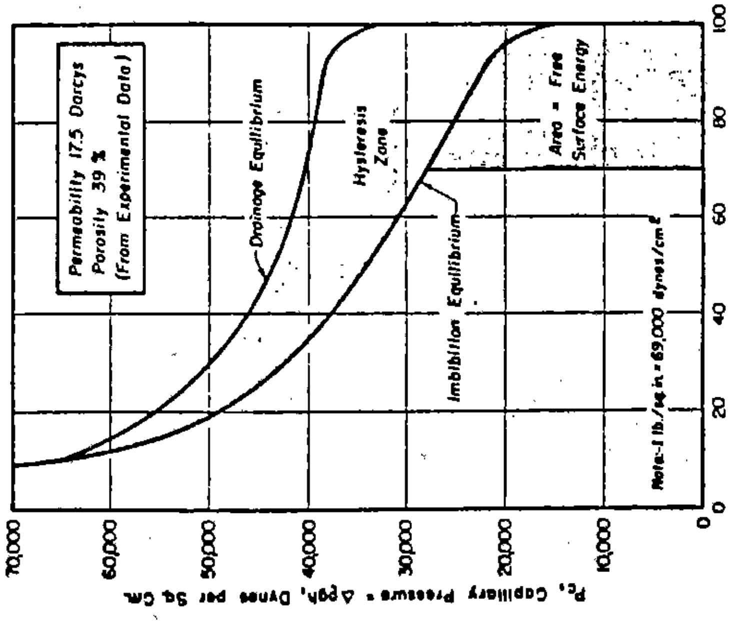

FIG. 6.—EQUILIBRIUM DISTRIBUTION OF AIR AND WATER IN UNIFORM UNCONSOLIDATED SAND, PERMEABILITY 17.5 DARCYS.

face are obtained from the curves of Fig. 7, the order of magnitude of this area is well defined. Also shown on Fig. 7 is the surface area of the dry sand, computed by the method of Carman.[14] The two-fluid interfacial area is seen to be less than that of the sand itself over the region of application of eq. 8.

Occasionally, it will be necessary to choose between the curvature-saturation data as obtained by imbibition and drainage experiments. In this connection it is helpful to note that since the states in the hysteresis zone persist indefinitely if undisturbed, but are permanently altered if a small but finite disturbance occurs in the system, these states represent *metastable equilibria*. It appears likely that the conditions under which hydrocarbons accumulate in and are produced from the earth will lead to distributions of the fluids corresponding more closely to the imbibition equilibrium than to the drainage equilibrium. Where, therefore, it is necessary to choose between the two sets of data we shall use the lower. Computations made for this paper are on this basis.

EQUILIBRIUM DISTRIBUTION OF THREE FLUIDS IN SANDS

Although only two-fluid systems have so far been discussed, an analogous treatment of three fluids may be made. It may be shown that eq. 2*d* applies equally well to the oil-water, oil-gas, and water-gas interfaces; when so applied the physical constants appearing in it must, of course, be those for the two fluids bounding the interface under question. Since the interfacial curvature is fixed (within the limits of saturation hysteresis) by the geometry of the system, as pointed out above, it is reasonable to assume that the relation between total liquid saturation and interfacial curvature at the gas-liquid interface is independent of the number or proportions of the liquids which, together, comprise the total liquid saturation.* This assumption fixes the slope (at a given total liquid saturation) of the total liquid saturation versus height curve for fluids of definite densities and interfacial tensions. The vertical position of the $(S_o + S_w)$ (total liquid) curve is fixed by the amount of oil present.

In order to illustrate the application of these principles to the determination of the original fluid distribution within a reservoir, the distribution of gas, oil, and water at equilibrium has been calculated for a clean, uniform, unconsolidated sand containing a relatively small amount of oil. The conditions assumed were as follows: oil-water, gas-oil, and water-gas interfacial tensions: 35, 20, and 65 dynes per centimeter, respectively; specific gravities oil, water, and gas: 0.7, 1.0, and 0.1 respectively; sand permeability: 1 darcy; porosity: 35 per cent; total thickness of oil interval: 8.5 feet.

The results of these computations are shown in Fig. 8, from which it may be observed that the vertical transition from gas to oil is sharper than that from oil to water, but that both the gas-oil and water-oil contacts are zones of rapid transition from a region saturated primarily with one fluid to a region saturated primarily with the second fluid, rather than levels of saturation discontinuities. The thickness of the transition zones depends upon the amounts of the fluids present and upon the character of the fluids and of the reservoir rock. It is interesting to observe that these calculations indicate that some oil may be contained in portions of the sand that may be expected from their saturations to produce only gas or water, an observation that has been confirmed by analyses of cores taken from above the "gas-oil contact" and below the "water-oil contact" in producing oil fields. It should be borne in mind that Fig. 8 represents no attempt to portray the conditions in any actual reservoir, but is illustrative only. Had the calculations

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* The oil must spread on the water for this assumption to be completely valid.

been made on the basis of a greater assumed quantity of oil in the sand, the transitions from one saturation region to another would have been similar, but small quantities of oil would have been found in the gas sand at points higher relative to the gas-oil contact.

Additional theoretical and experimental work remains to be done on the three-fluid static distribution problem before it can be considered solved; however, certain qualitative deductions may be made with respect to the conditions encountered in oil reservoirs. Thus, it is to be expected that in any particular fairly uniform sand the transition zones from gas to oil and from oil to water will be fairly definite. Because of the shapes of the permeability-saturation[12,13] plots, the transition with height, of the composition of the fluids produced will be much more rapid than the corresponding transition of saturation with height. Probably the complete transition zone from 100 per cent water to 100 per cent oil in the produced fluids will often be only a few feet thick. However, even in a continuous reservoir these levels may vary several feet from one part of the sand to another as the permeability varies. It is probable that in nearly all cases the gas-oil contact will be more sharply defined and will exhibit less variation than the water-oil contact. Except in thin sands, where there may be partial overlapping of the contacts, it is to be expected that the existence of these transition zones will not materially interfere with proper well completion and not seriously impair reserve estimates based upon apparent thickness of the oil sand.

MOTION OF FLUID MIXTURES IN POROUS SOLIDS

Previous work on the flow of fluid mixtures in porous solids has failed adequately to account for all of the three influences that cause motion of the fluids: capillarity, gravity, and impressed external pressure differentials. We shall show briefly how these influences may be properly evaluated, with the aid of the concept of capillary pressure.

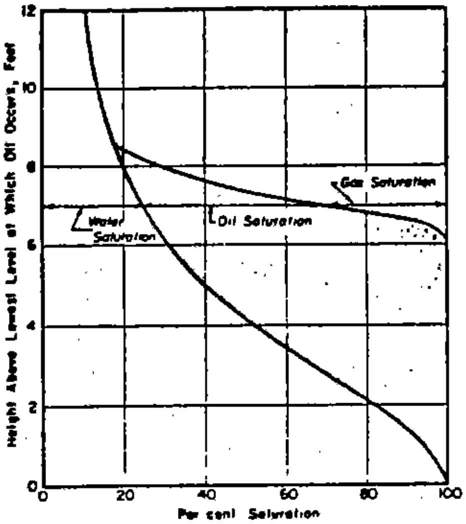

FIG. 8.—CALCULATED DISTRIBUTION OF OIL, GAS, AND WATER IN A UNIFORM UNCONSOLIDATED SAND.

Equations for Two-component Mixture Flow

Let us consider, for the sake of simplicity, the flow of a mixture of only two fluids, for example water and oil, in a porous solid in a gravitational field. By analogy to the well-known D'Arcy's law, we may write for the oil

$$q_{ou} = -\frac{K_o}{\mu_o}\left[\frac{\delta P_o}{\delta u} - g\rho_o \sin\alpha\right] \quad [9]$$

and for the water

$$q_{wu} = -\frac{K_w}{\mu_w}\left[\frac{\delta P_w}{\delta u} - g\rho_w \sin\alpha\right] \quad [10]$$

where q_{ou} and q_{wu} are the rates of oil and water flow in the direction u, per unit of cross-sectional area normal to u; $\left(\frac{\delta P_o}{\delta u}\right)$ and $\left(\frac{\delta P_w}{\delta u}\right)$ are the pressure gradients in the u direction in the oil and water, respectively; μ_o and μ_w are the oil and water viscosities;

α is the angle made by the direction u with the horizontal; K_o and K_w are the effective permeabilities[11] to oil and water, respectively, and the other symbols have their previous significance. Eqs. 9 and 10 are to be regarded as algebraic definitions of the effective permeabilities, and are statements of the fundamental law of viscous flow of fluid mixtures through porous media.

Since the water and oil are separated by curved interfaces the pressures in the two phases are not in general equal in the same plane normal to u. As a reasonable simplification, we shall *assume* that this pressure differential between the fluids is P_c, the capillary pressure, which would be calculated knowing the interfacial tension and curvature of the interface. The latter may, as shown previously, be determined approximately from the water saturation existing. Since, as defined, $P_c = P_o - P_w$, obviously

$$\left(\frac{\delta P_c}{\delta u}\right) = \left(\frac{\delta P_o}{\delta u}\right) - \left(\frac{\delta P_w}{\delta u}\right) \qquad [11]$$

Hence the pressure gradients in the two fluids are related by a quantity which, according to the above assumption, is a function of saturation gradient and saturation only. Further, the quantities K_o and K_w, effective permeabilities, have been shown to depend in steady mixture flow principally on the saturations existing.[11,18,19,20] A secondary effect of pressure gradient and interfacial tension on the effective permeabilities has been previously reported.[18] However, it is advisable tentatively to disregard this effect, since it now appears that it may possibly be merely a manifestation of the "boundary effect," and therefore not typical of the behavior of the interior of a large mass of sand. It is reasonable and convenient to *assume* that the effective permeabilities are functions of saturation only, for unsteady flow as well as steady. These two assumptions permit numerical evaluation of the rate of flow of both fluids at any point at which the saturation, saturation gradient and pressure gradient in one fluid are known. However, because of the necessity for evaluating the pressure gradient in one or the other fluid at every point in the system, these equations are not actually very useful. But this difficulty disappears for the special case of mixture flow in which (1) the total fluid rate per unit cross-sectional area

$$q_t = q_o + q_w \qquad [12]$$

is constant over each cross section normal to the direction of net flow, or varies in an explicitly known fashion, and (2) no motion of fluids occurs normal to the net flow direction. In this simplified case we may combine eqs. 9, 10 and 11 to give an expression for f_w, the fraction of water in the flowing stream passing any point in the sand:

$$f_w = \frac{1 + \dfrac{K_o}{q_t\mu_o}\left[\left(\dfrac{\delta P_c}{\delta u}\right) - g\Delta\rho \sin\alpha\right]}{1 + \dfrac{K_o}{K_w}\dfrac{\mu_w}{\mu_o}} \qquad [13]$$

This equation provides a relation between f_w, stream composition, and, by assumption, implicitly, water saturation and saturation gradient. It therefore suffices, together with appropriate boundary conditions, for the solution of any flow problem falling within the restrictions stated above. Such solutions are obtainable by numerical means.

Eq. 13 conveys a considerable amount of information regarding certain problems in oil production, but we shall forego detailed discussion of it until it can be shown to be quantitatively applicable. Good qualitative correspondence between theory and experiment have, however, already been observed in many cases.

THE BOUNDARY EFFECT

Discussion of capillarity in sands would be incomplete without particular mention of the special behavior of the fluids as they flow past a discontinuity in the capillary properties of the porous medium. Such a discontinuity, for example, is the outflow face of a sand column.

In the interior of a uniformly saturated, uniform sand mass, no fluid flow due to capillarity occurs, since the pressures due to capillarity act equally in all directions, and hence exactly cancel each other.

At the outflow face of the sand column, however, there is a discontinuity in the capillary properties of the sand, since the water passes abruptly from a region of relatively high capillary pressure (the sand) into a void in which (since the restraint imposed by the sand grains is absent) the oil-water interface has no sensible curvature, and the capillary pressure therefore vanishes. Capillarity in the sand tends to draw the water into the sand from the void, a tendency that must be overbalanced by the impressed pressure gradient if water is to pass from the sand. Since part of the impressed pressure gradient goes to overcome the capillary pressure and hence is ineffective for overcoming frictional energy losses in the water, the water moves less rapidly than normally in the boundary. The water thus accumulates in the boundary grain layers, and the increased water saturation causes a decrease in the permeability to oil. The boundary thus makes egress of both oil and water more than normally difficult. This whole behavior will be called the "boundary effect."

Where water and oil are flowing steadily through the boundary, it is possible to show, and has been observed experimentally, that there is a saturation gradient, from a relatively high water saturation in the boundary to the lower one to be predicted for steady flow in the absence of capillary forces, or at a very large distance from the boundary. Similar behavior is observed in unsteady flow. The boundary effect thus involves distortion of the "normal" saturation profile in the sand. The distance to which appreciable distortion takes place can be shown (eq. 13) to vary directly with the interfacial tension of the fluids and the permeability of the sand, and inversely with oil viscosity and total liquid rate. Calculations show that, at ordinary reservoir flow rates, the boundary effect is confined to a zone a few feet in diameter near the well, therefore probably is not an important factor in behavior of large-scale reservoirs. However, it is extremely important to recognize its existence and nature in interpreting the results of small-scale laboratory experiments. Indeed, it seems likely that many such experiments reported in the literature have been improperly interpreted because of failure adequately to account for the boundary effect.

Summary

The static equilibrium vertical distribution of fluids of different densities in porous solids has been discussed from a largely thermodynamic standpoint. The abandonment of the "capillary tube" concept of sand structure is urged, and the substitution of the concept of a characteristic distribution of interfacial two-fluid curvatures with water saturation is suggested. Experimental determination of this curvature-saturation relation for unconsolidated sands is described, and the results obtained are correlated so as to apply to all clean unconsolidated sands. The extent of the two-fluid interfacial surface area is shown to be determinable from thermodynamic consideration of the curvature-saturation relation.

The concepts developed are applied briefly to problems in the flow of mixtures of immiscible fluids in porous media, with emphasis on the proper accounting for the effects of capillarity on mixture flow. The existence of a *boundary effect*, characteristic of any discontinuity in the capillary properties of the solid medium, is pointed out. The importance of adequately accounting for its influence in the interpretation of data from small-scale flow experiments is stressed.

ACKNOWLEDGMENT

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DISCUSSION

D. L. KATZ,* Ann Arbor, Mich.—Dr. Leverett's paper is a timely one and of particular interest to me. The percentages of oil saturation remaining in depleted oil sands based on flow experiments are of the order of 30 to 60 per cent liquid saturation. This concept has led us to neglect the ability of oil and water to drain of their own accord down to a final saturation of 8 to 10 per cent in the upper portion of thick sand sections. This means that oil will drain from thick permeable sands and reduce the final saturation much lower than any fluid drive could reduce it. It follows that claims for efficient recovery of oil from thick sands by fluid drives probably are unsound if compared with the recovery by drainage of the oil to the final saturations indicated in the paper.

It should be noted that Dr. Leverett bases the water-oil-sand relations on the preferential wetting of the sand by the water but states that exceptions to this preferential wetting by water may occur. This possibility that water does not preferentially wet the sand should not be forgotten when working with naturally occurring systems.

S. C. HEROLD,* Los Angeles, Calif.—Dr. Leverett's paper contributes to our knowledge of events within a producing reservoir in a manner aptly stated by S. E. Buckley just a year ago in the following words:[21]

"Regardless of the geometrical complexity of the conditions met in actual practice and the resulting difficulty in drawing exact conclusions, the underlying physical principles may be discovered through laboratory investigation, and once delineated and understood may be relied upon for the interpretation of the behavior of individual wells and of complete reservoirs. In fact, a knowledge of these principles is absolutely essential to any intelligent study of the drainage of oil and gas, the spacing of wells, the value of gas injection, or the use of water-flooding in secondary recovery operations."

The patient investigations of Muskat, Botset, Wyckoff and Lewis likewise clarify our conceptions of reservoir behavior. Field reservoirs are too complex and too erratic in their behavior, and there are too many factors in simultaneous action for us to rely upon them. In the laboratory it is a simple matter to eliminate in turn all the disturbing factors except the selected one for each particular investigation. A subsequent compilation of the results of necessity will reveal the performance of the well or that of the reservoir. The method is comparatively new in the oil industry, although it has had a general application in other sciences since the fourth century B. C. The industry is fortunate in having the work of these investigators. No longer need we deal with the uncertainties of field data,

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* Assistant Professor of Chemical Engineering, University of Michigan.

* Consulting Petroleum Geologist and Engineer.

[21] S. E. Buckley: *Trans.* A.I.M.E. (1940) 136, 104.

particularly where these data originate in observations by untrained individuals.

Mr. Leverett's suggestion that we discard the analogy between a sand and a bundle of straight, cylindrical capillary tubes is timely. Any such analogy is misleading. Uren first pointed this out some years ago in the following words:[12] "An oil sand is not a 'bundle of capillary tubes' converging on a well."

Furthermore, the idea that the Jamin effect can stop flow was discarded by Versluys in the following terms:[13] "J. Plateau proved that Jamin had not taken all the necessary precautions with his experiments. With the precautions Plateau took, the effect was much less. The writer believes that the Jamin effect would not be observed in a cylindrical tube, if it were possible to work more accurately than Plateau did." As a matter of fact, Plateau did the best he could to see that the tubes were clean. With the laboratory refinements of today, undoubtedly it is possible to improve upon Plateau's methods. This should in itself prove that the application of any such effect is now unwarranted. Botset came to this conclusion by experimentation with an ingenious electrical apparatus which showed very clearly that:[14] " . . . even in the case of mixtures any pressure gradient however small will cause fluid to move through a porous medium."

Buckley apparently agrees with this, for he said:[11] "It follows that so long as a pressure gradient exists in a continuous body of sand, flow will continue."

The preponderance of opinion obviously is against the concept of the capillary tube and in favor of the more realistic one; namely, "the concept of a characteristic distribution of interfacial two-fluid curvatures with water saturation," as offered by Leverett. This is clearer and in exact agreement with laboratory results. We cannot explain all that we observe in the field, but laboratory experimentation, supported by the integrations of the simpler partial differential equations of the second order and second degree, in time will reveal with precision that which we desire to know.

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