# Soil Moisture Transfer in the Vapor Phase Upon Freezing

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In this study the validity of the assumption serving as a basis for the soil freezing experiment is examined, namely, that the upward flow of soil moisture from ground water toward the freezing ice lenses takes place virtually unaccompanied by vapor diffusion.

Two cases were studied: (1) upward diffusion of vapor to air (voids in soil not filled with water), and (2) upward diffusion of vapor through water (soil voids filled with water).

The study reveals that upon freezing the amounts of soil moisture transferred in the vapor phase are small. Therefore the mechanism of vapor diffusion in the soil freezing experiment can be considered as being of little significance.

• UPON freezing of the soil moisture flowing upward from the ground water to the freezing ice lenses within a certain soil system a fundamental change in phase of state takes place, namely, water changes from liquid to ice.

Soil moisture in the form of vapor may also be present in that soil system. Upon freezing, aqueous vapor also undergoes a fundamental change in phase, namely, vapor moisture transforms into ice. It is obvious that in the process of changing the phase temperature is always one of the necessary factors.

In order that an upward flow of soil moisture may take place, there must be, besides temperature difference, a potential as well, viz., the presence of a pressure difference between the lower and upper parts of the system.

The potential or driving force to cause the process of an upward flow of the soil moisture may be a hydraulic one (or, more precisely, a hydrodynamic pressure), or it may be a vapor pressure gradient with a pressure drop from the lower part to the upper part of the system, that is, in the direction from the ground-water table towards the freezing ice lenses.

In order to study the physical process of the upward flow of soil moisture upon freezing, and particularly to learn what are the magnitudes of the pressure differences, viz., subpressures for various types of soil at various environmental conditions, and because all physical laws are derived from experiment, it is believed that soil freezing should be studied experimentally.

<u>Assumption</u>—In studying physical processes in a complex system such as the freezing process in soil, and because of lack of certain scientific information which would serve as a basis for such studies, it is necessary to make some assumptions at the outset in order to agree on certain facts.

In theorizing about the migration of the soil moisture and in planning a soil freezing experiment, one of the assumptions the author made is that the soil moisture transfer in the vapor phase ( = vapor diffusion) upon freezing is negligible, and therefore it can be ignored (1, 2).

<u>References to Other Authors</u>—The aforementioned assumption was based on information given by several authors in their works. Thus, for example, the noted geologist Gunnar Beskow, a Swedish authority on soil freezing and frost heaving (3), reasoning from his research and many field and laboratory observations, believes that in many cases the transfer of soil moisture towards the cold front in the soil takes place by vapor diffusion, but that this is not always necessarily so, and that vapor diffusion is not a necessary step in the process of the upward migration of soil moisture towards the forming and downward-progressing ice lenses upon freezing.

A. W. Porter (4), a former professor of physics at the University of London, writes: "All surface-tensions with which we have to deal are in reality interfacial tensions, since a liquid is always in contact with its own vapor or the gas in which it is immersed. The effect due to the gas is known, however, to be very small."

Another reference relative to this subject is found in the works of H. F. Winterkorn (5), who writes that the phenomenon of the soil moisture diffusion in the vapor phase, caused by vapor pressure differences, is of little practical importance.

The Problem—In order to learn the significance and the effect of vapor pressure and vapor diffusion in the soil freezing process, and in order to examine the validity of the assumption that the upward flow of soil moisture upon freezing is virtually unaccompanied by vapor diffusion, this assumption was studied theoretically, using assumed values for physical constants.

In this study only soil freezing with water supply solely from the ground water is considered because freezing under such conditions, subsequently followed by thawing, causes the greatest damage to highways.

#### Vapor Diffusion

<u>Two Kinds of Soil Freezing</u>—In thermal soil mechanics two principal types of soil freezing can be distinguished: (1) freezing with possible upward water supply from the ground-water table (real or perched) to the downward-freezing ice lenses, and (2) freezing when there is no ground water present, or when the ground water is too deep to affect the soil freezing, i.e., no water supply from ground water to the freezing ice lenses is available.

As previously explained, only the first case is examined here.

The soil voids proper may be considered as substantially a network of small, irregular cellular units or, for simplicity and convenience of explanation, as irregular capillary voids or tubes. The soil voids communicate with each other through narrow necks at the contact points of the soil particles (Figs. 1, 2 and 3).

The voids of a soil may be filled with water, gas (for example, air, moisture vapor, or gases dissolved in ground water), or both moisture and gas. Thus, the principal constituent parts of a soil are: the solid soil particles, or simply solids, the water and the gas. It is generally assumed that most of the volume of the voids of frost-susceptible soils such as silt, clayey silt and silty clay 1s derived from capillaries filled with soil moisture, assuming that ground water is present in the soil.

If a certain volume of air, vapor or gas points of an is entirely surrounded by water it is called a globule or bubble.

NECK AT CONTACT VOID SOIL PARTICLE MOISTURE FILM Figure 1. Narrow necks at the contact points of the soil particles.

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Thus soil can be considered as a porous medium, and thereby as a disperse system. As such, it can be considered as a carrier of soil moisture, aqueous vapor or gas. Vapor and gas are transferred through the voids of the soil, filled or not filled with moisture, by way of diffusion. Diffusion, in its turn, is effected by aqueous vapor pressure difference as a driving force.

<u>Vapor Pressure</u>—Diffusion of aqueous vapor in a soil system generally takes place when there exists a vapor pressure difference. Hence, vapor pressure difference can be considered, among other potentials which are available for the transference of moisture in soil, as one of the potentials or driving forces causing the soil moisture to move upward in the vapor phase, It is obvious that in a laterally insulated system consisting of a soil sample in the form of a vertical cylinder (where the moisture films are connected with the ground water table) and subjected to freezing from its top, the vapor pressure must be larger at the lower end of the system and smaller at the upper end (Fig. 4). This is because in wintertime, when temperatures of the air, viz., ground surface, are at or below freezing, the upper layers of the soil are cooler than the lower ones. Thus during a freezing season heat in soil is flowing upward.

<u>Diffusion Caused by Several Factors</u>—The upward diffusion of soil moisture in the vapor phase by vapor pressure can take place under the following conditions:



Figure 2. Idealized capillary network.

1. There might be a difference in temperature  $(T_1 - T_2)$  at the bottom and top of the freezing soil system, the bottom being at a higher temperature (viz., ground-water temperature, which, depending upon the depth below the ground surface, varies during a winter, according to the author's observation, from about 6 deg C to 10 deg C) than the top (freezing temperature at about 0 deg C as it would be during a freezing season). Such temperature differences cause a vapor pressure difference  $(p_1 - p_2)$ under the influence of which aqueous vapor diffusion in soil takes place. Thus,  $p_1 - p_2$ =  $f(T_1 - T_2)$ .

2. There might be a vapor pressure difference in soil due to a difference or variation in capillary moisture surface tension, S, i.e.,  $p_1 - p_2 = f(S)$ .

Upon the commencement and prevalence of such conditions the assumed continuous threads, paths or capillaries of soil moisture, particularly the weaker stressed part which is located farthest from the soil particles and may merge with that absorbed to



Figure 3. Sketch illustrating the concept of the upward flow of soil moisture toward an ice crystal.

the surface of an adjacent soil particle, can under certain circumstances be interrupted by the formation of vapor or gas bubbles. Thus, diffusion and condensation of soil moisture would take place within the freezing soil system.



Figure 4. The freezing soil system-upward diffusion of vapors.

## I. Diffusion as a Function of Temperature

<u>Diffusion System</u> – Assume that at the beginning of the freezing period and at the beginning of observation there is present in an idealized soil capillary, besides soil moisture, also some water vapor in the form of bubbles which are surrounded by water. Assuming also that those voids which are not occupied by water communicate with each other through the narrow necks at the contact points of the particles and that in these voids there is some vapor present, this case becomes essentially a problem of diffusion of one gas into another, or, in other words, diffusion of aqueous vapor to air (Fig. 4).

<u>Temperature Conditions</u>—Now, upon freezing, the soil gradually chills from the ground surface down (see tautochrone, Fig. 4). However, because the air in the bubble has a relatively smaller coefficient of thermal conductivity than the chilling soil (including air in the voids) above the bubble, there is established a relatively large temperature difference across the bubble between its temperature and that of the soil above the bubble. Because the temperature within the bubble is greater than that of the soil above it, the aqueous vapor within the bubble is also greater than that outside and above the bubble. Such a condition may cause more vaporization and consequently cause the aqueous vapor in the soil to flow upward. Thus, the aqueous vapor has a tendency to diffuse from places of higher pressure to places of lower pressure until a pressure equilibrium is achieved. Also when the moisture content of the soil is uniform throughout the system vapor diffuses with the temperature gradient, i. e., in the direction of heat flow. These conditions are illustrated schematically in Fig. 4.

Soil temperature measurements during the years 1949 to 1955 at Rutgers University show that the average soil temperature gradient during several winters in 34 types of New Jersey soils for depths from zero to about 30 inches below the ground surface vary from  $i_T = 0.038$  to 0.078 deg C/cm, or approximately from  $i_T = 0.04$  to 0.08 deg C/cm.

Because of the physical quantities involved, as well as for convenience, let us in

this study avail ourselves of the significance of the soil moisture diffusion in the vapor phase by vapor pressure as the driving force to the c.g.s.-system.

Thermal Properties-Assuming for air containing some aqueous vapor a coefficient

of thermal conductivity of  $K_{air} = (5.1) \cdot (10^{-5}) \left[ \frac{cal}{cm \cdot sec \cdot {}^{\circ}C} \right]$ , and one for a moist soil near freezing temperature of  $K_{\text{soil}} = (252) \cdot (10^{-5}) \left[ \frac{\text{cal}}{\text{cm} \cdot \text{sec} \cdot {}^{\circ}\text{C}} \right],$  $\frac{K_{\text{air}}}{K_{\text{soil}}} = \frac{(5.1) \cdot (10^{-5})}{(252) \cdot (10^{-5})} \approx \frac{1}{50},$ 

their ratio

shows that in this example the coefficient of thermal conductivity of air is approximately 50 times less than that of the soil.

Upon chilling the soil downward, such a ratio of thermal conductivities would give us a thermal gradient across the aid space or bubble of vapor or gas between  $2-4 \deg C/cm$ .

Vapor Pressures—It is known that the pressure of a saturated vapor is determined only by its temperature. Also the pressure is independent of its volume if the temperature is unchanged. Thus, the vapor determines its own volume for any given temperature. The saturation vapor pressure of an aqueous vapor is defined as the pressure at a given temperature when completely saturated.

Aqueous vapor can be admixed to the soil air or to the atmospheric air in a limited amount only. This is true because its partial pressure can never be greater than the saturation pressure at a given temperature. Therefore, it is satisfactory in this study to neglect the consideration of the degree of saturation and/or the relative humidity and to operate here merely with the saturation vapor pressure. which are the maximum pressures.

Table 1, Column 2, gives an idea of the magnitudes of the saturation vapor pressures  $p_{max}$  in mm of mercury at various temperatures and  $p_0 = 760$  mm Hg under standard pressure conditions. These pmax -values were taken from the International Critical Tables (6). Column 3 of Table 1 shows pressure differences of water vapor in mm Hg. Column 4 shows the weight of water in grams per cubic meter of saturated



Figure 5. Vapor pressure and density curves.

aqueous vapor (= absolute moisture)  $D_v$ , which is also known as the density or unit weight of vapor at a given temperature. Vapor densities  $D_v$  as in Column 4 were calculated by the combined Boyle's-Charles'-Gay Lussac's general gas law by means of the following equation (7):

$$D_v = (288.9) \cdot (\frac{p_{max}}{0 K}), (1)$$

where  ${}^{\circ}K = 273{}^{\circ}C + T{}^{\circ}C$ 

is the absolute temperature of the vapor D<sub>v</sub>. In Column 5 it is shown that the average aqueous vapor pressure differences for 1 deg C temperature difference within a temperature range from 0 deg C to 5 deg C is approximately 0.38 mm Hg.

Aqueous vapor pressures pmax and vapor densities D<sub>v</sub> as a function of temperature are also shown in Fig. 5. From this graph it can be seen that as the temperature of the soil moisture increases, the vapor ex-

pands and the pressure of the saturated vapor increases. Vice versa, when the vapor is cooled heat is abstracted from it and the vapor will contract.

Whenever the temperature of the soil moisture, viz., soil, is known the vapor pressure can be found from Fig. 5 or from Table 1.

# TABLE 1

# SATURATED AQUEOUS VAPOR PRESSURES

Soil Air Temper- ature <sup>o</sup> C	Satura Vapo	ted Aqueous r Pressure	Vapor Density D <sub>V</sub> in g/m <sup>3</sup>	Average Vapor Pressure Difference in mm Hg/ <sup>o</sup> C
	pmax, in mm Hg	Differences, in mm Hg		
1	2	3	. 4	5
-5 -4 -3 -2 -1 0 1 2 3 4 5 6	3. 163 3. 410 3. 673 3. 956 4. 258 4. 258 4. 579 4. 926 5. 294 5. 685 6. 101 6. 543 7. 013	0. 247 0. 263 0. 283 0. 302 0. 321 0. 347 0. 368 0. 391 0. 416 0. 442 0. 470	$\begin{array}{c} 3.353\\ 3.615\\ 3.893\\ 4.193\\ 4.513\\ 4.854\\ 5.222\\ 5.612\\ 6.026\\ 6.467\\ 6.934\\ 7.434\end{array}$	0. 380

<u>Pressure Differences</u>—For temperatures of 2 deg C to 4 deg C (near freezing), as seen from Columns 3 and 5 of Table 1, the average difference in aqueous vapor pressure is about 0.38 mm Hg per degree centigrade. Thus, for temperatures from 2 deg C to 4 deg C per width x of the air space, that is, "thickness" of the bubble, the corresponding average vapor pressure differences can be calculated

as 
$$2 \times 0.38 = 0.76 \text{ mm Hg}$$

and

 $4 \ge 0.38 = 1.52 \text{ mm Hg},$ 

respectively. This corresponds to a variation in unit pressure gradient of  $1.034 \text{ g/cm}^2$  and  $2.06 \text{ g/cm}^2$ , respectively, or, assuming that the unit weight of one cubic centimeter of water is one gram, the above pressures, expressed in terms of pressure heads of a column of water, are: dp = 1.034 cm and dp = 2.06 cm, respectively.

<u>Diffusion Theory</u>—The phenomenon of upward diffusion of soil vapor is analogous to diffusion of a gas through another gas. In this study the two gases are the aqueous vapor and air. Thus, our vapor diffusion problem in the soil freezing experiment can be treated by Fick's first law of diffusion (8). In this law it is assumed that the diffusion of matter 1s analogous to the heat transfer in the steady state through a slab according to Fourier's law, the difference being that the coefficient of gas (vapor) diffusion D takes the place of the coefficient K of the thermal conductivity.

Thus, according to Fick's law the quantity W of a gas or vapor in a translational perpendicular diffusion through a given cross-sectional area A of the diffusion capillary, in a short time interval dt, and at constant temperature, is proportional to this area, to the time and to the concentration gradient  $\frac{dc}{d}$ . Generally,

$$W = -D \cdot A \cdot \frac{dc}{dx} \cdot dt$$
 (3)

where

- W = quantity of a substance in grams diffused during time t through area A;
- D = constant of proportionality, in  $cm^2/sec$ ;
- A = cross-sectional area, in cm<sup>2</sup>;
- c = the concentration of the diffusing substance given as amount of substance per cubic centimeter;

- x = coordinate perpendicular to a reference plane, or distance in cm along the path of diffusion; and
- $\frac{dc}{dx}$  = concentration gradient (Fig. 6).

The minus sign indicates that diffusion takes place from a region of higher concentration to one of lower concentration.

The term "concentration" is a very important concept for the understanding of the solution of a problem. This term means a quantity of matter, expressed in moles or grams contained in a unit of volume, for example, cubic centimeter, or liter, or cubic meter.

According to Jost (9), the unit chosen for the quantity of a substance in the definition of diffusion W given above is not specified, since the law of diffusion is independent of the special choice. Therefore, the following units, generally, can be chosen: mass (in grams or any other unit); number of molecules; cubic centimeters of gas at standard temperature and pressure conditions; or whatever unit may seem most convenient in the case under consideration.

The coefficient of proportionality, D, is termed the coefficient of diffusion for one



Figure 6. Vapor diffusion.

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gas to another gas,  $\ln \frac{cm^2}{Sec}$ . In this problem the two gases are vapor to air. Here, this coefficient represents a quantity of gas by weight diffusing one cm per second through an area of one square centimeter when the concentration gradient is a unity. At 0°C and 760 mm Hg pressure, the coefficient of vapor diffusion into air is

D = 0.203 as determined by H. Houdaille (10), and

D = 0.198 as determined by A. Winkelmann (11).

For this study it is satisfactory to assume a value for vapor to air diffusion of D = 0.20, which is an average of the two values just given.

Application of Diffusion Theory to Soil Mechanics, viz., Soil Freezing, Problem-In order to apply the diffusion theory to our soil system the molar concentration gradient dc/dx is replaced by the partial pressure gradient dp/dx. According to the general gas law (12),  $\mathbf{p} = \mathbf{c} \cdot \mathbf{R} \cdot \mathbf{T} \left[ \frac{\mathbf{g}}{\mathbf{c} \mathbf{m}^2} \right] ,$ (4)

where

**R** = gas constant in  $\frac{cm}{K}$ , and

T = absolute temperature in degrees Kelvin.

Expressing from Equation\_4 the concentration c,

$$\mathbf{c} = \frac{\mathbf{p}}{\mathbf{R} \cdot \mathbf{T}} \quad \left[ \frac{\mathbf{g}}{\mathbf{cm}^3} \right] , \tag{5}$$

and substituting it in Equation 3, obtain

$$W = -D \cdot A \cdot \frac{1}{R \cdot T} \cdot \frac{dp}{dx} \cdot t \left[ g \right]$$
 (6)

The minus sign now accounts for diffusion that takes place from higher values of pressure to lower ones. Because diffusion is a slow process, instead of dt, time t is used. The unit of time was chosen to be the day = 86,400 seconds. Equation 6 is now rewritten showing the proper units:

$$W (g) = -D \cdot (cm^{2}/sec) \cdot A \cdot (cm^{2}) \cdot \frac{1}{R \cdot (cm/K) \cdot T(K)}$$
$$\frac{dp (g/cm^{2})}{dx (cm)} \cdot t (sec), \qquad (7)$$
$$W (g) = -D \cdot A \cdot t(cm^{3}) \cdot \frac{1(g/cm^{2})}{R(cm/K) \cdot T(K)} \cdot \frac{dp \cdot (1)}{dx \cdot (1)} \cdot (8)$$

From Equation 8 it can be noted that the expression

$$\frac{1}{RT} \frac{g}{cm^3} = \frac{p_v - \frac{1g}{cm^2}}{RT} \left(\frac{g}{cm^3}\right)$$
(9)

represents the density of vapor,  $D_v$ , at pressure of  $p_v = 1 \text{ g/cm}^2$ . Therefore Equation 9 can be equated to Equation 1, and the latter substituted into Equation 8:

$$\mathbf{W} = -\mathbf{D} \cdot \mathbf{A} \cdot \mathbf{t} \frac{d\mathbf{p}}{d\mathbf{x}} \cdot \mathbf{D}_{\mathbf{V}} \cdot$$
(10)

Amount of Vapor Diffused—Since  $1 \text{ g/cm}^2$  of pressure corresponds to 0.735 mm Hg, the vapor density D<sub>w</sub> is calculated as follows (at 0° C and 760 mm Hg):

$$D_{v} = (288. g) \cdot \frac{0.735}{273} = 0.755 \left[ g/m^{3} \right]$$
(11)  
$$D_{v} = (0.755) \cdot 10^{-6} \left[ g/cm^{3} \right] .$$
(12)

or

Thus, the amount in grams of aqueous vapor, W, diffused through an area of  $A = 1 \text{ cm}^2$ , during a day (t=86,400 sec.), under a driving force of  $\frac{dp}{dx} = 1.034 \text{ g/cm}^2 \cdot \text{cm}$  at a vapor density of  $D_v = 0.775 \cdot 10^{-6} \text{ g/cm}^3$  with a coefficient of diffusivity of D = 0.20, is a) in the first case;  $W = \left| -(0.20) \cdot (1) \cdot (86,400) \cdot (1.034) \cdot (0.775) \cdot (10^{-6}) \right| = 0.0138(g)$ (13)

b) in the second case:

$$W = \left| -(0.20) \cdot (1) \cdot (86,400) \cdot (2.06) \cdot (0.775) \cdot (10^{-6}) \right| = 0.0276(g) \quad (14)$$

These quantities correspond to a sheet of water of . 14 mm per day and . 28 mm per day, respectively, which quantities, indeed, seem to be of too little practical significance to take them into consideration in the soil freezing experiment.

#### **II.** Diffusion as a Function of Moisture Surface Tension

<u>General Considerations</u>—Diffusion of soil moisture in the vapor phase with vapor pressure as a driving force can take place owing to the difference in capillary moisture surface tension. In essence, this case presents a problem of upward diffusion of water vapor through water. Now, in order that such a diffusion may take place, there must prevail a certain relationship between the aqueous vapor pressure and the soil moisture tension. Further, consider that within a soil system containing in its voids some water, there are scattered many bubbles of gas (air, or vapor, or gas). According to the minimum principle in nature the surface of these small bubbles should tend to decrease. This tendency results in merging together of the small bubbles into a single bubble upon their direct contact with each other. The shape of the bubble then tends to approach a



Figure 7. Water in contact with its own vapor.

sphere which, according to geometry, has the least surface area as compared with the equivalent volume of the sum of the small bubbles.

If the small bubbles do not make contact, then it is possible that their merger into a single bubble would take place upon vaporization.

The following study is based on the general concepts of capillary theory. According to this theory the capillary water in a capillary tube is in contact (through its meniscus) with its own vapor (Fig. 7). It is then assumed that upon freezing there is enclosed vapor present between the upper meniscus and the lower 0° C-isothermal surface or bottom plane of the frozen soil (Fig. 8). This assumption, however, is a pretty weak point to defend: this is because upon the attachment of water molecules to the ice lens no meniscus or (vapor) space between the ice lens and the water in the capillary tube can be observed, unless incidentally there happens to be a larger air

void in the soil directly underneath the ice lens. However, if we assume (a) that upon freezing the water is in contact with the solid ice, (b) that water is connected to the ice lenses directly without the vapor phase, and (c) that the removal of water molecules from the capillary water and their attachment to the growing ice crystal or lens would cause an effect equivalent to that which would occur if there were actually vapor pressure present, then this problem can be studied by means of the capillary theory.

<u>Pressure, Surface Tension and Curvature of Meniscus</u>—Suppose now that there is a spherical bubble of gas present in the soil water. Assume that the diameter of the bubble, viz. the capillary tube, is 2r. Also, assume that the bubble interrupts the continuity of the capillary water in the tube so that there is no water contact between the upper meniscus and the ground-water table (Fig. 9).

Theoretically the spherical shape of the bubble is possible because of the existence of an internal pressure  $p_V$  inside the bubble. This internal pressure, for example vapor pressure, acts on the inside surface of the sphere. Besides, the internal or vapor pressure, viz. gas pressure, must be greater than the external or outside pressure  $p_L$ .

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Under these conditions, there exists inside the bubble a pressure difference or resulting (=excess) pressure,  $p_{V} - p_{L}$ , expressed in physical units of dynes per cm<sup>2</sup>.

The total pressure tending to force the two hemispheres apart is

$$(p_{\tau \tau} - p_{\tau}) \cdot \pi \cdot r^2$$

dynes ,

(15)

(16)

where r is the radius of the spherical bubble, viz. capillary tube. This total pressure is balanced by the surface tension of the hemispherical gas-moisture film which acts circumferentially around a circle through the largest diameter plane. The magnitude of this total surface tension force is

where S<sub>\*</sub> is surface tension in dynes per cm.

At force equilibrium,

$$(\mathbf{p}_{\mathbf{v}} - \mathbf{p}_{\mathbf{L}}) \cdot \boldsymbol{\pi} \cdot \mathbf{r}^2 = 2 \cdot \boldsymbol{\pi} \cdot \mathbf{r} \cdot \mathbf{S}_{\mathbf{*}}.$$
(17)

Then the difference in vapor pressure and water pressure is

$$p_{V} - p_{L} = \frac{2 \cdot S_{*}}{r}$$
  $\left[\frac{dynes}{cm^{2}}\right] \cdot$  (18)

This equation represents Laplace's law, and establishes the relationship between the pressure on the liquid and its meniscus surface curvature. In Equation 18,  $\frac{2 \cdot S_*}{r}$ 

is the excess pressure on one side of the film (directed from inside to outside of the spherical bubble) of constant surface tension. To increase the gas bubble in size or



# a) VAPOR BETWEEN ICE LENS AND CAPILLARY WATER.

# b) CAPILLARY WATER IN DIRECT CONTACT WITH ICE LENS.

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Figure 9. Bubble in capillary water.

to expand it within a void in the soil, an excess pressure increment is needed, so that

$$(p_v - p_L) > \left(\frac{2 \cdot S_*}{r}\right)$$
 (19)

At this point, however, it is pertinent to remember that at the outset of this problem nothing was said as to the cause of the internal pressure  $p_V$ , viz. pressure difference  $(p_V - p_{L_i})$ .

If we assume that the cause of the pressure is vapor, then the following general relationship (based on work consideration) between vapor pressures  $p_1$  and  $p_2$  and surface tension S (or radius of the curved surface of the meniscus) as given by Kelvin (<u>13</u>) is applicable:

$$\mathbf{R} \cdot \mathbf{T} \cdot \mathbf{1n} \quad \frac{\mathbf{p}_1}{\mathbf{p}_2} = \frac{2 \cdot \mathbf{S}}{\mathbf{\gamma}_{\mathbf{W}} \cdot \mathbf{r}} \quad , \qquad (20)$$

where

p1 = vapor pressure over a plane reference surface of water, for example, ground-water table;

- p<sub>2</sub> = vapor pressure over a concavely curved capillary meniscus surface;
- $\mathbf{R} = \mathbf{gas \ constant}, \ \mathbf{in \ cm/deg \ T},$
- T = absolute temperature in degrees Kelvin;
- $\gamma_w$  = unit weight of water, in grams per cubic centimeter, and
- S = surface tension at temperature T, in grams per cm.

These conditions are illustrated in Figure 10.

Developing 
$$\ln \frac{p_1}{p_2}$$
:  
 $\ln \frac{p_1}{p_2} \quad \ln \left( \left| - \frac{p_2 - p_1}{p_2} \right| \right) \approx \frac{p_1}{p_2} - \right|$  (21)  
(for small pressures).

obtain

$$p_1 - p_2 = \frac{2 \cdot S \cdot p_2}{\gamma_{W} \cdot r \cdot R \cdot T} \cdot \left[\frac{g}{cm^2}\right]$$
(22)

According to the general gas law, the expression

$$\frac{\mathbf{p}_2}{\mathbf{R}\cdot\mathbf{T}} = \mathbf{D}_{\mathbf{V}}$$

represents the density or unit weight of vapor,  $D_v$  (14).

Thus, Equation 22 can be rewritten as

$$p_1 - p_2 = \frac{2 \cdot S}{\gamma_w} \cdot D_v \cdot \frac{1}{r} . \qquad (23)$$

The interpretation of this equation is that the vapor pressure over a concave meniscus in a capillary tube is less than that over a plane surface by an amount of 2 S  $D_v/\gamma_w$  r. The effect of surface tension on the vapor pressure is to vary the latter as the curvature  $\frac{1}{2}$  of the capillary meniscus varies. However, because the variation in surface tension due to small soil temperature variations in winter below the frozen is small, the variation in pressure difference is also relatively small.

The pressure differences  $(p_1 - p_2)$  can now be calculated, provided that the quantities 2. S.  $D_{V/Y}$  w and 1/r are known. These quantities are obtained from the capillary theory.

Capillary Pressure-According to Laplace, the capillary pressure Pc, or the carrying capacity of the meniscus, is equal to the weight of the capillary water column (Fig. 11):



ship between vapor pressure and surface ten- as one dyne equals (1.0197) . (10<sup>-3</sup>) grams. sion, viz. radius of curvature.

 $\mathbf{P}_{c} = \mathbf{Y}_{w} \cdot \mathbf{g} \cdot \mathbf{H}_{c} = \frac{2 \cdot \mathbf{S}_{*}}{r} \left[ \frac{\mathrm{dynes}}{\mathrm{cm}^{2}} \right], \quad (24)$ where

 $\gamma_{w}$  - unit weight of water, in g/cm<sup>3</sup>;

= 981.4  $\rm cm/sec^2$  = acceleration of gravity:

 $H_c$  = capillary height, in cm;

= surface tension, in dynes/cm, and S\_

= radius of meniscus, in cm, which, r when normally developed, equals the radius of the capillary tube.

It follows that

$$H_{c} = \frac{2 \cdot S_{*}}{\gamma_{w} \cdot g} \cdot \frac{1}{r} \left[ cm \right], (25)$$
  
or  
$$H_{c} = \frac{2 \cdot S}{\gamma_{w} \cdot r} \left[ cm \right], (26)$$

Figure 10. Kelvin's condition for relation- where S is now in grams per centimeter, The term H<sub>c</sub> is also called the capillary

suction height, or capillary coefficient.

Multiplying  $H_c$  by a unit area and by the unit weight of water  $Y_W = 1$  g/cm<sup>3</sup>, one obtains  $H_c$  as a unit pressure in g/cm<sup>2</sup>, which is also termed the capillary pressure.

Stress in Capillary Water-It is interesting to note that the capillary phenomenon presupposes a tensile resistance of the capillary water (observe in Fig. 12 that the capillary water column seems to be hanging with its full weight at the meniscus). Besides, physically, with the ascent of the vapor from the plane surface of water the vapor pressure decreases. i. e. . vapor pressure decreases when rising from a lower to a higher level. Thus, for the conditions it can be said that the larger the negative capillary pressure or subpressure, the larger is the curvature of the capillary meniscus and the larger is the vapor pressure p<sub>2</sub> as compared with p1.

<u>Bubble in a Capillary Tube</u>—Assuming that the continuity of the capillary water column in a capillary tube is interrupted by a confined air space or a large void in the form of an entrapped, spherical

σ



Figure 11. Illustrating weight of the capillary water columns.

bubble (Fig. 9), it becomes apparent to the reader that in order that an upward diffusion of soil moisture in the vapor phase upon freezing may take place, there should exist a vapor pressure difference, viz. capillary pressure difference between the plane surface of reference or the ground-water table and the curved meniscus surface of the capillary water. Further, referring back to the study of vapor diffusion in air caused by temperature variations, it can also be inferred that in order to bring about some appreciable amount of vapor diffusion one would expect that the vapor pressure difference in the freezing soil system should be of a high order of magnitude.

<u>Stresses in Capillary Water at the Position of the Bubble</u>—The stress  $\sigma_{a-b}$  in the capillary water at the position a-b of the bubble is

$$\mathbf{a}-\mathbf{b} = \mathbf{\gamma}_{\mathbf{W}} \cdot (\mathbf{H}_{\mathbf{c}} - \mathbf{h}_{\mathbf{c}}) \qquad \left[ \mathbf{g}/\mathbf{cm}^2 \right] \qquad (27)$$

The vapor pressure within the bubble is  $p_v g/cm^2$  (Fig. 13).

At force static equilibrium in section a-b c-d of the capillary column the following equation applies:

$$\mathbf{p}_1 - (\mathbf{H}_c - \mathbf{h}_c) \cdot \mathbf{\gamma}_w = \mathbf{p}_v - \frac{2 \cdot \mathbf{S}}{r} , \qquad (28)$$

and the vapor pressure difference in such a case is

$$\mathbf{p}_1 - \mathbf{p}_{\mathbf{V}} = (\mathbf{H}_{\mathbf{C}} - \mathbf{h}_{\mathbf{C}}) \cdot \mathbf{Y}_{\mathbf{W}} - \frac{2 \cdot \mathbf{S}}{\mathbf{r}}$$
(29)

Again, from this equation it can be seen that if the variation in surface tension S due to the soil temperature variations is small, the vapor pressure difference  $(p_1 - p_V)$  is likewise small.

Vice versa, from Equation 29 it can also be seen that should large vapor pressure differences be needed, there should be concurrently also available large capillary pressure differences. These, of course, are not available in wintertime below the frozen soil layer because of the narrow temperature range above freezing (from about



a) CAPILLARY HEIGHT b) WATER c) VAPOR PRESSURE PRESSURE DIAGRAM DIAGRAM

Figure 12. Tension in capillary water.

0 deg C to about 6 deg C to 8 deg C).

<u>Capillary Constant</u>—Referring now back to Equation 23, the quantity  $2 \cdot S/\gamma_w$  is customarily termed the capillary constant, and is designated

$$\frac{2 \cdot S}{\gamma_W} = a^2 \qquad \qquad \left[ cm^2 \right] \qquad (30)$$

Thus, the capillary height H<sub>c</sub> in Equation 26 can now be expressed as

and the vapor pressure difference based on work considerations as in Equation 23 now is

$$p_1 - p_2 = \frac{2 \cdot S}{\gamma_W} \cdot D_V \cdot \frac{1}{r} = a^2 \cdot D_V \cdot \frac{1}{r}$$
(32)

The capillary constants,  $a^2$ , are computed and compiled in Column 4, Table 2. The  $(p_1 - p_2)$ -values are computed as a function of r and are compiled in Column 6, Table 2. From Columns 2 and 4, it can be seen that as the temperature decreases the surface tension and the capillary constants increase. Also, it can be observed that within a temperature range from -5 deg C to +5 deg C the capillary constants vary very little. Therefore an average capillary constant, namely,  $a^2 = 0.1545$  cm<sup>2</sup> at 0 deg C can be used in calculating the radius of the meniscus, viz. the radius of an ideal capillary tube (-size of uniform voids in a soil) for different capillary heights, H<sub>c</sub>:

ТΑ	B	L	E	2
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CAPILLARY CONSTANTS AND (p1 - p2)-VALUES

T⁰C	Surface Tension S g/cm	W ater Density Y <sub>W</sub> g/cm <sup>3</sup>	Capillary Constant $a^2 = \frac{2S}{\gamma_w}$	Vapor Density D <sub>V</sub> g/cm <sup>3</sup>	$p_1 - p_2 = a^2 \cdot D_{\mathbf{v}} \cdot \frac{1}{r}$ $g/cm^2$			
1	2	3	4	5	6			
-5	*77.91·10 <sup>-3</sup>	0,9992	0.1562	3, 353, 10 <sup>-6</sup>	$0.522 \cdot 10^{-6} \cdot \frac{1}{r}$			
-4	77.76·10 <sup>-3</sup>	0. 9994	0.1559	3.615.10 <sup>-6</sup>	$0.562.10^{-6}.\frac{1}{r}$			
-3	77. 61 <sup>.</sup> 10 <sup>-3</sup>	0 9996	0. 1556	3.830·10 <sup>-6</sup>	$0.594 \cdot 10^{-6} \cdot \frac{1}{r}$			
-2	77.45·10 <sup>-3</sup>	0. 9997	0. 155 <b>2</b>	4. 193 · 10 <sup>−6</sup>	$0.649 \cdot 10^{-6} \cdot \frac{1}{r}$			
-1	77. 29 <sup>.</sup> 10 <sup>-3</sup>	0. 9998	0. 1549	4.513·10 <sup>-6</sup>	$0.697 \cdot 10^{-6} \cdot \frac{1}{r}$			
0	77. 13 <sup>.</sup> 10 <sup>-3</sup>	0. 99986	0. 1545 <sup>+</sup>	4.854·10 <sup>-6</sup>	$0.748 \cdot 10^{-6} \cdot \frac{1}{r}$			
1	76.99•10 <sup>-3</sup>	0. 99992	0. 1543	5. 222· 10 <sup>-6</sup>	0.803 $\cdot 10^{-6} \cdot \frac{1}{r}$			
2	76.83·10 <sup>-3</sup>	0.99996	0.1540	5.612.10 <sup>-6</sup>	$0.864 \cdot 10^{-6} \cdot \frac{1}{r}$			
3	76.69·10 <sup>-3</sup>	0. 99999	0. 1536	6.026·10 <sup>-6</sup>	$0.924 \cdot 10^{-6} \cdot \frac{1}{r}$			
4	76. 54·10 <sup>-3</sup>	1. 00000	0. 1533	6.467·10 <sup>-6</sup>	$0.989 \cdot 10^{-6} \cdot \frac{1}{r}$			
5	76.40·10 <sup>-3</sup>	0. 99999	0. 1530	6. 934·10 <sup>-6</sup>	$1.059 \cdot 10^{-6} \cdot \frac{1}{r}$			
6	76. 25· 10 <sup>-3</sup>	0. 99996	0. 15 <b>2</b> 7	7.434·10 <sup>-6</sup>	$1.133 \cdot 10^{-6} \cdot \frac{1}{r}$			

+ Values calculated from International Critical Tables

\* Average  $a^2 = 0.1545$  at 0 deg C

$r = \frac{a^2}{H_c} = \frac{0.1545}{H_c}$ [ cm ] . (1)	33)
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The "r's" as seen in Table 3, are calculated for capillary pressure differences of  $H_c = 1$  cm, 10 cm, 50 cm, 100 cm, 500 cm and 1,000 cm, respectively.

Pressure Differences—One observes from Table 3 that the vapor pressure differences for each particular capillary pressure difference  $H_c$  and at temperatures at or near freezing ( $\approx 0 \deg C$ ) (a condition that pertains to soil freezing and in which we are particularly interested) are very small. In order to have vapor pressure differences of 1.035 g/cm<sup>2</sup> to 2.06 g/cm<sup>2</sup> (as we had in the case of vapor diffusion into air) to diffuse 0.0138 g and 0.0276 g per day, we ought to have at about 0 deg C a pressure difference about 1,000 times larger than those at  $H_c = 250 \text{ cm}$  and  $H_c = 500 \text{ cm}$ , respectively, that is to say, we must have a capillary pressure difference of 250,000 cm per cm and 500,000 cm per cm of the thickness, viz. width of the air space, respectively, or 250 m to 500 m per one millimeter, respectively, which would give us a 1.21g/cm<sup>2</sup> and 2.42 g/cm<sup>2</sup> vapor pressure difference, respectively. The values of these would then be approximately equal to 1.035 g/cm<sup>2</sup> and 2.06 g/cm<sup>2</sup>, respectively.

Diffusion as a Function of S-As the capillary pressure is equal to

$$\mathbf{P}_{\mathbf{C}} = \mathbf{Y}_{\mathbf{W}} \cdot \mathbf{H}_{\mathbf{C}} \quad \left[ \frac{\mathbf{g}}{\mathbf{cm}^2} \right]$$
(34)

#### TABLE 3

(in cm and inches)							
H <sub>C</sub> in	c m	1	10	50	100	500	1000
	inches	0.39	3.94	19.70	39.37	196.85	393.70
Ra	dius r	0. 1545	0.01545	0.0031	0.001545	0.00031	0.0001545
	1	2	3	4	5	6	7
Тd	T deg C *DIFFERENCE IN VAPOR PRESSURE, $p_1 - p_2 = f(S)$ , in $\frac{g}{Cm^2}$ FOR VARIOUS RADII AND AT DIFFERENT TEMPERATURES					a <u>g</u> RATURES	
	-5	3.37	33.7	168	337	1685	3370
	-4	3.63	36.3	181	363	1815	3630
	-3	3.84	38.4	192	384	1920	3840
	-2	4.20	42.0	210	420	2100	4200
	-1	4.51	45.1	225	451	2255	4510
	0	4.84	48.4	242	484	2420	4840
	1	5.19	51.9	259	519	2595	5190
	2	5.57	55.7	278	557 <sup>.</sup>	2785	5570
	3	5.98	59.8	299	<b>598</b>	2990	5980
	4	6.40	64.0	320	640	3200	6400
	5	6.85	68.5	342	685	3425	6850
6		7.46	74.6	373	746	3730	7460

# RADIUS OF MENISCI, r, IN CM AS A FUNCTION OF VARIOUS CAPILLARY HEIGHTS

\*The  $(p_1 - p_2)$  in this table consist of the true  $(p_1 - p_2)$ -values multiplied by 10<sup>6</sup>. To obtain the real  $(p_1 - p_2)$ -values, multiply the figures in this table by 10<sup>-6</sup>. For example,  $p_1 - p_2 = 6.40 \times 10^{-6} = 0.00000640$  at T = 4 deg C for  $H_C = 1$  cm.

For 
$$H_c = 250$$
 cm,  $p_1 - p_2 = 1210 \cdot 10^{-6}$  g/cm<sup>2</sup> = 0.00121 g/cm<sup>2</sup>.

which at equilibrium is in balance with the difference in vapor pressure  $(p_1 - p_2)g/cm^2$ , then, substituting into the diffusion Equation 6 the vapor pressure symbol dp by its equivalent capillary pressure,  $H_c \cdot \gamma_W$ , obtain the amount of moisture in grams per 86,400 seconds (=24 hours) transferred in the vapor phase:

$$W = -D \cdot A \cdot t \cdot \frac{1}{R \cdot T} \cdot \frac{\gamma_{W} \cdot H_{c}}{x}$$
(6)

$$= D \cdot A \cdot t \cdot D_{v} \cdot \frac{H_{c}}{x} \qquad \left[g\right],$$

$$W = \left|-(1) \cdot (1) \cdot (86, 400) \cdot (0.755) \cdot (10^{-6}) \cdot \frac{H_{c}}{100 \cdot x}\right|$$

or

= (0.0006696) 
$$\cdot \frac{H_c}{x} \qquad [g]$$
 (36)

Here  $H_c$  is now expressed in meters, and x is the width of the air space, which is the diameter of the spherical bubble (=2  $\cdot$  r), in cm.

The small amount of soil moisture diffused in the vapor phase as a function of surface tension is to be interpreted as follows: in order to diffuse 6.7 g/cm of soil moisture during one day, theoretically 1,000 m of capillary pressure would be needed. However, such an immense capillary pressure is practically very rarely available under normal conditions. On the other hand, if the length of the freezing season is to be of 100 days duration, and the capillary pressure  $H_c = 1 \text{ m} = 3.28$  feet, then the moisture transferred during this time would be 0.067 grams. One sees that the diffused quanti-

(35)

ties of soil moisture, considering surface tensions, are really very insignificant. Therefore, it seems that this kind of mechanism for the upward supply of soil mois-

ture toward the freezing ice lenses can be ignored. Effect of Capillary Radius on Vapor Diffusion-Expressing  $\frac{2 \cdot S}{r}$  from Equation 29 obtain

$$\frac{2 \cdot S}{r} = p_{V} - p_{1} + (H_{C} - h_{C}) \gamma_{W}$$
(37)

It can be observed that the smaller  $h_c$  is, the larger is  $\frac{2 \cdot S}{r}$ , and the smaller is r, in turn. When  $h_c$  becomes zero, r is at its minimum.

For these conditions Equation 37 can be rewritten as follows:

$$\frac{2 \cdot S}{r_{\min}} = H_{c} \cdot \gamma_{w} + p_{v} - p_{1}$$
(38)

But

$$H_{c} \cdot \gamma_{w} = \frac{2 \cdot S}{r_{2}}$$
(39)

where  $r_2$  is the upper meniscus in the tube, causing the capillary column, the height



Figure 13. Stresses in capillary water at the position of the bubble.

of which is  $H_c$ , to rise. Note that  $r_2 \neq r$  (see Fig. 14). Hence Equation 38 can be rewritten as

$$\frac{2 \cdot S}{r_{\min}} = \frac{2 \cdot S}{r_2} + p_v - p_1 .$$
 (40)

From here one sees that

$$\frac{2 \cdot S}{r_{\min}} < \frac{2 \cdot S}{r_2} \quad , \tag{41}$$

and therefore

 $r_{min} > r_2$ 

From Equations 40 and 42 we deduce that no matter what the position of the bubble, its radius  $r_{min}$  will always be larger than the radius  $r_2$  of the capillary. This requires revision of Figure 9 as now shown in Figure 14.



Figure 14. Revision of Figure 9.

Besides, physically  $r_2$  cannot be less than the radius  $\frac{d}{2}$  of the capillary tube. These considerations lead to the deduction that formation of aqueous vapor and/or gas in soil is more likely to take place in coarse voids than in fine ones, for example such silty sands, silt, silty clay, clayey silt or clay.

#### **Evaluation** of Study

<u>Comparison of Calculated Values with</u> <u>Possible Field Conditions</u>—Variation in soil temperature may cause soil moisture vapor in soil voids to vary in density and pressure. However, as seen from Table 1, as well as from observations, soil temperature below the frozen layer does not vary appreciably. Consequently, vapor pressures during the freezing season are not of great magnitude, nor do they vary appreciably. Vapor diffusion is probably more pronounced in spring and fall, when temperatures change more rapidly.

The intensity of vapor exchange in soil depends upon the texture of the soil. In soils with large sizes of voids (= function of coarse soil particles and loose packing) vapor exchange would take place more intensively than in a soil, the void sizes of which are of very fine dimensions.

Because the most troublesome soils relative to upward migration of soil moisture upon freezing are the fine silty sands, the silts in particular, and the silty clays, all of which can be broadly classified as fine soils, it can be deduced that soil moisture transport in the vapor phase in such soils would be of lesser quantity than in coarsegrained soils.

The amount of soil moisture transferred in the vapor phase upon freezing is indeed very small as compared with the high moisture contents in the frozen soil where groundwater supply for the formation of ice lenses is available. The calculated values here can be taken as the maximum ones. Actually they would be even less if we consider the following.

Upon freezing the downward-progressing freezing surface of the frozen soil is at a

(42)

temperature of about 0 deg C = 32 deg F. During a cold snap the temperature at the 0 deg C-isothermal surface of the frozen soil layer drops somewhat below 0 deg C. Under these conditions more ice lenses are formed.

Upon formation of ice latent heat is set free and the temperature at the downwardprogressing freezing isothermal surface returns to 0 deg C. Thus during a cold snap the freezing process is a slow one and the increase in frost penetration with depth is relatively small. From what has been said above it can be reasoned that during the seasons of freezing and thawing, temperature variations on the soil or road surface have, practically speaking, little influence on the soil temperature conditions below the 0 deg C-line, which in turn explains the small order of magnitude of the soil moisture diffused in the vapor phase.

<u>Comments</u>—Owing to the small amount of vapor transferred, it seems that for simplicity the factor vapor diffusion within the freezing soil system can be disregarded. Because of some unavoidable uncertainties contained in the fundamental assumptions of the theories as well as in the assumed numerical values for the various coefficients, it seems that in this instance simplicity is of much greater importance than accuracy at the start of our studies of the complex soil-freezing problem. In a simplified theory it is easier to evaluate the practical consequences of various deviations from the assumptions, and then this would permit introducing improvements as our knowledge increases.

#### CONCLUSIONS

This study considers two cases of soil moisture diffusion in the vapor phase, namely

- 1. (a) diffusion of vapor to air as a function of temperature differences, i.e., the driving force or vapor pressure difference is a function of temperature variation,  $p_1 p_2 = f(T_1 T_2)$ ,
  - (b) diffusion across an air space (bubble) in soil water as a function of capillary moisture surface tension, i.e.,  $p_1 - p_2 = f(S')$ .

2. The study brings out the relatively small order of magnitude of the pressure differences when operating with such assumed values, which from experience indicates that they are optimum, reflecting pretty nearly the actual or real conditions.

3. The amounts of soil moisture transferred upward in the vapor phase toward the freezing ice lenses upon freezing can in both cases be considered as very insignificant. Therefore upward vapor transfer in soil upon freezing can be considered as an ineffective mechanism of moisture transport.

4. Moisture diffusion in the vapor phase in soil would take place in soil with larger void sizes rather than with fine void sizes.

5. This study reveals that the assumption made to serve as a basis for the soil freezing experiment, namely, that the upward flow of soil moisture from ground water toward the freezing ice lenses in a frost-susceptible soil takes place virtually unaccompanied by vapor diffusion, can be considered as justified.

6. Other possible transport mechanisms for the upward flow of soil moisture upon freezing should be investigated.

### A CKNOW LEDGMENT

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#### REFERENCES

1. A.R. Jumikis, "The Frost Penetration Problem in Highway Engineering," Rutgers University Press, New Brunswick, New Jersey, 1955, p. 111.

2. A.R. Jumikis, "The Soil Freezing Experiment," Paper, presented before the 35th Annual Meeting of the Highway Research Board, Washington, D. C., January, 1956, p. 12.

3. G. Beskow, "Tjälbildningen och Tjälliftningen, Statens Vaginstitut," Stockholm, 1935, p. 9.

4. A. W. Porter, "Surface Tension." Encyclopedia Britannica. Vol. 21. Enclyclopedia Britannica, Inc., Chicago, 1952, p. 597.

5. H. F. Winterkorn, "Appendix C, Earth Environment, ERDL Project Contract No. DA-44-009 Eng. 1773," November 28, 1953, Department of Engineering Research, The Pennsylvania College, College Park, Pennsylvania, p. 185.

6. "International Critical Tables of Numerical Data, Physics, Chemistry and Technology, for the National Research Council of the U.S.A., "McGraw-Hill Book Co., New York, 1928, Vol. III, p. 211.
7. O. Maas and E.W.R. Steacie, "An Introduction to the Principles of Physical

Chemistry," John Wiley and Sons, New York, 1931, page 11-20.

8. S. Glasstone, Textbook of Physical Chemistry, 2nd Edition, D. Van Nostrand Company, Inc., New York, 1946, p. 1257. 9. W. Jost, "Diffusion in Solids, Liquids and Gases," Academic Press, Inc.,

Publishers, New York, 1952, p. 1.

10. G.W.C. Kaye and T.H. Laby, "Tables of Physical and Chemical Constants," Longmans, Green and Co., London, 10th Ed., 1948, p. 47.

11. F.E. Fowle, "Smithsonian Physical Tables," 7th Ed., The Smithsonian Institution, City of Washington, 1920, p. 167.

12. F. H. Macdougal, "Thermodynamics and Chemistry," John Wiley and Sons, Inc., New York, 1926, p. 13.

13. S. Brunauer, "The Absorption of Gases and Vapors," Princeton University Press, Princeton, New Jersey, 1943, p. 120.

14. J.K. Vennard, "Elementary Fluid Mechanics." John Wiley and Sons, New York. 1950, p. 6.