

# Review of Some Elements of Soil-Moisture Theory

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GEOLOGICAL SURVEY PROFESSIONAL PAPER 411-D



# Review of Some Elements of Soil-Moisture Theory

By IRWIN REMSON *and* J. R. RANDOLPH

F L U I D   M O V E M E N T   I N   E A R T H   M A T E R I A L S

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## LIST OF SYMBOLS

$a$ acceleration	$r$ radius of a capillary tube
$A$ area of a liquid surface	$r_0$ critical distance of separation between the molecules of a liquid
$b$ mole fraction of dissolved material	$R$ radius of curvature of a hemispherical liquid surface
$C$ a constant	$R_1$ and $R_2$ principal radii of curvature of a liquid surface
$d$ a digit or group of digits	$R$ the gas constant
$dS$ area of an infinitesimal element of capillary surface	$dS$ area of a small element of capillary surface
$D$ density of a liquid or gas	$T$ absolute temperature
$D(\Omega)$ diffusivity as a function of concentration of ions or molecules	$t$ time
$e$ the exponential base, 2.71828 . . .	$u$ a scalar point function such as potential
$f$ a digit	$v$ volume of a mass of water
$F$ force or resultant force	$v_l$ specific volume of a liquid
$F_a$ force of adhesion	$v_v$ specific volume of a vapor
$F_c$ force of cohesion	$\bar{V}$ mass flow of moisture (a vector)
$F_g$ force of gravity	$V_x, V_y, V_z$ components of the mass flow of moisture in the $x, y, z$ directions
$g$ acceleration of gravity	$\bar{V}_v$ volume flow of moisture (a vector)
$G$ gravitational potential	$W$ work or energy
$G_m$ gravitational potential in ergs per gram of water	$x, y, z$ distances in a rectangular coordinate system
$G_v$ gravitational potential in ergs per cubic centimeter of water	$z$ distance above or below a datum
$h$ water-table elevation	$\alpha$ angle between a force and direction of movement
$\Delta h$ difference in water-table elevation	$\beta$ moisture content on a dry-weight basis
$\bar{i}, \bar{j}, \bar{k}$ a system of unit direction vectors	$\frac{\partial \beta}{\partial \Sigma}$ specific moisture capacity
$K$ coefficient of capillary conductivity	$\gamma$ density of a gas or vapor
$l$ length of a capillary tube	$\Delta$ operator indicating change in value of a quantity
$m$ mass	$\epsilon$ osmotic-pressure potential
$M$ molecular weight	$\eta$ coefficient of viscosity
$o$ a digit	$\theta$ (1) angle of contact; or (2) angle between the inclination of the water table and the horizontal
$p$ (a) pressure; (b) pressure on the concave side of a curved liquid surface; (c) pressure of the vapor in a capillary opening; (d) pressure of the vapor a distance above a free flat water surface; or (e) vapor pressure of a solution	$\kappa$ diffusivity
$p_0$ (a) pressure of the vapor immediately above a flat water surface; (b) pressure on the convex side of a curved liquid surface; or (c) vapor pressure of a free pure solvent	$\lambda$ heat of vaporization at constant temperature
$p'$ pressure of the liquid on the convex side of a meniscus	$\xi$ adsorption potential
$p_a$ pressure just over an element of capillary surface	$\pi$ 3.14159 . . .
$p'_a$ pressure just under an element of capillary surface	$\rho$ density of liquid water
$P$ hydrostatic pressure	$\rho_s$ bulk density of a soil
$Q$ discharge or flow rate	$\sigma$ surface tension
	$\Sigma$ capillary potential
	$\phi$ total potential
	$\psi$ hydrostatic-pressure potential
	$\Omega$ concentration of ions or molecules
	$\nabla$ the vector operator del, or nabla

## FLUID MOVEMENT IN EARTH MATERIALS

### REVIEW OF SOME ELEMENTS OF SOIL-MOISTURE THEORY

By IRWIN REMSON and J. R. RANDOLPH

#### ABSTRACT

This review was assembled from the existing literature to make available a convenient introduction to this subject, which is of interest to workers in many diverse fields of hydrology.

Surface tension at the liquid-vapor interfaces largely controls the occurrence and movement of moisture in unsaturated soils. Surface tension is defined as the amount of work or energy required to produce a unit increase in the area of a liquid surface. The pressure on the concave side of a liquid-vapor surface in a round capillary tube exceeds the pressure on the convex side by an amount equal to twice the surface tension divided by the tube radius. The rise of liquid in a round capillary tube, if the angle of contact is assumed to be zero, is predicted by the capillary-rise equation  $\rho g z = \frac{2\sigma}{r}$ ; where  $\rho$  is the density of the liquid,  $g$  is the acceleration of gravity,  $z$  is the height of capillary rise,  $\sigma$  is surface tension, and  $r$  is the radius of the tube.

Important soil-moisture phenomena result from the transfer of water molecules across liquid-vapor surfaces and from the diffusion of water vapor within the system. Vapor pressure decreases with increasing height above a free water surface according to the barometric equation. The vapor pressure over a water meniscus is less than the vapor pressure over a flat water surface by an amount that increases with surface curvature according to the Kelvin equation. When the barometric and Kelvin equations are compared, the capillary-rise equation shown above is obtained. This equation holds at equilibrium throughout the zone of aeration.

The total potential of soil water is the minimum energy per gram needed to transport a test body of water from a water-table datum to any point within the liquid phase of a soil-water system at equilibrium. It is the scalar sum of six main component potentials: (a) gravitational potential, which increases with height above the water table; (b) hydrostatic-pressure potential, which is associated with surface tension at liquid-vapor interfaces; it becomes increasingly negative with increasing height above the water table at equilibrium, and the force associated with its negative gradient exerts a suction on any external body of water with which it is in contact; (c) osmotic-pressure potential, which is present in soil that shrinks upon drying; it is produced by osmotic pressures resulting from differences in ion concentrations at surfaces of soil particles having electric (Gouy) double layers; the force associated with its negative gradient also exerts a suction on externally applied bodies of water; (d) adsorption or adhesion forces, which strongly retain water near the surfaces of soil particles; adsorption potential is important only in soils that are drier than those normally encountered in nature; (e) gradients of thermal poten-

tial, which occur when temperature differences occur in the system; they are relatively unimportant in causing moisture movement except when the temperature gradients are large; (f) finally, chemical potential, which is due to the osmotic energy of free ions in the aqueous solution; it is usually unimportant in nonsaline soils because solutes generally move more readily than the water with respect to the soil.

In a hypothetical distribution of vertically swelling and pinching horizontally disconnected capillary tubes, there are positions of both minimum and maximum capillary rise. These are the most common positions of the top of the capillary fringe, which is generally at the maximum or minimum position according to previous fluctuations of the water table, whether rising or falling. A hypothetical model of rhombohedrally packed spheres differs from the vertically pinching and swelling tubes mainly in that isolated wedges of water remain above the capillary fringe as the water table falls. Water is either added to or taken away from the water wedges by vapor diffusion so that the capillary-rise equation is satisfied at equilibrium.

Water may move in the zone of aeration as a liquid, a vapor, or both a liquid and a vapor. Vapor transfer occurs where a vapor continuum fills the pores. Where only the pore necks are filled with water, movement occurs by vapor transfer in the pores and by liquid transfer in the necks. Where the pore necks and parts of the pores are filled with liquid water, movement may occur by discontinuous jumps of liquid water from neck to neck. Finally, where a moisture continuum fills the pores, water may move completely as a liquid.

The hydraulic conductivity of a wet soil decreases very rapidly as the moisture content decreases from its saturation value. Field-capacity and wetting-front phenomena are largely a result of this decrease of hydraulic conductivity with moisture content.

The differential equation for unsaturated flow is derived from the equation of continuity and Darcy's law.

#### INTRODUCTION

This report is not an exhaustive treatise on soil moisture. It is not meant to display a full understanding of the physics of the basic phenomena. Indeed, the writers do not possess such a thorough knowledge of this adjacent but alien field. Rather, it is intended to provide for the hydrologist a concise and easily mastered picture of some of the important phenomena and practical manifestations of soil-moisture theory.

The Seabrook investigation of the U.S. Geological Survey, of which this report is a product, was made under the supervision of Allen Sinnott, district geologist, U.S. Geological Survey, Trenton, N.J. The cooperation of the Seabrook Farms Co. in all phases of the investigation is acknowledged with gratitude.

### ZONE OF AERATION

The zone of aeration is between the water table and the land surface. It is "the zone in which the interstices of the functional permeable rocks are not filled (except temporarily) with water. The water is under pressure less than atmospheric" (Am. Geol. Inst., 1957, p. 325; after Meinzer, 1923b, p. 31). Thus, three physical phases exist in an unsaturated soil in the zone of aeration: the solid soil matrix, the liquid water, and the soil air which includes the vapor of the liquid. Because of the presence of these phases and the interfaces between them, the occurrence and movement of water in the zone of aeration are more complex than in saturated flow.

The zone of aeration (vadose zone), according to Meinzer (1923a, p. 81; 1923b, p. 26), has three divisions: the capillary fringe, the intermediate belt, and the belt of soil water. The lowermost or capillary fringe is "a zone, in which the pressure is less than atmospheric, overlying the zone of saturation and containing capillary interstices some or all of which are filled with water that is continuous with the water in the zone of saturation but is held above that zone by capillarity acting against gravity" (Am. Geol. Inst., 1957, p. 44; after Meinzer, 1923b, p. 26). The intermediate belt is "that part of a zone of aeration that lies between the belt of soil water and the capillary fringe. It contains intermediate vadose water" (Am. Geol. Inst., 1957, p. 151; after Meinzer, 1923b, p. 26). The uppermost belt, or belt of soil water, is "that part of the lithosphere, immediately below the surface, from which water is discharged into the atmosphere in perceptible quantities by the action of plants or by soil evaporation" (Am. Geol. Inst., 1957, p. 29; after Meinzer, 1923b, p. 23).

This report reviews some of the elements of soil-moisture theory, which deals largely with the unsaturated occurrence and movement of water in the zone of aeration. It reviews also some of the background physics needed for an understanding of this theory.

### BACKGROUND PHYSICS

#### SURFACE TENSION

Surface-tension phenomena associated with the liquid-vapor interfaces within the soil matrix have important effects upon the occurrence and movement

of soil water. Part of the following description of these surface-tension phenomena is based upon Sears (1950, p. 319-330).

#### MOLECULAR CAUSES OF SURFACE TENSION

Whereas the average distance between the molecules of a gas at atmospheric pressure is about 10 times the size of each molecule, the molecules of a liquid are almost touching. The forces between the individual liquid molecules are largely electrical. As shown in figure 1,

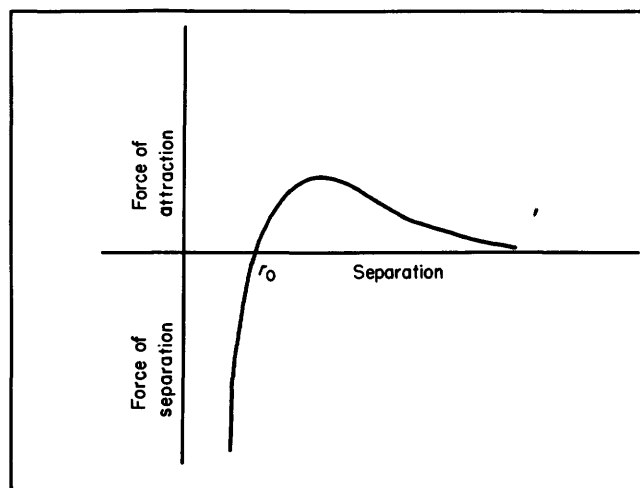


FIGURE 1.—Intermolecular force as a function of molecule separation. (After Sears, F. W., 1950, *Mechanics, heat, and sound*; 2d ed., Addison-Wesley Pub. Co., Inc., Reading, Mass., p. 321.)

an attractive force exists between two molecules that are separated by a distance greater than some value,  $r_0$ . (See "List of symbols.") As the separation distance increases from  $r_0$ , the attractive force first increases to a maximum and then gradually decreases.

When the separation between two molecules of a liquid is less than  $r_0$ , there is a large repulsive force. This repulsive force is responsible for the high pressures that are needed to compress a liquid. When the separation distance is  $r_0$ , the repulsive and attractive forces equate to zero, and the molecules are in a state of equilibrium.

A molecule in the interior of a liquid is surrounded by similar molecules. The molecule has thermal energy that tends to make it move (to become displaced from the equilibrium separation,  $r_0$ ). However, when displaced from  $r_0$ , it is attracted by the adjacent molecules on one side and repelled by the adjacent molecules on the other side in accordance with the relation shown on figure 1. The combination of attractive and repulsive forces tends to restore the molecule to the equilibrium separation. As a consequence of the displacing effect, due to the thermal energy, and the restoring effect, due to the intermolecular forces, the molecules

in the interior of a liquid tend to oscillate about their equilibrium separation,  $r_0$ .

A molecule at the surface of a liquid generally has a component of vibration normal to that surface. When the molecule is moving outward from the surface, it is attracted back to the surface by the molecules below. However, there are no molecules above the liquid surface to give the repulsive force shown in figure 1. Therefore, the molecule may move out a greater distance than molecules within the body of the liquid. If the surface molecule has sufficient thermal energy it may escape (evaporate) from the liquid. The molecule performs a series of excursions out to a distance slightly greater than that of normal separation, and spends most of its time in a region where an inward force of attraction is exerted on it in accordance with the relation shown in figure 1. "The fact that the environment of those molecules in or very near the surface differs from that of the molecules in the interior gives rise to the surface effects we are now considering" (Sears, 1950, p. 322).

#### DEFINITION OF SURFACE TENSION

A definite amount of work per unit area is required to increase the area of a liquid surface. The work can be recovered when the area decreases, so that the surface layer appears capable of storing potential energy. The enlarged liquid surface is not stretched like a balloon. Instead, additional molecules move into the surface layer and the final molecular spacing is unchanged. Unlike a balloon or rubber membrane, the work done, or energy of the surface, is directly proportional to the increase in the surface area of the liquid. The proportionality constant, or the work per unit area, is known as the surface tension,  $\sigma$ . It is expressed in units of energy per unit area such as ergs per square centimeter, which is equivalent to dyne-centimeters per square centimeter or dynes per centimeter. Expressed mathematically,

$$dW = \sigma dA \quad (1)$$

where  $dW$  is the work, or energy, necessary to increase the area of the liquid surface by an amount  $dA$ .

The free energy of a liquid-vapor surface is a fundamental property of the surface (Adam, 1930, p. 4). "The free energy of a substance is a property that expresses the resultant of the energy (heat content) of the substance and its inherent probability (entropy)" (Pauling, 1958, p. 650). It exists because work must be done to extend the surface, as the extension is accomplished by bringing molecules from the interior to the surface of the liquid against the inward attractive forces. As a mathematical device, a hypothetical

tension parallel to the surface and equal to the free energy is sometimes substituted for the free energy. This is known also as the surface tension, but it is merely a convenient mathematical fiction that does not really exist. Surface tension is correctly defined as the proportionality constant in equation 1 (Sears, 1950, p. 322). Actually,  $W$  in equation 1 should be the free energy for a rigorous definition of surface tension.

A system is in stable equilibrium when its potential energy is a minimum (Sears, 1950, p. 322). Liquid-vapor interfaces tend toward a condition of minimum potential energy and minimum free energy. Because the energy is proportional to the area, as shown in equation 1, the condition of minimum energy corresponds to a surface of minimum area for a given volume. Thus, the inward attraction causes the number of molecules in the surface to diminish to a minimum by contraction of the surface. "This tendency is shown in the spherical form of small drops of liquid, in the tension exerted by soap films as they tend to become less extended, and in many other properties of liquid surfaces" (Adam, 1930, p. 1).

In discussing the work of Plateau, Adam (1930, p. 1) points out that liquid surfaces always assume a curvature such that

$$\frac{1}{R_1} + \frac{1}{R_2} = \text{Constant} \quad (2)$$

when the disturbing effect of gravity is absent.  $R_1$  and  $R_2$  are the principal radii of curvature at any point. It is a geometrical fact that surfaces for which this relation holds are surfaces of minimum area.

It is customary to show  $R_1$  and  $R_2$  as positive when the liquid surface is convex to the vapor as for a water bubble in air. In this report it will be more convenient to take  $R_1$  and  $R_2$  as positive when the liquid surface is concave to the vapor, as for a capillary meniscus for water.

#### PRESSURE DIFFERENTIAL ACROSS A LIQUID-GAS INTERFACE

The pressures above and below a flat liquid-gas interface are equal at equilibrium. For convenience the discussion will be limited to the case where the liquid is water. In a vacuum the pressure of the water vapor above the interface equals the very small hydrostatic pressure immediately below the interface. Where the system is open to the atmosphere the pressure above the surface is the sum of the partial pressures of the water vapor and the atmospheric gases. The hydrostatic pressure immediately below the surface is the result of the combined weight of the overlying water vapor and atmosphere.



"If a liquid surface be curved the pressure is greater on the concave side than on the convex, by an amount which depends on the surface tension and on the curvature. This is because the displacement of a curved surface, parallel to itself, results in an increase in area as the surface moves toward the convex side, and work has to be done to increase the area. This work is supplied by the pressure difference moving the surface" (Adam, 1930, p. 12). "The magnitude of this pressure differential across a curved surface can be derived at once from the fact that work must be done to create fresh surface" (Sears, 1950, p. 323).

In figure 2 the pressure,  $p$ , of the air plus its water

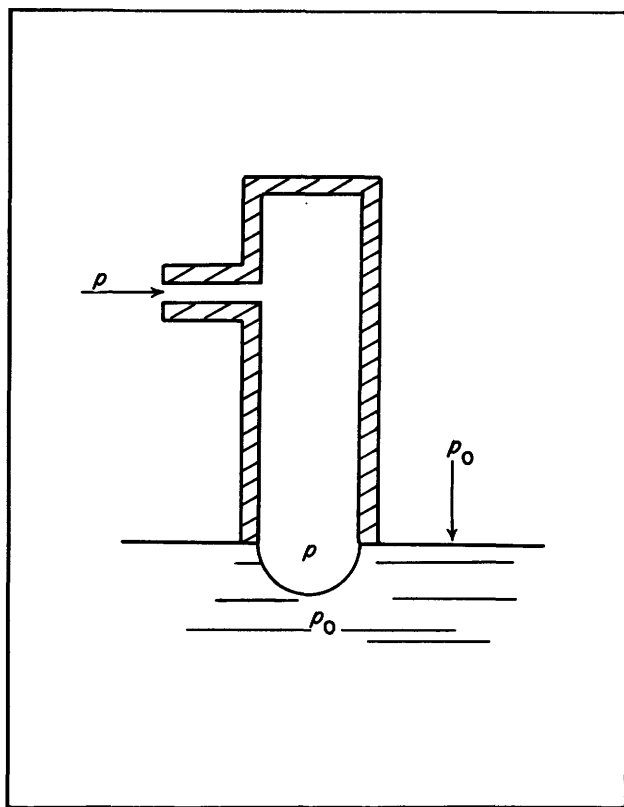


FIGURE 2.—A bubble of air blown at the end of a capillary tube.  $p_0$  is the normal pressure of the air and its water vapor, and  $p$  is increased pressure in the tube of the air and its water vapor. (After Sears, F. W., 1950, *Mechanics, heat and sound*: 2d ed., Addison-Wesley Pub. Co., Inc., Reading, Mass., p. 323.)

vapor in the capillary tube is increased over the normal pressure,  $p_0$ , of the air and its water vapor. An air bubble is formed at the lower end of the tube. When the bubble becomes unstable and is about to break away, its shape is very nearly that of a hemisphere of radius  $R$ . If  $A$  is the surface area of the hemisphere,

$$A = 2\pi R^2 \quad (3)$$

If the radius is increased to  $R + dR$ , the surface is increased by

$$dA = 4\pi R dR \quad (4)$$

Substituting this into equation 1, the work done in creating this additional surface is

$$dW = 4\pi\sigma R dR \quad (5)$$

Let us now find the work done by the pressure difference,  $p - p_0$ . The net force against a small element of the hemispherical surface of area  $dS$  is

$$(p - p_0)dS \quad (6)$$

This assumes that the increase of hydrostatic pressure from the water surface to the bottom of the bubble is negligible. In increasing the size of the bubble, this element of surface moves out radially through a distance  $dR$ . The work on this small element of the surface is the product of force and distance, or

$$(p - p_0)dS dR \quad (7)$$

When this work is integrated over all the bubble-surface elements (see equation 3), the total work done by the pressure forces is

$$dW = (p - p_0)2\pi R^2 dR \quad (8)$$

Equations 5 and 8 may be equated and simplified. Furthermore  $R$ , the radius of the hemispherical bubble, is very nearly the same as  $r$ , the radius of the tube. Therefore, the pressure difference between the concave and convex sides of the liquid interface is

$$(p - p_0) = \frac{2\sigma}{R} = \frac{2\sigma}{r} \quad (9)$$

As shown by Adam (1930, p. 14), for any curved surface (shaped like a blowout patch, for example) the pressure difference is

$$(p - p_0) = \sigma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \quad (10)$$

where  $R_1$  and  $R_2$  are the principal radii of curvature.

$R_1$  and  $R_2$  are here taken as positive for a meniscus whose interface is concave to the vapor. However in normal usage  $R$  is taken as positive when the interface is convex to the vapor, as for a water bubble in air or a mercury meniscus. If normal usage were followed, it would be necessary to have minus signs in equations 9 and 10 to have the pressure over the meniscus come out greater than the pressure below the meniscus, using the negative value of radius. It is largely to

avoid the use of these minus signs that  $R$  is taken as positive for the case of a meniscus concave to the vapor.

#### ANGLE OF CONTACT

The molecules in a liquid-vapor interface near a solid are affected by forces of cohesion (attractive forces of p. D2) exerted upon them by other molecules of the liquid and by forces of adhesion exerted upon them by the molecules of the solid

The dot in figure 3 represents a molecule in the surface layer of a liquid, and the vectors  $F_a$  and  $F_c$

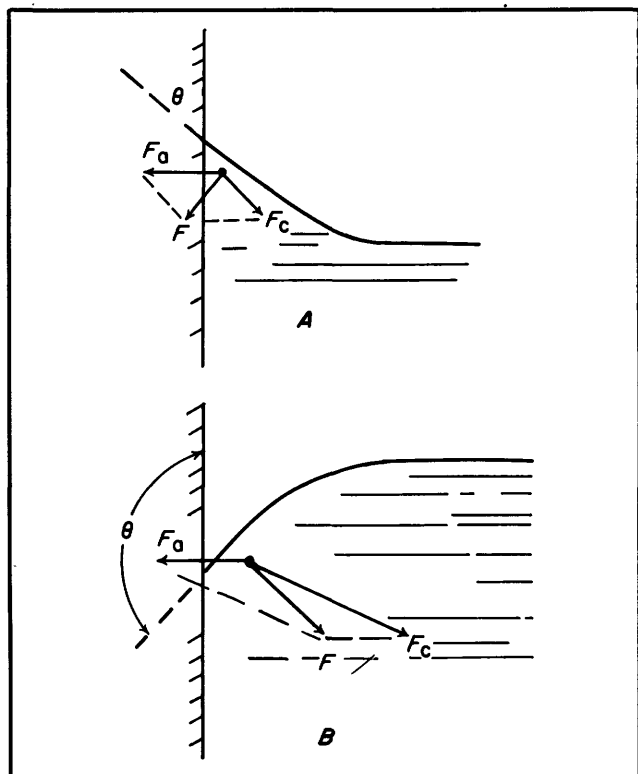


FIGURE 3.—Contact angle of a liquid-vapor surface near a solid.  $F_a$  is the adhesion force;  $F_c$ , the cohesion force,  $F$ , the resultant force, and  $\theta$ , the angle of contact, (After Sears, F. W., 1950, Mechanics, heat, and sound: 2d ed., Addison-Wesley Pub. Co., Inc., Reading, Mass., p. 325.)

represent the adhesive and cohesive forces acting on that molecule.

If the magnitudes of  $F_a$  and  $F_c$  are as shown in figure 3A, the resultant force is  $F$ . The liquid surface will curve upward near its contact with the solid because a liquid can be in equilibrium only when the force on its surface is perpendicular to the surface. The surface must be perpendicular to  $F$  and the angle of contact,  $\theta$ , is acute. If the forces of adhesion and cohesion have the relative magnitudes shown in figure 3B, the liquid surface curves down near the solid contact, and  $\theta$  is obtuse.

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When the forces of adhesion and cohesion are such that the angle of contact is zero, the liquid tends to spread over a solid surface, or to "wet" the surface. When the forces are such that the angle is large, the liquid tends to bunch up in beads or droplets on the solid surface and is said to be nonwetting.

#### RISE OF WATER IN A CAPILLARY TUBE

Figure 4 shows a glass capillary inserted in water. If the radius of the tube and the forces of cohesion and

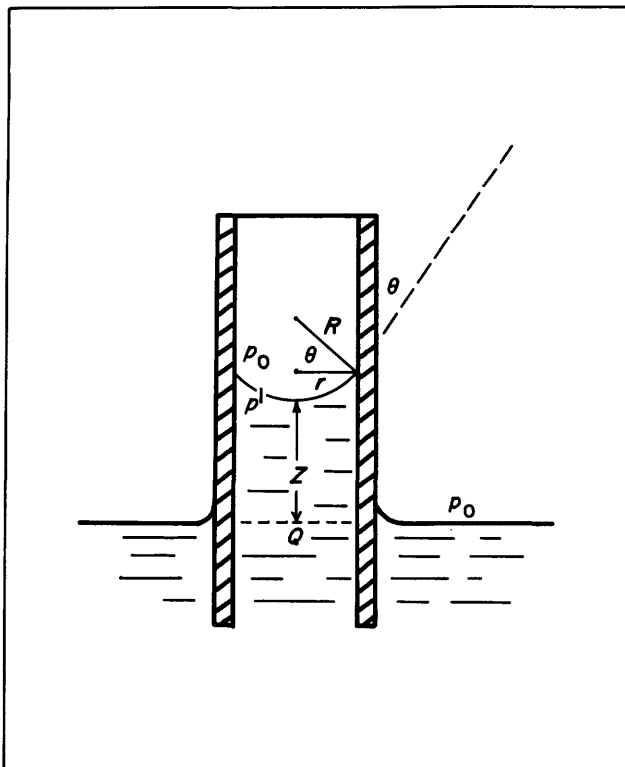


FIGURE 4.—Rise of water in a capillary tube.  $p_0$  is the atmospheric pressure,  $p'$ , the pressure under the meniscus,  $z$ , the height of capillary rise,  $R$ , the radius of curvature of the meniscus,  $r$ , the radius of the tube, and  $\theta$ , the angle of contact. (After Sears, F. W., 1950, Mechanics, heat and sound: 2d ed., Addison-Wesley Pub. Co., Inc., Reading, Mass., p. 326.)

adhesion are such as to give a meniscus that is curved concave upward, the water will rise in the tube. The following explanation of this capillary rise is adapted from Sears (1950, p. 327-328).

Let  $p_0$  be the total pressure of the atmosphere plus its water vapor above the flat surface outside the capillary tube. Under the flat surface, the hydrostatic pressure also is  $p_0$ . Neglecting the small variation of water-vapor pressure and air pressure over the small height, the total pressure above the meniscus also is  $p_0$ . Finally, for hydrostatic equilibrium the pressure at the level  $Q$  in the capillary tube also must equal  $p_0$ .

In figure 4,  $R$  is the radius of curvature of the curved surface,  $r$  is the radius of the capillary tube, and  $\theta$  is the angle of contact. Therefore (Adam, 1930, p. 15):

$$R = \frac{r}{\cos \theta} \quad (11)$$

where the tube is so narrow that the meniscus may be taken as spherical. Equation 9 gives the pressure difference across a meniscus. In the narrow tube,  $p_0$ , atmospheric pressure, is on the concave side of the meniscus. Thus it is the greater pressure. Let  $p'$  be the lesser pressure on the convex side just below the meniscus. Then using this terminology in equation 9,

$$p' = p_0 - \frac{2\sigma}{R} \quad (12)$$

Substituting the value of  $R$  from equation 11,

$$p' = p_0 - \frac{2\sigma \cos \theta}{r} \quad (13)$$

From hydrostatics, the pressure at  $Q$  is

$$p_0 = p' + \rho g z \quad (14)$$

where  $z$  is the height of capillary rise,  $\rho$  is the density of liquid water, and  $g$  is the acceleration of gravity. Substituting the value of  $p'$  from equation 13 into equation 14,

$$p_0 = p_0 - \frac{2\sigma \cos \theta}{r} + \rho g z \quad (15)$$

Rearranging, the final equation for the rise of water in the capillary tube is

$$z = \frac{2\sigma \cos \theta}{\rho g r} \quad (16)$$

The angle of contact between clean water and clean glass is nearly zero. Therefore, as a convenient approximation, equation 16 is often written as

$$z = \frac{2\sigma}{\rho g r} \quad (17)$$

or as

$$\rho g z = \frac{2\sigma}{r} \quad (18)$$

These equations state in effect that the liquid "rises or falls in the tube, until the height of the meniscus is such that the weight of the column of liquid adjusts the pressure inside and outside the tube to equality" (Adam, 1930, p. 295).

For a noncircular capillary interstice, equation 10 instead of equation 9 would be used in 12, and the final form would be

$$\rho g z = \sigma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \quad (19)$$

Therefore, other things being equal, the height of capillary rise increases as the radius of the capillary tube decreases.

"Most organic liquids and water form zero angles with clean glass and silica; exceptions to this rule may occur if the glass has become dry and the liquid is advancing over the surface" (Adam, 1930, p. 180). The contact angle of water with a mineral surface varies with the state and cleanliness of the mineral surface.

"The angle assumed when a liquid advances to a position of rest over a dry solid surface is larger than the angle when the liquid recedes to a position of rest over a wetted surface, and this was called by Sulman (1919) the *hysteresis of contact angle*; he suggested that the advancing or retreating contact angles are unstable forms of a definite equilibrium contact angle (*static angle*)" (Partington, 1951, p. 166). Edser (1922, p. 290), citing Sulman (1919), gives values for water from 13° to 58° receding and from 62° to 95° advancing for different mineral surfaces.

Partington (1951, p. 167) credits Langmuir and Bartell and co-workers for stating that, with proper precautions, equilibrium contact angles can be obtained and measured. Wark and Cox (1932), reviewing more recent work than that of Edser, say that really clean surfaces of most minerals have very small contact angles. Throughout this report, it will be assumed that the contact angles between water and the mineral grains of the soil are small, so that their cosines may be taken as unity and equations 18 and 19 are applicable.

#### WATER VAPOR IN UNSATURATED SOILS

Important phenomena in unsaturated soils result from the transfer of water molecules across liquid-vapor surfaces and the diffusion of water vapor.

#### MOLECULAR CAUSES OF VAPOR PRESSURE

When a liquid evaporates, or vaporizes, molecules fly off against the forces of molecular attraction into the overlying vapor. If the vapor is confined over the liquid, some vapor molecules return to the surface and become liquid again (condense). Eventually, when the density of the vapor is such that the average number of molecules returning to the liquid per unit time is equal to the average number leaving per unit time, the vapor is in equilibrium with the liquid. A vapor in equilibrium with its liquid is said to be saturated, and the equilibrium pressure is called the vapor tension or vapor pressure.

#### VAPOR PRESSURE AND TEMPERATURE

The pressure of a vapor in equilibrium with its liquid depends largely upon the temperature, and this depend-

ence is described by the Clausius-Clapeyron equation. As written by Fermi (1937, p. 66), the equation is

$$\frac{dp}{dT} = \frac{\lambda}{T(V_v - V_l)} \quad (20)$$

where

$dp$  = change in vapor pressure

$dT$  = change in absolute temperature

$\lambda$  = heat of vaporization of the liquid at constant temperature

$T$  = absolute temperature at which the change of state occurs

$V_v$  = specific volume of the vapor

$V_l$  = specific volume of the liquid

If it is assumed that  $V_l$  is negligible as compared with  $V_v$ , that the vapor satisfies the equation of state of an ideal gas, and that the heat of vaporization,  $\lambda$ , is constant over a wide range of temperatures, a simple approximate formula shows the manner in which vapor pressure is related to temperature. As written by Fermi (1937, p. 67), it is

$$p = Ce^{-\frac{\lambda M}{RT}} \quad (21)$$

where

$C$  = a constant

$R$  = the gas constant

$M$  = the molecular weight of the vapor

$e$  = the exponential base, 2.71828 . . .

Thus, vapor pressure increases with temperature.

#### VAPOR PRESSURE AND AMOUNT OF DISSOLVED SOLUTE

Let  $p_0$  be the vapor pressure of a free pure solvent. Add an amount of dissolved material whose value is given by the mole fraction  $b$ . The vapor pressure of the solvent will be lowered to  $p$  according to the equation,

$$p = p_0 e^{-b} \quad (22)$$

as written by Edlefsen and Anderson (1943, p. 129).

#### VAPOR PRESSURE AND HYDROSTATIC PRESSURE IN THE LIQUID

According to Edlefsen and Anderson (1943, p. 136), the relation

$$\left(\frac{dp}{dP}\right)_T = \frac{v_l}{v_v} \quad (23)$$

is true where  $dp$  is the change in vapor pressure caused by a change of hydrostatic pressure,  $dP$ . The subscript  $T$  denotes that these changes occur at constant temperature.  $v_v$  and  $v_l$  are the specific volumes of the vapor and liquid, respectively.

The fraction  $v_l/v_v$  is in general very small. Therefore, the effect of a change in the hydrostatic pressure

upon the pressure of the vapor in equilibrium with a liquid is small.

Edlefsen and Anderson (1943, p. 138) describe an equation that gives the increase in vapor pressure of water,  $\Delta p$ , in atmospheres, corresponding to the application of a hydrostatic pressure of  $P$  atmospheres. It is assumed that the normal vapor pressure  $p_0$ , in atmospheres, of free water at the temperature  $T$ , is known. The equation is

$$\Delta p = \frac{1.002(P - 2 \times 10^5 P^2)}{p_0 + \left[1 - 26.3 \left(\frac{373}{T}\right)^{10/3}\right]} \quad (24)$$

According to Edlefsen and Anderson this formula shows that, if a hydrostatic pressure of 20 atmospheres is applied to water at 27°C, the vapor pressure of the water is increased from 0.035 to approximately 0.03551 atmosphere. Thus, a relatively large change in hydrostatic pressure causes a relatively small change in vapor pressure. Similarly, if a tension of 20 atmospheres is placed on the water, the vapor pressure of the water will be decreased by 0.00051 atmosphere, and the humidity will be 98.5 percent of the humidity over a free water surface at the same temperature. A soil in this condition is close to the permanent wilting percentage, which is commonly taken at a suction of 15 atmospheres. Thus, as a soil dries, the vapor pressure and the humidity relative to that over a free water surface are decreased by only a small amount.

#### BAROMETRIC EQUATION

The barometric equation, or Laplace law of atmospheric pressure, gives the variation of gas pressure with height in a uniform gravitational field. It is usually used to determine the variation of air pressure with height. According to Edlefsen and Anderson (1943, p. 129), "It applies equally well, however, to the variation of vapor pressure with height above a free liquid surface, as, for example, water, when the whole system has come to equilibrium at the same temperature, in a uniform gravitational field." Because of the importance of the Laplace law in this development, the following derivation is included.

Consider a vertical column of gas of unit cross-sectional area (fig. 5).

According to the ideal-gas law,

$$pv = RT \quad (25)$$

where

$p$  = the pressure, in dynes per square centimeter, at a distance  $z$  above the reference point

$v$  = specific volume of the gas

$T$  = absolute temperature

$R$  = gas constant, in ergs per degree gram

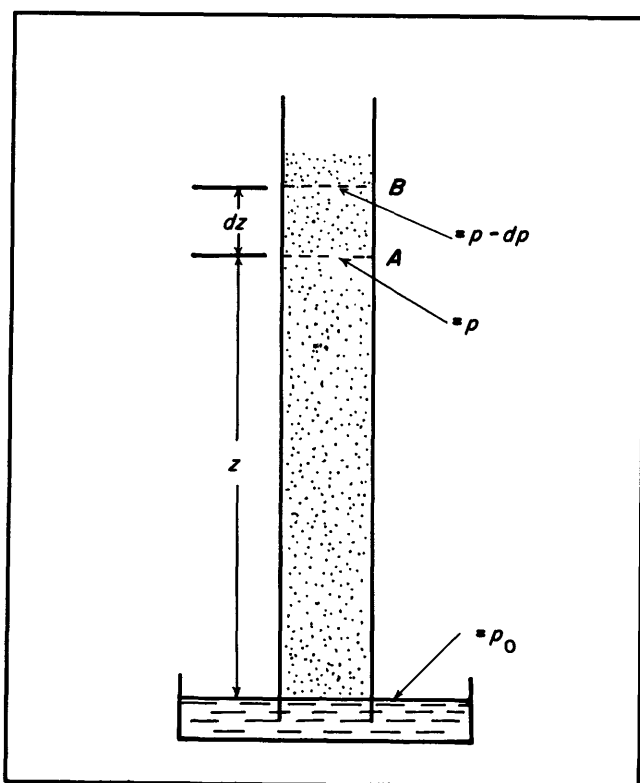


FIGURE 5.—Column of vapor in a gravitational field.  $p_0$  is the vapor pressure at the free water surface and  $p$ , vapor pressure at a height,  $z$  above the free water surface. (After Edlefsen and Anderson, 1943, p. 129.)

$R$  is equal to the universal gas constant, 83,140,000 ergs per degree gram mole divided by the weight of a gram mole. The molecular weight, or the weight of a gram mole of water vapor, is 18.02 grams. For water vapor,  $R$  would therefore be about 4,620,000 ergs per degree gram.

Rewriting equation 25, and remembering that specific volume is the inverse of density,

$$\gamma = \frac{p}{RT} \quad (26)$$

where  $\gamma$  is the density of the gas, in grams per cubic centimeter.

The vapor pressure of the gas in the column in figure 5 changes by the amount  $-dp$  in going from  $A$  to  $B$ . This decrease in pressure is equal to the weight of the gas or vapor in the length of column represented by  $dz$ . The weight is  $\gamma g dz$ . Thus,

$$-dp = \gamma g dz \quad (27)$$

Eliminating  $\gamma$  by means of equation 26 and rearranging,

$$-\frac{dp}{p} = \frac{g}{RT} dz \quad (28)$$

Integrating from  $z=0$  at the free water surface where  $p=p_0$ , to  $z=z$  where  $p=p$ ,

$$[\ln p]_{p_0}^p = -\frac{g}{RT} [z]_0^z \quad (29)$$

and

$$\ln \frac{p}{p_0} = -\frac{gz}{RT} \quad (30)$$

(Edlefsen and Anderson, 1943, p. 130).

Equation 30 can be put into the final form

$$p = p_0 e^{-\frac{gz}{RT}} \quad (31)$$

Thus, if  $p_0$  is the vapor pressure at the free water surface, where  $z=0$ , equation 31 determines the pressure  $p$  at a height  $z$ . It is interesting that the rate of change of vapor pressure with height outside a capillary tube is much smaller as predicted by equation 31 than the rate of change of hydrostatic pressure with height within the tube,  $\rho g z$ . This is as predicted by equation 23.

#### KELVIN EQUATION

##### DERIVATION

The vapor pressure over a concave water meniscus is less than the vapor pressure over a free flat water surface. Thus, a vapor-pressure deficiency exists over a meniscus in a capillary tube when compared with the vapor pressure over a free flat water surface. The relation between the vapor pressure and the radius of curvature of the meniscus is described by the Kelvin equation (Thompson, 1871). Because of the importance of this equation, it is now derived for a capillary surface connected to a flat surface following the derivation of W. O. Smith (1936, p. 228–230).

Let the system in figure 6 be isolated so that there is no air pressure. Then  $p_0$  is the water-vapor pressure over the flat surface. The hydrostatic pressure in the liquid just under the flat surface also is equal to  $p_0$  and is due to the weight of the overlying water vapor. Let  $p_a$  be the water-vapor pressure just over an element,  $dS$ , of capillary surface, and let  $p'_a$  be the hydrostatic pressure just under the element,  $dS$ , of capillary surface. The hydrostatic pressure,  $p'_a$ , under the element of curved surface equals the vapor pressure,  $p_a$ , minus the pressure difference across the curved surface due to surface tension.

If the system in figure 6 were open to the air, all the pressures would be increased by the atmospheric pressure. Furthermore, the change in atmospheric pressure with height would have to be considered, as well as the change in water-vapor pressure with height. Therefore when suitable adjustments are made the

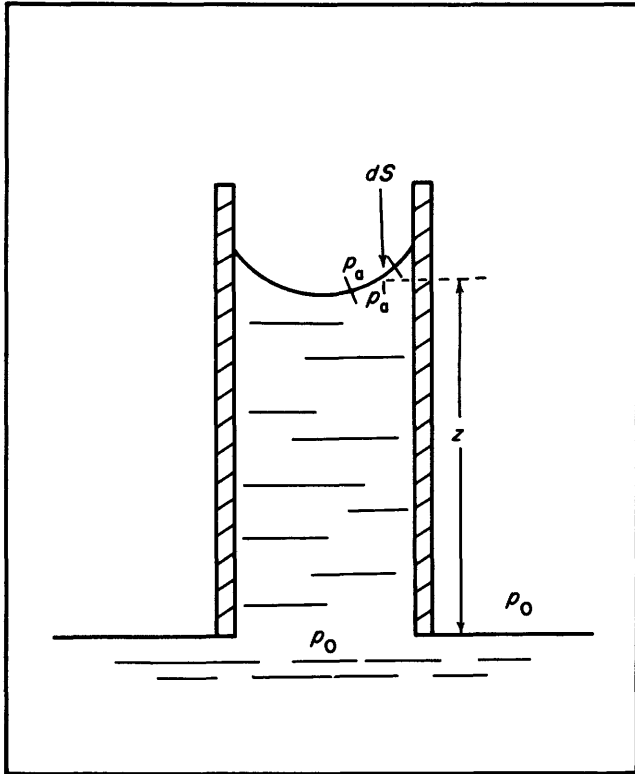


FIGURE 6.—A curved liquid-vapor surface in contact with a free flat liquid surface.  $p_0$  is the water-vapor pressure over the flat surface,  $p_a$ , the water-vapor pressure just over and  $p'_a$ , the hydrostatic pressure just under an element,  $dS$ , of capillary surface at a height,  $z$ , above the flat surface. (After Smith, W. O., 1936, p. 229).

following derivation is applicable regardless of the type of gas in the system:

The pressure in the water in the capillary tube at the same level as the flat surface is

$$p_0 = p'_a + \rho g z \quad (32)$$

Similarly, the pressure in the vapor outside the capillary tube just over the flat surface is

$$p_0 = p_a + \int_0^z \gamma g dz \quad (33)$$

where  $\gamma$  is the density of the vapor. Equating equations 32 and 33,

$$p_a + \int_0^z \gamma g dz = p'_a + \rho g z \quad (34)$$

This can be rearranged to

$$p_a - p'_a = \rho g z - \int_0^z \gamma g dz \quad (35)$$

The value for the difference of pressure across the curved surface can now be substituted from equation 10:

$$\sigma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) = \rho g z - \int_0^z \gamma g dz \quad (36)$$

taking the radii of curvature as positive.

The two terms on the right side of equation 36 give the pressure differences between the flat and curved water surfaces in the water and vapor columns, respectively. To make them more usable, everything will be put in terms of pressure. This can be done by starting with the simple relationship between pressure and height in the vapor, equation 27.

$$dp = -\gamma g dz \quad (37)$$

Integrating between 0,  $p_0$  and  $z$ ,  $p$ ,

$$\int_{p_0}^p dp = - \int_0^z \gamma g dz \quad (38)$$

and

$$(p - p_0) = - \int_0^z \gamma g dz \quad (39)$$

Equation 39 may be substituted for the second term on the right side of equation 36, giving

$$\sigma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) = \rho g z + (p - p_0) \quad (40)$$

To put the first term on the right side of equation 40 into terms of pressure, equation 37 is rewritten as

$$dz = - \frac{dp}{\gamma g} \quad (41)$$

Setting up the integral between 0,  $p_0$  and  $z$ ,  $p$ ,

$$\int_0^z dz = - \int_{p_0}^p \frac{dp}{\gamma g} \quad (42)$$

Integrate the left side, and

$$z = - \int_{p_0}^p \frac{dp}{\gamma g} \quad (43)$$

We cannot integrate the right side of equation 43 because  $\gamma$ , the density of the vapor, varies with pressure. To eliminate  $\gamma$  from equation 43, consider Boyle's law:

$$\frac{\gamma}{\gamma_0} = \frac{p}{p_0} \quad (44)$$

or

$$\gamma = \frac{\gamma_0 p}{p_0} \quad (45)$$

Putting this value of  $\gamma$  into equation 43, it becomes

$$z = - \frac{p_0}{g \gamma_0} \int_{p_0}^p \frac{dp}{p} \quad (46)$$

Integrating,

$$z = - \frac{p_0}{g \gamma_0} \ln \frac{p}{p_0} \quad (47)$$

Substituting into equation 40, the Kelvin equation is

$$\sigma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) = -\frac{\rho p_0}{\gamma_0} \ln \frac{p}{p_0} + (p - p_0) \quad (48)$$

Equation 40 can be simplified if it is assumed that  $(p - p_0)$  is negligible and that  $R_1 = R_2 = r$ , as is approximately true for a capillary tube of circular cross section. Then 48 becomes

$$-\ln \frac{p}{p_0} = \frac{2\sigma}{r} \frac{\gamma_0}{\rho p_0} \quad (49)$$

From the ideal gas law,

$$p_0 v_{v0} = RT \quad (50)$$

where  $v_{v0}$  is the specific volume of the vapor at  $p_0$ . Then,

$$p_0 = \frac{RT}{v_{v0}} = \gamma_0 RT \quad (51)$$

Substituting for  $p_0$  in equation 49 and remembering that  $\rho$ , the density of water, is the inverse of  $v_i$ , the specific volume of water, we arrive at the following forms of the Kelvin equation:

$$-\ln \left( \frac{p}{p_0} \right) = \frac{2\sigma}{r} \frac{v_i}{RT} \quad (52)$$

and

$$p = p_0 e^{-\frac{2\sigma}{r} \frac{v_i}{RT}} \quad (53)$$

The minus is in equation 53 because the values of  $R_1$ ,  $R_2$ , and  $r$  were assumed as positive if the meniscus is concave to the vapor. If positive values of  $r$  are substituted into equation 53, the pressure over the meniscus comes out less than that over a flat surface. Using the form shown in 53, the radius of curvature is negative when the meniscus is convex to the vapor, as in a raindrop. If a negative value of  $r$  is inserted in the equation, the vapor pressure over a raindrop comes out greater than that over a flat surface.

Equation 53 applies where the capillary surface is in liquid continuity with the flat water surface. The equation may be derived, from thermodynamic considerations (Edlefsen and Anderson, 1943, p. 142-146), for a curved liquid-vapor interface that is separated from the flat liquid surface.

For the discontinuous-liquid system, we again take the radius of curvature of the interface to be positive for a liquid surface concave to the vapor and negative for a surface convex to the vapor. From the equation, the smaller the radius of curvature of a capillary meniscus, or the greater the curvature of the meniscus,

the greater is the vapor-pressure deficiency above the meniscus.

#### SIGNIFICANCE

Equating the exponential terms in equation 53, the Kelvin equation, and equation 31, the barometric equation, rearranging terms, and substituting density for the inverse of the specific volume of the water, we arrive back at equation 18

$$\rho g z = \frac{2\sigma}{r} \quad (54)$$

Equation 54 does not contain any of the properties of the gas. Thus, the height of capillary rise of a given liquid in a tube or interstice of given radius is the same whether the surrounding atmosphere consists of water vapor alone or water vapor and air.

The Kelvin equation may be looked at in several ways. If suction is applied to a wet sand, the vapor pressure is decreased. Therefore, the radii of curvature of the equilibrium minisci are greatly reduced, and the menisci are drawn deeper into the narrowing necks of the soil pores. The hydrostatic pressure in the water on the convex sides of the menisci also is decreased because of the pressure differentials across such curved surfaces.

Adam (1941, p. 13-14) gives a physical explanation of these phenomena:

The vapor pressure over a convex surface is greater than that over a plane; and over a concave surface it is less. The difference depends on the fact that condensation of vapor on a small convex drop of a liquid increases its surface area, so that the surface tension tends to oppose the condensation and to increase the vapor pressure. On a plane surface condensation does not alter the surface area, and on a concave surface the surface area is diminished by condensation of more vapor, so that the surface tension aids condensation in this case.

Adam (1930, p. 22) gives solutions of the Kelvin equation for the increase of vapor pressure,  $p/p_0$ , over a drop of water of radius  $r$ , at 20° C, with  $p_0$  equal to 17.5 mm of mercury:

$r$ (cm)	$p/p_0$
$-10^{-4}$	1.001
$-10^{-5}$	1.011
$-10^{-6}$	1.114
$-10^{-7}$	2.95

Thus, a small change in vapor pressure greatly changes the radius of the equilibrium meniscus.

To demonstrate the use of these equations, assume that a suction equivalent to 15 atmospheres is applied to a soil. This value of negative hydrostatic pressure is commonly taken for the permanent wilting percentage. Let us compute the radius of the circular pore in which the menisci will be lodged at equilibrium.

For this case,

$$\begin{aligned}v_i &= 1 \text{ cm}^3 \text{ per gram} \\v_o &= 57,800 \text{ cm}^3 \text{ per gram} \\dP &= 15 \text{ atmospheres} = 15,194,000 \text{ dynes per cm}^2\end{aligned}$$

Therefore, the vapor-pressure deficiency can be computed from equation 23. It is  $dp = 263$  dynes per  $\text{cm}^2$ . Thus, even at the permanent wilting percentage, the vapor-pressure deficiency in the soil is very small. (See also p. D7.)

To determine the equilibrium meniscus, or the pore that has a sufficiently small radius to support the equilibrium meniscus, we refer to the Kelvin equation. For a temperature of  $20^\circ\text{C}$ ,  $p_0$ , the vapor pressure over a flat water surface, may be taken as 17.5 mm of mercury.

$$\begin{aligned}p_0 &= 17.5 \text{ mm of mercury} = 23,300 \text{ dynes per cm}^2 \\ \sigma &= 73.5 \text{ dynes per cm for water} \\ v_i &= 1 \text{ cm}^3 \text{ per gram} \\ T &= 293^\circ \text{ Kelvin} \\ R &= 83,100,000 \frac{\text{ergs}}{\text{degree gram-mole}} \left( \frac{18.0 \text{ gram}}{\text{gram mole}} \right) \\ &= 4,620,000 \frac{\text{ergs}}{\text{degree gram}} \text{ for water vapor} \\ p &= p_0 - dp = 23,100 \text{ dynes per cm}^2\end{aligned}$$

Substituting into equation 52 or 53, the radius of the equilibrium meniscus is about 0.00001 cm, or 0.0001 mm.

The same result can be found by substituting into equation 54 a value of  $z$  equivalent to 15,500 cm. This is the height of a hanging column of water that would give a tension of 15 atmospheres if the hanging column of water could support such tensions.

As will be discussed later, other forces are generally more important than surface tension in pores of this small size. Therefore, this computation is more of a demonstration than an accurate portrayal of the meniscus size in a soil at the permanent wilting percentage.

Because the Kelvin and barometric equations apply whether or not a liquid continuum exists, equation 54 also applies to both cases. Whether or not a pore is in liquid continuity with the water table, the radius of curvature of the meniscus at equilibrium can be computed from the pore height above the water table by equation 54.

It may seem surprising that equation 54 applies equally when there is a liquid continuum, as in the capillary fringe, and when there is not, as above the capillary fringe. However, as discussed later, both regions fall within the same gravitational field. If the value of  $g$  is assumed to be constant the gradient of

gravitational potential is constant throughout both regions.

Equation 54, in the case of a liquid continuum, may be looked upon as a statement of the equivalence of the pressures exerted by surface tension and by the weight of a hanging column of water in continuity with the water table. If a break occurred halfway up this column, equation 54 would apply to the lower half of the column and would predict the radius of curvature of the meniscus at the top of the half column. The value of  $z$  in equation 54 would be smaller for the meniscus at the top of the half column than for the meniscus at the top of the whole column. Therefore, the radius of curvature would be larger for the meniscus at the top of the half column. This radius of curvature would be greater than the radius of the tube and would develop on the cutoff lip at the top of the lower half-column tube. The meniscus at the bottom of the upper half column would be in vapor equilibrium with the meniscus at the top of the bottom half column and would have the same radius of curvature. Therefore, the forces at the midpoint of the column would be the same as if there were no break in the column, and equation 54 would apply to the entire column. The same reasoning can be projected to cases where there are progressively increasing numbers of breaks in the column. Eventually, as the limit is approached, we arrive at the case of an isolated pore separated from the water table by vapor-filled pores.

Equations 31, 53, and 54 may be looked at in another way. Figure 7 shows a capillary tube immersed in water. The pressure of the water vapor relative to that at the water table decreases with height according to equation 31.

Because the capillary tube has a fixed radius, only one radius of curvature is possible for the meniscus. A given vapor-pressure deficiency is associated with that meniscus curvature according to equation 53. At equilibrium, the meniscus must be located so that the vapor-pressure deficiency above it is the same as the pressure deficiency in the adjacent exterior vapor as given by equation 31.

Assume that the radius of the tube is such that the vapor-pressure deficiency above the meniscus is 10 dynes per  $\text{cm}^2$ . Assume also that water is run into the tube until it is filled to level *A*. Then the vapor-pressure deficiency over the meniscus would be less than that in the adjacent exterior vapor, and a condition of unbalance would exist. Water would drain from the tube immediately, and the meniscus would fall until it stabilized at position *B*. The vapor-pressure deficiency over the meniscus would then be the same as that in the adjacent exterior vapor, and the system would be in equilibrium.



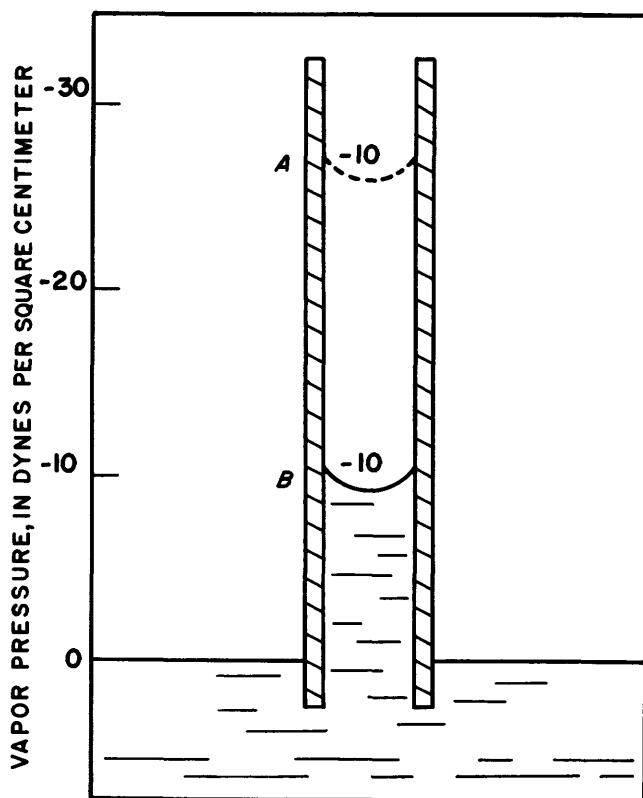


FIGURE 7.—Position of the meniscus in a capillary tube and adjacent vapor pressures.

An analogous situation exists in the wedge-shaped pore in figure 8. Because the wedge is fixed in space relative to the water table, the vapor-pressure deficiency over it must be the same as that in the adjacent exterior vapor, 20 dynes per  $\text{cm}^2$ , at equilibrium. If the wedge is filled to the dashed line, where the meniscus curvature is smaller than that required for equilibrium, the vapor-pressure deficiency might be only 10 dynes per  $\text{cm}^2$ . Water would evaporate and diffuse away from the meniscus, which would be drawn into the narrower part of the wedge. At equilibrium, the curvature would be increased so that the pressure deficiency over the meniscus would be 20 dynes per  $\text{cm}^2$ .

For a capillary tube immersed in mercury, the meniscus would be convex to the vapor. According to the Kelvin equation, the vapor pressure over the meniscus in the capillary tube would be greater than that over a flat surface. Therefore, the meniscus would have to be depressed below the flat surface to a level where the increase of hydrostatic pressure in the exterior liquid would equal the increase in pressure over the meniscus.

The foregoing development and equation 54 apply where surface-tension forces are dominant. In clay soils, in very small interstices, and very close to the particle surfaces, other forces become more important.

Then equation 54 no longer applies, as is discussed later.

As a result of analyses similar to the foregoing it is sometimes assumed that the water in an unsaturated soil is under considerable tension. Although under certain conditions water has considerable tensile strength, the tensile strength is very small when the water contains dissolved gases. It is small also if the absolute pressure approaches the vapor pressure of the water, and bubbles of water vapor form and disrupt the liquid phase. It is likely "that the fraction of water which is actually in tension is never large except perhaps at very high water contents and small tension. This conclusion was also reached by Edlefsen and Anderson. We regard apparently large values of soil-moisture tension or soil suction to be artifacts accounted for by the influence of the electrical double layer" (Bolt and Miller, 1958, p. 928). (See p. D20.)

#### DIFFUSION

Water vapor moves by diffusion. The distribution of solutes throughout a liquid also occurs by diffusion. Finally, osmotic effects are due to diffusion. Therefore, the nature of the diffusion process will be considered in this report.

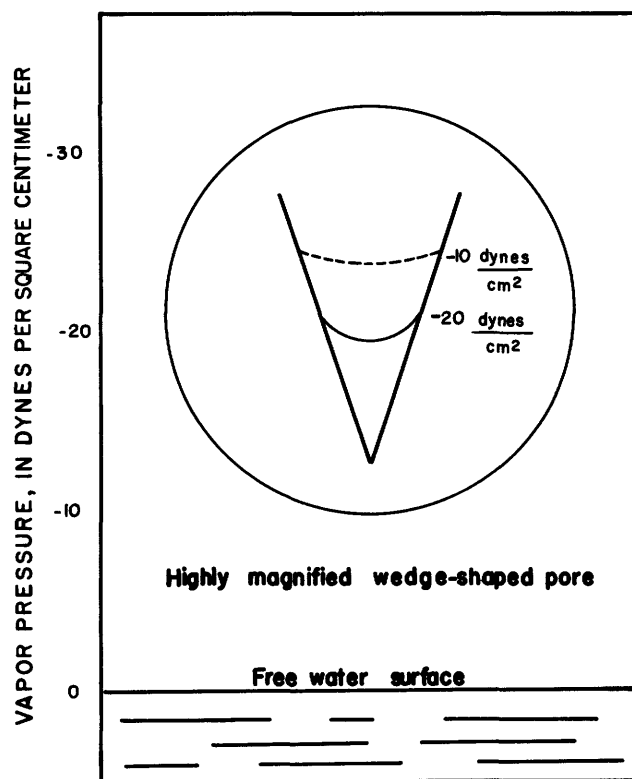


FIGURE 8.—Position of the meniscus in a wedge-shaped pore and adjacent vapor pressures.

Gas released in an evacuated vessel distributes itself uniformly throughout the vessel, as explained by Meyer and Anderson (1939, p. 83-92) in their elementary discussion of diffusion. The distribution is accomplished by the thermal activity of the gas molecules and is an example of diffusion.

If the gas is released in a vessel containing air, it takes longer for the gas to move to all parts of the vessel. The freedom of movement of the gas molecules is impeded by the air molecules, and the diffusion is retarded. If the pressure of air in the jar is increased by reducing its volume (which is equivalent to increasing the concentration of air molecules), the rate of diffusion is still less.

Two gases in separate vessels mix by diffusion when the vessels are put in communication. Liquids also diffuse into each other, though more slowly than gases because of the closeness of the molecules. Solids also exhibit diffusion (Duff, 1937, p. 104).

If the temperature remains constant, the partial or diffusion pressure of a gas, solvent, or liquid is directly proportional to its own concentration, or the number of molecules per unit volume. Dalton's law of partial pressures states that the total pressure exerted by a mixture of real gases is the sum of the pressures that the gases would exert if each occupied the whole space alone. To visualize this, assume that the molecules of a gas are far apart. Molecules of other gases may be slipped in among them without perceptibly altering the frequency with which they collide with the vessel wall and without altering the pressure that the first gas exerts (Deming, 1944, p. 85). Hildebrand (1947, p. 50) explains this by pointing out that the molecules of one gas species would "maintain the same average kinetic energy at the same temperature regardless of the presence of any other species of molecules, and therefore the part of the pressure which is due to the impacts on the vessel walls of one species, called the partial pressure of that gas, would be the same no matter what other gases are present."

Diffusion occurs only when the concentration or partial pressure of the diffusing substance is not uniform throughout the system. It is different from mass movements such as wind, current, or convection. In mass movement the moving units are not single molecules, but generally extensive assemblages of molecules.

Each substance in a system diffuses in a direction and at a rate that depends on its own gradient of diffusion pressure (partial pressure) or on the gradient of concentration. The diffusion-pressure gradient equals the difference in diffusion pressure between two regions, divided by the distance through which the diffusing molecules travel. According to the principle of independent diffusion, the direction in which any

substance will diffuse is unaffected by the gradients or the directions or rates of diffusion of other substances in the system. In any system several substances may diffuse in different directions at the same time. In fact a substance can diffuse into a region of smaller partial pressure but greater total pressure, and the total pressure in the region will then be even greater than the total pressure in the area from which diffusion occurred.

The rate of diffusion of a gas varies directly with its diffusion gradient, directly with its temperature, inversely with the square root of its density, and inversely with the concentration of the medium through which it is diffusing. The diffusion of a solute through a solvent is much slower than the diffusion of gases because of the densely packed molecules of the liquid which impede the diffusion of the dissolved molecules or ions. The diffusion of solute particles is governed by principles very similar to those which control the diffusion of gases. Although the freedom of movement of liquid molecules is to some extent restrained by internal cohesive forces, the molecules also possess thermal energy. Like gases and solutes, liquids exhibit diffusion phenomena. If water is brought into contact with another liquid, such as ether, with which it is only slightly miscible, a slow diffusion of the molecules of the ether takes place into the water and of water into the ether, and the process continues until the two liquids are mutually saturated.

Diffusion is described by the well-known one-direction, nonlinear, concentration-dependent diffusivity equation (see, for example, Bruce and Klute, 1956, p. 458-459):

$$\frac{\partial \Omega}{\partial t} = \frac{\partial}{\partial x} \left[ D(\Omega) \frac{\partial \Omega}{\partial x} \right] \quad (55)$$

where

$\Omega$  = the concentration of ions or molecules

$t$  = time

$x$  = distance

$D(\Omega)$  is the diffusivity which is a function of the concentration,  $\Omega$ . This equation states that the change in concentration with time,  $\frac{\partial \Omega}{\partial t}$ , is a function of the rate of change with distance,  $\frac{\partial}{\partial x}$ , of the product of the diffusivity,  $D(\Omega)$ , and the concentration gradient,  $\frac{\partial \Omega}{\partial x}$ .

#### OSMOSIS

Suppose a vessel containing a sucrose solution is placed in contact with one containing plain water. There will be a diffusion-pressure gradient for sucrose

from the solution toward the water and a diffusion-pressure gradient for water from the water toward the solution. According to the principle of independent diffusion, water molecules and sucrose molecules will diffuse in opposite directions until the solute concentration and the diffusion pressure become uniform.

Suppose that the two vessels are connected through a differentially permeable or semipermeable membrane that is permeable to the solvent (water) but impermeable to the solute (sucrose). Water will diffuse into the sucrose solution but the sucrose will not be able to penetrate the membrane and diffuse into the pure water. This is called osmosis. As a result of the net movement of solvent into the solution, the total pressure in the solution becomes greater than that in the pure solvent at equilibrium. We say net movement because solvent actually moves in both directions across the membrane. However, at equilibrium, the movements in both directions are equal. Thus, osmosis may be considered as the building up of a differential total pressure in one part of a system through the restricting of diffusion in one direction and the allowing of diffusion in the other direction by means of a differentially permeable membrane.

"Osmotic pressure may be defined as the maximum pressure which can be developed in a solution when separated from pure water by a rigid membrane permeable only to water" (Meyer and Anderson, 1939, p. 94). The osmotic pressure of a solution can be determined by enclosing it in a vessel formed of a rigid membrane permeable only to water, immersing this vessel in pure water, and exerting just enough pressure on the solution to prevent any increase in its volume due to the entrance of water. The osmotic pressure of the solution is quantitatively equal to the imposed hydrostatic pressure (Meyer and Anderson, 1939, p. 94-95).

It is common practice to speak of solutions possessing osmotic pressures whether or not they are under such conditions that a hydrostatic pressure can develop within them. In other words, the term "osmotic pressure" is commonly used to denote the potential maximum hydrostatic pressure which would develop in a solution were it placed under the necessary conditions. It will be used in this way in this report.

Osmotic pressure is used sometimes to designate also the actual hydrostatic pressures or turgor pressures developed as a result of osmosis. Actual hydrostatic (turgor) pressures developed during osmosis seldom equal the osmotic, or potential maximum, pressure. For example, assume that a solution having an osmotic, or potential maximum, pressure of 12 atmospheres is enclosed in a stoppered vessel formed of a membrane permeable only to water. Assume further that the vessel in turn is immersed in a solution having an

osmotic pressure of 8 atmospheres. Water will diffuse inward until, at equilibrium, the actual hydrostatic (turgor) pressure developed in the internal solution will be 4 atmospheres. Its osmotic, or potential maximum, pressure will still be nearly 12 atmospheres. Even if the external liquid is pure water, the actual hydrostatic (turgor) pressure developed in the internal solution will not be equal to its original osmotic pressure unless the membrane is completely inelastic (Meyer and Anderson, 1939, p. 94-95).

Because osmotic pressures are defined in terms of final hydrostatic (turgor) pressures developed by osmosis, flow occurs in the direction of greater osmotic pressure. For example, flow occurs from pure water (lower osmotic pressure) into a solution (higher osmotic pressure). However, flow is always from the region of greater to the region of lesser partial pressure of the diffusing substance. This is because the region of greater osmotic pressure is the region of lesser partial pressure of the diffusing substance.

When a substance is dissolved in water, the diffusion pressure of the water in the resulting solution is decreased and its osmotic pressure increased as compared with that of pure water at the same temperature and pressure. The diminution of diffusion pressure is proportional, within a wide range of solution concentrations, to the number of solute particles in a given volume of the solvent.

The osmotic pressure of a solution is a measure of the diffusion-pressure deficit of the water in that solution. Suppose that solution *A* has an osmotic pressure of 20 atmospheres and solution *B* an osmotic pressure of 12 atmospheres. Then the diffusion-pressure deficit of *A* is 20 atmospheres, and that of *B* is 12 atmospheres. Water moves toward solution *A* where the diffusion-pressure deficit, or the osmotic pressure, is greater. After the water movement, solution *A* will exert an actual hydrostatic (turgor) pressure of 8 atmospheres at equilibrium, and the membrane will exert a wall pressure of 8 atmospheres to contain it. Because the actual pressure is greater in *A* at equilibrium, the diffusion pressure of water in *A* will increase, and the diffusion-pressure deficit of the water in *A* will no longer be 20 atmospheres, but will be 12 atmospheres. Thus at equilibrium the increase in actual hydrostatic, or turgor, pressure inside the solution raises the diffusion pressure of the water in the solution to equal that in the outside water (Meyer and Anderson, 1939, p. 97).

#### **FORCE, WORK, ENERGY, POTENTIAL, AND GRADIENT**

The following sections of this report are devoted largely to discussions of potentials and forces in soil water. Therefore, it is advisable to discuss first the meaning of force, work, energy, potential, and gradient.

Force is commonly defined as a push or pull (Sears, 1950, p. 1). It may be thought of as the cause of acceleration or the cause of a change in the state of rest or state of uniform motion of a body. The relation between the force on a body and its mass and acceleration is described by Newton's second law of motion (Sears, 1950, p. 78)

$$F=ma \quad (56)$$

where

$m$ =mass, in grams

$a$ =acceleration, in centimeters per second squared

$F$ =force, in gram centimeters per second squared  
=dynes

When a force acts on a body the product of the force and the distance the body moves in the direction of the force is the work performed by the force. Mathematically,

$$W=Fx \cos \alpha \quad (57)$$

where

$F$ =the force causing the motion, in dynes

$x$ =the distance that the body is moved by the force, in centimeters

$\alpha$ =the angle between the direction that the force is acting and the direction that the body is moving

$W$ =the work done, in dyne centimeters, or ergs

Energy is the capacity for doing work. A moving body possesses kinetic energy equal to the work it can do before it is brought to rest. By definition it is equal to the product of one-half the mass and the square of the velocity of the body.

Potential energy is the capacity that a body or system of bodies has for doing work by virtue of its position or configuration (Smith, A. W., 1948, p. 45). For example, a spring expanded beyond its unstretched length has potential energy because it can do work when it contracts. Similarly, a body at some elevation above a gravitational datum has potential energy with respect to that datum because it can do work as it falls from the higher elevation to the datum. The amount of potential energy it has is proportional to the height above the datum. In other words, the higher it is, the more work it can do upon falling to the datum. Because energy is the capacity to do work, it has the same dimensional units as work, ergs.

A scalar "is any quantity which although having magnitude does not involve direction. For example, mass, density, temperature, energy, quantity of heat, electric charge, potential, ocean depths, rainfall, numerical statistics such as birth rates, mortality or

population, are all scalar quantities" (Coffin, 1911, p. 1). Any quantity which involves both magnitude and direction is a vector quantity. "Any vector quantity may be represented graphically by an arrow" (Coffin, 1911, p. 1).

According to d'Abro (1951, p. 71), the name "field" is given to the continuous distribution of some "condition" prevailing throughout a continuum. When the condition is adequately described at each point of space by a scalar, it is known as a scalar field. Temperature is such a condition and the temperature distribution throughout a volume is a physical illustration of a scalar field. In many cases the condition at each point of space has a direction as well as a magnitude, and the field is a vector field. A field of force or the field defined by the instantaneous velocities of the different points of fluid in motion are illustrations of vector fields.

Consider a number of points in space. Suppose that with each of those points there is an associated value of potential. Potential is the work required to take a unit mass or volume from a datum to the point in question against the field forces. The potential might be due to gravitational, mechanical, or electrical causes. The potential at a point may be thought of as the potential energy of a unit body at the point. Because energy has no direction, the potential at the point is a scalar property or a scalar point function. Its value depends only upon the values of the coordinates of the point. Suppose further that the scalar point functions together with their first space derivatives are continuous and singly valued functions. Then the ensemble of points in the given region together with the corresponding values of the scalar point function "constitute what is called the Field of the Scalar Point Function" (Wills, 1931, p. 75). Examples of such fields are gravitational or electrical fields.

A level or equipotential surface of a scalar point function is a surface for all points of which the function has the same value (Wills, 1931, p. 76). For example, all points at the same elevation have the same gravitational potential and can be connected by such an equipotential surface. For another example, the equipotential surfaces around an isolated electrostatic point charge would consist of concentric shells.

Consider next an ensemble of points each of which is associated with a vector function the value of which depends only upon the coordinates of the point. Examples would be the gravitational force field associated with a field of gravitational potential, the velocity of a moving fluid associated with a field of pressure potential, or an electric force field due to a distribution of electric charges. The ensemble of points in the given region, together with the corresponding values of the vector

point function, constitute "the Field of the Vector Point Function in the region" (Wills, 1931, p. 75).

The potential gradient at a point is the rate of change of potential with distance measured in the direction in which this variation is a maximum (Gray, 1958, p. 219). As shown in figure 9, the ground-water gradient would

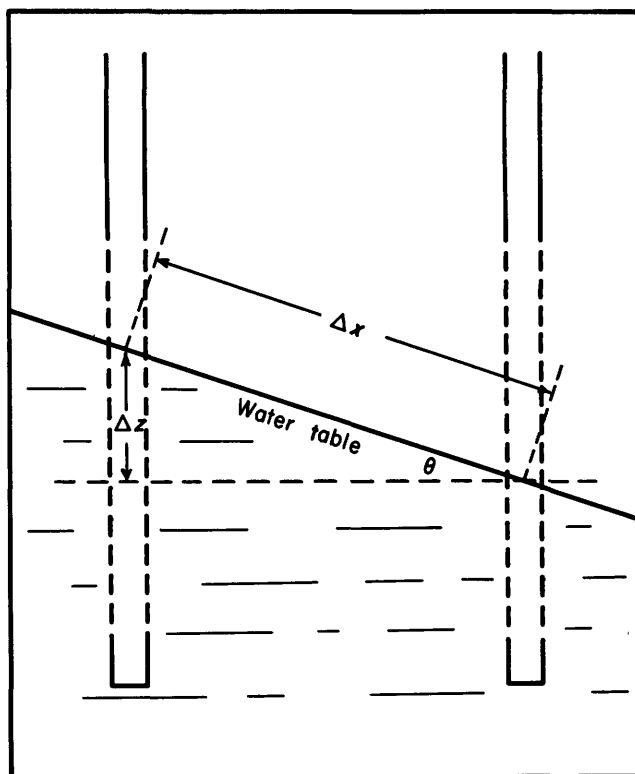


FIGURE 9.—Ground-water gradient =  $\frac{\Delta z}{\Delta x}$ .

be  $\frac{\Delta z}{\Delta x}$ , where  $\Delta z$  is the difference in elevation of the water table at two wells a horizontal distance  $\Delta x \cos \theta$  apart, where  $\theta$  is the angle between the inclination of the water table and the horizontal.

"The symbol  $\nabla$ , read 'del,' defined by writing:

$$\nabla = \bar{i} \frac{\partial}{\partial x} + \bar{j} \frac{\partial}{\partial y} + \bar{k} \frac{\partial}{\partial z} \quad (58)$$

is an operator which, acting upon the scalar point function  $u$ , produces the gradient of this function" (Wills, 1931, p. 77).  $x$ ,  $y$ , and  $z$  are the rectangular coordinates of the system in which  $u$  is defined.  $\bar{i}$ ,  $\bar{j}$ , and  $\bar{k}$  are three mutually perpendicular unit vectors, which are present in the operator because the gradient of the scalar function is a vector. A bar over a term indicates that the term is a vector quantity. Therefore, the gradient of  $u$  is

$$\nabla u = \bar{i} \frac{\partial u}{\partial x} + \bar{j} \frac{\partial u}{\partial y} + \bar{k} \frac{\partial u}{\partial z} \quad (59)$$

where  $u$  is a scalar point function such as potential. "Thus, the gradient of a scalar field is a vector field, the vector at any point having a magnitude equal to the most rapid rate of increase of \* \* \* the scalar point-function \* \* \* at the point and in the direction of this fastest rate of increase, i.e., perpendicular to the level surface at the point" (Hague, 1939, p. 35).

The total change of the value of  $u$  in a distance  $d\bar{r}$ , is  $du$ . This is the scalar product of the gradient and the distance, or

$$du = d\bar{r} \cdot \nabla u \quad (60)$$

where the dot indicates the scalar product (Wills, 1931, p. 77).

The gradient of a scalar field is a vector field as shown by equations 58 and 59. Furthermore, because the direction of maximum change is perpendicular to the equipotential surfaces, the gradient of a scalar field denotes a vector field such that the vectors are normal to the equipotential surfaces. Such fields, where the equipotential surface and the vectors are perpendicular, are said to be orthogonal. In effect, for hydraulics this simply expresses the fact that water flowing down a hill follows the steepest grade. It is often valuable to map fields of associated scalar and vector point functions. An example is given in figure 10. In studies of gravi-

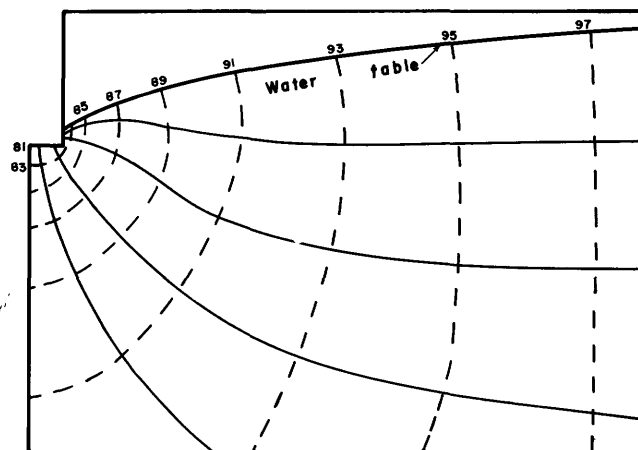


FIGURE 10.—Approximate flow net in the vicinity of an irrigation pond. The dashed lines are equipotential lines, or lines of equal hydraulic head, in feet. The solid lines are flow lines which enclose areas of equal ground-water flow.

tation, the lines or surfaces of equal potential are lines or surfaces of equal gravitational potential. The orthogonal vectors are lines of equal gravitational force.

In hydraulics, a map of scalar and vector point functions is called a flow net (fig. 10). The scalar field consists of distributions of values of pressure or head. Equipotential surfaces are surfaces of constant pressure or head. The lines orthogonal to the scalar field map the vector field and are streamlines which indicate directions of flow.

In hydraulics, a velocity potential is often defined as a scalar function of space and time such that its space rate of change with respect to a given direction, or its gradient in that direction, is the fluid velocity in that direction. It is analogous to the force potential, whose gradient in a given direction is the force intensity in that direction. In such a flow net, as in figure 10, flow lines, or streamlines or flow tubes, include elements of equal flow. Therefore they are closer together in areas of greater velocity.

Rewriting equation 57, and changing the notation so that  $\bar{F}$  stands for force, which is always a vector,

$$W = \bar{F}x \cos \alpha \quad (61)$$

Because potential energy is the ability a body has to do work by virtue of its position or configuration,  $W$  is the potential energy of the body after it is moved a distance from a datum. The negative of the work done by a conservative field of force is the potential  $u$ , and according to Joos (1934, p. 81)

$$dW = \bar{F}dx = -du \quad (62)$$

The minus sign is necessary because the potential decreases in the direction of the force or flow.

Suppose we want the force. It is simply obtained from

$$\bar{F} = -\nabla u \quad (63)$$

Thus, "every conservative force may be represented as the negative of the gradient of a scalar point function, the potential" (Joos, 1934, p. 81).

#### POTENTIALS IN SOIL WATER

In soil moisture, the

total potential is defined as the minimum energy per gram of water which must be expended in order to transport an infinitesimal test body of water from a specified reference state to any point within the liquid phase of a soil-water system which is in a state of rest. The reference state is commonly taken to be a pool of pure water at the same temperature with a flat surface exposed to atmospheric pressure at a known elevation. Under conditions in which the soil will spontaneously adsorb water from the reference state, the potential is a negative quantity. In any soil-water system in a state of rest, the total potential does not vary from point to point in the system (Bolt and Miller, 1958, p. 918).

The total potential depends upon the individual potential fields and upon individual force fields which affect the test body of water as the transfer is made. In unsaturated soils these potentials are presumed to be due to (a) gravitational attraction, (b) hydrostatic-pressure difference, or gradient of pressure potential, (c) osmotic-pressure differences due to differences of content both of soluble salts and of anions and cations

in Gouy double layers associated with the solid surfaces, (d) adhesion of water to the solid surfaces, (e) temperature gradients, and (f) gradients of chemical potential due to changes in solute concentration. If the last two of these are considered to be negligible, the total potential at any point is the scalar sum of the potentials due to the first four effects (Childs and Collis-George, 1948, p. 78). Thermodynamic considerations and the use of the free-energy concept are necessary to include the thermal and chemical potentials (Edlefsen and Anderson, 1943).

#### GRAVITATIONAL POTENTIAL

All terrestrial water lies within the earth's gravitational field. Gravitational potential is the energy required to move an infinitesimal mass or volume of water from a datum where gravitational potential is arbitrarily taken as zero, to a given position in the field against the attraction of gravity. According to this definition of gravitational potential,

$$G = F_g z \quad (64)$$

where

$G$  = the gravitational potential, or gravitational energy, at an elevation  $z$  above the datum, where the gravitational potential is arbitrarily taken as zero. It is the work done, in ergs, in moving an infinitesimal mass or volume of water from the datum to the height  $z$ , in centimeters.

$F_g$  = the force of the gravitational field against which the water is moved, in dynes.

The relation between  $G$  and  $z$  is positive because the gravitational potential increases as the given mass or volume of water is moved in the direction of increasing  $z$ , or vertically upward.

According to Newton's second law of motion,

$$F_g = ma = mg \quad (65)$$

where

$m$  = the mass of water moved, in grams.

$a = g$  = the acceleration of gravity, in centimeters per second squared. The acceleration is assumed to be constant within the relatively small range of values of  $z$  normally encountered in soil-moisture work.

Combining equations 64 and 65, the energy, in ergs, to move any mass of water,  $m$ , from the datum to the height  $z$  centimeters is the scalar quantity

$$G = mgz \quad (66)$$

To find the gravitational potential in ergs per gram of water,  $G_m$ , divide equation 66 by  $m$ . Then

$$G_m = \frac{G}{m} = gz \quad (67)$$

To find  $G_v$ , the gravitational potential, in ergs per cubic centimeter of water, divide equation 66 by  $v$ , the volume of the test mass of water, and

$$G_v = \frac{G}{v} = \frac{mgz}{v} = \rho gz \quad (68)$$

where  $\rho$  = density of the liquid water.

The gravitational potential, in ergs per gram of water, or in ergs per cubic centimeter of water, depends only upon the height within the field above the datum. Furthermore, it increases at a uniform rate with increasing  $z$ , assuming  $g$  to be constant. The gravitational potential is not affected by the contents of the field, whether liquid, vapor, or solid. It depends only upon the energy required to move vertically a unit test mass or volume from a datum to any position in the field.

To determine the gravitational force on a mass  $m$  of water at elevation  $z$  in the field one applies the operator  $\nabla$ , equation 58, and differentiates the potential. For equation 66 operated upon by 58,

$$\bar{F}_g = -\bar{k} \frac{\partial mgz}{\partial z} \quad (69)$$

The  $x$  and  $y$  terms present in equation 58 do not exist because the gravitational force operates only in the vertical, or  $z$ , direction. The minus sign shows that the force is directed downward while height,  $z$ , increases upward and the potential increases with  $z$ . In other words, the force is directed in a direction opposite to that of increasing potential.

Differentiating, the gravitational force on the mass of water,  $m$ , is

$$\bar{F}_g = -\bar{k}mg \quad (70)$$

where  $F_g$  is in dynes. Changing the notation to represent the magnitudes of the quantities only, we arrive back at equation 65,

$$F_g = mg \quad (71)$$

Similarly, if  $F_g$  is force per gram of water,

$$F_g = g \quad (72)$$

Thus, the gravitational force, in dynes per gram of water, is numerically equal to the acceleration of

gravity. Finally, if  $F_g$  is the gravitational force per unit volume of water,

$$F_g = \rho g \quad (73)$$

The force on a unit mass or volume at any point in the field is constant because of the assumption that  $g$  is constant. This independence of the gravitational potential of the contents of the field explains why equation 54 is equally applicable whether or not there is a liquid continuum. It explains why equation 54 applies equally to the continuous liquid phase below the capillary fringe and to the discontinuous liquid phase above the capillary fringe.

The acceleration of gravity,  $g$ , may be taken as 980 cm per sec<sup>2</sup>. Therefore, according to equation 67, the change in gravitational potential per gram equals 980 ergs per gram per centimeter of change in height. The density of water,  $\rho$ , is 1 gram per cm<sup>3</sup>. Therefore, according to equation 68, the change in gravitational potential per cubic centimeter of water is 980 ergs per cm<sup>3</sup> of water per centimeter of change in height.

The datum for gravitational potential is usually taken as the water table. At this point  $z=0$  and  $G=0$ . Therefore  $z$  is the height above the water table and  $-z$  is the depth below the water table. Below the water table the gravitational potential is negative by an amount equal to 980 ergs per gram of water per centimeter depth below the water table, or 980 ergs per cm<sup>3</sup> of water per centimeter depth below the water table, times the depth below the water table. Above the water table, it is equal to 980 ergs per gram of water per centimeter height above the water table, or 980 ergs per cm<sup>3</sup> of water per centimeter height above the water table, times the height above the water table, regardless of whether the liquid phase is continuous or discontinuous.

According to equations 72 and 73, the force on the water is equal to 980 dynes per gram of water, or 980 dynes per cm<sup>3</sup> of water throughout the field.

Although the gravitational potential and force at any point in the gravitational field are independent of the material filling the field, this is not true for the pressure within the field. The variation of pressure with height is directly proportional to the density of the phase filling the field. In equation 73 the force on each cubic centimeter of water is constant. However, when the water is in a liquid state, there are more of these cubic centimeters of water per unit change in height than if the water were in a vapor state. Therefore, the forces add up more quickly in the liquid phase, and the changes in pressure are greater than in the vapor phase. Looked at in another way, a column of liquid water weighs more than a column of water vapor, and the pressure

is a function of the weight of the overlying column of water. According to elementary hydrostatics,

$$\Delta p = Dgz \quad (74)$$

where

$\Delta p$  = change in pressure between two points a vertical distance  $z$  apart

$D$  = density of the liquid or vapor

The soil is saturated for some distance above the water table. For a somewhat greater distance above the water table, some interconnecting systems of pores are in liquid continuity with the water table. Because the density of water is 1 gram per  $\text{cm}^3$ , the pressure in the water above the water table changes at the rate of 980 dynes per  $\text{cm}^2$  per centimeter of change in height, according to equation 74.

In the unsaturated soil outside the interconnecting systems of liquid-filled pores, the pores are partly filled with water vapor. Taking the density of saturated water vapor, at a temperature of  $20^\circ\text{C}$  and at atmospheric pressure, as 0.000017 grams per  $\text{cm}^3$ , equation 74 shows that the change in the pressure in a vapor-filled continuum is about 0.02 dyne per  $\text{cm}^2$  per centimeter of change in height. For greater accuracy, the compressibility of water vapor should be considered by using the barometric equation.

#### HYDROSTATIC-PRESSURE POTENTIAL

According to Childs (1957, p. 14), a suction must be applied in order to withdraw water from a soil or to prevent the soil from imbibing water. The greater the applied suction, the more water is withdrawn, and the lower will be the moisture content when the soil has reached equilibrium at the applied suction.

If water is withdrawn from a soil that does not shrink upon drying, air must enter the pore space and air-water interfaces must be present in the pore space. Such curved interfaces can be maintained only by capillary forces. Hence, surface tension acting in the interfaces provides a mechanism of soil-water retention against externally applied suctions (Childs, 1957, p. 14). This is one of several types of force that retain water against externally applied suctions. Furthermore, this is the mechanism whereby a negative hydrostatic pressure and pressure potential are developed within the soil.

As in the case of gravitational potential, hydrostatic-pressure potential may be taken as zero at the water table. Of course the absolute pressure at the water table is atmospheric pressure, equivalent (at sea level) to that of a column of mercury 76 cm high, or 1,013,000 dynes per  $\text{cm}^2$ . Because this pressure is taken as zero,

all pressures are relative to atmospheric pressure or are gage pressures. Below the water table at equilibrium hydrostatic pressures are positive because the hydrostatic-pressure potential increases with increasing depth. Above the water table at equilibrium the water is under a negative hydrostatic pressure, or tension, because the hydrostatic-pressure potential becomes increasingly negative with increasing height above the water table (Baver, 1948, p. 204).

At the water table, then, the gravitational potential and the hydrostatic-pressure potential are arbitrarily taken as zero. In the absence of other forces the total potential at the water table is therefore zero. Under equilibrium conditions the total potential must also be equal to zero at all points above and below the water table. Thus, at equilibrium and where other forces are not present, the gravitational potential and the hydrostatic-pressure potential must everywhere be numerically equal (Baver, 1948, p. 204; Childs and Collis-George, 1950b, p. 243).

According to equation 67, the gravitational potential per gram of water decreases at the rate  $gz$  with increasing depth below the water table. Therefore at equilibrium the hydrostatic-pressure potential per gram of water must increase at the same rate with increasing depth below the water table, or

$$\psi = -gz \quad (75)$$

where  $\psi$  = the hydrostatic-pressure potential. It is the energy, in ergs per gram of water, to move a gram of water from the water table to a depth  $-z$  below the water table against the hydrostatic-pressure forces. The minus sign is present because the pressure potential increases downward, whereas  $z$  is measured upward.

In similar fashion from equation 68,

$$\psi = -\rho gz \quad (76)$$

$\psi$  is now the hydrostatic-pressure potential, in ergs per cubic centimeter of water. It must be remembered that below the water table  $z$  is negative, and according to equations 75 and 76 the hydrostatic-pressure potential,  $\psi$ , is therefore positive.

A liquid continuum extends to a height above the water table that is determined by the pore sizes and by equation 54, as will be discussed later. This is the same capillary rise that occurs when a capillary tube is immersed in water. This region, where some or all of the pores are filled with water that is continuous with water in the zone of saturation, is the capillary fringe. At equilibrium, and in the absence of other potentials, the hydrostatic-pressure potential equals the gravitational potential in the capillary fringe, and its value is given by equations 75 and 76. In this case  $z$  is positive,



and the hydrostatic-pressure potential is negative. This situation corresponds to the fact that in the zone of aeration the soil exhibits a negative pressure, or hydrostatic-pressure deficiency, or suction, or tension.

The liquid-water system is discontinuous above the capillary fringe. It consists of isolated capillary interstices, or groups of such interstices, that are filled with water and separated from similarly filled interstices by others that are filled with soil air and water vapor. In this part of the zone of aeration, equations 75 and 76 also hold at equilibrium and give negative values of hydrostatic-pressure potential for positive values of  $z$ . Curved liquid-vapor interfaces are present in many of the pores and equation 54 also applies. The actual pressures in the water vapor in this belt can be determined from the barometric equation 31. The pressures in the water on the convex sides of the menisci can be determined from equations 9 or 10.

Above the water table the hydrostatic pressure in the liquid is negative relative to atmospheric pressure. The greater the height above the water table, the greater will be the curvature of the equilibrium liquid-vapor interfaces. The interfaces are drawn deeper into the smaller interstices, and the larger interstices are emptied of water, giving larger hydrostatic-pressure deficiencies in the pore water. However at a sufficiently great height above the water table, or at sufficiently great values of externally applied suction, only very small pores remain full of water. Other forces then become more important than surface tension as discussed below. Thus extremely high negative hydrostatic pressures, or tensions, do not exist in the soil water. In fact, as shown by Edlefsen and Anderson (1943, p. 205), much of the water is actually under compression, even though it is in equilibrium with an extremely large applied suction.

#### OSMOTIC-PRESSURE POTENTIAL

A third type of potential found in soil water is osmotic-pressure potential. It is due to differences in content of both soluble salts and anions and cations in Gouy double layers associated with the solid surfaces of soil particles (Childs and Collis-George, 1948).

According to the concept of Gouy (Adam, 1941, p. 342), cations, or positively charged particles, frequently become dissociated from soil particles of clay size (Childs, 1957, p. 7-8). The surface of the soil particle then has a negative charge. Such particles are called micelles. Particles having similar electrical charges repel each other and particles having opposite electrical charges attract each other. Therefore, in the vicinity of negatively charged soil-particle surfaces, there is an increased concentration of cations (positively charged

ions) and a decreased concentration of anions (negatively charged ions), whereas cation and anion concentrations are equal in parts of the solution that are more remote from the solid-liquid interface. The arrangement of charges at the surface of the micelles is known as an electric, or Gouy, double layer. Because the total ion concentration increases as the solid-liquid interface is approached, the osmotic pressure also increases.

Because the negatively charged soil micelles attract cations from the soil solution, the net concentration of ions in the space between any two given micelles is greater than that in the solution remote from the micelles. Because of this difference in concentration, an osmotic force tends to force water into the space between the micelles, thereby tending to force them apart. Thus the hydrostatic pressure between the micelles is in excess of the hydrostatic pressure in the remote solution. If suction is applied to a soil that exhibits this phenomenon, removal of water as a result of application of the external suction relieves the hydrostatic pressure on the space between the micelles. Therefore, the soil contracts upon drying (Childs, 1957, p. 23-28).

The ultimate ionic concentration at equilibrium in the neighborhood of a Gouy double layer at the surface of a clay-size particle represents a balance between the segregating forces and the diffusing forces. The segregating, or ion-concentrating, forces are those due to the mutual electrical attraction between the micelle and oppositely charged ions and to adsorptive forces. The diffusing, or ion-diluting, forces include the normal ionic diffusion that would occur from a region of higher ion concentration to one of lower ion concentration and the diffusion of water in the direction of the higher concentration. Corresponding to this equilibrium, there is an osmotic-pressure gradient which is a function of distance from the solid surface. The osmotic pressure at any point corresponds to a negative hydraulic-pressure potential. It must be regarded as a hydrostatic-pressure deficiency because it tries to force water in the direction of greater ion concentration—that is, toward the particle and into the electric double layers. This contribution to total potential might be appreciable within as much as 50 Å (Å=1 Angstrom unit =  $10^{-8}$  cm) from the dissociating surface (Childs and Collis-George, 1948, p. 79).

Osmotic-pressure potential due to differences in ion concentration is important in soils that shrink upon drying. Such soils contain clay minerals and humus. Childs (1957, p. 23) refers to water retention in such soils as the mechanism of "water retention by particle repulsion." It is the main source of the negative hydrostatic pressure that is exerted against an externally applied suction applied to a soil that shrinks upon drying. It could be of importance also in extremely dry

sandy soil, where the remaining water is retained in very small wedges or close to the particle surfaces.

#### ADSORPTION POTENTIAL

"Attractive (adsorptive) forces between solids and water can be divided in two categories, short-range forces and long-range forces" (Bolt and Miller, 1958, p. 918). The short-range forces are effective in a range less than 100 Å from a solid surface, whereas the long-range forces may extend beyond 100 Å.

Of the two types of short-range forces, one consists of chemical forces, which are "caused by localized interactions between the electron clouds of surface atoms and water molecules" (Bolt and Miller, 1958, p. 918-919). These forces are localized close to the surfaces of the particles and have little effect on adsorption.

The second type of short-range force consists of Van der Waals forces. They have their origin in the electrostatic attraction of the nucleus of one molecule for the electrons of another. Because of the geometry of the molecule this attraction is largely but not completely compensated for by the repulsion of electrons by electrons and of nuclei by nuclei (Pauling, 1958, p. 321). These short-range

forces, although not as localized as the chemical forces, are in the case of interaction between water and a solid surface still of short range as a result of the destructive interference with fields from other atoms as the distance between the atoms under consideration increases. Although such forces account for the cohesive strength of the water and the phenomenon of surface tension, it seems unlikely that the effective range with regard to the adsorption of water on solid surfaces extends beyond the first few molecular layers adjacent to the interface (Bolt and Miller, 1958, p. 919).

In general, the short-range forces may be neglected except at low water contents usually encountered only in the laboratory. It must be noted, however, that other workers ascribe the cohesive strength of water and the phenomenon of surface tension to the molecular hydrogen bonding, or dipole nature of the molecule (Hendricks, 1955, p. 11-12).

To understand the long-range forces, consider the nature of the water molecule. "\* \* \* The water molecule may be supposed to have a localized distribution of electrical charge in its outer parts. The concentrations of charge are located at the apexes of a tetrahedron, two being positively charged with two negatively. The molecule is thus a dipole; i.e., it is, as a whole, electrically neutral but the 'center of gravity' of the negative charge is separated from that of the positive" (Childs, 1957, p. 9). The long-range adhesive forces are due to the attraction between the positive ends of the water dipoles and the electrostatic field emanating from the negatively charged soil particles. The relatively small separation between

the oppositely charged ends of the dipole becomes less important the farther away the dipole is from the soil particle. At some distance the dipole acts as a neutral particle because, for all practical purposes, the two opposite charges can be considered to coincide. Therefore, even these "long-range" adhesive forces must be of rather short range even though they may attain large values near the soil particle. This attractive or negative force may extend to a maximum distance from the soil particle of more than 100 Å (Bolt and Miller, 1958, p. 919).

The adsorptive forces strongly retain water near the solid surfaces, and large forces may be required to remove this water. However, these adsorptive forces become prominent only when soils are dried far beyond the state of dryness that is normally found in nature.

#### THERMAL POTENTIAL

According to Edlefsen and Anderson (1943), the free energy of soil moisture, or any other fluid, increases with the temperature. Furthermore, temperature and other thermodynamic variables of state help determine phase changes in the soil fluids. Therefore, thermal potential must be accounted for in determining the total potential of soil water. Unfortunately, "There can be little doubt that the most complex and least understood area in the field of soil-water relationships is that of the effect of temperature gradients applied to moist soils" (Winterkorn, 1958b, p. 113).

Moisture movement by vapor diffusion or by a combination of vapor diffusion and capillarity can be appreciable when thermal gradients are present (Smith, W. O., 1943; Gurr and others, 1952; Taylor and Cavazza, 1954). However, thermal transfer of water occurs in great quantity only when relatively large thermal gradients are present in the soil water. Furthermore, evidence suggests that moisture flow in response to temperature gradients occurs mainly or completely in the vapor phase (Hutcheon, 1958, p. 114; Kuzmak and Sereda, 1958, p. 146). It is most important near the land surface where the largest thermal gradients are found. At depth, thermal gradients are generally small (Baver, 1948). The moisture transfer due to these small thermal gradients at depth may be quantitatively substantial over a period of time and for a given area. However, it is relatively small when compared with the moisture transfer due to the other gradients. As stated by Richards and Richards (1957, p. 53), "There is evidence that, except very near the soil surface and then mainly for longtime effects involving weeks or months, vapor transfer of water in soil in the root zone of growing crops is not very significant agriculturally." Therefore,

it will be assumed that thermal gradients are negligible and that moisture movement occurs isothermally.

### CHEMICAL POTENTIAL

By chemical potential is meant the potential due to the osmotic energy of ions free in the aqueous solution. This is distinct from the potential due to the osmotic energy of ions held in the electrical double layers on the solid particle surfaces (Winterkorn, 1958a, p. 330).

If free salts are absent or are uniformly distributed, chemical potential may be ignored (Low, 1958, p. 56). In addition, it "is usually omitted in considering water movement because the solutes generally move more readily than the water with respect to the soil" (Gardner, 1958, p. 78).

### TOTAL POTENTIAL AND ITS MEASUREMENT

The advantages of using potentials in the soil water rather than the forces on the soil water now become apparent. Assuming isothermal conditions and uniform solute concentration, the total force on the soil water would be the sum of the forces due to gravity, hydrostatic pressure, osmosis, and adsorption. Because forces are vectors and have direction, a vectorial addition would be required at every point. On the other hand, potential is a scalar property, and the total potential at any point in an unsaturated soil is the scalar sum of the four component potentials discussed above:

$$\phi = \rho g z + (\psi - \epsilon - \xi) \quad (77)$$

where

$\phi$  = total potential, in ergs per cubic centimeter

$\rho g z$  = gravitational potential, in ergs per cubic centimeter

$\psi$  = hydrostatic-pressure potential, in ergs per cubic centimeter

$\epsilon$  = osmotic-pressure potential, in ergs per cubic centimeter

$\xi$  = adsorption potential, in ergs per cubic centimeter

(Childs and Collis-George, 1948, p. 79.)

The total force can be determined from the gradient of the total potential.

The potential of soil water can be measured by bringing the soil water into equilibrium with a manometer. Because all unsaturated soils have some continuous air-filled pore space, a manometer would read zero, or atmospheric pressure, in contact with an unsaturated soil. Therefore, a porous membrane made of sintered glass spheres, unglazed ceramic, cellophane, porvic, or sausage casing is interposed between the

soil on one side and an external body of water which is in contact with the manometer. The membrane to be used should have pores sufficiently small to remain full of water at all values of negative pressure to be encountered in an experiment. Because these pores remain full of water, air cannot enter them and put the manometer out of operation. On the other hand, the water in the soil is continuous with the water in the membrane, with the body of water on the manometer side of the membrane, and with the manometer. Thus, pressures are transmitted from the soil water to the manometer.

In unsaturated soils a negative pressure or suction must be maintained on the manometer side of the porous membrane for equilibrium to be achieved with the soil water. One commonly speaks of measuring soil-water suction because one measures "the suction prevailing in an external body of water which is in equilibrium with the soil. In some cases, as in sand, we shall see that we may safely infer the internal soil water suction from such measurements, while in others, as in clays, we may not; but in the latter case the true internal suction is almost meaningless because [of its] varying from point to point within wide limits, while the equilibrium suction of an external water body is definable and significant" (Childs, 1957, p. 16). The "internal soil water suction" refers to the actual tension or hydrostatic-pressure deficiency in the water.

When a sand or other soil that does not shrink upon drying is brought into equilibrium with such a manometer, the suction in the external water body comes to equilibrium with the resultant of the forces due to gravity and to hydrostatic-pressure deficiency from surface-tension effects. In these nonshrinking soils the osmotic effect is unimportant. The adsorptive effects are also unimportant at normal moisture contents. In this case, the external suction is a measure of the hydrostatic-pressure deficiency resulting from the surface tension at the curved air-water interfaces.

When a clay or other soil that does shrink upon drying is brought into equilibrium with such a manometer, the suction in the external water probably comes to equilibrium with the resultant of the forces due to gravity, to hydrostatic-pressure deficiency from surface-tension effects, and to osmotic pressure (or pressure involved in water retention by particle repulsion). Where the shrinkage effect is completely dominant, the necessary external suction required to bring about equilibrium is equal to the osmotic repulsive pressure (Childs, 1957, p. 27).

The relation between the external suction applied to a soil and the amount of water that the soil retains against that dewatering suction (the moisture content) is the moisture characteristic. A typical moisture

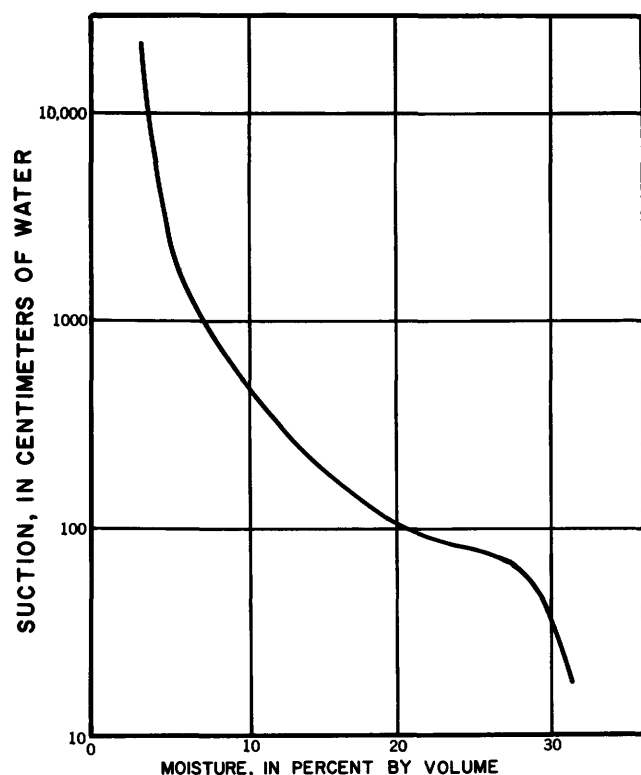


FIGURE 11.—Moisture characteristic of a fine sand. (Courtesy of N. A. Willits, assistant professor of soils, Rutgers University.)

characteristic is shown in figure 11. The moisture characteristic of a nonshrinking soil is related to the withdrawal of moisture from pores against the forces of surface tension. Therefore it is an indication of the pore-size distribution of the soil. For soils that do shrink upon drying, it is related to the osmotic pressure and to the separation of the clay micelles (which depends upon the amount of water between the micelles). Thus, when shrinkage experiments show that water loss is not accompanied fully by the entry of air into the pore space, the soil suction may be interpreted either as repulsive pressure between the micelles due to osmosis or as hydrostatic-pressure deficiencies due to surface tension.

In nonshrinking soils the contribution of osmotic potential,  $\epsilon$ , and adsorption potential,  $\xi$ , to total potential,  $\phi$ , can be ignored. The moisture characteristic can be used as if it were a curve of moisture content,  $\beta$ , versus negative hydrostatic-pressure potential due to surface tension,  $\psi$ . Thus it can be used to determine the pore-size distribution. Childs and Collis-George (1950a, p. 396) use this derived pore-size distribution to determine the hydraulic, or capillary, conductivity. For clays, where the suction removes water by drawing the grains closer together, by orientation of clay-mineral plates into lower potential energy positions or by the

interpenetration of double layers, the moisture characteristic cannot be used to determine the pore-size distribution.

The term  $(\psi - \epsilon - \xi)$  in equation 77 is expressed as a pressure deficiency because it is determined from the suction in an external body of liquid at equilibrium. However, this does not mean that there are large hydrostatic-pressure deficiencies in the soil. As discussed above, it is doubtful that water can exist in a state of tension greater than 1 atmosphere under normal conditions. The true internal hydrostatic-pressure deficiency of the water, in a clay especially, varies greatly from point to point. In fact the water is probably under great compression in many parts of the system.

Consider equation 77 when moving from point to point in either a shrinking soil or close to the particles in a nonshrinking soil at a fixed elevation. At the fixed elevation  $\rho g z$  is constant. If the system is in equilibrium the total potential,  $\phi$ , must be zero, and the term in parentheses must everywhere be the negative equivalent of  $\rho g z$ . Near a solid surface or in a clay micelle  $-\epsilon$  and  $-\xi$  may have extremely large negative values. To keep the term in parentheses constant and equal to  $\rho g z$ ,  $\psi$  would have a very large positive value. Thus the water would be under considerable positive hydrostatic pressure—that is, under compression—near the solid surface.

Moisture-characteristic curves relating external suction and moisture content exhibit hysteresis. The hysteresis in nonshrinking soils can be explained by considering a small capillary interstice that is hydraulically connected to the rest of the system through a larger interstice. If a relatively large suction is applied during drying, both interstices will empty. During a subsequent wetting the overall suction might decrease to some intermediate value. Assume that the smaller interstice would normally fill with water at this intermediate suction but the larger interstice would not. Because water cannot fill the larger interstice, it cannot reach and fill the smaller, and both interstices remain empty. Therefore the moisture content may be lower at a given suction during wetting than at the same suction during drying. In soils that shrink upon drying, the hysteresis might reflect the irreversible orientation of the clay plates during drying and wetting cycles, respectively (Childs, 1957, p. 28).

Several instruments measure potentials in soil water by bringing the soil water into equilibrium with a manometer as described above. The most important are the tensiometer, the asbestos tension table, the porous-plate pressure apparatus, and the pressure membrane apparatus (Baver, 1948, p. 211; Childs and Collis-George, 1950b, p. 239). Another method con-

sists of measuring the pressure of vapor in equilibrium with the soil vapor when the soil vapor is at equilibrium with the soil liquid. A variation of this method consists of measuring the freezing-point depression, because the freezing point and vapor pressure are lowered with increasing hydrostatic-pressure deficiency or increasing osmotic-pressure deficiency (Edlefsen and Anderson, 1943, p. 113).

Caution is necessary in using the vapor-pressure or the freezing-point-depression methods because they measure the total free energy of the soil water (Edlefsen and Anderson, 1943, p. 201). The total free energy is the potential shown by equation 77 plus energy components due to temperature and to the presence of free solutes. The energy potential due to the presence of free solutes is distinct from that due to the osmotic pressure attributable to the ions held in the Gouy double layer. However it is also commonly called an osmotic potential and is attributable to the energy changes stemming from the changes in solute concentration (Schofield, 1948, p. 129). This free-solute component of the total free energy does not contribute to the pressure deficiency in the water and does not cause water movement. Therefore it must be subtracted from the total free energy as measured by the vapor-pressure or freezing-point methods, to get the actual pressure deficiency in the water due to the surface tension or osmotic forces discussed above.

By means discussed above, the total potential,  $\phi$ , can be measured. The gravitational potential,  $\rho gz$ , also can be determined. Under equilibrium conditions the total potential at the water table and elsewhere in the system is zero, and the gravitational potential is everywhere equal to the sum of the terms in parentheses in equation 77. Even under nonequilibrium conditions, if the total potential and the gravitational potential are known, the term in parentheses can be evaluated. However it is usually not possible to resolve the term in parentheses into its component potentials. Therefore equation 77 is most commonly used in the form

$$\phi = \rho gz + \Sigma \quad (78)$$

where

$$\Sigma = (\psi - \epsilon - \xi) \quad (79)$$

and  $\Sigma$  is the capillary potential. Its interpretation for shrinking and for nonshrinking soils is outlined above. In most situations, as discussed above, it equals the suction potential. The gradient of the sum of the gravitational and capillary potentials gives the water-moving forces in unsaturated soils.

#### EQUILIBRIUM DISTRIBUTION OF POTENTIAL AND WATER IN SOIL

The distribution of component potentials within an unsaturated soil is discussed by Bolt and Miller (1958).

The distribution of water and potentials at equilibrium in a nonshrinking sand is discussed below.

In a nonshrinking sand the capillary potential,  $\Sigma$ , is equal to the hydrostatic-pressure potential,  $\psi$ , because osmotic and adsorption potentials are negligible. At equilibrium the total potential,  $\phi$ , is everywhere equal to zero because there are no gradients of total potential at equilibrium, and the total potential is equal to zero at the water table. Therefore, letting  $\phi$  equal zero in equations 77 and 78, the gravitational potential,  $\rho gz$ , is everywhere equal to the negative value of the capillary potential ( $-\Sigma$ ), or to the negative value of the hydrostatic-pressure potential ( $-\psi$ ). Furthermore, equation 54 also applies;  $\rho gz$  in 54 may be interpreted as the gravitational potential, in ergs per cubic centimeter, and  $2\sigma/r$  may be interpreted as the negative of the hydrostatic-pressure potential, in ergs per cubic centimeter.

#### DISTRIBUTION IN THE ZONE OF SATURATION

The datum for gravitational potential and for capillary potential is usually taken as the water table. In the zone of saturation below (the zone filled with water under atmospheric or greater pressure), the gravitational potential decreases at the rate of 980 ergs per  $\text{cm}^3$  of water per centimeter of increase in depth below the water table according to equation 68. Therefore the capillary potential  $\Sigma$ , in this case equivalent to the hydrostatic-pressure potential  $\psi$ , increases at the rate of 980 ergs per  $\text{cm}^3$  of water per centimeter of increase in depth below the water table. This corresponds to the rate of increase of hydrostatic pressure with depth in a body of water, 980 dynes per  $\text{cm}^2$  per centimeter of increase in depth.

#### DISTRIBUTION IN THE CAPILLARY FRINGE

The capillary fringe is an irregular belt of saturation extending above the water table. The water in this belt is at less than atmospheric pressure. Interconnected systems of saturated pores exist, making a continuum of saturated interstices extending to the water table. Here, as elsewhere in the system, the gravitational potential increases at the rate of 980 ergs per  $\text{cm}^3$  of water per centimeter of increase in height above the water table. Therefore the negative value of the hydrostatic-pressure potential, or the capillary potential, increases at the rate of 980 ergs per  $\text{cm}^3$  of water per centimeter of increase in height above the water table. The hydrostatic pressure in the liquid continuum decreases at the rate of 980 dynes per  $\text{cm}^2$  per centimeter of increase in height above the water table.

# DISTRIBUTION IN PINCHING AND SWELLING TUBES WITHOUT HORIZONTAL CONNECTIONS

The following discussion describes the capillary rise of water in pinching and swelling tubes of circular cross section. It is greatly simplified and is designed only to illustrate the general type of occurrence of water in such a system. A more rigorous description of capillary rise in a somewhat more realistic soil model is presented by W. O. Smith and others (1931).

Equation 54 describes the capillary rise in a tube of uniform cross section, the angle of contact being assumed equal to zero. It may be rewritten as

$$z = \frac{2\sigma}{\rho g r} \quad (80)$$

The pinching and swelling tubes have cross sections that vary with height. However, assuming that the cross sections are circular, equation 80 must be satisfied at any possible meniscus position. For purposes of illustration, it is implied also that the contact angle is always zero regardless of the pore geometry.

Taking

$$\begin{aligned} \sigma &= 73.5 \text{ dynes per cm for water at } 20^\circ\text{C} \\ \rho &= 1 \text{ gram per cm}^3 \text{ for water} \\ g &= 980 \text{ cm per sec}^2 \end{aligned}$$

equation 80 becomes

$$rz = 0.15 \text{ cm}^2 \quad (81)$$

Figure 12 is a plot of equation 81 showing the possible meniscus positions, or possible heights of capillary rise, that correspond to different pore sizes under the simplifying assumption.

Before a meniscus can lodge in a pore of radius  $r$  at a height  $z$  above the water table, another condition besides that indicated by equation 81 must be satisfied. A pore of the proper size must exist at the corresponding distance above the water table. To demonstrate this point, consider a hypothetical distribution of pores.

Assume for example that the pores are distributed in vertical sequences that are completely isolated from adjacent vertical sequences. Assume further that the radii of the pores vary in the vertical direction according to a sine-curve distribution. Thus, we are replacing the pores by vertical tubes that pinch and swell like a sine curve. Let

- $a$  = the minimum neck radius
- $b$  = the height from one neck to the next or from one swell to the next
- $c$  = the difference between the maximum and minimum neck radii.

(See fig. 13.)

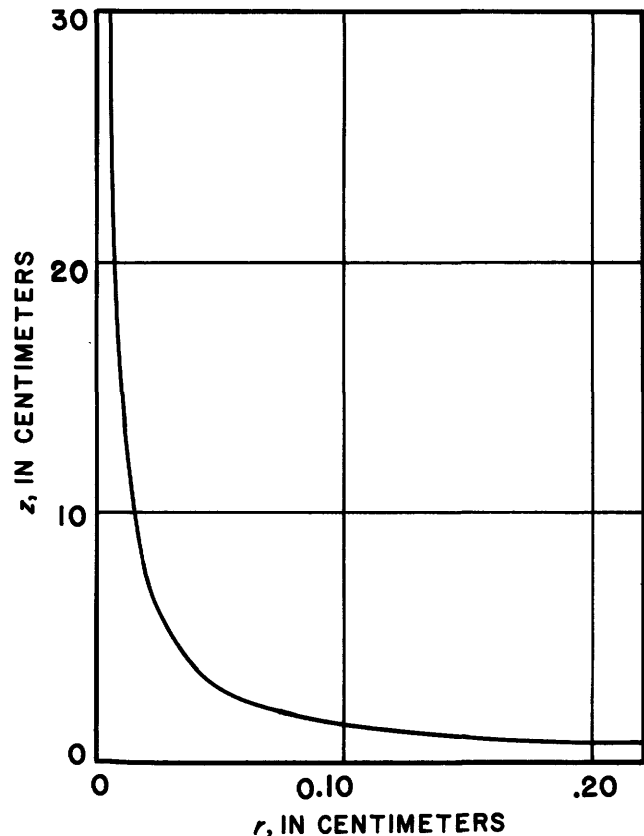


FIGURE 12.—Plot of the capillary-rise equation for water,  $rz=0.15 \text{ cm}^2$ .  $z$  is the height of capillary rise, in centimeters, for a pore of given circular radius ( $r$ ) in centimeters.

The neck radius at any height,  $z$ , is

$$r = a + c \sin \frac{\pi z}{b} \quad (82)$$

where  $\pi = 3.14159 \dots$

The vertical lines around the trigonometric term indicate that the absolute value of that term is to be used.

Consider the hypothetical case where

$$\begin{aligned} a &= 0.01 \text{ cm} \\ b &= 0.1 \text{ cm} \\ c &= 0.1 \text{ cm} \end{aligned}$$

Equation 82 becomes

$$r = 0.01 + 0.1 |\sin 10\pi z| \quad (83)$$

which is expanded in figure 13.

Equation 81 and figure 12 show the equilibrium hydraulic relationship between  $z$  and  $r$ . Equation 83 and figure 13 show the actual geometrical relationship between  $z$  and  $r$ . When both are reproduced on the same scale and one is superimposed on the other, the points of intersection of the two curves satisfy both equations 81 and 83. They indicate the possible

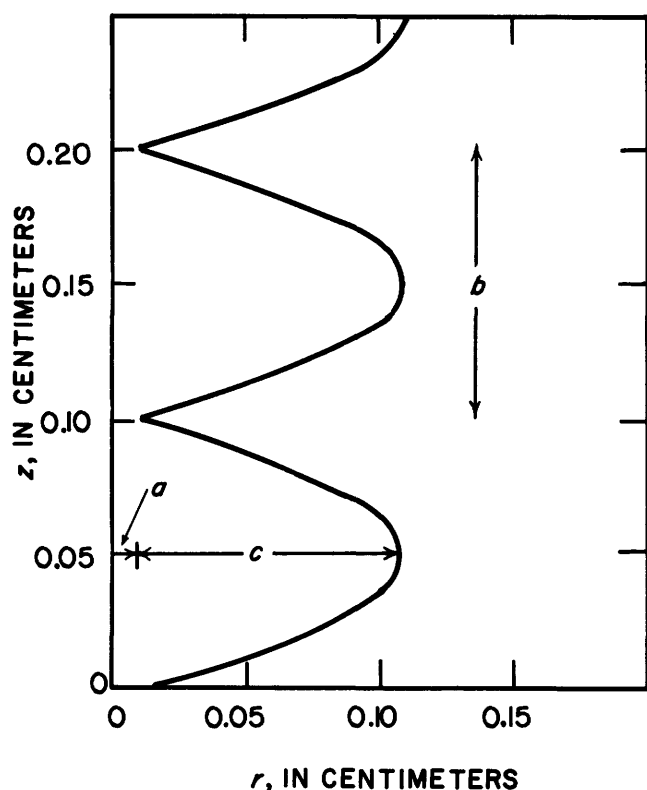


FIGURE 13.—Hypothetical variation of pore radius ( $r$ ) with height above the water table,  $z$ , according to the relation  $r=0.01+0.1|\sin 10\pi z|$ .

meniscus positions, or the possible heights of capillary rise. However, because the menisci can occupy only the lower halves of the pores, the intersections with the upper parts of the pores must be ignored. This principle can be expressed mathematically by saying that, in equation 83,  $z$  is a number of the form

$$z=dfo$$

where  $d$ ,  $f$ , and  $o$  are digits or groups of digits such that

$$d=0 \text{ to } n$$

$$f=0.0 \text{ to } 0.9$$

$$o=0.00 \text{ to } 0.05$$

Figure 14 shows equation 81 plotted on the same scale as figure 13, between  $z=2.00$  and  $z=2.25$ . When overlaid on figure 13, the three points of intersection are  $z=2.022$  and  $r=0.074$ ,  $z=2.121$  and  $r=0.071$ , and  $z=2.220$  and  $r=0.68$ . These are possible solutions of the two equations and show possible heights of equilibrium menisci and the radii of the interstices required at those heights above the water table.

Substituting equation 80 into equation 82, the possible values of pore size that satisfy the two equations are expressed by

$$r=a+c\left|\sin \frac{2\sigma\pi}{\rho g r b}\right| \quad (84)$$

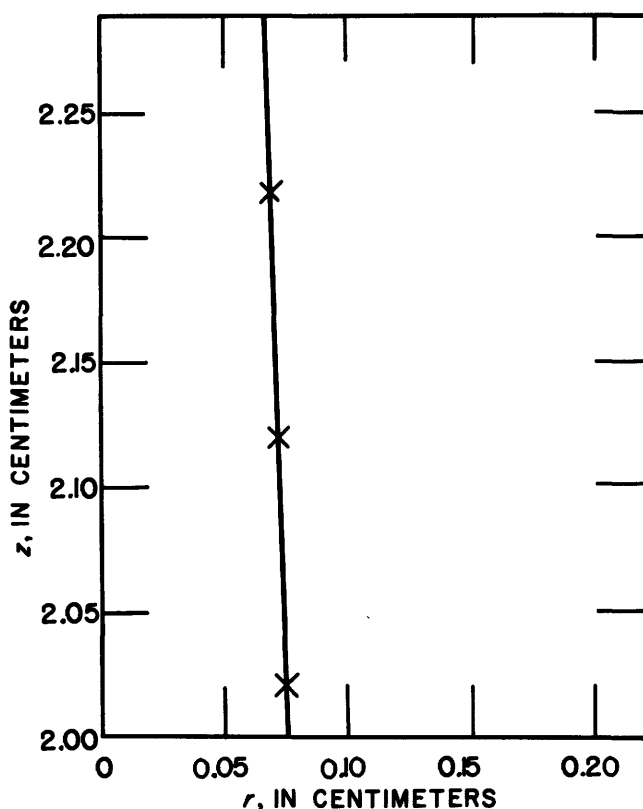


FIGURE 14.—Plot of the capillary-rise equation,  $rz=0.15 \text{ cm}^2$ , on the same scale used in figure 13.

Or, substituting equation 81 into equation 82,

$$r=a+c\left|\sin \frac{0.15\pi}{rb}\right| \quad (85)$$

Any possible pore radius in the given pore-size distribution that can support a water column in equilibrium with gravity must satisfy this equation subject to the limitations of the simplifying assumptions.

Applying equation 85 to the hypothetical example,

$$r=0.01+0.1\left|\sin \frac{1.5\pi}{r}\right| \quad (86)$$

Solving by trial and error, the largest radius that satisfies the relation is  $r=0.1042 \text{ cm}$ . Substituting this value of  $r$  into equation 81, the minimum height of capillary rise is 1.44 cm.

The largest radius in the hypothetical distribution of pinching and swelling tubes is 0.11 cm. This would hold a meniscus at a height of 1.36 cm according to equation 81. According to equation 83 the pore extends from 1.30 to 1.40 cm. However, the part of the pore that has a radius of 0.11 cm (the widest part of the pore) is at a height of 1.35 cm above the water table and not at a height of 1.36 cm as required by equation 81. At both 1.35 cm and 1.36 cm above the water table the

radii are smaller than those required for equilibrium. Because this situation pertains throughout this pore, the water would rise above the pore into the next pore. The equations indicate that it would rise to a height of 1.44 cm into the next pore, which goes from 1.40 to 1.50 cm, and reach stability where the radius is 0.1042 cm. This would be the height of "minimum capillary rise" as it is called by some investigators (Smith, W. O., and others, 1931, p. 18).

The maximum height of capillary rise is determined in similar fashion. The smallest pore radius is 0.01 cm, and this can hold a meniscus at a height of 15 cm above the water table according to equation 81. A neck of this radius is located at exactly 15 cm according to equation 83, and this is the maximum height of capillary rise. In this case, there can be no capillary rise above this height because there is no pore small enough to support an equilibrium meniscus above this height.

Other possible positions of capillary rise exist between the maximum and minimum heights. In fact there is a possible meniscus position in each of the intervening pores. Consider which of these possible positions the top of the capillary fringe will assume.

Assume that the top of the capillary fringe is at the height of minimum capillary rise, 1.44 cm above the water table. If the water table then slowly rises, the meniscus moves upward toward the center of the pore that extends from 1.40 to 1.50 cm above the water table. As discussed above, when the center of the pore is 1.36 cm above the water table the meniscus is lodged in that pore center where the radius is 0.11 cm. If the water table continues to rise, the meniscus rapidly passes through the upper part of the pore and lodges at an equilibrium position in the next pore. Thus, for a rising water table, the top of the capillary fringe in this hypothetical distribution of pores remains a distance above the water table about equal to the minimum height of capillary rise.

Suppose that the water table after rising reaches equilibrium where the top of the capillary meniscus is 1.36 cm above the water table and the pore radius is 0.11 cm. If the water table then falls, the meniscus is gradually drawn downward into the lower half of the pore in order to develop a greater curvature. When the water table is 15 cm below the top of the capillary fringe the meniscus is in the narrowest part of the pore, the neck, where the radius is 0.01 cm. If the water table continues to fall, the meniscus is pulled rapidly through the neck into the pore below, where it lodges close to the neck of the lower pore. Thus, for a falling water table, the top of the capillary fringe in this hypothetical distribution of pores remains a distance above the water table about equal to the maximum height of capillary rise.

The most common positions of the capillary fringe are at the maximum and minimum positions of capillary rise. However, other positions are possible. Examples were given above where intermediate positions were assumed as the water table changed from a rising to a falling or from a falling to a rising condition.

As the water table falls in this hypothetical simplified model, the meniscus is pulled through successive pores, and the pores left above the meniscus are empty. Thus, the moisture content changes abruptly from saturation to near dryness, at the top of the capillary fringe.

The illustration above is a simple example of soil-moisture hysteresis. The moisture content of the region between the positions of maximum and minimum capillary rise depends upon the previous history of water-table fluctuation. In this extreme case of pinching and swelling tubes a region may be saturated when the water table falls, and it may be dry when the water table rises. Similarly, actual soils exhibit hysteresis and are wetter on dewatering than on rewetting, even though the suctions applied are the same.

#### DISTRIBUTION IN TIGHTLY PACKED SPHERES

Consider perfect spheres in the most compact, or rhombohedral, packing as shown in figures 15 and 16 (Slichter, 1899, p. 309-310). The arrangement of the pores differs in several ways from that of the nonuniform vertical tubes postulated previously.

1. The interstices no longer have smooth walls. They are complicated wedge-shaped openings having wedge-shaped reentrants.
2. The interstices are no longer isolated horizontally but are connected in a continuous system. It is as if lateral capillary tubes connect the vertical capillary tubes.
3. Although the individual pores are all similar, a horizontal plane through the system intersects different pore widths and shapes if the unit rhombohedron is tilted.

These differences from the previous model have only minor effects on the height and shape of the capillary fringe. Instead of being at a uniform elevation, the top of the capillary fringe rises and falls as it goes from pore sections of smaller radius to those of larger radius. However, because all the pores are similar, the undulations of the top of the capillary fringe are minor and do not exceed one sphere diameter in height. Another difference between the two models is that the interstices can no longer be assumed to be circular, and equation 87 would have to be used instead of equation 80 for a more rigorous solution. It is

$$z = \frac{\sigma}{\rho g} \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \quad (87)$$



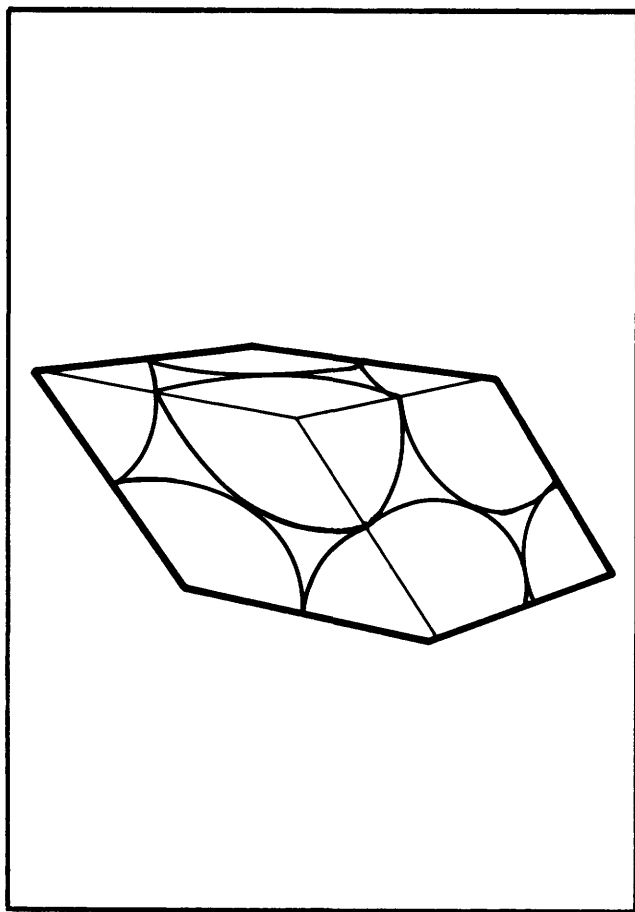


FIGURE 15.—Unit rhombohedron formed by passing surfaces through the centers of eight contiguous spheres in the most compact packing of a mass of spheres. (After Slichter, 1899, p. 309.)

where  $R_1$  and  $R_2$  are the principal radii of curvature of the meniscus.

The main differences between the two models are shown by the dewatering process. When the water table falls in rhombohedrally packed spheres or in an actual soil, the interstices are not completely dewatered. As the meniscus is pulled down through the main part of a given pore, little wedges of water remain in the reentrants of the pore.

Figure 17 shows a pore having horizontally inclined reentrant wedges of gradually decreasing cross section leading to adjacent pores. Assume that the capillary fringe is in the position of maximum capillary rise with the meniscus in the neck at the top of the large pore, thereby satisfying equation 80 or 87. The reentrant wedges will be completely full of water, as shown in figure 17A.

As the water table falls, the meniscus is drawn through the main pore into the neck below. The continuous water film is separated, and there are separate menisci in the pore and in the reentrant wedges,

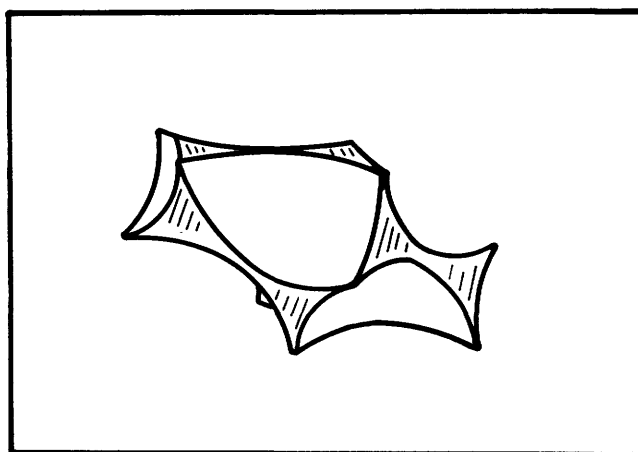


FIGURE 16.—Unit element of the pore space in a mass of spheres packed in the most compact manner possible, a plaster cast of the interior of the rhombohedron in figure 15. The spheres are not quite in contact; their surfaces are separated about 0.5 cm. (After Slichter, 1899, p. 310.)

as shown in figure 17B. The curvature of the menisci in the pore and in the wedges is governed by equations 80 and 87. As the water table continues to fall, the meniscus at the top of the capillary fringe is pulled into the underlying pore. However, little isolated wedges of water remain in the reentrants.

#### DISTRIBUTION ABOVE THE CAPILLARY FRINGE

##### DISTRIBUTION IN TIGHTLY PACKED SPHERES

Consider the little isolated wedges of water in the pore reentrants that are now above the liquid continuum. The water wedges must come to equilibrium with the vapor that fills the pores at the same height above the water table. Transfer of water into and out of the reentrant wedges occurs by vapor movement until equation 87 is satisfied.

Suppose that the water table stabilizes at a depth of 100 cm below the reentrant pore. If circular cross sections are assumed for illustrative purposes, according to equations 80 or 81 the equilibrium pore size would be 0.0015 cm. Water would evaporate and

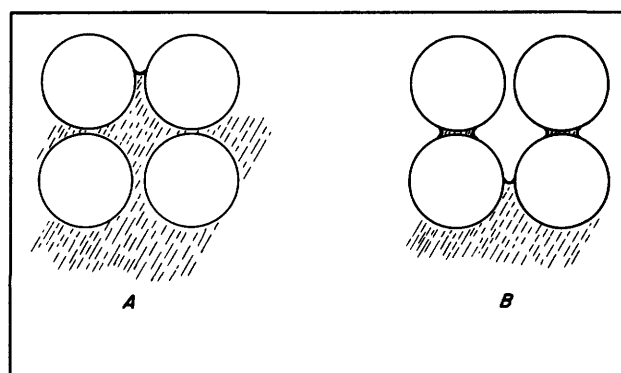


FIGURE 17.—Dewatering of a main pore and of the reentrants.

diffuse away from the liquid surfaces in the wedge-shaped reentrants until the menisci were drawn into the wedges to a point where their radii were 0.0015 cm. If the smallest parts of the reentrants had radii greater than 0.0015 cm, water would evaporate and diffuse away from the menisci until the reentrants were completely dewatered. Only those reentrants having radii of 0.0015 cm or smaller would retain any water that is in equilibrium with the gravitational potential at that level. Of course this assumes that water is retained in the pores only by the surface-tension forces and that adsorptive and other forces are negligible.

Equation 78 provides another way of looking at this problem. At equilibrium,  $\phi$  is zero and  $\Sigma$  must equal the gravitational potential. The required value of negative capillary potential, or hydrostatic-pressure potential, can develop only in a pore 0.0015 cm in radius. If there is no pore that small, sufficient retaining capillary or hydrostatic-pressure force cannot be developed to balance the dewatering gravitational force. Equilibrium is not possible, and the interstice is dewatered by gravity flow.

At 100 cm above a rising water table, water vapor would diffuse to any meniscus in a pore less than 0.0015 cm in radius. The vapor would condense on the meniscus, reducing its curvature and energy of water retention until the equilibrium meniscus size of 0.0015 cm was reached.

#### DISTRIBUTION IN RANDOMLY DISTRIBUTED PORES

Consider next the hypothetical extreme case where there is a random distribution of pore sizes. Furthermore, assume that the soil is of infinite horizontal extent. As a final simplification, assume circular pores so that equation 81 may be used.

Somewhere in the system, a pore having a radius greater than that required by equation 81 will be located close above the water table. At that point, there will be no capillary fringe and no capillary rise. Elsewhere, it will be possible to find a continuum of small pores extending to a great height above the water table. Furthermore, each pore radius will be equal to or smaller than the radius required by equation 81 at that height above the water table. There will be a saturated continuum filling these pores and thus a very large height of capillary rise. Finally, all heights of capillary rise between these two extremes will occur, and the top of the capillary fringe will be a very uneven surface. Of course the exact height and shape of the capillary fringe will depend upon whether the soil is in a dewatering or rewetting phase. Above a falling water table, for example, very large pores can remain full of water provided that the required meniscus

is maintained in an overlying pore of sufficiently small radius.

In this random distribution of pore sizes, occasional isolated water-filled pores will be surrounded by vapor-filled pores. Similarly, occasional isolated vapor-filled pores will be surrounded by water-filled pores. In general, however, at a given level there will be different combinations or groups of water-filled pores whose menisci are sufficiently small to satisfy equation 81. Here again hysteresis is important. For example, consider a region containing a group of relatively large pores completely surrounded by pores small enough to retain water at a particular elevation and to satisfy equation 81. At a given stage in a rewetting phase, water might diffuse toward and condense in the smaller pores until they were filled with water. However the larger internal pores might not be filled at that stage of the rewetting phase, and menisci might face inward toward the larger pores. In dewatering from a state of saturation, on the other hand, the situation would be similar to that at the top of the capillary fringe for a falling water table. The surrounding smaller pores might reach equilibrium according to equation 81 and retain the water in their own pores and in the larger interior pores as well. Therefore the entire region might remain saturated even though the larger internal pores would normally be dewatered at that elevation. An analogous hysteresis effect would prevail in a region consisting of small pores surrounded by larger pores.

Two extremes have been presented. One consists of uniform interstices having a capillary fringe of virtually uniform height and individual reentrant wedges retaining water above the capillary fringe. The other consists of a random distribution of pores having a capillary fringe the top of which is extremely uneven. Water would be retained erratically above the capillary fringe in all combinations from single filled pores to very large webs of water filling great numbers of pores. The actual situation at equilibrium in the field lies between these extremes. Most soils have some sorting and horizontal stratification. Therefore, in most cases, the water distribution at equilibrium should be closer to the first case than to the second. In extremely variable material the actual water distribution at equilibrium might approximate more closely the random situation.

#### MOVEMENT OF SOIL MOISTURE

##### PHYSICAL PICTURE

Soil moisture can exist and move in three ways—as liquid water, as water vapor, and as adsorbed water. “It seems probable that, in soils, moisture transfer in

the adsorbed phase can be significant only under rather special conditions, such as where the soil is very dry and possesses a large specific surface" (Philip, 1958, p. 157). Thus in the following discussion it is assumed that movement of adsorbed water is negligible and that the water moves chiefly in the liquid and vapor phases.

Soil moisture moves in response to gravitational, hydrostatic-pressure, adsorption, osmotic, temperature, and chemical potential gradients. As discussed previously, temperature and solute concentration are taken as constant throughout the system. In addition, the discussion is restricted to a sand, where the osmotic and adsorption potentials are negligible. Moisture movement is then governed by the gradient of the total potential, which according to equation 78 is

$$\phi = \rho g z + \Sigma \quad (88)$$

Here,  $\Sigma$  is the capillary potential of a nonshrinking soil. It is virtually equivalent to  $\psi$ .

#### PORE UNDERLAIN BY A CAVITY

Assume that a given pore has the general shape shown in figure 18 and is underlain by a cavity. Figure 18A shows the pore neck partly filled with water and at

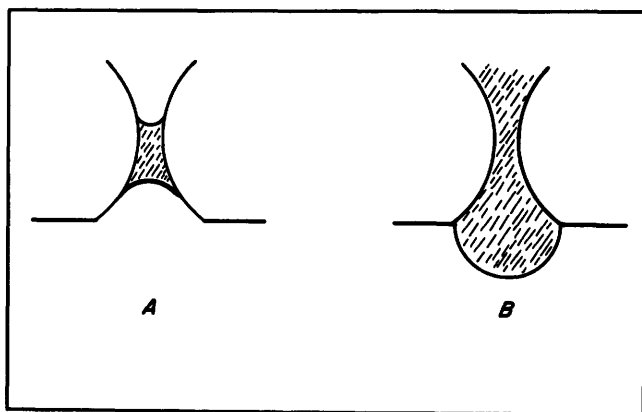


FIGURE 18.—Pore underlain by a cavity.

equilibrium. Therefore the upward and downward forces on the water are equal.

The downward forces are the pull of the lower meniscus and the weight of the water in the pore,  $\rho g z$ , where  $z$  is now the height of the water in the neck. If the pore is circular, this pull is denoted by equation 9, which is

$$(p - p_0) = \frac{2\sigma}{r} \quad (89)$$

The upward force is the pull of the upper meniscus, also denoted by equation 9. The upward pull by the upper meniscus must exceed the downward pull by the

lower meniscus by an amount equal to  $\rho g z$ . Consequently the radius of the upper meniscus must be smaller according to equation 9, and it will be lodged in a smaller part of the neck than will the lower meniscus.

Suppose water is added to the system until the soil overlying the cavity becomes saturated. Eventually the upward meniscus will not be able to develop a small enough radius to support the growing weight of water in the pores in addition to the pull of the lower meniscus. Therefore the lower meniscus will move to the bottom of the pore and become convex toward the cavity, as shown in figure 18B.

The pressure in the cavity is atmospheric pressure. At equilibrium, the pressure on the upper side of the lower meniscus (concave to the liquid) is greater than atmospheric pressure according to equation 9. Thus the upper and lower menisci act in the same direction—to support the weight of water in the pore.

Positive hydrostatic pressure due to the weight of the overlying liquid is required to overcome the pressure differentials across the menisci before water can flow into the cavity. Thus the soil above a cavity must be saturated and under sufficient head to overcome the pressure differences across the interfaces before water can move into the cavity. If the pore radius is large, it will take very little positive pressure to overcome the pressure difference, according to equation 89. If the pore is small, it might take considerable hydrostatic pressure—a considerable zone of saturation over the cavity—to overcome the larger interfacial pressure differences associated with pores of smaller radius.

Assume that the pore is in the moisture condition shown in either A or B of figure 18 and that the cavity is underlain by pores having a lower moisture content. No liquid movement can occur across the cavity as discussed above. However, equilibrium does not exist because the pores are drier below the cavity than above it. The water menisci below the cavity are drawn farther into the pore necks and their radii of curvature are smaller than above the cavity. According to the Kelvin equation, vapor pressures are therefore smaller below the cavity than above it. A vapor-pressure gradient would be established across the cavity, and water would evaporate from the upper menisci, diffuse across the cavity, and condense on the lower menisci. Movement would cease at equilibrium when all the moisture contents and menisci are such that equation 80 is satisfied everywhere in the system (assuming the validity of the simplifying assumptions).

Once the upper pore has sufficient positive hydrostatic head for liquid flow to occur, it occurs very quickly. On the other hand, the diffusion of water vapor is very slow. Thus water moves at greatly different rates under these different conditions.

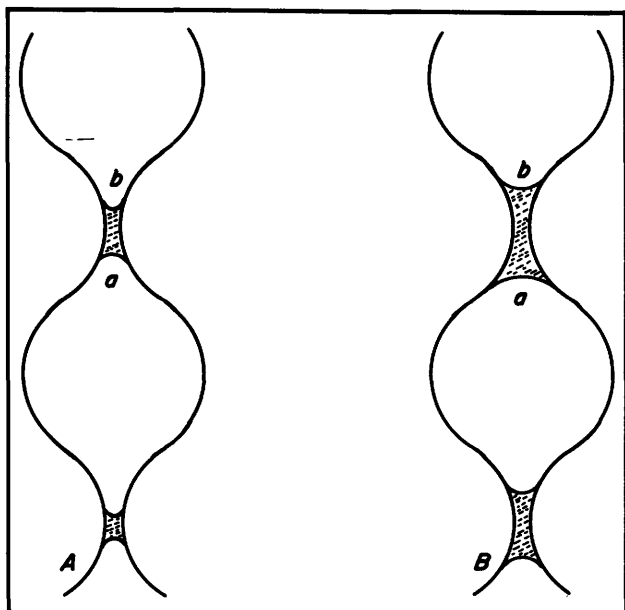


FIGURE 19.—Pore underlain by a pore of similar size.

**PORE UNDERLAIN BY PORES OF SIMILAR SIZE**

Figure 19 shows two similar necks separated by a pore. There is less water in the lower neck than in the upper. The balance of forces in each neck is similar to that described for the case of the cavity. In each neck the capillary pull of the lower meniscus plus the weight of the water in the neck equals the capillary pull of the upper meniscus; the upper meniscus exerts a greater pull than does the lower meniscus and must be lodged in a narrower part of the neck. As in the case of the cavity, water cannot flow as a liquid across the pore, and moisture equilibration occurs by slow evaporation at the upper neck, diffusion to the lower neck, and condensation at the lower neck.

Assume that entrapped air can be bled from the pores by lateral connections. As water is added to the upper neck in figure 19A, meniscus *b* moves into the upper pore and meniscus *a* moves into the lower pore. Meniscus *b* is always lodged in a narrower neck section than meniscus *a*, however, because it must balance the weight of the water in the neck as well as the pull of meniscus *a*.

If insufficient water is added to move meniscus *a* to the midpoint of the lower pore, liquid flow does not occur. Instead, relatively slow downward movement of water occurs across the pore by evaporation, diffusion, and condensation. Because the radius of curvature of meniscus *a* in figure 19B is larger than in figure 19A, vapor pressure at this meniscus is greater and a diffusion occurs more rapidly than in figure 19A.

If sufficient water is added to move meniscus *a* past the midpoint of the pore, water will flow rapidly

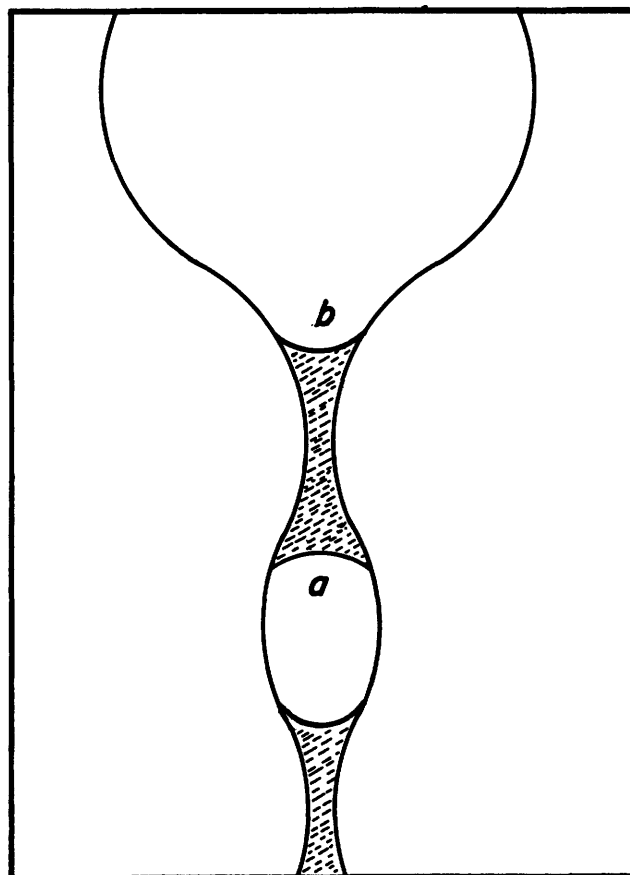


FIGURE 20.—Pore underlain by a smaller pore.

to the lower part of the pore. At equilibrium the amount of water in the lower neck will be slightly greater than in the upper neck in order to satisfy equation 80.

If sufficient water is added to fill all the pores and entrapped air is removed, surface tension ceases to be a factor. Water movement through the pores then follows the rules of saturated flow.

**PORE UNDERLAIN BY PORES OF DISSIMILAR SIZE**

The upper pore in figure 20 is underlain by a smaller one. Meniscus *a* will reach the midpoint of the lower pore while meniscus *b* is still in the neck of the larger pore. After meniscus *a* reaches the midpoint of the smaller pore, water will flow rapidly to the lower part of the small pore. Thus liquid flow will occur at a moisture content which is lower than that required for liquid flow where the upper pore is underlain by a pore of equal or larger size. In fact, if the lower pore is sufficiently smaller than the upper, it can fill with water while the upper pore remains almost empty.

If the lower pore is larger than the upper, the reverse situation is present. In figure 21, for example, it would be necessary for the upper pore to be full

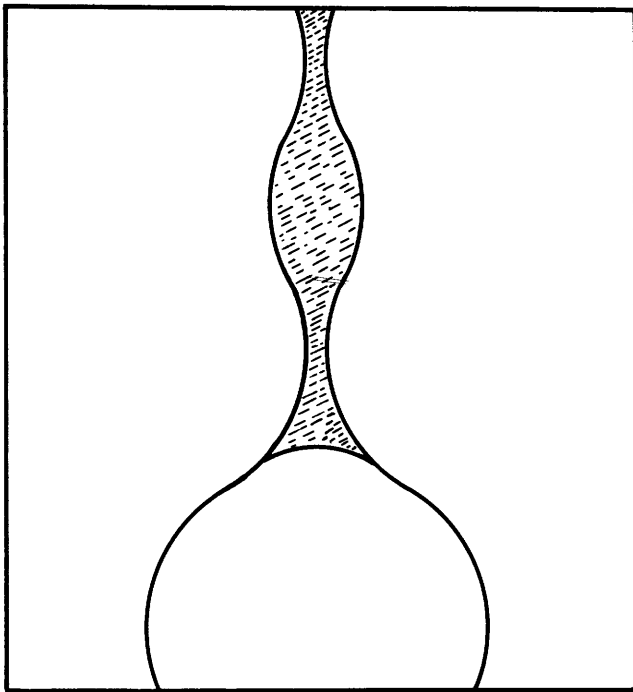


FIGURE 21.—Pore underlain by a larger pore.

and to have sufficient hydrostatic head before the water could move as a liquid into the larger pore below. Vapor diffusion would occur across the underlying large pore as long as there was any difference in the vapor pressures above and below. This is similar to the case of the pore underlain by a cavity.

#### RANDOMLY DISTRIBUTED PORES

Several conclusions are possible from the considerations discussed above. For a given pore size and distribution, there is a moisture content below which liquid movement through the pores does not occur. Movement occurs exclusively by vapor transfer or else by vapor transfer from neck to neck and by liquid transfer through the necks. At higher moisture contents, the liquid movement occurs as a series of discontinuous jumps from neck to neck as discussed above. At sufficiently high moisture contents, a series of pores might be filled so that the flow through them follows the laws of saturated flow. For some types of soil geometry there might be a continuous vapor bypassing liquid-filled wedges. Similarly there might be liquid-filled passages bypassing vapor-filled pore centers.

The following description pertains to a soil containing a random distribution of pores. Some passageways are filled only with water vapor, and water moves through them slowly only as a vapor. Some passageways contain vapor-filled pores and liquid-filled necks. The movement through these channels occurs by vapor

transfer through the pores and liquid transfer through the necks. Some passageways are in a similar condition except that there is enough water for the menisci to jump across the pores. Water movement then occurs relatively rapidly by the mechanism of liquid jumps. Finally, some passageways are completely full of water and movement occurs rapidly by saturated flow.

A given arrangement of pores at a given moisture content transmits water at a given velocity under a given head difference. The ability to transmit water under a unit head difference is known as the capillary conductivity, or unsaturated conductivity, of the soil at the given moisture content. Capillary conductivity describes the sum of the movement by the different mechanisms described above. It includes movement by vapor flow, by vapor flow in the pores and liquid flow in the necks, by liquid jumps, and by liquid flow. As moisture content increases, more systems of pores contain more water. Therefore more systems of pores transmit water by the liquid-flow mechanisms, and capillary conductivity increases. Abundant experimental data show that capillary conductivity increases with increasing moisture content and with decreasing suction.

#### Poiseuille's law

$$Q = \frac{\pi r^4}{8\eta l} (P_1 - P_2) \quad (90)$$

gives the discharge rate through a capillary tube under conditions of viscous flow, where

$Q$  = the discharge rate

$r$  = the radius of the tube

$\eta$  = the absolute or dynamic coefficient of viscosity

$l$  = the length of the tube

$P_1$  and  $P_2$  = the pressures at the ends of the tube

The largest pores empty first as soil moisture decreases. Because of the fourth-power relationship between  $Q$  and  $r$  in equation 90, saturated flow through a soil decreases very rapidly as the radii of the saturated pores diminish in size. In addition, as moisture content decreases " \* \* \* the chance of water occurring in pores or wedges isolated from the general three-dimensional network of water films and channels increases. Once continuity fails, there can be no flow in the liquid phase, apart from flow through liquid 'islands' in series-parallel with the vapor system \* \* \*" (Philip, 1958, p. 153).

Most of the conductivity of a wet soil stems from pores in material of silt size and larger. When a soil is dry the only pores that are filled and capable of liquid flow are the smaller pores. Liquid movement

through these pores is very small. The larger pores, substantially dewatered, transmit water only by the slow mechanisms of (1) vapor transfer, and (2) vapor transfer through the pores and liquid flow through the necks. At such low moisture contents the conductivity is very small.

In field soils, drainage and water transmission occur rapidly at high moisture contents. At a critical range of moisture contents, where pores of silt size and larger are being virtually dewatered, the rate of drainage becomes very small. For some soils this critical moisture content corresponds to field capacity. Field capacity, or field moisture capacity, is the "amount of water remaining in a well-drained soil when the velocity of downward flow into unsaturated soil has become small" (Soil Sci. Soc. America, 1956, p. 433).

Applied water distributes itself uniformly throughout a soil only if it is sufficient in quantity to bring the entire soil to a certain critical moisture content or range of moisture contents. These critical moisture contents correspond to those at which values of capillary conductivity become small during drainage. The applied water percolates downward as a belt, whose moisture content is between the critical one and saturation. It leaves the overlying soil near the critical moisture content. After the applied water moistens a certain depth to this moisture content, movement practically ceases. More water must be applied to obtain further rapid penetration as a liquid (Veihmeyer, 1939, p. 544).

According to Bodman and Colman (1944, p. 117), downward moving water advances behind a "wetting-front," or sharp differential in moisture content (Remson and others, 1960, p. 153). If only enough water is applied to wet a certain depth of soil to the critical moisture content, movement of the wetting front practically ceases. Further moisture movement occurs only by vapor transfer and other slow processes discussed above. More water must be applied to obtain further penetration as a liquid. Of course, all movement finally stops at static equilibrium, when only enough moisture has been left behind so that the capillary forces equal the gravitational forces.

This behavior results because a certain degree of saturation is necessary before any given distribution of pore sizes can begin to transmit water rapidly as a liquid. At lower moisture contents, water movement through the larger of these pores depends upon slow vapor diffusion. Water movement through the smaller of these pores is negligible even when the pores are filled. Therefore rapid water transmission can occur only at moisture contents where series of larger pores are sufficiently wet for water to move through them as a liquid. Below these moisture contents, water

movement as a vapor through the larger pores and as a liquid through the smaller pores is very slow, and the wetting front remains practically stable.

## DIFFERENTIAL EQUATION FOR UNSATURATED FLOW

### HISTORICAL BACKGROUND

In order to understand the derivation and meaning of the unsaturated-flow equation, it is helpful to consider first the derivation and meaning of the similar equation for saturated flow. This is because "the simplest type of porous flow problem deals with 'saturated' media in which all of the pores are completely filled with one homogeneous liquid" (Miller and Miller, 1956, p. 324). Historically, the equation was first derived for the saturated case and later adapted to the unsaturated case.

Henry Darcy discovered in 1856 an empirical proportionality between macroscopic flow rate and driving force (Darcy, 1856). By adding a conservation-of-matter condition for steady flow to Darcy's law written in differential form, Slichter in 1899 obtained an equation identical in form with the Laplace equation (Slichter, 1899, p. 330). Finally, by adding a conservation-of-matter condition for unsteady flow to Darcy's law written in differential form, Theis obtained an equation identical in form with the heat-flow equation (Theis, 1935). "This has since formed the basis for the successful development of saturated flow technology" (Miller and Miller, 1956, p. 324). This type of equation is known as the equation of heat conduction in studies of heat conduction, as the diffusion equation in studies of chemical diffusion, and as the nonequilibrium equation in studies of ground water.

Several difficulties delayed the development of the analogous equation for unsaturated flow. The first difficulty stems from the nature of the potentials and the driving forces in unsaturated systems. In saturated systems the potentials are relatively simple, involving only position and pressure, and are easily measured by means of water wells and piezometers. The potentials in unsaturated flow systems are much more complicated and involve components of gravitational, hydrostatic-pressure, osmotic-pressure, adsorption, temperature, and chemical potentials. Unsaturated-flow potentials also vary in a complicated way with moisture content, and hysteresis enters into the relationship between them. Furthermore, measurements of potential and moisture content in soils are difficult and tedious to make. An additional difficulty not encountered in saturated flow is due to the fact that the transmission constant, or capillary conductivity, is dependent upon the moisture content and thus is variable.

Buckingham (1907) recognized the analogy between potentials in unsaturated-flow systems and in other flow systems and introduced the concept of capillary potential. Richards (1931, p. 323-324) was able to adapt the heat-flow or diffusion type of equation to unsaturated flow by writing the moisture content and capillary conductivity as unspecified independent functions of the capillary potential or the suction. In this way, he arrived at the type of equation that forms the basis for unsaturated-flow studies. Richards assumed that Darcy's law holds for unsaturated systems and subsequent work has shown the validity of this assumption (Philip, 1958, p. 153).

As has been discussed, unsaturated flow involves several different mechanisms. The particular mechanism that dominates varies with the moisture content. It may seem surprising that a single equation can describe flow under these different conditions, but it can be done because of the fortunate circumstance that the equation for saturated flow is of the same form as the equation governing the diffusion of water vapor. Thus by proper specification of the transmission coefficient as a variable to cover the sum of the different mechanisms operating at different moisture contents a single equation can be used (Philip, 1958, p. 158).

It is recognized by some investigators (Edlefsen and Anderson, 1943) that the thermodynamic specification of the liquid and vapor phases is incomplete in current use of the equation. However, no solution to this difficulty is currently available.

The best answer available for the hysteresis problem has been to confine the solution of the equation to periods of either soil drying or soil wetting so that moisture content and capillary conductivity can be treated as single-valued functions of the capillary potential.

Because of the importance of the unsaturated-flow equation, its derivation is presented. It is derived from the equation of continuity and the Darcy equation, which are discussed first.

#### EQUATION OF CONTINUITY

The equation of continuity is chiefly a statement of the law of conservation of matter. It "states that the fluid mass in any closed system can be neither created nor destroyed" (Muskat, 1937, p. 121). It can be derived from the fact that the change of mass in a small unit rectangular parallelepiped equals the difference between the mass entering and the mass leaving.

Figure 22 shows a unit rectangular parallelepiped with center at  $x, y, z$ . The mass flow of moisture through the parallelepiped is to be computed first. This is the net flow of moisture out of the volume element per unit time, in grams of water per square centimeter per second.

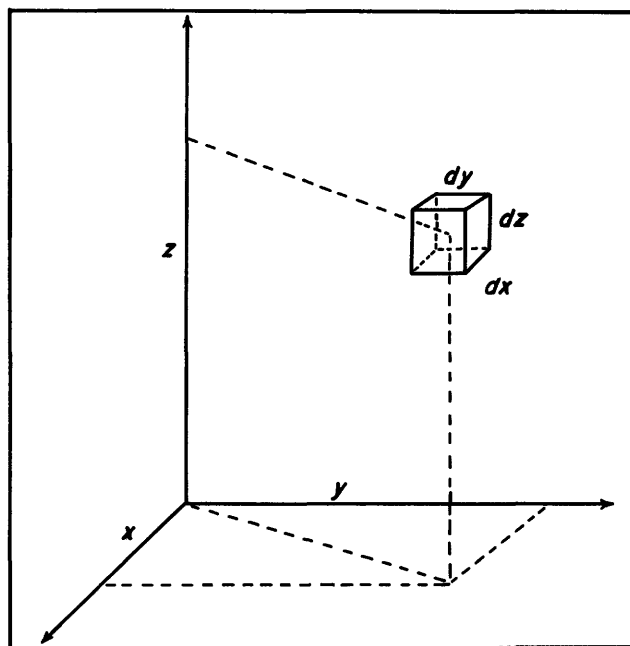


FIGURE 22.—Unit rectangular parallelepiped.

Let  $V_x$  equal the mass flow of moisture per unit time in the  $x$  direction, through a unit cross-sectional area at a distance  $x$  from the  $yz$  plane.  $V_x$  is measured in grams per square centimeter per second.

Then, the expression

$$\frac{\partial V_x}{\partial x}$$

equals the change in the mass flow of moisture per unit time per unit cross-sectional area in the  $x$  direction, with distance from the  $yz$  plane.

The mass flow through an elemental plane of the parallelepiped parallel to the  $yz$  plane and cutting the point  $x, y, z$  is  $V_x dydz$ , in grams per second. The mass flow into the side  $dydz$  at a distance  $x - \frac{dx}{2}$  from the  $yz$  plane is

$$V_x dydz - \frac{\partial V_x}{\partial x} \frac{dx}{2} dydz \quad (91)$$

or

$$\left[ V_x - \frac{\partial V_x}{\partial x} \frac{dx}{2} \right] dydz \quad (92)$$

Similarly, the flow out of the side  $dydz$  at a distance  $x + \frac{dx}{2}$  from the  $yz$  plane is

$$\left[ V_x + \frac{\partial V_x}{\partial x} \frac{dx}{2} \right] dydz \quad (93)$$

The net mass flow in the  $x$  direction out of the unit rectangular parallelepiped per unit time is the flow out,

equation 93, minus the flow in, equation 92. Making the subtraction, it is

$$\frac{\partial V_x}{\partial x} dxdydz \quad (94)$$

Similarly, let

$V_y$  = the mass flow of moisture per unit time in the  $y$  direction, through a unit cross-sectional area at a distance  $y$  from the  $xz$  plane.

$V_z$  = the mass flow of moisture per unit time in the  $z$  direction, through a unit cross-sectional area at a distance  $z$  from the  $xy$  plane.

Then the net mass flow in the  $y$  direction out of the unit parallelepiped per unit time is

$$\frac{\partial V_y}{\partial y} dxdydz \quad (95)$$

The net mass flow in the  $z$  direction out of the unit parallelepiped per unit time is

$$\frac{\partial V_z}{\partial z} dxdydz \quad (96)$$

The total mass flow out of the unit parallelepiped per unit time, in grams per second, is the sum of equations 94, 95, and 96. Adding and simplifying, it is

$$\left[ \frac{\partial V_x}{\partial x} + \frac{\partial V_y}{\partial y} + \frac{\partial V_z}{\partial z} \right] dxdydz \quad (97)$$

The loss of mass of water in the unit parallelepiped per unit time is to be computed next. Let

$\rho\sigma$  = the bulk density of the medium or soil, in grams per cubic centimeter.

$\beta$  = the moisture content on a dry-weight basis. This is a decimal fraction obtained by dividing the mass of water in grams by the mass of dried soil in grams.

The mass of water per volume of soil, in grams per cubic centimeter, is

$$\rho\sigma\beta \quad (98)$$

The mass of water in the unit parallelepiped of volume  $dxdydz$  is

$$\rho\sigma\beta dxdydz \quad (99)$$

The loss of mass of water in the unit parallelepiped per unit time, in grams per second, is

$$-\frac{\partial(\rho\sigma\beta)}{\partial t} dxdydz \quad (100)$$

where  $t$  = time, in seconds.

According to the law of conservation of matter, the mass loss of water in the parallelepiped equation 100 must equal the flow out of the parallelepiped equation 97, or

$$-\frac{\partial(\rho\sigma\beta)}{\partial t} dxdydz = \left[ \frac{\partial V_x}{\partial x} + \frac{\partial V_y}{\partial y} + \frac{\partial V_z}{\partial z} \right] dxdydz \quad (101)$$

Dividing by  $dxdydz$ ,

$$-\frac{\partial(\rho\sigma\beta)}{\partial t} = \frac{\partial V_x}{\partial x} + \frac{\partial V_y}{\partial y} + \frac{\partial V_z}{\partial z} \quad (102)$$

which is the equation of continuity.

Let  $\bar{V}$  be a vector giving the mass flow of moisture, in grams per second per square centimeter, in the direction of the line of flow. Then,

$$\bar{V} = \bar{i}V_x + \bar{j}V_y + \bar{k}V_z \quad (103)$$

Using the vector operator defined in equation 58 on equation 103,

$$\nabla \cdot \bar{V} = \bar{i} \frac{\partial}{\partial x} \cdot (\bar{i}V_x) + \bar{j} \frac{\partial}{\partial y} \cdot (\bar{j}V_y) + \bar{k} \frac{\partial}{\partial z} \cdot (\bar{k}V_z) \quad (104)$$

But,

$$\bar{i} \cdot \bar{i} = \bar{j} \cdot \bar{j} = \bar{k} \cdot \bar{k} = 1 \quad (105)$$

Therefore,

$$\nabla \cdot \bar{V} = \frac{\partial V_x}{\partial x} + \frac{\partial V_y}{\partial y} + \frac{\partial V_z}{\partial z} \quad (106)$$

Comparing equations 102 and 106

$$-\frac{\partial(\rho\sigma\beta)}{\partial t} = \nabla \cdot \bar{V} \quad (107)$$

$\nabla$  is the vector operator known as del or nabra. It will be recalled also that the product of this operator and a scalar such as potential is a vector known as the gradient. The scalar product of this operator and a vector, such as velocity above, is known as the divergence (Brand, 1947, p. 183).

The divergence operator applied to a vector function gives at each point the rate per unit volume at which the physical entity is issuing from that point. If the divergence is positive, as in equation 107, there must be a source of water located at the point, or else water must be leaving the point. If water is leaving the point the storage of water at that point must be decreasing as shown by the negative time derivative on the left side of equation 107. If the divergence is zero and there are no sources or sinks, equation 107 shows that the rate of change of storage also is zero and that steady-state conditions pertain.



## DARCY'S LAW

As stated by Richards (1931, p. 323), "Darcy, working with mediums under saturated conditions, found that the flow of water through a column of soil is directly proportional to the pressure difference and inversely proportional to the length of the column. For low pressure gradients it has been found by numerous investigators (Stearns, 1927; King, 1899) that this law is in exact agreement with experiment and it is entirely analogous to the well-known law of Poiseuille for the flow of liquids through capillary tubes. However, both of these laws fail to hold for high pressure gradients. The limits within which they are true and the modifications which a second approximation requires can be determined only by exhaustive experiments on a wide range of materials. In view of the experimental data now available it is assumed that Darcy's law holds for the low velocities and pressure gradients dealt with in this paper."

Darcy's law may be written as

$$\bar{V}_v = -K \nabla \phi \quad (108)$$

where

$\bar{V}_v$  = a vector giving the volume flow of moisture, in cubic centimeters per square centimeter per second

$K$  = the coefficient of capillary conductivity

$-\nabla \phi$  = the negative gradient of the total potential

If  $\phi$  is in ergs per gram,  $K$  is in seconds.

## FLOW EQUATION

The mass flux is the product of the fluid density and the volume flux, or

$$\bar{V} = \rho \bar{V}_v \quad (109)$$

where  $\rho$  = the density of the water, in grams per cubic centimeter.

Therefore, equation 107 can be changed to

$$\frac{\partial(\rho\beta)}{\partial t} = -\nabla \cdot [\rho \bar{V}_v] \quad (110)$$

where  $\bar{V}_v$  is the vector giving the volume flow of moisture.

The value of  $\bar{V}_v$ , the volume flow, can be replaced by means of Darcy's law, equation 108. Then the equation of continuity, equation 110, becomes

$$\frac{\partial(\rho\beta)}{\partial t} = \nabla \cdot (\rho K \nabla \phi) \quad (111)$$

This is the general equation for unsaturated flow.

For a system in which flow is occurring in the vertical direction only, and for which  $\rho_v$  is constant, equation 111 becomes

$$\rho_v \frac{\partial \beta}{\partial t} = \frac{\partial}{\partial z} \left[ \rho K \frac{\partial \phi}{\partial z} \right] \quad (112)$$

Equation 78 may be rewritten as

$$\phi = gz + \Sigma \quad (113)$$

where

$\phi$  = the total potential, in ergs per gram

$z$  = the vertical height above the datum

$gz$  = the gravitational potential, in ergs per gram

$\Sigma$  = the capillary potential, in ergs per gram

Substituting this into equation 112,

$$\rho_v \frac{\partial \beta}{\partial t} = \frac{\partial}{\partial z} \left[ \rho K \frac{\partial \Sigma}{\partial z} \right] + \frac{\partial}{\partial z} [\rho K g] \quad (114)$$

Assuming  $g$  and  $\rho$  to be constant and dividing by  $\rho_v$ , we have

$$\frac{\partial \beta}{\partial t} = \frac{\partial}{\partial z} \left[ \frac{\rho}{\rho_v} K \frac{\partial \Sigma}{\partial z} \right] + \frac{\rho}{\rho_v} g \frac{\partial K}{\partial z} \quad (115)$$

If  $\beta$  and  $\Sigma$  may be considered to be related by a single-valued function, equation 115 can be rewritten as

$$\frac{\partial \beta}{\partial t} = \frac{\partial}{\partial z} \left[ \frac{\rho}{\rho_v} K \frac{\partial \Sigma}{\partial \beta} \frac{\partial \beta}{\partial z} \right] + \frac{\rho}{\rho_v} g \frac{\partial K}{\partial z} \quad (116)$$

If

$$\kappa = \frac{\rho}{\rho_v} K \frac{\partial \Sigma}{\partial \beta} \quad (117)$$

the equation for vertical flow is

$$\frac{\partial \beta}{\partial t} = \frac{\partial}{\partial z} \left( \kappa \frac{\partial \beta}{\partial z} \right) + \frac{\rho}{\rho_v} g \frac{\partial K}{\partial z} \quad (118)$$

Similarly, for unidirectional horizontal flow, the flow equation is

$$\frac{\partial \beta}{\partial t} = \frac{\partial}{\partial x} \left( \kappa \frac{\partial \beta}{\partial x} \right) \quad (119)$$

$\kappa$  is known as the diffusivity. The reciprocal of the term  $\frac{\partial \Sigma}{\partial \beta}$  is analogous to specific heat in the theory of heat flow, and Klute (1952a, p. 106) proposes the name specific moisture capacity for it.

Under conditions of steady-state flow the mass loss of water, or the change in moisture content with time,  $\frac{\partial \beta}{\partial t}$ , is zero. Therefore, the left sides of equations 102, 107, 111, 118, and 119 are equal to zero. This was discussed previously in regard to equation 107, the continuity equation. It was pointed out that if the

divergence is zero and there are no sources or sinks, the rate of change of storage of water also is zero and steady-state conditions pertain.

Under steady-state conditions the general equation for unsaturated flow, equation 111, becomes

$$0 = \nabla \cdot (\rho K \nabla \phi) \quad (120)$$

When the density of water,  $\rho$ , and the coefficient of capillary conductivity,  $K$ , are constant, equation 120 can be rewritten as

$$\nabla^2 \phi = 0 \quad (121)$$

or

$$\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} + \frac{\partial^2 \phi}{\partial z^2} = 0 \quad (122)$$

This is the well-known Laplace equation. Similarly, for steady-state conditions, the equation for vertical flow of soil moisture, equation 118, becomes

$$\frac{\partial}{\partial z} \left( \kappa \frac{\partial \beta}{\partial z} \right) + \frac{\rho}{\rho_w} g \frac{\partial K}{\partial z} = 0 \quad (123)$$

Finally, for steady-state conditions the equation for unidirectional horizontal flow, equation 119, becomes

$$\frac{\partial}{\partial x} \left( \kappa \frac{\partial \beta}{\partial x} \right) = 0 \quad (124)$$

These equations are difficult to use because the capillary conductivity,  $K$ , the specific moisture capacity,  $\frac{\partial \beta}{\partial \Sigma}$ , the total potential,  $\phi$ , the diffusivity,  $\kappa$ , and the capillary potential all depend on the moisture content. To solve the equations, the functional dependence of capillary conductivity, specific moisture capacity, potential, and diffusivity on moisture content must be determined by empirical or other means. Exact solutions of equation 123 under given boundary conditions are available from Richards (1931, p. 329), Remson and Fox (1955, p. 308), Wind (1955), and Gardner (1958a).

In the past few years, numerical, or iterative, methods have been devised for the solution of the flow equation for the nonequilibrium or transient case under given boundary conditions (Klute, 1952a, Klute, 1952b; Luthin and Day, 1955; Day and Luthin, 1956, p. 445; Philip, 1957; Youngs, 1957). It is hoped that a large number of solutions applicable to soil-moisture flow under different conditions will be available within a few years.

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