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THERMODYNAMICS OF SOIL MOISTURE

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THERMODYNAMICS OF SOIL MOISTURE¹N. E. EDLEFSEN² AND ALFRED B. C. ANDERSON³

INTRODUCTION

THE WORKER who attempts to study the basic principles of thermodynamics with reference to soil moisture has considerable difficulty because both the nomenclature and the method of treatment in existing literature vary greatly. Writers on thermodynamics have usually had in mind specific purposes quite foreign to soil-moisture studies; their conclusions and equations, being adapted to some other particular field, are not easily applied to soil moisture. This paper aims to eliminate at least part of the difficulty and also to make certain helpful original applications. It applies the well-grounded principles of thermodynamics to a study of the soil-moisture system. The first part includes, for the convenience of the reader, some material that can be found scattered in numerous published reports and books. Such material, it is hoped, is here presented in such a way as to be more readily available.

Probably the most useful thermodynamic function, as far as the student of soil moisture is concerned, is free energy. The following treatment has been built, accordingly, around that function. The chief purpose of this paper, aside from the presentation of the basic thermodynamic principles, is to develop quantitative expressions for the dependence of the free energy of soil moisture on such factors as the adsorptive force field that surrounds a soil particle, the hydrostatic pressure on the soil moisture, the dissolved material present, and the temperature.

In mathematical treatments of physical systems, the inexperienced student cannot always distinguish clearly between the parts that result from pure mathematical manipulation and the parts that can be deduced, either directly or indirectly, from experimental measurements. Certain aspects of mathematical analysis used in this paper are difficult

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for the student of soil moisture to find elsewhere in the literature, especially in a form immediately applicable to his own research. At the beginning of this discussion are presented, therefore, several mathematical articles that do not depend on any physical or chemical facts relative to soil moisture. They are, however, used later in the paper in analyzing certain aspects of the thermodynamics of soil moisture. Since they are presented early, the reader may be more easily able to distinguish between the deductions that are purely mathematical and those that are physical. Since the mathematical developments are used only in certain parts of the treatment, the reader may well scan them over but need not necessarily master every detail before reading the general discussion that follows. He may even skip the first section entirely until he is referred back to it at some later point.

To be most useful, any treatment of thermodynamics of soil moisture must recognize certain phenomena related in some ways to plant physiology and in other ways to soil hydrodynamics. In the present treatment, three types of phenomena have been distinguished.

The first deals with the vapor pressure of soil moisture as a function of moisture content (2, 46, 104, 119, 123, 153, 154, 169).⁴ When the soils are very wet, the vapor pressure is approximately that of free water at the same temperature. As the moisture content is decreased, the vapor pressure decreases very slightly with respect to changes in moisture content until a certain value is reached that is characteristic of the soil. At this point the decrease in the vapor pressure with respect to a decrease in moisture content becomes and remains very great. In other words, there is a moisture content where the second derivative of the vapor pressure with respect to moisture content is a maximum, which means that, at this point, the slope of the vapor-pressure-moisture-content curve changes most rapidly.

The second might be classed as a plant-physiological type of phenomenon. The extensive work of Veihmeyer, Hendrickson, and co-workers (33, 40, 73, 74, 75, 157, 158, 161, 162) has demonstrated that plants seem to grow normally (assuming other conditions to be favorable) until the moisture content is reduced to a certain value that, because of the manner in which it is defined, can be fixed only within a narrow range of moisture contents. Other work, in general, seems to support this view (15, 16, 29, 47, 152, 174). When this value is reached, the plants begin to evidence their need of water by drooping of leaves, by lack of growth, or by some other fairly obvious sign; they will no longer function normally unless water is added to the soil. According to available data (46, 153, 154), the point on the curve mentioned in the previous paragraph, where

⁴ Italic numbers in parentheses refer to the Bibliography at the end of this paper.

the vapor pressure of the soil moisture changes most rapidly with respect to changes in moisture content, falls in this narrow range where plants wilt. This moisture content has been characterized as the "permanent wilting percentage," and might be regarded as the lower limit above which moisture is readily available to plants. This does not mean, of course, that plants cannot dry the soil out to lower moisture contents than the permanent wilting percentage. They may continue to use some water, but at a markedly reduced rate, while their normal functioning is markedly inhibited. The permanent wilting percentage is approximately independent of the kind of plant grown in the soil, and seems to depend only upon the type of soil, being a characteristic of a given soil.

The third type of phenomenon concerns the hydrodynamics of soil moisture. If a field is saturated by irrigation or rain and then allowed to drain freely, water will at first filter through the soil rather rapidly until a certain moisture content is reached; then the drainage will practically cease (19, 20, 32, 82, 96, 97, 157, 159, 163). This moisture content is also a characteristic of the particular soil. It too is represented by a narrow range in moisture content and, when applied to field conditions, will here be called "field capacity." The "moisture equivalent" (21, 28, 87, 155, 163, 164, 165, 170, 173) is a convenient and for most soils a fairly accurate method of evaluating the field capacity. The marked slowing of the downward motion is usually reached within two or three days after a heavy rain or irrigation, the time depending on the type of soil. Any further downward movement is so slow that, from the agricultural point of view, it may be neglected. The field capacity represents the maximum amount of water that can be stored for long periods, in the absence of plants, in a soil having free drainage. This statement applies only to the soil below the depth to which evaporation is effective. Loss by evaporation is extremely small below the top 6 inches of soil (91, 157). Earlier literature (76, 97, 170), however, seemed to stress this loss.

For practical purposes in agriculture, the amount of water that is readily available to plants and that can be stored in a soil is represented by the difference in moisture content between field capacity and permanent wilting percentage. This range of what is termed "readily available water" is likewise characteristic of a given soil and nearly independent of the kind of plants grown.

After heavy irrigations amounts of water larger than field capacity can, of course, be held in the soil for short periods; but since moisture above field capacity drains out soon after application, very little of it can be used by plants. Likewise, plants can extract water to moisture contents below the permanent wilting percentage. In that case, however, they usually evidence need for water and fail to function normally.

"Field capacity" and "permanent wilting percentage," as we use these terms, are recognized by most students of soil moisture as significant in agriculture. They are not always, however, known by these names, some investigators (76, 97, 143) selecting other soil-moisture contents near these as having similar significance. These terms are either arbitrary or, like those mentioned above, less specific than one might wish; they are merely narrow ranges of moisture content. In reporting data, however, they are customarily given a specific value. This practice of reporting single values that really represent narrow ranges is sometimes misleading. The student of soil moisture bears in mind, however, that the measurement might vary by plus or minus a slight amount. For certain purposes

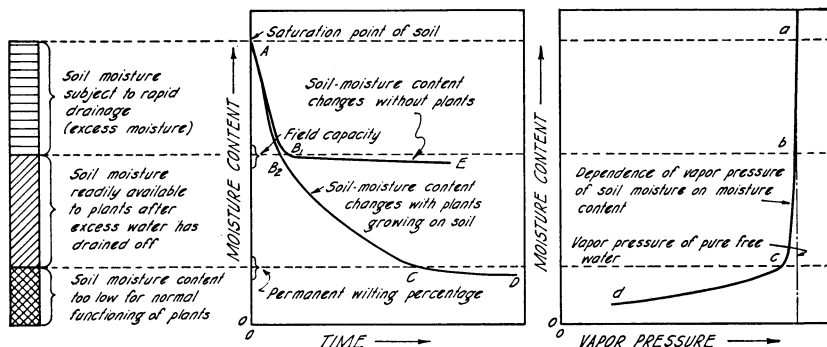


Fig. 1.—Relation between permanent wilting percentage, field capacity, range of readily available moisture, drainage, vapor pressure, and moisture content.

some investigators might find other nomenclature convenient, but for this discussion the terms mentioned above will serve.

Figure 1 summarizes graphically the three foregoing types of phenomena. It shows how the drainage, the vapor pressure, and the amount of moisture available to plants all change after a soil planted to a crop has been saturated by irrigation. It shows the relation between the field capacity, the permanent wilting percentage, and the readily available water. It also points out the nearly constant time rate of use of readily available water by a crop growing on the soil. Suppose we consider a soil immediately after irrigation in the nearly saturated state as represented by the point A. At this point the soil will possess its maximum moisture content; and the vapor pressure of its moisture will be that of free, pure water as represented by the point a. If desired, the osmotic pressure equivalent to the vapor pressure can be readily calculated from the expressions given in articles 35 and 36.

Consider first the case of a soil immediately after an irrigation with no plants growing on it. As time goes on, the soil moisture content will de-

crease very rapidly by free drainage until it reaches the point B_1 , corresponding to the field capacity or the moisture equivalent. (For most agricultural soils, the moisture equivalent is nearly equal to the field capacity.) Where evaporation is unimportant, as is usually the case, the soil moisture content would remain for an indefinite period relatively constant near field capacity, as illustrated by the nearly horizontal section of the part B_1E of the curve. The vapor pressure of the soil moisture at field capacity is still practically that of free water, as given by the point b .

If, on the other hand, a crop is growing on the soil, the field capacity will be reached sooner at B_2 because of transpiration. Transpiring plants will reduce the moisture content still further, eventually to the permanent wilting percentage C along some curve such as B_2C , without showing appreciable inhibition of their normal functions. At the permanent wilting percentage, the vapor pressure of the soil moisture is still relatively near that of free, pure water, as represented by the point c . With decrease of moisture content below the permanent wilting percentage, the energy required to remove the soil moisture begins to increase so rapidly and to such a high value that neither the plant nor gravity is able normally to remove much additional moisture. What little might be removed by the plant below the permanent wilting percentage is sufficient only to permit the plant to function at a greatly inhibited rate. The approximate constancy of the soil moisture content after the permanent wilting percentage is reached is represented by the almost horizontal section CD . Simultaneously the vapor pressure of the soil moisture decreases tremendously, as represented by cd . As will be shown later, the free energy of the soil moisture, being proportional to the logarithm of the vapor pressure, also begins to decrease very rapidly at the point c . These conditions and behavior are what one normally finds a few inches below the soil surface, where evaporation into the atmosphere is negligible.

The field capacity and the permanent wilting percentage may, of course, vary slightly with such factors as the temperature and the nearness of the soil moisture to the water table. The small ranges covered by the terms "field capacity" and "permanent wilting percentage" are illustrated in the diagram by the small brackets.

MATHEMATICAL THEOREMS TO BE USED IN THE THERMODYNAMIC ANALYSIS OF SOIL MOISTURE⁵

1. Single-valued Functions and Perfect Differentials

Two types of functions are used in thermodynamics. The first may be represented as a single-valued function of one or more variables, as follows:

$$\phi = \phi(x, y, \dots). \quad (1)$$

A particular set of values (x, y, \dots) will represent and determine a definite state of the system and will therefore determine uniquely a single value of ϕ . In consequence any infinitesimal change in ϕ , which we shall represent by $d\phi$, depends solely upon the initial and final state or the initial and final sets of values of (x, y, \dots) . For example, the change $d\phi$ caused by changing (x, y, \dots) to $(x + dx, y + dy, \dots)$, which means that $\phi(x, y, \dots)$ becomes $\phi(x + dx, y + dy, \dots)$, may be expressed as follows:

$$d\phi = \phi(x + dx, y + dy, \dots) - \phi(x, y, \dots). \quad (2)$$

Assuming that the partial derivatives

$$\frac{\partial \phi}{\partial x}, \frac{\partial \phi}{\partial y}, \dots$$

exist and are continuous in the vicinity of the point (x, y, \dots) , equation 2 may be written in terms of the differentials (dx, dy, \dots) in the form

$$d\phi = \frac{\partial \phi(x, y, \dots)}{\partial x} dx + \frac{\partial \phi(x, y, \dots)}{\partial y} dy + \dots \quad (3)$$

Purely as a mathematical consequence, therefore, $d\phi$ may be expressed as above in terms of the changes (dx, dy, \dots) in the variables (x, y, \dots) representing the state of the system. If ϕ is a function of but one variable, x , we have the following almost trivial case:

$$\begin{aligned} \phi &= \phi(x), \\ d\phi &= \phi(x + dx) - \phi(x), \end{aligned}$$

and

$$d\phi = \frac{d\phi}{dx} dx.$$

⁵ This section contains a number of mathematical articles that do not depend on any physical or chemical facts relative to soil moisture. They are, however, used later in the paper in analyzing certain aspects of the thermodynamics of soil moisture. The reader may well scan them over and then revert to them only as the occasion demands.

When the differential $d\phi$ of a function may be represented in terms of the differentials of its dependent variables (eq. 3), we say that $d\phi$ is a "perfect differential." For example, the independent variables x and y may represent the temperature T and specific volume v , respectively; the dependent variable ϕ , the internal energy e of the system. Other properties of a function that may be represented as a perfect differential will be found in succeeding articles.

The other type of function, which we shall, for generality, here represent by θ , is not a single-valued function of the variables of state (x, y, \dots)

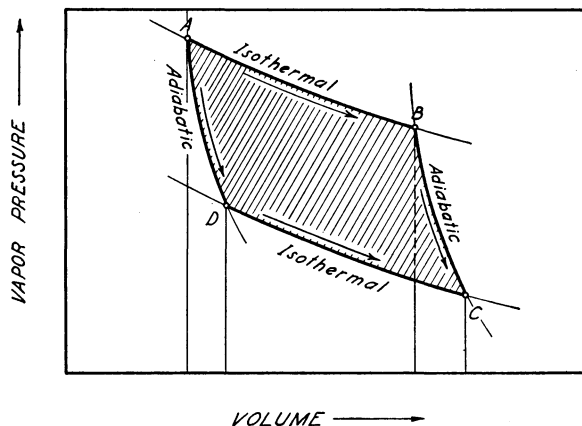


Fig. 2.—Carnot cycle for an ideal gas engine.

and cannot be represented in the form of equation 1. Instead, its values depend solely on the path followed by the process causing the change of state. Thus a change $d\theta$ in θ caused by going from one state to another depends not upon the initial and final values of the variables of state (x, y, \dots), but solely on the path followed in going between the two states. Consequently, the differential $d\theta$ can never be represented in the differential form of equation 3 above; that is, it is not a perfect differential. As an illustration from thermodynamics of such functions as these, we have the heat energy q added to the system, and the work w done by the system, whose differentials depend not upon the initial and final states of the system, but rather upon the path followed during the thermodynamic process. Consider, for example, figure 2, which represents the Carnot cycle of an ideal gas engine. The work done by the system dw on its surroundings in going from A to C along the path ABC is greater than along the path ADC by the area $ABCD$ of the figure, although the initial and final points A and C are the same. Likewise, the heat added to the system dq in going from the state A to the state C depends upon the

path taken and not upon the initial and final states A and C . More heat is taken in by the system in going along the path ABC than along the path ADC . We therefore distinguish thermodynamic functions as to whether their differentials are perfect or not.

To fix our ideas and to bring out the meaning and importance in thermodynamics of the functions of the former type, let us consider some of the more common single-valued thermodynamic functions with which we shall be dealing.

Such variables as the temperature T , the pressure P , and the specific volume v serve to define the state of a system and correspond to the variables (x, y, \dots) used previously. For simple substances such as water, any two of these variables will, in general, define the state. If, for example, the pressure P and temperature T are given, the volume v of the water is immediately fixed. If, on the other hand, we have a simple solution composed of a solvent and solute, three variables will define the state of the system; and, in this case, they might be P , T , and the mol fraction X of solute. To define the state of a more complicated system, more than three variables will, of course, be necessary.

Expressed in terms of the variables of state given above are a number of thermodynamic functions such as the internal energy e , the heat content h , the free energy f , the maximum work a , and the entropy s .

The internal energy e , by the very nature of its definition, must depend on the variables of state, for it represents the internal energy of the substance, which is due to such factors as molecular attraction, kinetic energy, molecular vibration, and intramolecular and intra-atomic attraction. Experience has shown that these forms of energy are fixed by any two of the variables: specific volume, pressure, or temperature. The internal energy of water, for example, is immediately fixed when its specific volume and temperature have been given. The entropy s is likewise determined by the specific volume and temperature, as will be shown later. Evidently, therefore, the differentials of the internal energy e and the entropy s are perfect, since the functions e and s may be expressed in terms of the variables of state, T , P , and v .

The other three thermodynamic functions, whose meaning is considered in detail later in this paper, are there shown to be defined by the following equations:

$$\left. \begin{aligned} h &= e + Pv \\ f &= h - Ts = e - Ts + Pv \\ a &= e - Ts \end{aligned} \right\} (4)$$

The differentials of such functions as h , f , and a above are called "perfect differentials" because, as equations 4 show, the functions are com-

pletely determined by the variables of state such as T , P , and v ; it has already been pointed out that the internal energy e and the entropy s may be expressed in terms of these same variables of state. Thus the right-hand side of equations 4 is composed of quantities which either are or can be expressed in terms of the variables of state T , P , and v . For example, if T , P , and v are given, h is fixed. Thus equations 4 are each perfectly analogous to equation 1 and have all the same mathematical properties. In analogy to equation 3, for instance, we have the following perfect differentials, which we shall merely accept for the present but which are derived in articles 11, 21, and 44:

$$\left. \begin{aligned} dh &= Tds + vdP \\ df &= -sdT + vdP \\ da &= -sdT - Pd v \\ de &= Tds - Pd v \end{aligned} \right\} (5)$$

The last equation follows immediately from a combination of the First and Second laws of thermodynamics, since the First Law (art. 11) states that $de = dq - Pd v$, where dq is the amount of heat added to the system; and the Second Law (art. 14) states that $ds = \frac{dq}{T}$.

2. The Interrelations of the Properties of a Substance

Several properties or quantities, such as P , v , T , s , and h , serve to describe the state of a substance or system. Offhand, therefore, it would seem that many of these quantities would have to be known before the state of a system could be fixed and described quantitatively. Generally, however, as previously stated, any two of such quantities as those given above will quantitatively describe and uniquely fix the state of a simple substance such as water. Such descriptive quantities are usually so inter-related that to determine any two of them will for a simple substance immediately fix the others. The state of free, pure water, for example, is immediately fixed if any two of the quantities named above are known. If both the pressure and the temperature are given, the water can exist in but one state; and therefore all its other properties, such as its specific volume v , its entropy s , and its heat content h , are simultaneously fixed.

In mathematical language we speak of such a system as having two degrees of freedom or two independent variables, because two variables are needed to fix the state of the system. All the other quantities, properties, or variables of the system are then called dependent variables because their value depends on the independent variables. If, for example, the pressure and temperature of water are given, the volume, which is then the dependent variable, is immediately fixed. It is usually imma-

terial, except for convenience, which variables are taken as independent. Those remaining then become the dependent variables.

If we take T and P as the independent variables of state for water, with v , the specific volume, as the dependent variable of state, we have $v = f(P, T)$, which expresses the specific volume as a single-valued function of the variables of state T and P . To fix our ideas for the present, we might assume that we are dealing with water vapor, the specific volume of which will be determined by the pressure and temperature. Then from the general theorem of mathematics, stated at the beginning of article 1, we should have

$$dv = \left(\frac{\partial v}{\partial T} \right)_P dt + \left(\frac{\partial v}{\partial P} \right)_T dP.$$

If, instead, P and s had been taken as independent variables, then $v = f(P, s)$; and we should have

$$dv = \left(\frac{\partial v}{\partial s} \right)_P ds + \left(\frac{\partial v}{\partial P} \right)_s dP.$$

It will be noticed that $\left(\frac{\partial v}{\partial P} \right)$ is not the same in the two equations: $\left(\frac{\partial v}{\partial P} \right)_T$ refers to the variation of v with respect to P with T constant, whereas $\left(\frac{\partial v}{\partial P} \right)_s$ refers to the variation of v with respect to P with the entropy s kept constant. When the differential of the dependent variable of a function can be expressed in a form such as dv above, in terms of the differentials of the independent variables, dv is called a "perfect differential." This fact leads us to an important mathematical theorem in thermodynamics presented in article 3.

3. Properties of Single-valued Functions of Two Variables

Single-valued functions of but two independent variables have an important mathematical property, arising from the fact that the function may be expressed as a perfect differential. Suppose

$$d\phi = Xdx + Ydy, \quad (6)$$

where ϕ is a function of x and y —that is, $\phi = \phi(x, y)$ —and likewise where X and Y are each functions of both x and y . We shall now show that

$$\left(\frac{\partial X}{\partial y} \right)_x = \left(\frac{\partial Y}{\partial x} \right)_y.$$

To prove this theorem, consider the single-valued function $\phi = \phi(x, y)$. According to equation 3, we may express $d\phi$ in the form of a total differential as follows:

$$d\phi = \left[\frac{\partial \phi(x, y)}{\partial x} \right]_y dx + \left[\frac{\partial \phi(x, y)}{\partial y} \right]_x dy. \quad (7)$$

Comparing equation 6 with 7, we have

$$X = \left[\frac{\partial \phi(x, y)}{\partial x} \right]_y \text{ and } Y = \left[\frac{\partial \phi(x, y)}{\partial y} \right]_x. \quad (8)$$

Differentiating equations 8, we get

$$\left(\frac{\partial X}{\partial y} \right)_x = \frac{\partial^2 \phi(x, y)}{\partial y \partial x} \text{ and } \left(\frac{\partial Y}{\partial x} \right)_y = \frac{\partial^2 \phi(x, y)}{\partial x \partial y}. \quad (9)$$

Since the order of differentiation is immaterial, the right-hand sides of equations 9 are equal. We conclude, therefore, from 9 that when $d\phi = Xdx + Ydy$, it follows that

$$\left(\frac{\partial X}{\partial y} \right)_x = \left(\frac{\partial Y}{\partial x} \right)_y. \quad (10)$$

An application of equation 10 to each of the four perfect differentials of equations 5 gives the four following, which are often referred to as Maxwell's equations:

$$\left(\frac{\partial T}{\partial P} \right)_s = \left(\frac{\partial v}{\partial s} \right)_P \quad (11)$$

$$\left(\frac{\partial s}{\partial P} \right)_T = - \left(\frac{\partial v}{\partial T} \right)_P \quad (12)$$

$$\left(\frac{\partial s}{\partial v} \right)_T = \left(\frac{\partial P}{\partial T} \right)_v \quad (13)$$

$$\left(\frac{\partial T}{\partial v} \right)_s = - \left(\frac{\partial P}{\partial s} \right)_v \quad (14)$$

To illustrate the usefulness of these equations, let us show that the Clausius-Clapeyron equation (given by eq. 15 and considered in detail in art. 27) falls immediately out of equation 13, the third of Maxwell's equations above. From article 19 we have, by definition (eq. 70),

$$\Delta s = \frac{\Delta q}{T} = \frac{l}{T},$$

Dividing through by an increment in the volume while the temperature T remains constant, we have to a first approximation

$$\left(\frac{\partial s}{\partial v}\right)_T = \frac{l}{T} \frac{1}{\Delta v},$$

and therefore, since the left-hand side of this is equal to the left-hand side of equation 13, we obtain

$$\frac{dP}{dT} = \frac{l}{T\Delta v}. \quad (15)$$

The restriction of the constancy of volume may be omitted because the equilibrium pressure is independent of the volume. This is the Clausius-Clapeyron equation showing the relation between changes of temperature and pressure if two phases are to remain in equilibrium. Here l is the latent heat of transformation and Δv is the change in volume per gram (when the c.g.s. system is used) when one phase is transformed into the other.

As an application of the second of Maxwell's equations, let us derive the relation

$$\Delta s = -\int_{P_A}^{P_B} \left(\frac{\partial v}{\partial T}\right)_P dP,$$

which is used in article 77. As will be recalled, by applying equation 10 to the second of equations 5, we obtain equation 12, which is

$$\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P.$$

That is, a change ds when T is kept constant is given by

$$ds = -\left(\frac{\partial v}{\partial T}\right)_P dP,$$

which when integrated between the limits P_A and P_B gives

$$\Delta s = s_B - s_A = -\int_{P_A}^{P_B} \left(\frac{\partial v}{\partial T}\right)_P dP. \quad (16)$$

4. Simplest Conditions for the Maximum or Minimum of a Function of Any Number of Variables without Constraining Conditions

Let us consider first the simplest case where the function ϕ is a function of but one variable, x . That is,

$$\phi = \phi(x).$$

At any maximum or minimum, $x = x_0$ of ϕ , the first derivative of ϕ must be zero. In other words, when ϕ is a maximum or minimum at $x = x_0$, we have

$$\left(\frac{d\phi}{dx}\right)_{x=x_0} = 0. \quad (17)$$

That is, a slight change of x in either direction from $x = x_0$ will cause no change in ϕ except for infinitesimals of higher order than the first. That is, $\delta\phi = 0$ for infinitesimal variations δx about the point $x = x_0$, where x_0 corresponds to either a maximum or minimum value of ϕ . This is clarified

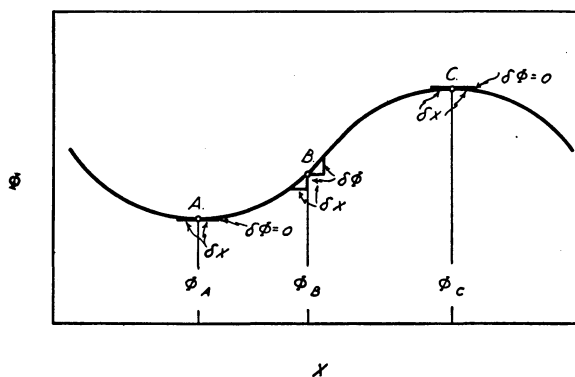


Fig. 3.—Properties of a function at a maximum and at a minimum.

by figure 3. Any infinitesimal variation δx in the neighborhood of either A or C, the minimum and maximum of ϕ , is seen to produce no variation $\delta\phi$ in the function ϕ ; that is, $\delta\phi = 0$ for infinitesimal variations δx about the point $x = x_0$, which corresponds to either a maximum or a minimum of the function ϕ . If, however, we focus attention on B, any other point of the curve, we note that slight variations δx do produce appreciable variations $\delta\phi$ of the function ϕ .

Considerations of the maximum or minimum of functions of any number of variables resemble those above. Let

$$\phi = \phi(x, y, \dots).$$

Then from article 1 it follows that the differential of ϕ may be represented as

$$\delta\phi = \frac{\partial\phi}{\partial x} \delta x + \frac{\partial\phi}{\partial y} \delta y + \dots \quad (18)$$

Now if the set of values (x_0, y_0, \dots) are such that $\phi = \phi(x_0, y_0, \dots)$ is either a maximum or minimum, then any slight variation $(\delta x, \delta y, \dots)$

of any or all the values (x, y, \dots) about the set of values (x_0, y_0, \dots) will cause no change in the function ϕ except for infinitesimals of higher order than the first. That is, $\delta\phi = 0$ for infinitesimal variations $(\delta x, \delta y, \dots)$ about the set of values (x_0, y_0, \dots) , which corresponds to either a maximum or minimum of the functions ϕ . Obviously, $\delta\phi$ must equal zero for variations $(\delta x, \delta y, \dots)$ about (x_0, y_0, \dots) , for if the variations $(\delta x, \delta y, \dots)$ produced a change $\delta\phi$ different from zero, the set of values (x_0, y_0, \dots) could not correspond to a maximum or minimum of ϕ .

Further, since $\delta\phi$ must equal zero for any arbitrary set of variations $(\delta x, \delta y, \dots)$ about (x_0, y_0, \dots) , according to equation 18 we must have

$$\frac{\partial\phi}{\partial x} = 0, \quad \frac{\partial\phi}{\partial y} = 0, \dots \quad (19)$$

in perfect analogy with equation 17. This follows because if any one of the partial derivatives—for example, $\frac{\partial\phi}{\partial x}$ —were not equal to zero at (x_0, y_0, \dots) , then $\phi(x, y_0, z_0, \dots)$, which is a function of x alone, would be either increasing as x passes through the value x_0 , or else decreasing, according to the sign of $\frac{\partial\phi}{\partial x}$. In neither case, therefore, could $\phi(x, y, \dots)$ have a maximum or a minimum at (x_0, y_0, \dots) .

That the conditions in equations 19 must hold also follows from the fact that if any of the partial derivatives were not equal to zero, the variations $(\delta x, \delta y, \dots)$ could not be carried out in any arbitrary manner but would have to be always so adjusted that $\delta\phi = 0$ in equation 18. There are no restrictions on the variations, for they are independent of each other. As will be remembered, the variations $(\delta x, \delta y, \dots)$ are independent and may be carried out in any arbitrary manner about (x_0, y_0, \dots) , still keeping $\delta\phi = 0$, if (x_0, y_0, \dots) is to correspond to a maximum or a minimum value of ϕ .

If, on the other hand, $\delta\phi = 0$ and equations 19 are not satisfied, then ϕ is merely a constant. This means that the variations $(\delta x, \delta y, \dots)$ must take place in such a way as to leave the value of ϕ unchanged. Under these conditions the variations cannot be made in an arbitrary manner, as we found to be the case above, at a maximum or minimum. This latter case can be stated mathematically from equation 18 by

$$\delta\phi = 0 = \frac{\partial\phi}{\partial x}\delta x + \frac{\partial\phi}{\partial y}\delta y + \dots$$

when

$$\phi(x, y, \dots) = \text{constant.}$$

**5. Determination of the Maximums or Minimums of a Function Subject to
One or More Constraining Conditions
(Lagrange's Method of Undetermined Multipliers)**

In article 49 on the statistical treatment of the properties of molecules, we shall have to determine the values of the independent variables $w_1, w_2, \dots w_n$, for which a certain function W has its maximum, subject to several restrictions or equations of constraint. Let us now consider the presentation and proof of a general method for making this determination.

Assume that we have a function $H_0 = H_0(w_1, w_2, \dots w_n)$ of the n variables $w_1, w_2, \dots w_n$ and that we wish to find the values of $w_1, w_2, \dots w_n$ for which $H_0 = H_0(w_1, w_2, \dots w_n)$ has a maximum or minimum value subject to h conditions, restrictions, or constraints. In applying the results of this article to the specific problem of article 49, we shall there set $H = W$. The h conditions, restrictions, or constraints, which are also to be functions of the n variables, may be denoted by

$$\left. \begin{aligned} H_1 &= H_1(w_1, w_2, \dots w_n) \\ &\dots\dots\dots \\ H_h &= H_h(w_1, w_2, \dots w_n) \end{aligned} \right\} (20)$$

Our h conditions will then be described by h fixed values $H_1, H_2, \dots H_h$, although the variables $w_1, w_2, \dots w_n$ may vary widely. Thus, we wish to find for what values of the variables $w_1, w_2, \dots w_n$ the function H_0 has a maximum subject to the h restrictions or conditions $H_1, H_2, \dots H_h$, each of which has a fixed or assigned value.

Having stated our problem, let us now recall from article 4 an important property of a function—namely, that when $H_0 = H_0(w_1, w_2, \dots w_n)$, for example, is at its maximum or minimum value, we can make small changes in the variables $w_1, w_2, \dots w_n$ without altering the value of H_0 . In general, according to article 1, we have

$$\delta H_0 = \frac{\partial H_0}{\partial w_1} \delta w_1 + \frac{\partial H_0}{\partial w_2} \delta w_2 + \dots\dots\dots + \frac{\partial H_0}{\partial w_n} \delta w_n.$$

When H_0 has a maximum value, we can carry out small changes, $\delta w_1, \delta w_2, \dots \delta w_n$, quite independently of each other without altering H_0 ; that is, $\delta H_0 = 0$, according to article 4. Hence, if H_0 is to be a maximum or a minimum, we must have

$$\delta H_0 = 0 = \frac{\partial H_0}{\partial w_1} \delta w_1 + \dots\dots\dots + \frac{\partial H_0}{\partial w_n} \delta w_n, \quad (21)$$

$$\left. \begin{aligned} &\frac{\partial H_0}{\partial w_1} \delta w_1 + \frac{\partial H_0}{\partial w_2} \delta w_2 + \dots + \frac{\partial H_0}{\partial w_n} \delta w_n = 0 \\ &\lambda_1 \frac{\partial H_1}{\partial w_1} \delta w_1 + \lambda_1 \frac{\partial H_1}{\partial w_2} \delta w_2 + \dots + \lambda_1 \frac{\partial H_1}{\partial w_n} \delta w_n = 0 \\ &\lambda_2 \frac{\partial H_2}{\partial w_1} \delta w_1 + \lambda_2 \frac{\partial H_2}{\partial w_2} \delta w_2 + \dots + \lambda_2 \frac{\partial H_2}{\partial w_n} \delta w_n = 0 \\ &\dots\dots\dots \\ &\dots\dots\dots \\ &\lambda_h \frac{\partial H_h}{\partial w_1} \delta w_1 + \lambda_h \frac{\partial H_h}{\partial w_2} \delta w_2 + \dots + \lambda_h \frac{\partial H_h}{\partial w_n} \delta w_n = 0 \end{aligned} \right\} (23)$$

Since each term in a given equation is multiplied by the same constant, the equations must still remain satisfied. The h quantities $\lambda_1, \lambda_2, \dots, \lambda_h$ are called Lagrangian multipliers; their values will be determined later. Suppose now we add all these equations 23 together, collecting terms having like coefficients of the variations δw —that is, all terms in the same vertical columns. We then have

$$\begin{aligned}
& \left(\frac{\partial H_0}{\partial w_1} + \lambda_1 \frac{\partial H_1}{\partial w_1} + \lambda_2 \frac{\partial H_2}{\partial w_1} + \dots + \lambda_h \frac{\partial H_h}{\partial w_1} \right) \delta w_1 \\
& + \left(\frac{\partial H_0}{\partial w_2} + \lambda_1 \frac{\partial H_1}{\partial w_2} + \lambda_2 \frac{\partial H_2}{\partial w_2} + \dots + \lambda_h \frac{\partial H_h}{\partial w_2} \right) \delta w_2 \\
& + \dots \\
& + \dots \\
& + \left(\frac{\partial H_0}{\partial w_n} + \lambda_1 \frac{\partial H_1}{\partial w_n} + \lambda_2 \frac{\partial H_2}{\partial w_n} + \dots + \lambda_h \frac{\partial H_h}{\partial w_n} \right) \delta w_n = 0. \quad (24)
\end{aligned}$$

It will be noticed that this equation contains h new variables $\lambda_1, \lambda_2, \dots, \lambda_h$.

We shall next see that by introducing the h variables or multipliers, we may change all the n variations $\delta w_1, \dots, \delta w_n$ of equation 24 independently of each other, while the right side of the equation still remains zero. This will mean that the coefficients of all the variations must be equal to zero at all times.

As will be recalled, there are h equations of constraint (see equations 20) and therefore h dependent variables. Let these be w_1, w_2, \dots, w_h . Each of the variations $\delta w_1, \delta w_2, \dots, \delta w_h$ is therefore dependent for its value on all the remaining $(n - h)$ variations $\delta w_{h+1} \dots \delta w_n$. Let us then make the coefficients of each of the h dependent variations in

There are $(n - h)$ of these equations, which, with the h equations of 25, give n equations in all. This is just sufficient to determine the values of the n variables w_1, w_2, \dots, w_n at the point where H_0 has a maximum or minimum subject to the h constraining conditions H_1, H_2, \dots, H_h .

We have thus not only solved our problem but justified the method of its solution. In practice, the h equations of constraint (eqs. 20) may be used for evaluating the h multipliers $\lambda_1, \lambda_2, \dots, \lambda_h$. The mathematical technique involved will depend upon the particular problem at hand.

To illustrate these methods in determining maximums and minimums, let us consider the following very simple example:

Let us find the greatest value of the volume $V = 8xyz$, subject to the condition that the sum of the squares of the sides of the solid is equal to unity; that is, $1 = x^2 + y^2 + z^2$. Here by analogy, $H_0 = V = 8xyz$; and we have only one constraining condition, which is $H_1 = 1 = x^2 + y^2 + z^2$. Applying equation 21, we have

$$dV = dH_0 = 8yz dx + 8xz dy + 8xy dz = 0.$$

The eight's can of course be dropped. Also applying equations 22, we have

$$dH_1 = 2x dx + 2y dy + 2z dz = 0.$$

The two's can of course be dropped. Multiplying the latter by λ and adding it to the former in accordance with equations 23, we have, corresponding to 24,

$$(yz + \lambda x)dx + (xz + \lambda y)dy + (xy + \lambda z)dz = 0$$

and in accordance with equations 25 plus 27

$$yz + \lambda x = 0; \quad xz + \lambda y = 0; \quad xy + \lambda z = 0.$$

We now wish to determine λ by means of the constraining condition. In this particular case, we can make the determination most easily by multiplying the three equations given above by x, y , and z , respectively:

$$xyz + \lambda x^2 = 0; \quad xyz + \lambda y^2 = 0; \quad xyz + \lambda z^2 = 0. \quad (28)$$

Substituting the values of x^2, y^2, z^2 from equations 28 into the equation of constraint, we have

$$\lambda = -3xyz, \quad (29)$$

which, with $H_0 = 8xyz = V$, becomes

$$\lambda = -\frac{3V}{8}.$$

Substituting 29 into each of the equations 28 we have, subject to the constraining condition, the values of x, y, z , for which V is a maximum.

$$x = \sqrt{\frac{1}{3}}; \quad y = \sqrt{\frac{1}{3}}; \quad z = \sqrt{\frac{1}{3}}.$$

From this,

$$V = \frac{1}{3}\sqrt{\frac{1}{3}}.$$

This paragraph should be read principally in connection with article 49. In that article we shall wish to find the maximum of a function $W = H_0$ subject to the two constraining conditions—namely, the constancy of the quantities $e = H_1$ and $N = H_2$. We will have, therefore, in accordance with equations 21 and 22, the following:

$$\left. \begin{aligned} \delta H_0 = \delta W = 0 &= (w_1 \ln w_1) \delta w_1 + (w_2 \ln w_2) \delta w_2 + \dots + (w_n \ln w_n) \delta w_n \\ \delta H_1 = \delta e = 0 &= \epsilon_1 \delta w_1 + \epsilon_2 \delta w_2 + \dots + \epsilon_n \delta w_n \\ \text{and} \\ \delta H_2 = \delta N = 0 &= \delta w_1 + \delta w_2 + \dots + \delta w_n \end{aligned} \right\} \quad (30)$$

where the terms W and ϵ have the same meaning as in article 49. In this case, for the i th term, we have

$$\frac{\partial H_0}{\partial w_i} = w_i \ln w_i, \quad \frac{\partial H_1}{\partial w_i} = \epsilon_i, \quad \text{and} \quad \frac{\partial H_2}{\partial w_i} = 1.$$

In accordance with the general solution just presented, we will introduce two multipliers, which will be called α and β corresponding to λ_1 and λ_2 in the previous general treatment, and get the following n relations, one for each variable w_1 to w_n :

$$\left. \begin{aligned} (w_1 \ln w_1 + \alpha \epsilon_1 + \beta) &= 0 \\ (w_2 \ln w_2 + \alpha \epsilon_2 + \beta) &= 0 \\ \dots \dots \dots \\ (w_n \ln w_n + \alpha \epsilon_n + \beta) &= 0 \end{aligned} \right\} \quad (31)$$

from which the values of w_1, w_2, \dots, w_n , when W has a maximum, are determined subject to the two constraining conditions, H_1 and H_2 .

6. Relation between a Partial Differential and Its Reciprocal

Suppose variables x, y, z to be connected by an equation so that only two of the variables are independent—that is, each of the variables is a function of the other two. We wish to prove that

$$\left(\frac{\partial z}{\partial x} \right)_y = \frac{1}{\left(\frac{\partial x}{\partial z} \right)_y}.$$

To do so, let us first assume that x is a function of both y and z . According to equation 3, we must then have

$$dx = \left(\frac{\partial x}{\partial y} \right)_z dy + \left(\frac{\partial x}{\partial z} \right)_y dz.$$

If z is a function of both x and y , we have similarly

$$dz = \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy.$$

Let us assume, from here on, that x and y are to be the independent variables, and z the dependent one. If we eliminate dz of the former equation by means of the latter, we have

$$dx = \left(\frac{\partial x}{\partial y} \right)_z dy + \left(\frac{\partial x}{\partial z} \right)_y \left[\left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy \right].$$

Rearranging,

$$dx = \left[\left(\frac{\partial x}{\partial y} \right)_z + \left(\frac{\partial x}{\partial z} \right)_y \left(\frac{\partial z}{\partial y} \right)_x \right] dy + \left(\frac{\partial x}{\partial z} \right)_y \left(\frac{\partial z}{\partial x} \right)_y dx$$

or

$$0 = \left[\left(\frac{\partial x}{\partial y} \right)_z + \left(\frac{\partial x}{\partial z} \right)_y \left(\frac{\partial z}{\partial y} \right)_x \right] dy + \left[\left(\frac{\partial x}{\partial z} \right)_y \left(\frac{\partial z}{\partial x} \right)_y - 1 \right] dx.$$

Since we assumed that x and y were to be the independent variables and z the dependent one, dx and dy may be varied independently of each other in any arbitrary manner. Under such a condition the only way in which this equation can remain zero at all times is for the coefficients of dx and dy to vanish for all values of dx and dy . That is, we must have

$$\left(\frac{\partial x}{\partial y} \right)_z + \left(\frac{\partial x}{\partial z} \right)_y \left(\frac{\partial z}{\partial y} \right)_x = 0,$$

which is of no immediate use, and

$$\left(\frac{\partial x}{\partial z} \right)_y \left(\frac{\partial z}{\partial x} \right)_y - 1 = 0,$$

from which

$$\left(\frac{\partial z}{\partial x} \right)_y = \frac{1}{\left(\frac{\partial x}{\partial z} \right)_y}. \quad (32)$$

We can obtain two other equations like 32 between x, y, z by assuming x and y in turn to be the dependent variables and carrying through the same process twice, as above. By cyclic permutation, however, we can write them down immediately as

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z} \quad \text{and} \quad \left(\frac{\partial y}{\partial z}\right)_x = \frac{1}{\left(\frac{\partial z}{\partial y}\right)_x}.$$

7. Another Theorem on Partial Differentiation

Suppose we have three variables such as x, y, z and suppose that z is a function of y and that y is a function of x . Also, x, y, z may each be functions of several other variables. The latter will be denoted by the symbols ϕ_1, ϕ_2, \dots . We want to prove that it is then possible to write

$$\left(\frac{\partial z}{\partial x}\right)_\phi = \left(\frac{\partial z}{\partial y}\right)_\phi \left(\frac{\partial y}{\partial x}\right)_\phi$$

where ϕ denotes that all the variables, ϕ_1, ϕ_2, \dots except x, y, z remain constant.

Since z is a function of y , we have for a change dz expressed in terms of a change dy , and the others, $d\phi_1, d\phi_2, \dots$

$$dz = \left(\frac{\partial z}{\partial y}\right) dy + \left(\frac{\partial z}{\partial \phi_1}\right) d\phi_1 + \left(\frac{\partial z}{\partial \phi_2}\right) d\phi_2 + \dots$$

We shall assume here that all the independent variables except y remain unchanged—that is, $d\phi_1 = 0, d\phi_2 = 0, d\phi_3 = 0, \dots$. We have then,

$$dz = \left(\frac{\partial z}{\partial y}\right)_\phi dy.$$

Similarly, since y is a function of x , we have

$$dy = \left(\frac{\partial y}{\partial x}\right)_\phi dx.$$

If we eliminate dy from the former by means of the latter, we have

$$dz = \left(\frac{\partial z}{\partial y}\right)_\phi \left(\frac{\partial y}{\partial x}\right)_\phi dx;$$

or, dividing through by dx and writing $\left(\frac{dz}{dx}\right)$ as $\left(\frac{\partial z}{\partial x}\right)_\phi$, since the ϕ 's remain constant during the differentiation, we find

$$\left(\frac{\partial z}{\partial x}\right)_\phi = \left(\frac{\partial z}{\partial y}\right)_\phi \left(\frac{\partial y}{\partial x}\right)_\phi. \quad (33)$$

8. Evaluation of Integrals to be Used in the Statistical Study of Molecules

We wish to evaluate a number of definite integrals to be used later. They are all based on the following one:

$$G = \int_0^{\infty} e^{-x^2} dx. \quad (34)$$

If we let $x = au$ and consider a in this equation to be a constant, we have

$$G = \int_0^{\infty} e^{-a^2 u^2} a du$$

where, instead of integrating x from zero to infinity, we now integrate u from zero to infinity, since $u = \frac{0}{a} = 0$ when $x = 0$ and $u = \frac{\infty}{a} = \infty$ when $x = \infty$. On the other hand, since a definite integral is only a function of the limits and does not depend on the letter used to symbolize the variable, we may write quite independently of equation 34:

$$G = \int_0^{\infty} e^{-a^2} da.$$

Both of the two latter definite integrals have the same numerical value G , since they have the same form and have corresponding limits of integration. Multiplying the two latter equations together, we have

$$G^2 = \int_0^{\infty} du \int_0^{\infty} e^{-a^2(1+u^2)} a da$$

which with any table of integrals reduces to

$$G^2 = \int_0^{\infty} du \cdot \frac{1}{2(1+u^2)}$$

and by further integration becomes

$$G^2 = \frac{1}{2} \left| \tan^{-1} u \right|_0^{\infty} = \frac{\pi}{4}.$$

Hence we obtain our first important integral,

$$G = \frac{\sqrt{\pi}}{2} = \int_0^{\infty} e^{-x^2} dx. \quad (35)$$

From the above we may obtain integration of other integrals. Consider the following, where a is a constant:

$$\int_0^{\infty} e^{-ax^2} dx = \frac{1}{\sqrt{a}} \int_0^{\infty} e^{-ax^2} d(\sqrt{a} x) = \frac{1}{2} \sqrt{\frac{\pi}{a}} \quad (36)$$

where we have applied equation 35 to integrate the second integral.

In the expression

$$\int_{-\infty}^{\infty} e^{-ax^2} dx$$

the integrand is symmetrical with respect to the y axis. The positive and negative half of the integral are therefore equal. We then have

$$\int_{-\infty}^{\infty} e^{-ax^2} dx = 2 \int_0^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}, \quad (37)$$

using 36 above.

If now we differentiate the first and last members of 36 with respect to a , we obtain

$$\int_0^{\infty} x^2 e^{-ax^2} dx = \frac{1}{4} \sqrt{\frac{\pi}{a^3}}. \quad (38)$$

Using this equation, we may immediately integrate the following. We shall find that since the integrand is symmetrical with respect to the y axis and since therefore the positive and negative half of the integrand are equal, we have

$$\int_{-\infty}^{\infty} x^2 e^{-ax^2} dx = 2 \int_0^{\infty} x^2 e^{-ax^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{a^3}}. \quad (39)$$

Differentiating 39 with respect to a again, we have

$$\int_0^{\infty} x^4 e^{-ax^2} dx = \frac{3}{8} \sqrt{\frac{\pi}{a^5}} \quad (40)$$

and, since the following integral is symmetrical with respect to the y axis,

$$\int_{-\infty}^{\infty} x^4 e^{-ax^2} dx = 2 \int_0^{\infty} x^4 e^{-ax^2} dx = \frac{3}{4} \sqrt{\frac{\pi}{a^5}}. \quad (41)$$

9. Determination of the Partial Specific Volume from the Specific Volume and the Mol Fraction

Let us first state the meaning of the terms to be used.

Weight Fraction.—If a solution contains n_1 grams of one substance, n_2 grams of another, and so on, then the weight fraction X_1 of the first substance is defined by

$$X_1 = \frac{n_1}{n_1 + n_2 + \dots}.$$

If the solution contains only one substance—that is, if we have now the pure solvent only—the value for the weight fraction becomes $X_1 = 1$.

Specific Volume.—If a solution contains n_1 grams of one substance, n_2 grams of another, and so on, and if V denotes the total volume of the solution, then the specific volume v of the solution is defined by

$$v = \frac{V}{n_1 + n_2 + \dots}.$$

Partial Specific Volume.—As above, let us suppose that a solution already contains n_1 grams of one substance, n_2 grams of another, and so

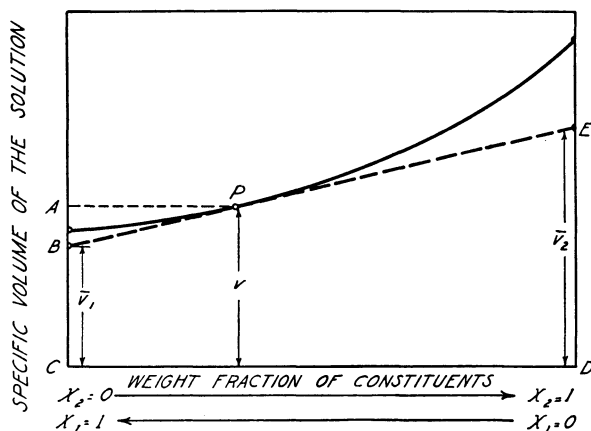


Fig. 4.—Relation of specific volume to the weight fraction of the constituents of a solution.

on, and that the total volume of the solution is V . Then the partial specific volume of the first substance, which we shall symbolize by \bar{v}_1 , is defined by

$$\bar{v}_1 = \frac{\partial V}{\partial n_1}.$$

That is, if we add a small amount of the first substance to the solution, keeping constant all other variables affecting the solution, the partial specific volume \bar{v}_1 is the total increase in volume of the solution per unit weight of the substance added. If the amount of the solution present is very large, \bar{v}_1 is the increase in volume of the solution when 1 gram of the first substance is added.

Having disposed in a preliminary way of these definitions, let us prove a theorem: if the specific volume v of a solution is plotted against the weight fraction of the constituents as shown in figure 4, we can determine the partial specific volumes of either constituent at any desired weight fraction as follows. Suppose we wish to determine the partial

specific volumes corresponding to the solution at P . We then erect the tangent at the point P . Its intercept CB on the ordinate $X_1 = 1$ is equal to the partial specific volume \bar{v}_1 of the first constituent; its intercept DE on the ordinate $X_2 = 1$, to the partial specific volume \bar{v}_2 of the second constituent.

The proof is mainly geometrical. The slope of the curve or (what is the same thing) the slope of the tangent, at any point P , for example, is given by $\frac{dv}{dX_2}$. Therefore $AB = X_2 \frac{dv}{dX_2}$. Consequently, we have for the segment $AC = v$:

$$v = \bar{v}_1 + X_2 \frac{dv}{dX_2}. \quad (42)$$

To prove this, let us recall that

$$v = \frac{V}{n_1 + n_2}.$$

If n_1 is changed,

$$dv = \frac{dV}{n_1 + n_2} - \frac{V dn_1}{(n_1 + n_2)^2}. \quad (43)$$

Also

$$X_2 = \frac{n_2}{n_1 + n_2}. \quad (44)$$

Therefore

$$dX_2 = -n_2 \frac{dn_1}{(n_1 + n_2)^2}. \quad (45)$$

Dividing equation 43 by 45 and multiplying the result by equation 44, we have

$$X_2 \frac{dv}{dX_2} = -\frac{dV}{dn_1} + \frac{V}{n_1 + n_2}. \quad (46)$$

Now, from the definitions given earlier, 46 becomes

$$X_2 \frac{dv}{dX_2} = -\bar{v}_1 + v$$

and

$$v = \bar{v}_1 + X_2 \frac{dv}{dX_2},$$

which is the same as 42 and therefore proves the theorem, since exactly the same procedure would be followed in showing that the intercept DE equals the partial specific volume \bar{v}_2 .

THE THREE FUNDAMENTAL LAWS OF THERMODYNAMICS AND THEIR BASIC CONSEQUENCES

10. Thermodynamic Concepts

For the present, attention will be confined to a single substance, such as water, in the solid, the liquid, or the gaseous phase, and consisting of any number of coexisting phases, all parts of which are in thermal equilibrium with one another. Some of the thermodynamic quantities with which we shall deal are proportional to the mass of water considered, such as the total internal energy of the water, its volume, its total heat content, and its weight, and will be symbolized by capital letters. When these quantities are referred to unit mass of water, they will be symbolized by small letters, such as e , v , and h . Other quantities used, which do not refer to unit mass, are the temperature T , the hydrostatic pressure P , the vapor pressure p , and the total volume V .

Since thermodynamics deals with energy and its transformations, the term "energy" must be clearly understood. Energy is the capacity of a body or system to perform work. Since the work done is a measure of the energy expended, both energy and work are measured in terms of the same unit, such as the erg. Energy stored in a system by virtue of motion, either of itself as a whole or of its parts, is known as "kinetic energy." Thus we may speak of the kinetic energy of a body of water moving through a pipe or the kinetic energy of the randomly moving molecules that make up the body of water. Energy stored in a system by virtue of the relative positions of the parts is called "potential energy." The energy contained in a body of water, for example, by virtue of its temperature and its molecular arrangement, is composed of both of the former kinds of energy. The sum of its internal kinetic and potential energies is known as its "internal energy." This includes all forms of energy due to molecular atomic and subatomic motions, as well as the potential energy of the system due to the existence of electrical and magnetic forces.

Classical thermodynamics is based entirely on the two fundamental laws that follow.

11. The First Law of Thermodynamics

The First Law of thermodynamics may be stated as follows: *The increase Δe in the internal energy of a substance, such as water, during any transformation is equal to the amount of heat Δq taken in, minus the work Δw done by the substance.* That is,

$$\Delta e = \Delta q - \Delta w \quad (47)$$

or

$$\Delta q = \Delta e + \Delta w. \quad (48)$$

Or if the only work done is that of expansion against a pressure P , we have

$$\Delta q = \Delta e + P \Delta v. \quad (49)$$

This is merely the law of conservation of energy generalized to include heat as a form of energy. Suppose, for example, we add some heat Δq to water vapor. This heat energy may appear partly as work Δw done by the vapor in changing its volume and partly as a change in its internal energy Δe due to a change in its temperature. The sum of the work Δw done by the water vapor in changing its volume and the change in its internal energy Δe is always equal to the amount of heat energy Δq added to the water vapor (eq. 48).

12. Specific Heat c , Internal Energy e , and Heat Content h

General Definition of Specific Heat.—Suppose the temperature of 1 gram of a substance rises from T to $T + \Delta T$ because of the intake of an amount of heat, Δq . Let us consider $\frac{\Delta q}{\Delta T}$. Then in the limit when ΔT approaches zero, we shall define c , the specific heat of the substance, at the temperature T as equal to $c = \frac{dq}{dT}$.

Since the amount of heat dq required to raise the temperature of the substance by an amount dT differs with the condition under which the heat is added, we shall have a corresponding number of different specific heats. If the heat is added while the volume of the material is kept constant, $\frac{dq}{dT}$ equals c_v , the specific heat of the substance at constant volume. If, on the other hand, the heat is added so that the pressure on the system is constant, $\frac{dq}{dT}$ equals c_p , the specific heat of the substance at constant pressure.

Let us now consider a homogeneous body undergoing a transfer of heat Δq and of mechanical work Δw either to or from the surroundings. According to the First Law of thermodynamics, we have

$$dq = de + Pdv$$

and for the specific heat c ,

$$c = \frac{dq}{dT} = \frac{de}{dT} + P \frac{dv}{dT}. \quad (50)$$

Specific Heat at Constant Volume c_v .—If heat is added to the substance while its volume is kept constant, dv in equation 50 will be zero. Thus,

$$c_v = \left(\frac{de}{dT} \right)_v. \quad (51)$$

Hence c_v , the specific heat at constant volume, is equal to the rate of change of the internal energy de .

Specific Heat at Constant Pressure c_p .—If, on the other hand, heat is added while the pressure P on the substance is kept constant, we have (eq. 50)

$$c_p = \left(\frac{dq}{dT} \right)_P = \left(\frac{de}{dT} \right)_P + P \left(\frac{dv}{dT} \right)_P \quad (52)$$

or, since P is constant,

$$c_p = \left[\frac{d(e + Pv)}{dT} \right]_P. \quad (53)$$

Let us introduce the following important abbreviation for the quantity in parenthesis and set:

$$h = e + Pv. \quad (54)$$

Because of its wide importance in thermodynamics, the quantity h has been given the special name "heat content." Using the heat content, h , equation 53 becomes:

$$c_p = \left(\frac{dh}{dT} \right)_P \quad (55)$$

or

$$dh = c_p dT. \quad (56)$$

Thus c_p , the specific heat at constant pressure, is equal to the rate of change of h , the heat content, with temperature; whereas, as indicated earlier, c_v , the specific heat at constant volume, is equal to the rate of change of e , the internal energy, with temperature.

Equation 56 also serves to define the heat content h , when the specific heat at constant pressure c_p is known as a function of the temperature. Since the heat content at the temperature of absolute zero is taken as zero, as shown in the consideration of the Third Law of thermodynamics (art. 20), we have

$$h_T = \int_0^T c_p dT. \quad (57)$$

Or, if we know the heat content at the temperature T_1 , we may write the heat content at some other temperature T_2 according to equation 57 as follows:

$$h_{T_2} = h_{T_1} + \int_{T_1}^{T_2} c_p dT. \quad (58)$$

13. Reversible Cycles

Throughout thermodynamics we continually deal with what is called a "thermodynamically reversible process." This is one carried out so slowly that the system is continuously in equilibrium with its surroundings, that is, with respect to temperature, pressure, or any other variables which determine its state. The process can therefore be made to proceed in the opposite direction by an infinitesimal change in any one of the conditions, such as temperature or pressure, that determine the direction of the process. If, for example, a gas is expanding reversibly, then an infinitesimal increase in the external pressure should cause the gas to contract. That is, the internal pressure differs only by an infinitesimal from the external pressure. Clearly, since the net force carrying on the reversible process is an infinitesimal, the process will be carried on with infinite slowness, so that all parts of the system remain at thermal equilibrium. Although this type of change never takes place in nature, we can make any change approach reversibility as closely as we please.

14. The Second Law of Thermodynamics

The Second Law of thermodynamics may be stated: *No self-acting device unaided by an external agency can transfer heat from a body of lower temperature to one of higher temperature.*

A self-acting device is one on which no work is done by an outside agency and which is so operated as to take the working substance through one or more complete cycles. After such a cycle, the final state of the working substance employed in the device is the same as at the start.

An alternative statement of the Second Law is: *Work can never be produced in a reversible cycle of changes operating in surroundings all at the same temperature.* Applying the First Law of thermodynamics to the Second, we arrive at a quantitative relation which states that when work is produced by a reversible cycle operating between two absolute temperatures T_1 and T_2 , where T_1 is greater than T_2 , the quantity of work performed spontaneously during the cycle, as will be proved later, is

$$w = q \frac{(T_1 - T_2)}{T_1},$$

where q is the heat absorbed at the higher temperature T_1 . We may arrive at this expression by considering any one of several reversible processes, among which the most common is probably the Carnot cycle, to be discussed later. Clearly, if T_1 is less than T_2 , then w , the work done by the process, is negative. This means that w units of work must be done on the working substance to transfer a quantity of heat from the lower temperature T_2 to produce a quantity of heat q at the higher T_1 . This agrees with the first statement (above) of the Second Law. The quantitative expression given above shows, likewise, that when T_2 equals T_1 —that is, when the surroundings are all at the same temperature— w equals zero. According to this, no work can be produced spontaneously by the system composed of the working substance and the surroundings when both are at the same temperature, a finding that agrees with the alternative statement of the Second Law given above.

Although mechanical work can always be transformed into heat, the reverse process of converting heat into mechanical work is by no means always possible. The First Law merely specifies the quantitative relation that must exist between any interchange of work and heat. The Second Law specifies the conditions under which it is possible to convert heat into work. That is, the Second Law limits the First. Whereas work may always be transformed into heat according to the First Law, the reverse change (heat into work) is subject to further restrictions, according to the Second Law. The Second Law also tells us the direction in which heat will flow when two bodies of heat are brought together.

To place the Second Law of thermodynamics on a quantitative basis and therefore to enable us to predict the amount of work w obtainable from a given quantity of heat q , as well as to predict the direction in which heat will flow spontaneously when two reservoirs of heat are interconnected, it has been necessary to introduce a term called "entropy," which we shall symbolize by s . The increase in entropy of a system ds is defined by

$$ds = \frac{dq}{T},$$

where dq is the amount of heat added to the system whose temperature is T . This concept will be discussed in detail later.

15. Carnot Cycle and Its Utility in Deriving Important Thermodynamic Relations

Definitions of Some Thermodynamic Terms.—Because of their repeated use, several new terms should be defined. A "cycle" is a succession of transformations that brings the working substance back to its original state. An "isothermal" transformation is one during which the tempera-

ture remains constant. An "adiabatic" transformation is one during which heat is neither taken in nor given out. A "Carnot cycle" (fig. 5) consists of two isothermal and two adiabatic transformations. During the isothermal expansion AB , the working substance takes in heat; during the isothermal contraction CD it gives out heat. During the adiabatic transformations the pressure, volume, and temperature always change in such a way that heat flows neither in nor out of the system, although mechanical work may be performed. The efficiency e_f of a heat engine or of a system acting as an engine gives the ratio of the work w done by the system on its surroundings, to the heat q taken in when the working substance goes through a complete cycle in the engine.

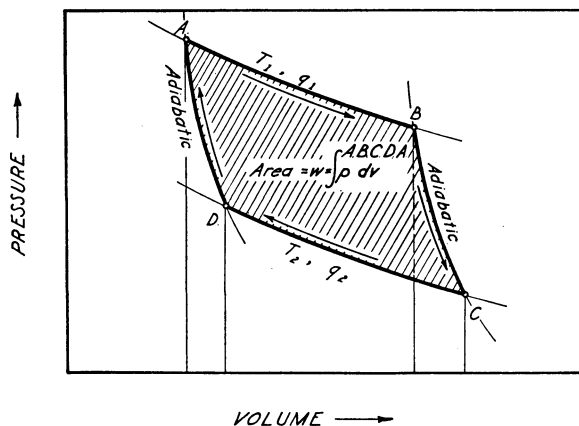


Fig. 5.—Relation of heat energy to useful work in a Carnot cycle.

Relation between the Heat, Work, and Efficiency of a Carnot Cycle.—The Second Law of thermodynamics and many of its implications are stated in terms of the Carnot cycle. Let us begin by determining the efficiency e_f of an engine operating in a reversible manner according to the Carnot cycle (fig. 5). We shall assume here that the working substance is a gas, though any substance may be put through a Carnot cycle. (Later in the discussion the conclusions will be applied to water vapor in equilibrium with soil moisture.) A quantity of heat q_1 is taken into the system during the isothermal expansion AB at T_1 , and a quantity of heat q_2 is given out by the system during the isothermal contraction CD at T_2 . No flow of heat q takes place during the adiabatic expansions or contractions BC and DA . The amount of work w done by the reversible engine in going through the cycle is represented by the area

$$w = \int^{(ABCD A)} P dv$$

enclosed by the curve. Since the gas arrives in the same condition, A (with respect to its internal energy) at the end of the cycle as at the beginning, we know, according to the First Law, that the $(q_1 - q_2)$ units of heat which have disappeared from the system during the cycle are completely converted into the work w performed by the system or engine. Of the original amount of heat q_1 given to the working substance by the surroundings, an amount $q_1 - q_2 = w$ has been converted into work. The efficiency e_f of a reversible engine or system following a Carnot cycle is given, therefore, by

$$e_f = \frac{q_1 - q_2}{q_1} = \frac{w}{q_1} . \quad (59)$$

We specify that the process be reversible because we wish the pressure and the temperature of the working substance at all times to equal those of the surroundings with which it is in contact, except for an infinitesimal amount. Otherwise the work performed by the working substance during the isothermal expansion will be somewhat greater than the work done by the working substance on the surroundings, the discrepancy depending (as will be shown later) upon the irreversibility of the process. The part of the work performed by the system during the irreversible expansion that does not reach the surroundings is converted into heat by friction. When the process is reversible, the work w performed by the system or engine in passing through a complete cycle [where $(q_1 - q_2)$ units of heat are absorbed from the surroundings] always equals the work w done on the surroundings.

Since the Carnot cycle is reversible, the engine may be made to run in the reverse direction $ADCBA$. In contrast to the previous case, if the cycle is carried out in the reverse direction, an amount of heat q_2 is now taken from the surroundings while an amount of work w is done on the working substance or engine, enabling the working substance to give out to the surroundings an amount of heat q_1 . In the latter case, instead of having the heat $(q_1 - q_2)$ added to the working substance and converted into work w on the surroundings, we now have an amount of work w being performed by the surroundings on the working substance, which work is in turn converted into an amount of heat $(q_1 - q_2)$ in the working substance; this amount of heat $(q_1 - q_2)$ is returned to the surroundings by the completion of the cycle.

Next we shall prove two fundamental theorems of great importance, based upon the Second Law of thermodynamics.

Theorem 1. No engine can be more efficient in converting heat into work than is the ideal Carnot engine just considered above.

Let us assume that we have two engines working between the same

two temperatures, T_1 and T_2 . One, which we shall call engine E , works in a reversible cycle; the other, E' , in a cycle either reversible or irreversible. Let us also assume that E' is connected so as to drive the reversible Carnot engine E . Thus the engine or working substance E' takes in an amount of heat q_1' from the surroundings, which are at the higher temperature T_1 , called the "source"; and it returns to the surroundings an amount q_2' , at the lower temperature T_2 here called the "sink." The source is at T_1 , a higher temperature than the sink, which is at the temperature T_2 . The working substance is of course subjected to T_1 and T_2 at different times.

The engine E' performs an amount of work w' on E which goes simultaneously to run the reversible engine E . In consequence, the engine E takes an amount of heat q_2 from the sink at the lower temperature T_2 and gives out a greater amount of heat q_1 to the source at the higher temperature T_1 . The efficiency e_f' of the engine E' is

$$e_f' = \frac{w'}{q_1'} = \frac{q_1' - q_2'}{q_1'}. \quad (60)$$

To obtain the efficiency e_f of the reversible engine E being run by E' , let us recall that E , being a reversible engine, would take up the same amount of heat q_1 from the reservoir or source at the higher temperature T_1 if it were running forward (that is, in the direction $ABCD$) about the cycle as it now gives up to the source at the higher temperature T_1 when running backwards (that is, in the direction $ADCB$). Also E would give up the same amount of heat q_2 to the sink, if driven forwards, that it now obtains from the sink while being driven backwards by the engine E' . For the efficiency e_f of the reversible Carnot engine E , we have, therefore,

$$e_f = \frac{w}{q_1} = \frac{q_1 - q_2}{q_1}.$$

Now the work w' done by E' during each cycle equals the work w done on E , since both engines are coupled without frictional losses. Also, according to the First Law of thermodynamics (eq. 48), since the internal energy e of the working substance in the engines after the completion of a cycle is again the same as at the start, we have

$$w = q_2 - q_1$$

and

$$w' = q_2' - q_1'$$

and therefore

$$q_1 - q_2 = q_1' - q_2'. \quad (61)$$

From equations 59 and 60 in combination with 61 we have

$$e_f q_1 = e_f' q_1'. \quad (62)$$

Now we wish to show that the efficiency e_f' of the engine E' cannot be greater than the efficiency e_f of the reversible engine. To demonstrate this let us assume the converse, that e_f' is greater than e_f , and then by the method of *reductio ad absurdum* show that we are led to an inconsistency which violates the Second Law of thermodynamics.

If we assume $e_f < e_f'$, then from equation 62 $q_1 > q_1'$. Therefore, from equation 61, $q_2 > q_2'$. As will be recalled, q_2' is the heat delivered by the engine E' to the sink at the lower temperature T_2 , whereas q_2 is the heat taken up from the sink at the lower temperature T_2 by the reversible Carnot engine E . Therefore, since $q_2 > q_2'$, there is a net transfer of heat from the sink at the lower temperature T_2 to the source at the higher temperature T_1 when we consider the two engines E and E' coupled together as a single self-acting engine. We are thus led to a direct contradiction of the Second Law of thermodynamics when we assume that the efficiency e_f' of any engine E' is greater than the efficiency e_f of a reversible engine, for, according to the Second Law, no self-acting engine (here composed of the two engines coupled together) can transfer heat from a body of lower temperature to one of higher temperature unaided by any external agency. The efficiency e_f' of any engine must be, therefore, either equal to or less than the efficiency e_f of a Carnot engine. That is,

$$e_f' \leq e_f.$$

Theorem 2. Every reversible engine, no matter what its construction or working substance, has the same efficiency when working between the same two temperatures.

Suppose that E_1 and E_2 are two reversible engines of quite different construction whose efficiencies are e_{f_1} and e_{f_2} , when working between the same two temperatures. Since both engines are reversible, either may replace the reversible engine E of the previous discussion, the other one then replacing E' of the previous discussion. If E_2 replaces E and if E_1 replaces E' , we have

$$e_{f_1} \leq e_{f_2}. \quad (63)$$

If we now interchange the engines E_1 and E_2 so that E_1 takes the place of E and E_2 that of E' , we have

$$e_{f_2} \leq e_{f_1}. \quad (64)$$

Now, obviously, the inequalities 63 and 64 can be satisfied simultaneously only if

$$e_{f_2} = e_{f_1}.$$

Since E_1 and E_2 were any two reversible engines, each working between the temperatures T_1 and T_2 , then all reversible engines working between the same two temperatures have the same efficiency. Since one of these engines might be a Carnot engine, therefore every reversible engine has the same efficiency as the Carnot engine when working between the same two temperatures.

16. Kelvin's Scale of Absolute Temperature

Up to now, nothing has been said about measuring temperature. If heat flows from T_1 to T_2 spontaneously, T_1 is said to be at the higher temperature. In practice the temperature is measured by the expansion of an arbitrary substance calibrated in terms of an arbitrary temperature scale. Two fixed temperatures (such as the freezing point and the boiling point of pure water under standard conditions of pressure) are chosen on the scale, and arbitrary values are assigned to them. Having established these two fixed points, we determine other temperatures merely by the relation of the length or volume of the thermometric substance at the unknown temperature to its change in length or volume in going from one of the fixed temperatures to the other. For example, the thermometric substance often taken is mercury; and the interval between the freezing point and the boiling point of pure water is then divided into 100 equal parts by so dividing the total change in length of the mercury column. If an unknown temperature causes the mercury to expand by 15 of these equal parts, we say that the temperature has changed by 15 degrees. Though we always assume that the expansion of the thermometric substance is proportional to the temperature, this assumption is not correct, and the deviation varies from one thermometric substance to another. Thus thermometers made from such thermometric substances as mercury, alcohol, water, and nitrogen all give slightly different readings in the same constant-temperature bath except at the two fixed temperatures.

Kelvin, on the basis of reversible heat engines working in a Carnot cycle, has introduced an absolute scale of temperature entirely independent of the thermometric substance used. Suppose, for example, we consider the two fixed temperatures, one at the freezing and the other at the boiling point of pure water. The associated Carnot cycle working between these two extremes is represented in figure 6. Let us divide this Carnot cycle into 100 equal parts such that *each of them has the same area on the pressure-volume diagram*. We thus have 100 reversible engines, each going through a Carnot cycle. Suppose the first engine takes in heat at the boiling point of water and rejects heat to the second engine; the second takes in the heat rejected by the first and rejects heat to the third;

the third takes in heat rejected by the second and rejects heat to the fourth; and so on. The last engine will then reject heat at the temperature of freezing water. Let the temperature of the boiling water, at which the first engine takes in heat, be 100° ; that at which the second takes in the heat given out by the first, 99° ; that at which the third takes in the heat given out by the second, 98° ; and so on. This will give us a temperature

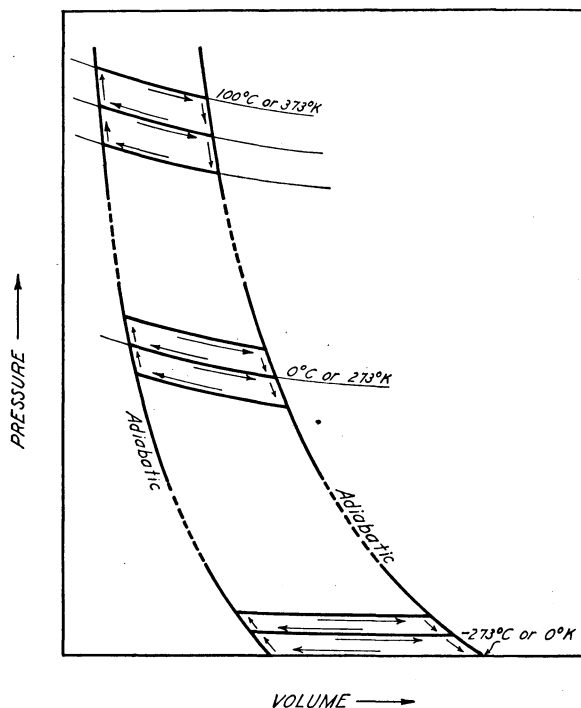


Fig. 6.—The Carnot cycle as the basis of Kelvin's scale of absolute temperature.

scale divided into 100 equal parts between the freezing and boiling points of pure water.

The 100 divisions are entirely independent of the thermometric substance used whether it be gas, mercury, alcohol, or any other substance, because (art. 15, theorem 2) the efficiency of all reversible engines working between the same temperatures is the same regardless of the working substance. No matter, therefore, what working substance is used in the set of 100 reversible engines, the temperatures they determine will always be the same. The temperature scale may in like manner be extended below and above the freezing and boiling point of pure water.

Experimental facts indicate that there is a lower temperature limit beyond which it is impossible to go. This temperature is found to be 273 of the above temperature units below the freezing point of water. At 272 units below, therefore, we should find the last reversible engine taking in heat rejected by the one above, but having no heat to reject at 273 units below. This lower limit of the temperature scale is known as the absolute zero.

Thus, as Kelvin has shown, the temperature difference between any two bodies can be measured in terms of the work performed by an ideal reversible engine working between the two temperatures, because equal temperature intervals are represented by equal areas on the pressure-volume diagram. Or—what is the same thing—equal areas on the diagram represent the performance of the same amount of mechanical work by a reversible engine. Thus in equal temperature intervals an ideal reversible heat engine performs the same amount of work per cycle. Hence the measurement of temperature on this scale is independent of the properties of any particular substance. This temperature scale is often called the “Absolute” or “Kelvin” scale. Temperatures measured on this scale (in contrast to the centigrade scale) are symbolized by the letter “A” throughout this paper. For most practical purposes, however, the divisions on the Kelvin scale can be regarded as equal in size to those on the centigrade scale.

17. Relation between the Efficiency, Heat, and Temperature in an Ideal Reversible Engine

To determine the relation between the efficiency, heat, and temperature in an ideal reversible engine, let us begin by finding the relation between the area $ABEF$ of figure 7 and the heat taken in during the isothermal transformation AB .

All points of the isothermal FE at 0° A may be considered as having zero internal energy e . The isothermal FE at 0° A coincides with the volume axis. This follows because in passing from one point to another on this axis, no heat is taken in or rejected by the engine or working substance, and no work is done by the engine, the pressure here being zero.

We shall now show that the area $ABEF$ (fig. 7) represents the heat q_1 taken in by the engine in going from A to B . Since no heat is taken in or given out by the engine in going along AF or BE , these being adiabatics, the increase in internal energy E_A of the working substance in going from F to A is equal to the work done on the working substance in going from F to A —that is, the area AHF . Likewise the increase in internal energy E_B of the working substance in going from E to B is equal to the work done on the working substance in going from E to B and is represented by

the area BKE . The change in internal energy ($E_B - E_A$) in going from A to B is represented by the difference in areas BKE and AHF , since the working substance has the same internal energy at F and at E . Also the work done w in going from A to B is represented by the area $ABKH$. Now, according to the First Law, equation 48, we have

$$q_1 = w + (E_B - E_A).$$

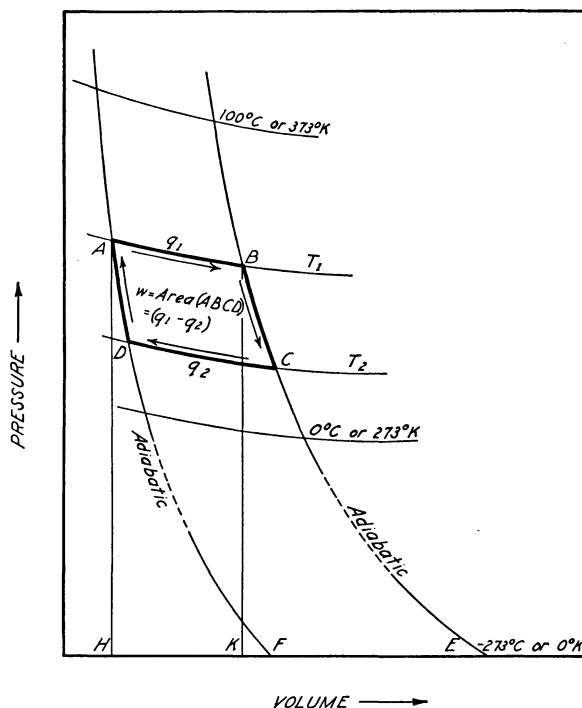


Fig. 7.—Relation between heat energy, maximum useful work, and temperature in a Carnot cycle.

Expressing this relation in terms of the areas of figure 7, we have q_1 represented by the area

$$q_1 = ABKH + (BKE - AHF)$$

or

$$= ABEH - AHF = ABEF.$$

Thus the heat q_1 taken in by the working substance while going from A to B is the area $ABEF$ included between the two adiabatics. Similarly, the heat q_2 taken in while going from D to C is the area $DCEF$.

Now we can express the total areas, q_1 and q_2 , between the adiabatics

in terms of the area of the small Carnot cycles considered in the previous article and in figure 6. Let Q represent the area of any one of the small cycles. Since there are T_1 small cycles below the temperature T_1 , the area $ABEF$, or q_1 , equals T_1Q . Likewise q_2 equals T_2Q .

Let us now calculate by equation 59 the efficiency e_f , in terms of temperature, of an ideal reversible engine operating in the Carnot cycle $ABCD$ such that heat q_1 is taken in by the working substance along AB and heat q_2 is given out by the working substance to the surroundings along CD , while during the cycle an amount of work w is performed by the surroundings on the working substance. We have

$$e_f = \frac{w}{q_1} = \frac{q_1 - q_2}{q_1} = \frac{T_1Q - T_2Q}{T_1Q} = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1}. \quad (65)$$

From the third and last of these members it follows that

$$\frac{q_1}{T_1} = \frac{q_2}{T_2}. \quad (66)$$

As equation 66 shows, when we are dealing with a reversible heat engine, the ratio of the amount of heat q_1 (taken in by the working substance at the temperature T_1) to the temperature T_1 always equals the ratio of the amount of heat q_2 (given out by the working substance at the lower temperature T_2) to the temperature T_2 .

In the previous discussion no formal convention was made as to the signs of the q 's. The expressions arrived at are in the same form as in most treatises on thermodynamics. Equation 66 may obviously be written in the following forms:

$$\frac{q_1}{T_1} - \frac{q_2}{T_2} = \frac{q_1}{T_1} + \frac{(-q_2)}{T_2} = 0. \quad (67)$$

Equation 67 shows that, in any reversible Carnot cycle, the heat taken in by a system divided by the temperature at which it is taken in, minus the heat given out by the system divided by the temperature at which it is given out, is zero.

18. Relation between the Energy Available for Mechanical Work and the Temperature in Any Reversible Process

For any ideal heat engine operating in a reversible cycle between the temperatures T_1 and T_2 , the maximum amount of work obtainable during the cycle is shown by equation 65, to be

$$w = \frac{q_1(T_1 - T_2)}{T_1} = q_1 - q_1 \frac{T_2}{T_1}. \quad (68)$$

The maximum efficiency, therefore, of an engine operating between the temperatures T_1 and T_2 is

$$e_f = \frac{w}{q_1} = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1} \quad (69)$$

where q_1 is the amount of heat taken in by the engine at the temperature T_1 . Since (art. 15) $w = q_1 - q_2$, we find from the first and last members of equation 68 that $q_1 \frac{T_2}{T_1}$ represents the total amount of heat q_2 given out by the engine at the temperature T_2 during the complete cycle—that is, the unavailable energy or the quantity of heat not convertible into work. Only if T_2 , the temperature of the sink, could be reduced to 0°A would q_2 be zero and the total amount of heat q_1 given to the engine be all converted into work w . In that event the efficiency of the engine would be unity, or, in the usual notation, 100 per cent.

From equation 69 we concluded that the maximum efficiency e_f obtainable from any engine is entirely determined by the temperatures T_1 and T_2 between which it works. As T_2 approaches 0°A , the efficiency of the Carnot engine approaches 100 per cent. Since T_2 can never be reduced to 0°A , the efficiency of the most efficient heat engine is always less than 100 per cent.

19. Entropy

Definition of Entropy.—Because of the frequent occurrence of the ratio of the amount of heat Δq taken in by a system, to the temperature T at which it is taken in, Clausius introduced the name entropy, Δs . This, as mentioned earlier, is defined by

$$\left. \begin{aligned} \Delta s &= \frac{\Delta q}{T} \\ \text{or} \quad s_B - s_A &= \int_A^B \frac{dq}{T} \end{aligned} \right\} (70)$$

where the small letters s and q refer respectively to the entropy and heat per gram of the substance and A and B are the initial and final states. By convention dq is positive (+) when heat flows into the substance and negative (−) when heat flows out of the substance and into the surroundings.

The Total Change in Entropy of a System or Working Substance in Passing Through a Reversible Cycle.—The system includes the engine or working substance together with its surroundings, the source and the sink. Let the working substance—water vapor, for example—pass through the re-

versible cycle represented by the closed figure 8. Divide the complete cycle into a number of small Carnot cycles bounded by adiabatics and isothermals as indicated. Thus we are replacing the single engine, working along the curve $ACBDA$, by a number of small reversible engines, each working on one of the cycles into which the area has been divided. It is clear from the figure that the greater the number of Carnot cycles into which the large cycle is divided, the more nearly is the effect of the sum of all the small Carnot cycles equivalent to the effect of the large

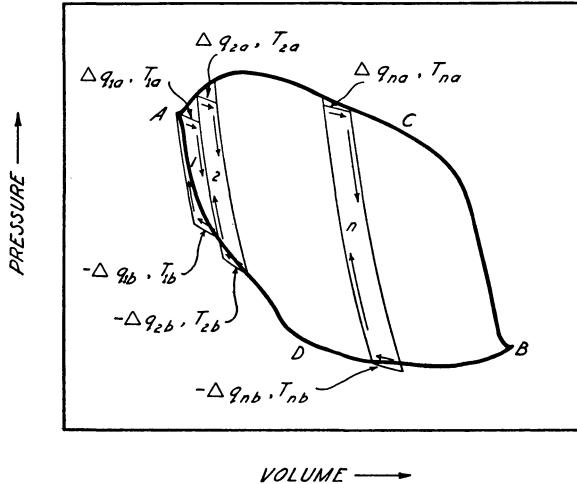


Fig. 8.—A generalized reversible cycle divided into little Carnot cycles.

single one. The sum of all the quantities of heat, Δq_a , Δq_{2a} , Δq_{3a} , . . . Δq_{na} , . . . taken in by all the small separate reversible engines from the source (that is, from the surroundings) at the different temperatures, T_a , T_{2a} , T_{3a} , . . . T_{na} , . . . respectively, equals the total amount of heat taken in from the source by the large single engine. The sum of all the quantities of heat, $-\Delta q_b$, $-\Delta q_{2b}$, $-\Delta q_{3b}$, . . . $-\Delta q_{nb}$, . . . given out to the sink (that is, to the surroundings) by the small separate reversible engines at the temperatures T_b , T_{2b} , T_{3b} , . . . T_{nb} , . . . respectively, equals the total amount of heat given out by the large single engine. Thus in the limit when the number of small cycles is extremely great, the system of small engines is thermodynamically equivalent to the single large one. The signs of the quantities Δq_a and Δq_b are defined in accordance with the conventions mentioned in connection with equation 70.

Consider the small single n th cycle. We have, according to equation 67,

$$\frac{\Delta q_{na}}{T_{na}} - \frac{\Delta q_{nb}}{T_{nb}} = 0. \quad (71)$$

To find the total change in entropy Δs in going around the complete cycle $ACBDA$, we must sum up all the small changes in entropy produced by all the small cycles. According to equation 71, the change in entropy in each small completed cycle is zero. We have, accordingly, for the following summation,

$$\Delta s = \left(\frac{\Delta q_a}{T_a} - \frac{\Delta q_b}{T_b} \right) + \left(\frac{\Delta q_{2a}}{T_{2a}} - \frac{\Delta q_{2b}}{T_{2b}} \right) + \dots + \left(\frac{\Delta q_{na}}{T_{na}} - \frac{\Delta q_{nb}}{T_{nb}} \right) + \dots = 0. \quad (72)$$

Hence we conclude that *the total change of entropy of a system or working substance in any reversible cycle, no matter what the path, is zero*. Equation 72 is equivalent in the limit to

$$\Delta s = \int^{(ACBDA)} \frac{dq}{T} = 0. \quad (73)$$

The Change in Entropy Δs of a Working Substance in Going Reversibly from a State A to a State B.—Consider the change in entropy in going around the complete cycle $ACBDA$, figure 8. This may be split up into two parts—one in going along ACB , the other along BDA . According to equation 73, we have then, for the total change,

$$\Delta s_{(ACB)} + \Delta s_{(BDA)} = 0$$

or

$$\Delta s_{(ACB)} = -\Delta s_{(BDA)}.$$

Since the sequence of the letters in the subscripts indicates the direction of the path followed and since when we change our path to the opposite direction we merely change the sign of the entropy change, Δs , without changing its magnitude, we therefore have

$$\Delta s_{(ACB)} = \Delta s_{(ADB)}. \quad (74)$$

Since ACB and ADB are any arbitrary paths, equation 74 says that no matter what path we take in going from the state A of the working substance to the state B , the change in entropy s is the same as long as the change is carried out reversibly. *The change in entropy Δs in any reversible process depends, therefore, only on the coordinates of the initial and final states, A and B .* This is unlike such quantities as the work w and the heat q , which depend wholly on the manner of going from A to B . The fact that the change in entropy Δs of a substance, in going from a state A to a state B , is independent of the manner in which the change is carried out, is what makes entropy so important in thermodynamics.

The Total Change in Entropy of a System or Working Substance in Passing through an Irreversible Cycle.—In all the previous considerations, we

have dealt with reversible processes. Spontaneous changes in nature, however, are always irreversible to a lesser or greater extent. In such cases, the system cannot be restored to its initial state solely by its own effort; mechanical energy must always be added from the outside. Thus in natural changes, mechanical energy is always dissipated. This does not violate the conservation of energy, since the energy itself is conserved. Part of the heat that is available for mechanical energy is dissipated or degraded; it passes into a form of heat energy too low in temperature to be available for the particular process being considered. In other words, no energy is lost—it is merely rendered unavailable.

We shall now show that in all natural processes, which are always irreversible to a greater or lesser extent, the change in entropy of the working substance plus its surroundings (including the source and the sink), in going through a complete cycle, is always greater than zero. This, as will be recalled, is in complete contrast to reversible cycles, where no entropy is lost.

Consider both a reversible and an irreversible engine operating in cycles between the same two temperatures T_1 and T_2 and such that the amount of heat q_1 passing from the surroundings into the working substance of the reversible engine is the same as the amount q_1' passing from the surroundings into the irreversible engine at the temperature T_1 . The quantities $\frac{q_1}{T_1}$ and $\frac{q_1'}{T_1}$ will obviously be the same in both cases. The quantity $\frac{q_2'}{T_2}$ of the irreversible engine is greater, however, than for the reversible one: in an irreversible engine, friction or its equivalent is always present, causing a greater amount of heat q_2' to be given back to its surroundings by the irreversible engine than q_2 , which is given out by the reversible engine. Thus we have both

$$\frac{q_1'}{T_1} = \frac{q_1}{T_1}$$

and

$$\frac{q_2'}{T_2} > \frac{q_2}{T_2}$$

By the addition of the two above and the recollection of equation 67, we secure

$$\frac{q_1'}{T_1} - \frac{q_2'}{T_2} > \frac{q_1}{T_1} - \frac{q_2}{T_2} = 0.$$

Hence

$$\frac{q_1'}{T_1} - \frac{q_2'}{T_2} > 0. \quad (75)$$

This inequality states that the total change of entropy in the irreversible cycle is greater than zero because, by our convention of signs used in arriving at equation 67, q_1' represents heat flowing from the surroundings into the working substance, whereas q_2' represents heat flowing from the working substance into the surroundings. Each of the terms on the left side of inequality 75 represents changes of entropy, according to their definition in equation 70. The first term of 75 represents an increase in the entropy of the system during the cycle whereas the second term represents a decrease in entropy of the system. Their difference is therefore the net increase in entropy of the system during the cycle.

In general, any irreversible cycle can be replaced thermodynamically by a group of small cycles as was done for the reversible cycle in arriving at equation 72. Each of these small cycles will behave in accordance with inequality 75. We have, then, for the total change in entropy Δs of any system when the working substance or engine passes through an irreversible cycle,

$$\Delta s = \left(\frac{\Delta q_a'}{T_a} - \frac{\Delta q_b'}{T_b} \right) + \left(\frac{\Delta q_{2a}'}{T_{2a}} - \frac{\Delta q_{2b}'}{T_{2b}} \right) + \dots + \left(\frac{\Delta q_{na}'}{T_{na}} - \frac{\Delta q_{nb}'}{T_{nb}} \right) + \dots > 0. \quad (76)$$

The primes are retained to indicate that the cycles are irreversible. Equation 76 is equivalent in the limit to

$$\Delta s = \int^{(ACBDA)} \frac{dq'}{T} > 0 \quad (77)$$

where the path (ACBDA) refers to a cycle similar to figure 8 but here considered irreversible. As we see, Δs of equation 77 above represents the total change in entropy of the source and the sink that make up the surroundings of the engine. The engine, with its surroundings, makes up a closed system. The total change in entropy of the system is synonymous with the total change in entropy of the surroundings, since the entropy of the working substance is the same at the end of the cycle as at the start.

As equation 77 above has shown, *in any irreversible cycle of operations, the total entropy change is positive* when both the surroundings and the working substance are considered together as a whole system. *That is, in any natural process the entropy always tends to increase.* Only in the limit when the process is reversible does the total change of entropy in a closed cycle of operations approach zero (eq. 73).

Calculation of Increase of Entropy in Natural Processes.—All natural processes are irreversible. The question then is, how are we to calculate the change in entropy undergone in such a case when the system passes from a state A to a state B? As will be recalled, equation 70 is applicable only

in calculating the change in entropy in going from the state A to the state B when the transformation is reversible. If, for example, water vapor confined at a fixed pressure is allowed to escape into a vessel at a lower pressure, the vapor undergoes an increase of entropy even though no heat passes into or out of the system. To calculate the change in entropy of a natural process by equation 70 in going from A to B in such a case, *we replace the irreversible transformation by a reversible one, connecting the same two states A and B .* The change of entropy can then immediately be calculated by means of equation 70 as will be illustrated below. As previously shown, it is immaterial what reversible path we take between A and B in calculating the change of entropy Δs . All paths will give the same value for Δs (eq. 74).

Change in Entropy When Heat Flows Spontaneously from a Hot to a Cold Body.—Consider two bodies in contact, one at a temperature T_1 , the other at T_2 . Both bodies are insulated so that there is no heat interchange with the surroundings. Assume that a quantity of heat dq flows by conduction from the body at the higher temperature T_1 to the other at T_2 . The decrease in entropy of the hotter body is

$$ds_1 = -\frac{dq}{T_1},$$

and the increase in entropy of the colder body is

$$ds_2 = \frac{dq}{T_2}.$$

The total change of entropy of the system as a whole is

$$ds = ds_1 + ds_2 = -\frac{dq}{T_1} + \frac{dq}{T_2} = dq \frac{(T_1 - T_2)}{T_1 T_2} > 0 \quad (78)$$

since $T_1 > T_2$. Thus the total change in entropy ds of the whole system is positive whenever an amount of heat dq flows spontaneously from one point to another.

Generalizing, therefore, in any irreversible process (that includes all natural processes) the entropy always increases. It will always tend toward a maximum. When this maximum is reached, the available energy will become zero, and all parts of the system will acquire a uniform temperature. The Second Law of thermodynamics, re-expressed in terms of entropy, states that in all natural processes the total entropy of a completely isolated system will increase. That is, a system is subject to spontaneous changes if any process can occur in which $ds > 0$. When the state of equilibrium has been reached by the system, $ds = 0$ for any conceiv-

able infinitesimal change that the system might undergo. Never in nature will entropy tend to decrease spontaneously. If it could, heat would tend to flow from a colder to a hotter body, and this would be in violation of the Second Law of thermodynamics. According to this law, as will be recalled from article 14, no self-acting device unaided by any external agency can transfer heat from a body of lower temperature to one of higher temperature.

Comparing the First and Second laws of thermodynamics, we may say that entropy stands in the same relation to the Second Law as energy stands to the First. Entropy and its characteristics, which embody the Second Law, predict in what direction the process or reaction will be carried out. On the other hand, the First Law, that of the conservation of energy, predicts the quantitative relation between the various kinds of energy involved in case the reaction is carried out.

Dependence of the Entropy of an Ideal Gas on the Temperature T , Volume v , and Pressure p .—The change in entropy is calculated according to the fundamental equation 70:

$$\Delta s = s_B - s_A = \int_A^B \frac{dq}{T}. \quad (79)$$

Since the change in entropy is a function entirely of the limits A and B and since only two of the variables T , V , and p are needed to define the state of an ideal gas (art. 1 and 2), dq then can always be expressed in terms of any two of the variables. Since the integrand of equation 79 contains T , let us express dq first, for example, in terms of T and v . From equation 49:

$$dq = de + pdv,$$

where we use p since it refers to pressure in a gas. From equation 51, $de = c_v dT$; and from the ideal-gas law (eq. 367), $p = \frac{RT}{v}$. Therefore

$$dq = c_v dT + RT \frac{dv}{v}.$$

Equation 79 therefore becomes:

$$\begin{aligned} s_B - s_A &= c_v \int_A^B \frac{dT}{T} + R \int_A^B \frac{dv}{v} \\ &= c_v \ln \frac{T_B}{T_A} + R \ln \frac{v_B}{v_A}. \end{aligned} \quad (80)$$

This gives the change of the entropy of an ideal gas in terms of the corresponding changes of temperature T and volume v . Eliminating v by means of the ideal gas equation, $pv = RT$, and eliminating R in equation

80 by equation 370, $c_p - c_v = R$, we can express the change in entropy in terms of corresponding changes of pressure p and temperature T (after again substituting R from equation 370), as follows:

$$s_B - s_A = c_p \ln \frac{T_B}{T_A} - R \ln \frac{p_B}{p_A}. \quad (81)$$

Similarly, equation 80, using the same two expressions, may be transformed into

$$s_B - s_A = c_v \ln \frac{p_B}{p_A} + c_p \ln \frac{v_B}{v_A}, \quad (82)$$

giving the change in entropy in taking a gas from a pressure p_A and volume v_A to another pressure p_B and volume v_B .

Dependence of Entropy s of Any Substance on the Temperature T While the Pressure P Remains Constant.—Recalling the analytic definition of entropy, equation 70, we have

$$s_B - s_A = \Delta s = \int_{T_A}^{T_B} \frac{dq}{T}. \quad (83)$$

The heat dq is here in too general a form. Let us secure a form more suitable to heat transformations carried out at constant pressure and involving the temperature T . From the First Law of thermodynamics, we have (eq. 49)

$$dq = de + dw = de + Pdv.$$

Since we are here postulating that P is constant, we may write

$$\begin{aligned} dq &= de + d(Pv) \\ &= d(e + Pv). \end{aligned}$$

The heat content h was defined by $(e + Pv)$ (eq. 54). At constant pressure, therefore,

$$dq = dh = c_p dT$$

because $dh = c_p dT$ (eq. 56). Equation 83 therefore becomes

$$s_B - s_A = \int_{T_A}^{T_B} \frac{c_p dT}{T} = \int_{T_A}^{T_B} \frac{dh}{T} \quad (84)$$

or

$$s_B = s_A + \int_{T_A}^{T_B} \frac{c_p dT}{T}. \quad (85)$$

Let us consider equation 85 when T_A is 0°A . We shall assume then that the entropy s_A will equal zero. This assumption, which forms the basis of

the Third Law of thermodynamics, will be discussed in article 20. Equation 85 then becomes

$$s_B = \int_0^{T_B} \frac{c_p dT}{T}. \quad (86)$$

Equation 86 gives the absolute value of the entropy per gram of a substance. To evaluate this, c_p must in general be known as a function of T . At the higher temperatures, c_p may be considered as nearly constant. This is by no means true in the neighborhood of 0° A , where the specific heat c_p approaches zero. The variation of the specific heat c_p at constant pressure with temperature T , particularly in the vicinity of 0° A , will be considered in article 20.

Change of Entropy during an Isothermal Process.—We shall use equation 84 for calculating the change in entropy Δs when ice is melted reversibly and isothermally at 273° A . In connection with an italicized statement earlier in this article, it will be recalled that to calculate the change in entropy of a substance in going from one state, A , to another, B , one must choose a reversible path between the two states and then carry out the integration of

$$s_B - s_A = \int_A^B \frac{dh}{T}. \quad (87)$$

At the melting point of ice, for example, the two phases, ice and water, are in equilibrium, and the process of fusion is therefore reversible: if the external temperature is raised by an infinitesimal amount, the solid will melt; and if it is lowered by an infinitesimal amount, the liquid will freeze. In other words, there is always a state of balance between the two opposing tendencies when the melting is carried out isothermally and reversibly at 273° A .

Since the process is isothermal, we have

$$s_B - s_A = \frac{1}{T} \int_A^B dh \quad (88)$$

where s_B denotes the entropy per gram of water and s_A the entropy per gram of ice. Here, obviously, the integral $\int_A^B dh$ is simply the heat of fusion of ice. It might also be regarded as the heat of reaction. Since the heat dh required to melt 1 gram of ice at 273° A is 79.6 calories per gram, $\int_A^B dh = 79.6$ calories per gram. Consequently,

$$\Delta s = \frac{79.6}{273} = 0.29 \text{ calories per gram per degree absolute.} \quad (89)$$

Thus at 273°A the entropy of a gram of water is 0.29 calories per degree greater than that of a gram of ice.

In the same manner, we may calculate the change in the entropy of a gram of water upon being vaporized. We must always remember that in calculating changes of entropy, the path of integration chosen for equation 87 must be reversible whether the process is isothermal or not.

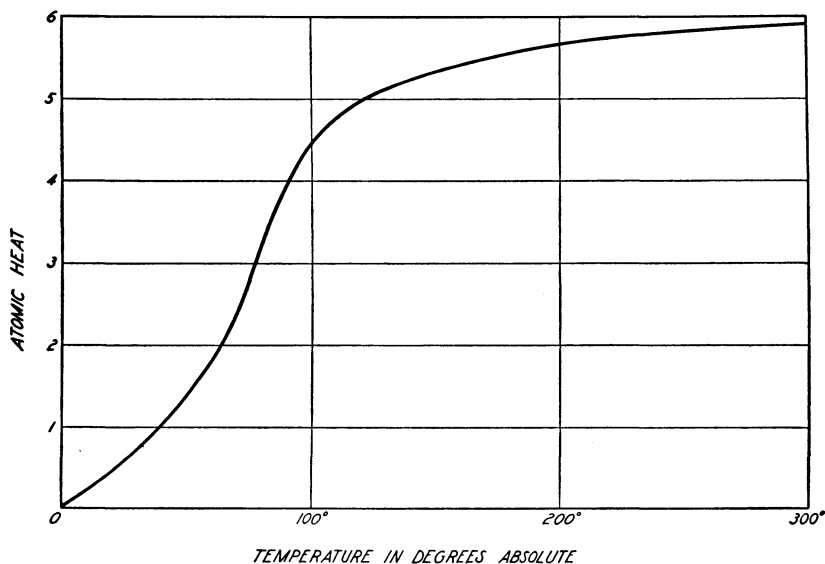


Fig. 9.—Typical way in which the atomic heat depends on temperature.

20. Specific Heat of Solids at Low Temperatures and the Third Law of Thermodynamics

Most of the chemical elements, particularly those of high atomic weight, show approximately the same value for the product of specific heat and atomic weight at ordinary temperatures. This product, usually called the atomic heat, was first shown experimentally by Dulong and Petit to be about 6.2 calories per gram atom. The value 6.2 was readily accounted for under the classical theory of thermodynamics and the kinetic theory of matter.

In 1911, however, Nernst's critical examination of the specific heat of many different substances at constant pressure over a wide range of temperatures showed that this rule held true only in special instances. At ordinary temperatures the atomic heat was constant—approximately 6 calories per gram atom. At very low temperatures, however, it was found to be very small and to approach zero at 0°A . A typical case is shown in figure 9. In 1912, Debye presented a theory of the variation of atomic

heat with change of temperature that gave curves coinciding very closely with those observed experimentally by Nernst. Debye's theory is based upon the quantum theory.

Figure 10 for water is a particular case of figure 9, taken from data in the International Critical Tables. According to figure 10, the specific heat

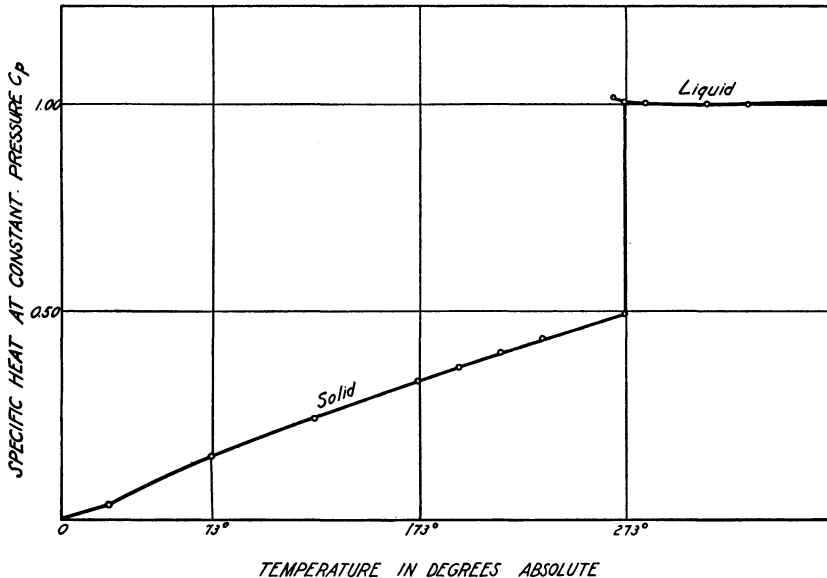


Fig. 10.—The dependence of specific heat of water at constant pressure, on temperature. Extension of the curve to the left for liquid represents supercooling.

of ice at constant pressure is zero at 0° A but gradually increases, until at 273° it is approximately 0.5 calorie per gram. Upon melting, the specific heat of the water suddenly jumps to approximately 1.0 calorie per gram.

A knowledge of the variation of the specific heat at constant pressure c_p is extremely important in computing the total value of such thermodynamic functions as entropy s , equation 90; total heat content h , equation 91; and the free energy f , equation 416. The total entropy s of a body, in general, is defined by

$$s = \int_0^T \frac{c_p dT}{T} + K$$

where K is an arbitrary additive constant, independent of the pressure, state of aggregation, and special chemical modification of the substance. This statement with respect to K has been amply verified by Nernst (1906) and by others.

The additive constant K can be arbitrarily taken as zero at 0° A. Such a selection makes the entropy s zero at absolute zero since, as was previously pointed out, the specific heat c_p becomes zero at 0° . This leads to the following expression for the value of the absolute specific entropy of a substance such as water:

$$s = \int_0^T \frac{c_p dT}{T}. \quad (90)$$

Equation 90 is merely the analytic expression and a special case of Nernst's general heat theorem, which serves to define the absolute value of the entropy. This theorem was stated by Planck as follows: "As the temperature diminishes indefinitely, the entropy of a chemical homogeneous body of finite density approaches indefinitely near to a definite value, which is independent of the pressure, the state of aggregation, and of the special modification." When we set the arbitrary constant K equal to zero (eq. 90), the theorem defining the absolute value of the entropy becomes, according to Planck: "As the temperature diminishes indefinitely, the entropy of a chemical homogeneous body of finite density approaches indefinitely near to the value zero." This basic theorem is often called the Third Law of thermodynamics. This means that at 0° A, we shall always assume the entropy of a substance to be zero.

Knowing the specific heat c_p at constant pressure as a function of the temperature, we can calculate the heat content h of a substance at any temperature T . The heat content has previously been defined according to equation 56, which becomes

$$h = \int_0^T c_p dT + h_0$$

where h_0 is the heat content at 0° A. Now if h_0 is arbitrarily put equal to zero at 0° , we have

$$h = \int_0^T c_p dT. \quad (91)$$

This arbitrarily makes the heat content h equal to zero at 0° .

PROPERTIES OF FREE ENERGY USEFUL IN A THERMODYNAMIC STUDY OF SOIL MOISTURE

21. Characteristics of Free Energy

Use of Free Energy in Describing Natural Processes.—As has been shown (art. 19), any natural process is characterized by an increase in the sum of the entropies ds of all parts of the system involved in the process. Also, if there is any possible change in the system for which $ds > 0$, the system is subject to spontaneous changes and cannot remain in equilibrium. If, furthermore, the system is in a state of equilibrium, its total change of entropy ds for all conceivable infinitesimal changes that the system might be made to undergo is zero—that is, $ds = 0$.

These facts are somewhat analogous to the conditions for spontaneous change and for equilibrium in the studies of mechanics, electricity, magnetism, and some aspects of the hydrodynamics of soil moisture. These studies make use of a quantity called “potential” that corresponds to entropy in the field of thermodynamics. A system is said to be subject to a spontaneous change if, in any conceivable infinitesimal change that it might be allowed to undergo, its total potential energy ψ will decrease—that is, $\Delta\psi < 0$. During a spontaneous change, as will be noticed, the entropy s of a system always increases, whereas the potential energy ψ of the system always decreases; that is, $\Delta s > 0$ and $\Delta\psi < 0$ describe the same conditions. If a system is in equilibrium, the change of the potential energy of the system $\Delta\psi$ for all conceivable infinitesimal changes that the system might undergo is zero; both $\Delta s = 0$ and $\Delta\psi = 0$ describe the conditions for equilibrium.

The term “entropy” was invented to describe and deal with energy changes associated primarily with the transformations of heat into other forms of energy in the field of thermodynamics. “Potential,” on the other hand, was invented to deal with changes of mechanical energy and of work in the fields of mechanics, electricity, and magnetism. The two terms and sets of criteria for equilibria arose originally somewhat independently of each other to deal with their respective types of energy changes as found in nature.

In studies on soil moisture and plant relations, the criteria set up by entropy alone, for energy changes and for equilibria, are far too general for most purposes, whereas those set up by potential are sometimes too limited and restricted. Potential, for example, takes no explicit account of the effect of temperature on the total energy change of a system. Fortunately, another function, called “free energy” f was invented many years ago in the field of thermodynamics. This function combines all the criteria and characteristics of both potential and entropy that are most

useful in the study of the thermodynamics of soil moisture and its use by plants. For example, it permits one to take account, explicitly, of the effect of temperature on the energy changes of a soil-moisture system, which may include several phases in equilibrium with each other. It is less general than entropy, which makes it more convenient and practical than entropy in the study of some actual problems. As will be shown below, the free energy f is defined in terms of entropy.

Thermodynamic Properties of Free Energy.—Absolute free energy f is defined by the two equations

$$f = e + Pv - Ts = h - Ts. \quad (92)$$

These are equivalent because $h = e + Pv$ (eq. 54). Here e represents the internal energy, v the specific volume, h the heat content, and s the entropy, of the substance under consideration.

The student might reasonably ask why such functions as heat content h and absolute free energy f are defined in such an apparently arbitrary manner with seemingly so little preliminary justification. Such functions, however, are usually arrived at during a mathematical analysis of a particular problem. Sometimes, in such analyses, a certain combination of mathematical terms describing physical quantities appears frequently in the equations, and the investigator may for convenience give it a particular name. The justification for introducing such quantities can become evident only as the student grows sufficiently familiar with their characteristics to appreciate their convenience and power in the analyses of problems. The genesis of such a function might be illustrated by the introduction of the term h for the combination $(e + Pv)$ in the expression of the specific heat at constant pressure c_p discussed in connection with equation 53.

Now the total work dw performed by a system may, in general, be separated into two parts: the work of expansion Pdv against a pressure P , and any other mechanical work dw_m , including electrical work, that the system might perform. In general, therefore, the total work dw may be represented by

$$dw = Pdv + dw_m. \quad (93)$$

Differentiating the first of equations 92, we have

$$df = de + Pdv + vdP - Tds - sdT. \quad (94)$$

According to the First Law of thermodynamics (eq. 47), we have

$$de = dq - dw. \quad (95)$$

Now, in any reversible process, since $ds = \frac{dq}{T}$ (eq. 70), we have $dq = Tds$, which, in combination with equation 93, makes equation 95 become

$$de = Tds - Pdv - dw_m. \quad (96)$$

Substituting 96 into 94, we have

$$df = -sdT + vdP - dw_m. \quad (97)$$

For isothermal changes, $dT = 0$, and equation 97 becomes

$$df = vdP - dw_m. \quad (98)$$

If the pressure P is constant during the change, then

$$df = -dw_m$$

or

$$-df = dw_m. \quad (99)$$

According to equation 99, if a reversible change is taking place in a system at a constant temperature and pressure, the work dw_m done by the system, excluding the work of expansion against the constant pressure P , equals the decrease of the free energy ($-df$) of the system during the change. Thus a finite decrease in the free energy $-\Delta f$ is a measure of the maximum work Δw_m (including both electrical and mechanical work but excluding any mechanical work of expansion against a constant pressure P) that can be performed by the system, at constant temperature and pressure, on its surroundings.

Let us now consider finite isothermal changes in a system from a state A to a state B . Since $dT = 0$, we therefore have, from equation 98,

$$\Delta f = \int_A^B df = f_B - f_A = \int_A^B vdP - \int_A^B dw_m. \quad (100)$$

If the pressure remains constant throughout the isothermal change of state, then $dP = 0$, and equation 100 becomes

$$\Delta f = f_B - f_A = - \int_A^B dw_m = -\Delta w_m. \quad (101)$$

According to equation 101, in finite isothermal, isobaric changes of state of a system from A to B , the increase in the free energy Δf of the system equals the work $\left(-\int_A^B dw_m\right)$ that must be performed on the system in carrying it from state A to state B . As already pointed out, this integral does not include work of expansion against a pressure P , as is seen from equation 93.

Equation 101 may also be interpreted as follows: if we let A represent the datum (see art. 40), the free energy Δf of a system in the state B with respect to the datum A is equal to the work that must be done on the system at constant temperature and pressure to bring it from the datum A to the state B . Another way of interpreting equation 101 is: the decrease in the free energy $-\Delta f$ of the system in going from state A to state B equals the total work done isobarically and isothermally by the system on the surroundings, excluding any work of expansion against a constant pressure P .

If, on the other hand, no work is performed during the isothermal change, but there is a change in the pressure P (that is, when $\int_A^B dw_m = 0$), then equation 100 becomes

$$\Delta f = f_B - f_A = \int_A^B v dP. \quad (102)$$

Thus the mere increase of the hydrostatic pressure P on the system will increase its free energy.

If a reversible process occurs at constant temperature and pressure, with no work done except an expansion against a constant pressure P , equation 102 becomes

$$\Delta f = f_B - f_A = 0. \quad (103)$$

Equation 103, as will be shown later, describes the conditions at equilibrium or where two or more phases remain in equilibrium. If, for example, water and vapor are in equilibrium at 100° C and if heat is added to the water so as to vaporize 1 gram of water at 100° C and at 1 atmosphere, then equation 103 says that the absolute free energy f_B in the vapor state equals that in the liquid state f_A . This follows because the temperature and pressure remain unchanged and because no work is done during the change except the expansion against the constant pressure P of the atmosphere.

Knowing the absolute value of the entropy s as defined by equation 90 and knowing the heat content h as defined by equations 57 and 91, we can express the absolute free energy f , previously defined by

$$f = h - Ts, \quad (104)$$

in another useful form. From equations 90 and 57, equation 104 becomes

$$f = \int_0^T c_p dT - T \int_0^T \frac{c_p dT}{T}. \quad (105)$$

Hence if c_p is known as a function of temperature, all three of the thermodynamic functions s , h , and f may be computed as indicated above.

At this point, the reader should clearly distinguish between the meanings of the absolute free energy f and what we shall simply call "free energy," Δf . The letter f defined by equations 92 denotes the absolute free energy (that is, the free energy of a substance when 0°A is used as the reference point), whereas we shall represent by Δf the difference in free energy between the substance in any particular state and the chosen reference point, both being usually at the same temperature. For simplicity we shall speak of Δf as the free energy of the substance. We shall always understand it to represent the difference between the absolute free energy f of the substance in the standard state and in the state in question.

Relation between Changes in Free Energy and Work Performed in Reversible and Irreversible Processes.—In all reversible processes (eq. 99), the maximum amount of work dw_m obtainable from a system equals the decrease in its free energy. That is,

$$-\Delta f = \Delta w_m. \quad (106)$$

In practice, however, all processes are irreversible to some extent; otherwise they would have to occur so slowly as never to be completed. If an isothermal process is to occur with a finite velocity, the process will be irreversible, and some of the mechanical work will be lost in the form of heat, so that we always find

$$-\Delta f > \Delta w_m'. \quad (107)$$

In other words, the mechanical work $\Delta w_m'$ performed in a natural process or transformation is less than the decrease in free energy occurring in the process. The difference $(\Delta w_m - \Delta w_m')$ represents a loss in mechanical energy. It generally becomes heat energy at a temperature too low to be available for work in the system under consideration.

A simple example in mechanics might clarify the preceding ideas. The relations given above may be illustrated by figure 11. By analogy, since temperature is here not involved, we shall take the level A where $h = 0$ as representing our absolute zero of free energy f . Here h has of course not the same meaning as it has been given previously. Our system is here composed of the weight M_1 , which by analogy we shall regard as the working substance, and the weight M_2 , which we shall regard as the surroundings, both weights being hung from the frictionless pulley P by a weightless rope. As M_1 moves downward, work dw_m is done on the surroundings M_2 . All changes in the system will be carried out at constant temperature and pressure. Reference to the discussion following equation 101 shows that the absolute free energy f , in ergs, of the working

substance M_1 at B with respect to the point A is given by the potential energy (in the c.g.s. system)

$$f = h M_1 g \text{ ergs.} \quad (108)$$

While M_1 travels downward, work Δw_m is performed on the surroundings M_2 ; numerically this is equal to

$$\Delta w_m = h M_2 g \text{ ergs.} \quad (109)$$

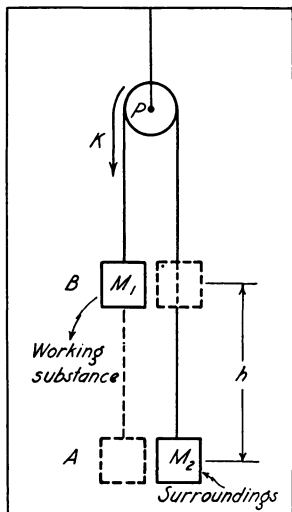


Fig. 11.—Mechanical model for illustrating the meaning of the term “free energy.”

We shall first consider an irreversible change represented by inequality 107 above. In order that M_1 may move downward with finite velocity, the weight M_1 must be greater than M_2 in order that there may be a net driving force K . The greater the disparity between M_1 and M_2 , the greater the force K , the greater the velocity of movement, and consequently (as we shall show) the greater the irreversibility of the process.

When M_1 moves from B to A , the decrease in free energy of the working substance is (eq. 108)

$$-\Delta f = h M_1 g \text{ ergs.} \quad (110)$$

The work done on the surroundings, consisting here of the weight M_2 , is

$$\Delta w_m' = h M_2 g \text{ ergs.} \quad (111)$$

Since $M_1 > M_2$,

$$h M_1 g > h M_2 g;$$

and therefore (eq. 110, 111) we have

$$-\Delta f > \Delta w_m',$$

which corresponds to inequality 107 for an irreversible process. The greater M_1 is with respect to M_2 (that is, the more irreversible the process), the greater the above inequality.

The question now is, when M_1 moves downward, what happens to the free energy that is lost and not stored in the surroundings as available energy? It is mainly dissipated as heat when M_1 strikes the bottom at B , since the directed kinetic energy of the downward motion of M_1 is converted into random heat movements of the individual molecules. In

addition, when M_1 strikes the bottom at B , some of the lost energy may go into energy of deformation of the bodies as well as into sound.

Let us now consider the case when the working substance M_1 moves down reversibly. Only in the limit when $M_1 = M_2$ and therefore when M_1 moves downward with infinite slowness will the decrease in the free energy $-\Delta f$ of the working substance M_1 equal the work dw_m performed by the system on M_2 , for, under these conditions, the net driving force K tending to move M_1 downward must be an infinitesimal, in order to develop only an infinitesimal amount of kinetic energy in M_1 . The decrease in the free energy of the working substance from equation 108 is

$$-\Delta f = h M_1 g \text{ ergs;} \quad (112)$$

and the work performed reversibly on the surroundings (eq. 109) is

$$\Delta w_m = h M_2 g \text{ ergs.} \quad (113)$$

Since $M_1 = M_2$, we have in the limit, from equations 112 and 113, for the reversible process, which must be carried out infinitely slowly,

$$-\Delta f = \Delta w_m,$$

corresponding to equation 106 of a reversible process.

The foregoing examples demonstrate that any natural spontaneous process must be to some extent irreversible. This follows because the forces of the system cannot all be completely balanced at all times. If they were, in order to satisfy the condition of reversibility, the process would go on with such infinite slowness that it would never be completed in a finite time. To carry out the process within a finite time, there must be an inequality in magnitude of opposing forces; in other words, there must be a resultant driving force K of the process. The greater K is, the greater the irreversibility. In all such cases, as is shown by the illustration above, the decrease of the free energy $-\Delta f$ is greater than the useful work accomplished $\Delta w_m'$. That is,

$$-\Delta f > \Delta w_m'.$$

We have considered above the change in the free energy $-\Delta f$ of the system when there has been interchange of useful work $\Delta w_m'$ with the surroundings. We shall now consider a case where $\Delta w_m' = 0$ —that is, where no work is done on the surroundings during the process, and the energy is instead dissipated into unavailable forms such as heat at too low a temperature to be available. In this case we have from inequality

$$-\Delta f = -(f_2 - f_1) > 0.$$

Assume a closed system in which spontaneous changes are taking place, where there is no interchange of work, and where, accordingly, $\Delta w_m' = 0$. This might correspond to a spontaneous change in a system such as one composed of a moist and a dry soil placed in contact. Suppose, for convenience, we have enough wet and dry soil so that the total weight of moisture in both is 1 gram. Moisture will spontaneously go from the moist to the dry soil, and the process will be irreversible. Here f_1 represents the average absolute free energy of the moisture in the entire system initially, and f_2 the average absolute free energy in the entire system after the spontaneous change has taken place. Since $\Delta w_m' = 0$, inequality 107 shows that

$$-\Delta f = -(f_2 - f_1) > 0 \quad (114)$$

or

$$\Delta f = (f_2 - f_1) < 0.$$

That is,

$$f_2 < f_1. \quad (115)$$

As moisture continues spontaneously to flow from the moist to the dry soil, the initial average absolute free energy f_1 of the entire system decreases to the final value f_2 .

We may thus conclude that when any spontaneous change occurs at constant temperature and external pressure, the absolute free energy of the system will invariably decrease; that is, the free-energy change Δf is always negative. Or, stated algebraically, we have for all spontaneous changes

$$\Delta f < 0. \quad (116)$$

Never in any spontaneous change will the free energy increase.

Condition of Equilibrium.—For an isothermal reversible process occurring at constant pressure, it was shown that $-\Delta f = \Delta w_m$. If we are dealing with an isolated system that can perform no net work on the surroundings except an expansion against constant pressure P , we must set $\Delta w_m = 0$; that is, $\Delta f = 0$.

Now, at equilibrium, all possible infinitesimal displacements of the system are also reversible—that is, all forces are completely balanced except for infinitesimal differences. The work done, Δw_m , in any possible infinitesimal displacement of the system, when at equilibrium, must accordingly equal zero, for there is no resultant force in any direction at equilibrium and hence $\Delta f = 0$. Therefore, since for any process occurring at constant temperature and pressure at equilibrium we have $\Delta f = 0$, the state of equilibrium may be defined by

$$\Delta f = 0. \quad (117)$$

Comparison of Free Energy with Potential.—The discussion above brings out another similarity of free energy to the potential energy as used in such fields as mechanics, electricity, magnetism, and soil moisture. The following tabulated comparisons between potential and free energy will illustrate some of their points of similarity. Earlier in this article we considered some of the differences between them that make free energy superior for present purposes. Other comparisons will be made later.

	Free energy f	Potential Φ
Condition for equilibrium	For any infinitesimal change of system, $\Delta f = 0$	For any infinitesimal change of system, $\Delta \Phi = 0$
Necessary condition for spontaneous change	$\Delta f < 0$	$\Delta \Phi < 0$
Usual conditions of system for spontaneous change	Constant temperature and pressure	Constant temperature and pressure
Typical spontaneous changes	Soil moisture moves spontaneously from wet soils, where f is high, to drier soils, where f is lower	Soil moisture moves spontaneously from wet soils, where Φ is high, to dry soils, where Φ is lower
	Electricity moves spontaneously from points where Φ is high to points of lower Φ
	Masses under influence of gravitational field move downward from points of high Φ to points of lower Φ

Specific Free Energy of Several Phases of the Same Substance in Equilibrium with Each Other.—Often we shall be concerned with several phases of a substance in equilibrium with each other, such as ice and water. In order to deal with the energy changes involved, let us give the absolute free energy term f additional meaning. In the past, the amount of mass to which the term f referred was not always specifically stated. It sometimes denoted the absolute free energy of the entire system, which in our present case would be composed of the total amount of the ice and water present. This definition of f is too general; it does not permit us to deal with the separate phases that compose the entire system or with their interrelations. For this reason we shall redefine f to mean the absolute specific free energy per unit mass of the substance in a single phase. We shall speak of this as absolute specific free energy, or as absolute free

energy of the substance in that phase. Changes in the free energy of our system will now consist of changes in absolute free energy of the unit mass within the same phase or of changes in absolute free energy of the unit mass in going from one phase to another. As was shown earlier, if two phases are in equilibrium with each other, any infinitesimal change in the variables of state of the system (for example T and p) will not change its total absolute free energy. Also, when a gram of ice melts by the addition of heat or a gram of water freezes by the removal of heat, no change in the total free energy of the system occurs so long as both the temperature and the pressure remain constant.

The change in the absolute free energy of the system when 1 gram of ice melts under equilibrium conditions of temperature and pressure is given (eq. 117) by

$$\Delta f = 0.$$

Here Δf represents the change in free energy of 1 gram of the substance when it changes state. That is, $\Delta f = 0$ simply states the fact that the free energy of the substance is the same in the two phases. As long as the two phases are present together, equilibrium will be maintained. For finite changes of the free energy of the system at equilibrium, we therefore have

$$\Delta f = (f_2 - f_1) = 0.$$

That is, if f_1 is the absolute specific free energy of the substance (ice) in the initial phase and if f_2 is the absolute specific free energy of the substance (water) in the final phase, we have

$$f_1 = f_2. \quad (118)$$

Thus, if two phases coexist at equilibrium, their absolute specific free energies are the same.

It will now be interesting to inquire how the absolute specific free energies f_1 and f_2 will be altered by changing the temperature of the system from the equilibrium temperature considered above, at which both phases are in equilibrium with each other, to some other temperature. Throughout the following considerations, we shall assume the pressure to remain constant. If the temperature of the two phases should be raised, the change of ice to water is of course spontaneous. That is (inequality 107), since $\Delta w_m' = 0$, we have

$$\Delta f = (f_2 - f_1) < 0$$

as the free-energy change of the reaction where f_1 is the absolute specific free energy of the initial state (ice) and f_2 is the absolute specific free energy of the final state (water), or

$$f_2 < f_1. \quad (119)$$

Thus, above 0° C the absolute free energy of the ice is greater than the absolute free energy of water. If one phase (ice) having the absolute free energy f_1 changes spontaneously to another (water) having the absolute free energy f_2 , the absolute free energy of the former must be the greater. This statement agrees with the generalization that the free energy decreases in all spontaneous changes.

If, on the other hand, the temperature should be lowered below 0° C, water will of course pass into ice spontaneously. If we now consider liquid water (f_2) as the initial state and ice (f_1) as the final state, we have (inequality 107 again)

$$\Delta f = (f_1 - f_2) < 0,$$

from which we can derive the relation for the free-energy change Δf for the imaginary reaction of ice melting into water below 0° C. It is clear, then, that

$$-\Delta f = (f_2 - f_1) > 0$$

or

$$f_2 > f_1. \quad (120)$$

Thus, below 0° C, the absolute free energy of water is greater than the absolute free energy of ice. If one phase (ice) having the absolute free energy f_1 cannot change spontaneously to another (water) having the absolute free energy f_2 , the absolute free energy of the former must be less. This agrees with the generalization that spontaneous changes never take place where the free energy of the system increases.

From the foregoing discussion, we may conclude that if several phases of the same substance are in equilibrium, the absolute specific free energies are the same in all phases of the system. More detailed and rigorous proof will be presented in article 22. If, however, the absolute free energy of any one phase should be greater than that of the others, then that phase will disappear into the others.

Negative Character of the Free Energy of Unsaturated Soils.—The discussion above shows clearly that the specific free energy of a system or substance decreases in any spontaneous change. Let us consider a body of free water in contact with an unsaturated soil. By common experience, water flows spontaneously from a body of free water (whose absolute specific free energy we shall call f_1) into an unsaturated soil (whose absolute specific free energy we shall call f_2). It is customary to use free, pure water under a pressure of 1 atmosphere (art. 62) as the zero point or datum for the free energy of soil moisture. Thus the free energy Δf of pure water under these conditions becomes zero. We have shown (inequality 107), in going from an initial state f_1 to a final state f_2 , that, for any spontaneous change in the case where $\Delta w_m' = 0$, it follows that

$$\Delta f = (f_2 - f_1) < 0. \quad (121)$$

Here $\Delta f = f_2 - f_1$ represents the free energy of the unsaturated soil with respect to the reference point f_1 . That is, the absolute free energy f_2 of the unsaturated soil moisture is less than that of free, pure water. The inequality 121 states the general fact that the free energy Δf of soil moisture in all unsaturated soils is negative with respect to the commonly accepted datum, since $\Delta f < 0$.

Going a bit further, let us consider the relation between the magnitude and sign of the free energy Δf of a wet soil and those of a drier one. Since, as is commonly known, moisture will flow spontaneously from the wet to the dry soil and since we are here considering spontaneous changes, let us take the wetter soil as the initial state of the soil moisture having the absolute free energy f_1 and the drier soil as the final state of the soil moisture having the absolute free energy f_2 . For spontaneous changes (inequality 121), we have

$$f_2 < f_1. \quad (122)$$

Inequality 122 states the general fact that the absolute free energy f_2 of the moisture in a comparatively dry soil is less than the absolute free energy f_1 of that in a wet soil.

As was shown previously, the free energy Δf of the moisture of all unsaturated soils is negative. The free energy of the moisture is therefore always more negative in a drier soil than in a wetter soil. Only if the wet soil is saturated can its free energy, at the most, be zero.

22. The Equality between the Free Energies of Several Coexistent Phases

We have previously shown (eq. 118) somewhat indirectly, in discussing the various characteristics of free energy, that the free energies of two or more phases coexisting at equilibrium must be the same. We shall now show this, for the case where the temperature and pressure are equal in all phases, in a much more rigorous and direct manner.

All substances exist in different modifications between which transitions may occur. These modifications are often called the different phases of a substance, the most important examples being the different states of aggregation—for example, gaseous, liquid, and solid. In addition, we have the different allotropic modifications of a substance, which make up still other possible phases.

From article 4 we recall that if we have a function ϕ of one or more variables and if we are at a maximum or minimum of the function ϕ , then any slight change in any one or more of the variables will not change ϕ . We shall represent slight variations in their magnitude by the symbol δ . At a maximum or minimum of the function ϕ we have

$$\delta\phi = 0$$

for any slight change of the variables. Conversely, $\delta\phi = 0$ serves to determine the values of the variables for which ϕ has a maximum or minimum. For example, taking the simplest case where ϕ is a function of but one variable, x , we find that at any maximum or minimum of ϕ the first derivative of ϕ is zero. Any infinitesimal variation δx in the neighborhood of either C or A (fig. 3), the maximum and minimum of ϕ , is seen to produce no variation $\delta\phi$ in the function ϕ ; that is, $\delta\phi = 0$ for infinitesimal variations of δx . If, however, we focus our attention on any other point B of the curve, we note that slight variations δx do produce appreciable variations $\delta\phi$ of the function ϕ .

We will also utilize the following mathematical fact: If ϕ is a function of one or more variables and if we wish it to remain constant for all possible variations of the independent variables, then

$$\delta\phi = 0$$

for all infinitesimal changes of the variables upon which ϕ depends. The changes in the variables must therefore so adjust themselves that $\delta\phi = 0$. If, for example, $\phi = xy$, and ϕ is to remain constant during changes of x and y , then $\delta\phi = 0 = x\delta y + y\delta x$, which serves to define the relation that must exist between changes of x and y .

We shall now prove that when two or more phases are in thermodynamic equilibrium with each other, and their temperatures and external pressures are equal, then their free energies must all be the same. To prove this we have merely to assume the First and Second laws of thermodynamics as well as the conservation of matter. It was shown for a specific case (connected with eq. 78) that *when a system has attained equilibrium, the total entropy S of the system has attained a maximum for the given values of the total mass, energy, and volume of the system.* This is a general characteristic of entropy at equilibrium. Our problem is thus to find the conditions which make S a maximum subject to the conditions that the total mass M , the total internal energy E , and the volume V remain constant. Hence one condition for the coexistence of several phases of a system in thermodynamic equilibrium is that

$$\delta S = 0. \tag{123}$$

That is, any slight displacement or change of the system composed of the several phases in equilibrium with each other does not alter the total entropy of the system. Certain almost self-evident subordinate conditions follow, furthermore, according to the previous paragraph. First,

$$\delta V = 0, \tag{124}$$

which states that the total volume of the system remains constant. Then, too,

$$\delta E = 0, \quad (125)$$

which states that the total internal energy of the system remains constant. Also,

$$\delta M = 0, \quad (126)$$

which states that the total mass M of the system remains constant—none is created or added and none is destroyed or taken away. That is, with a given mass, energy, and volume of the system, $\delta S = 0$ at equilibrium.

Let us now consider the simple example of a system composed of only two coexisting phases. Let s , v , and e represent the entropy, volume, and internal energy of the substance per unit mass—that is, the specific values. Let m represent the mass of the two phases, and let X be a fraction such that mX represents the mass of one of the phases. Then $m(1 - X)$ will represent the mass of the other phase. In what follows we shall assume for simplicity that m is unity; that is, we are dealing with only 1 gram of the substance. The quantities associated with one of the phases will be distinguished by a prime; those with the other by a double prime. The specific entropy of the system then becomes

$$s = Xs' + (1 - X)s'', \quad (127)$$

and the specific volume

$$v = Xv' + (1 - X)v'', \quad (128)$$

and the specific internal energy

$$e = Xe' + (1 - X)e'', \quad (129)$$

and the specific mass of the system m , which we shall set equal to unity

$$m = Xm + (1 - X)m. \quad (130)$$

Because of equation 123, 127 becomes

$$\delta s = 0 = X\delta s' + (1 - X)\delta s'' + (s' - s'')\delta X. \quad (131)$$

Similarly, we have

$$\delta v = 0 = X\delta v' + (1 - X)\delta v'' + (v' - v'')\delta X \quad (132)$$

and

$$\delta e = 0 = X\delta e' + (1 - X)\delta e'' + (e' - e'')\delta X \quad (133)$$

and

$$\delta m = 0 = m\delta X - m\delta X. \quad (134)$$

On the other hand, in accordance with the Second Law of thermodynamics stated by equations 49 and 70, we have

$$\delta s' = \frac{\delta q'}{T'} = \frac{\delta e' + P' \delta v'}{T'} \quad (135)$$

and

$$\delta s'' = \frac{\delta q''}{T''} = \frac{\delta e'' + P'' \delta v''}{T''}. \quad (136)$$

We want to express $\delta e''$ and $\delta v''$ in terms of $\delta e'$ and $\delta v'$. To do this, solve equations 132 and 133 for $(1 - X)\delta v''$ and $(1 - X)\delta e''$ respectively, and substitute these values in equation 136. We then have

$$(1 - X)\delta s'' = -\frac{X\delta e'}{T''} - \frac{XP''\delta v'}{T''} - \left[\frac{e' - e''}{T''} + \frac{P''(v' - v'')}{T''} \right] \delta X.$$

Substituting this as well as equation 135 into equation 131, we have

$$\begin{aligned} 0 = & X\delta e' \left[\frac{1}{T'} - \frac{1}{T''} \right] + X\delta v' \left[\frac{P'}{T'} - \frac{P''}{T''} \right] \\ & + \delta X \left[s' - s'' - \frac{e' - e''}{T''} - \frac{P''(v' - v'')}{T''} \right]. \end{aligned} \quad (137)$$

As may be seen from equations 131, 132, and 133, the variations $\delta e'$, $\delta v'$, and δX (the quantities associated with but one of the phases) can be carried out quite arbitrarily and independently of each other and still satisfy the three equations that define the states of equilibrium between the two phases. The reason is that no matter what values are given to $\delta e'$, $\delta v'$, and δX , the other variations in these equations can be given the proper values to still satisfy the three equations defining the state of equilibrium. Since the variations $\delta e'$, $\delta v'$, and δX of equation 137 are therefore quite independent of each other and can assume any arbitrary value, equation 137 can be satisfied at all times only when each of the three expressions in square brackets vanishes separately. This will be the case for the first two brackets when

$$T' = T'' \quad \text{and} \quad P' = P''. \quad (138)$$

For simplicity, let T and P denote the equal temperatures and pressures respectively of equation 138. The third bracket then becomes

$$s' - s'' - \frac{e' - e''}{T} - \frac{P(v' - v'')}{T} = 0$$

or

$$-s' + \frac{e'}{T} + \frac{Pv'}{T} = -s'' + \frac{e''}{T} + \frac{Pv''}{T}$$

or

$$-s'T + e' + Pv' = -s''T + e'' + Pv''. \quad (139)$$

Now it will be recalled (eq. 92) that we defined the absolute specific free energy f of a substance by

$$f = e - sT + Pv.$$

We see, therefore, that equation 139 above actually states that

$$f' = f''. \quad (140)$$

We thus conclude from the foregoing that if two phases are in equilibrium with each other and are at the same temperature and under the same pressure, then, as an inevitable consequence, both phases must possess the same absolute specific free energy. What was shown to hold for the free energies of two phases in equilibrium at the same temperature and pressure is readily seen to hold for any number of phases of a substance in equilibrium with each other.

This fact makes the quantity called "free energy" tremendously important when we are dealing with systems consisting of several phases in equilibrium with each other. Soil moisture, for example, may exist in the vapor, liquid, and solid states. If we know the free energy of the vapor in equilibrium with both the liquid and frozen soil moisture, we also know the free energy of the liquid soil moisture, as well as that of the solid soil moisture.

In the above proof, the pressure was made the same on the different phases at equilibrium to demonstrate the equality of free energy in the phases. This is not generally necessary. Cases when the pressures are not the same on the different phases at equilibrium will be discussed in articles 26, 30, and 41.

23. Effect of Temperature on the Free Energy

We wish to find how the free energy changes as the temperature is changed. Suppose we consider, for example, 1 gram of water at a given temperature and pressure, possessing a given amount of free energy. From equation 97 we have

$$df = -sdT + vdP - dw_m. \quad (141)$$

If the pressure remains constant and if no work is done on the surroundings, equation 141 becomes

$$df = -sdT \quad (142)$$

or

$$\left(\frac{\partial f}{\partial T}\right)_P = -s. \quad (143)$$

Thus the rate of change of the absolute free energy with respect to change of temperature equals the negative of the specific entropy. Applied to soil moisture, this means that the rate of change of the absolute free energy of soil moisture with temperature equals the negative of its specific entropy.

Suppose we go further and, instead of considering the change in the absolute free energy of water in going from one temperature to another, discuss the following case. At constant temperature T and pressure P , let a process (fig. 12) occur such that the absolute free energy in the initial

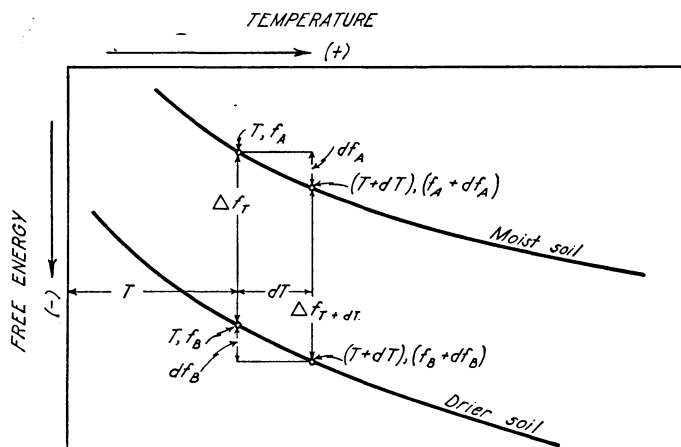


Fig. 12.—Dependence of specific free energy on temperature.

state is f_A , in the final state f_B , so that the change in the absolute free energy during the process is $\Delta f_T = f_B - f_A$. If the same process is carried out in exactly the same manner and at the same pressure, but at a different temperature $T + dT$, the absolute free energy in the initial and final states will be $f_A + df_A$ and $f_B + df_B$ respectively, giving a different value Δf_{T+dT} for the change in free energy at the temperature $T + dT$. We wish to find how the change in free energy Δf_T of the process depends on temperature. Suppose, for example, we have determined the change in free energy Δf_T of a gram of water in being carried from a drier soil to a wetter soil at the temperature T . We shall now wish to determine how this change of the free energy Δf_T involved in the transformation, change, or process is affected if the process is carried out at a different temperature $T + dT$. In the following discussion all changes of the process at the same temperature are denoted by Δ , whereas changes in the process in going from one temperature to another are denoted by d .

Since the process is carried out at constant pressure without the per-

formance of work, we have (eq. 142) the change df_A of the absolute free energy of the initial state A for a change dT of the temperature

$$df_A = -s_A dT \quad (144)$$

and for the change df_B of the absolute free energy of the final state B because of a change of temperature dT ,

$$df_B = -s_B dT. \quad (145)$$

The pressure in state A is to remain constant with all variations of temperature; so, likewise, is the pressure in state B . On the other hand, the pressure in state A will not in general be the same as in state B . The subscript P in equation 146 below denotes these facts.

From equations 144 and 145, we have

$$d(f_B - f_A) = d(\Delta f) = -(s_B - s_A)dT$$

or

$$\left(\frac{d(\Delta f)}{dT} \right)_P = -(s_B - s_A) = -\Delta s_P. \quad (146)$$

Thus, for example, the rate of change of the free energy Δf of soil moisture with respect to changes of temperature T , with the restrictions placed on the pressure as given above, equals the negative of the specific entropy, Δs_P , of the soil moisture, both Δf and Δs_P being measured with respect to free water in this example.

24. The Effect of Osmotic Pressure on the Free Energy of a Liquid

Suppose we have a pure solvent in contact with a solution through a semipermeable membrane as in figure 13. If the pressures on A and B are the same, the system will not be in equilibrium. Solvent will then flow from C into D . Also the vapor pressure p over A will be less than p_0 over B , which would cause a resultant movement of solvent from B to A through the vapor phase if the pistons were not present. Only when we increase the pressure on the solution by a definite amount ΔP —by means of a piston, for example—will the resultant flow of solvent through the semipermeable membrane from C to D be stopped and the vapor pressure p of the solvent over A become equal to p_0 over B . The pressure ΔP_O on the solution, which will just stop the movement of solvent from B to A in the vapor phase as well as from C to D in the liquid phase, is known as the “osmotic pressure” of the solution. It will be zero if no solute is present, and will increase as the amount of dissolved material increases.

From a kinetic viewpoint the situation may be described as follows, when we are not dealing with concentrated solutions. The presence of dissolved materials lowers the escaping tendency of the solvent molecules,

and thus holds back a definite fraction of those that would normally escape. On this basis, for example, if one fifth of the molecules of the solution were solute molecules, both the vapor pressure and escaping tendency of the solvent would be reduced to four fifths of their values for the pure solvent. Thus more of the solvent will move from *B* to *A* as well as from *C* to *D* than in the opposite direction, and there will consequently be a net flow of solvent into the solution. The escaping tendency of the solvent on the right side is the same throughout all parts of the solution. It is also the same throughout the pure solvent on the left side, but it has a higher value there than on the right. A quantitative measure of the

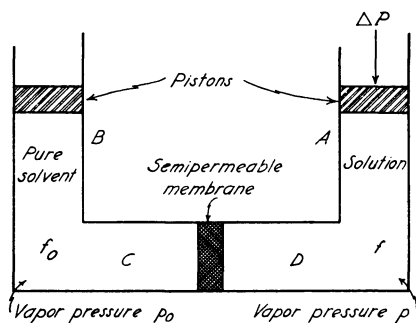


Fig. 13.—Equilibrium between a solution and the pure solvent through a semipermeable membrane.

escaping tendency of the solvent is its vapor pressure. Under the conditions postulated in the figure, the vapor pressure over *A* is less than that over *B*; that is, p is less than p_0 . Likewise the escaping tendency of the solvent on the right side is less than that on the left. Now, to establish equilibrium between the two sides, the vapor pressure or escaping tendency of the solvent on the right side must be increased. This may be accomplished by placing the solution under a hydrostatic pressure ΔP_0 , now called the osmotic pressure, such that the vapor pressure originally having the value p is raised to p_0 . The vapor pressure on the right, a measure of the escaping tendency of the solvent, is then equal to that on the left, and equilibrium is established. Incidentally the hydrostatic pressure ΔP_0 (that is, the osmotic pressure) required to raise the vapor pressure from p to p_0 can be immediately calculated according to equation 239.

The osmotic pressure ΔP_0 , which equals the hydrostatic pressure ΔP that must be applied to the solution to establish equilibrium, is by van't Hoff's law (eq. 226) given to a first approximation by

$$(\Delta P_0)v = x_2RT, \quad (147)$$

which is nothing more than the familiar ideal-gas equation. According to this equation, the dissolved material in a relatively dilute solution may be considered as behaving exactly like an ideal gas at the same temperature T and volume v as it occupies in the solution. The resultant solute pressure ΔP on the semipermeable membrane is found experimentally, for dilute solutions for which semipermeable membranes have been produced, to be approximately the same as the gas pressure or osmotic pressure ΔP_O given by equation 147.

Having considered above quantitatively some of the characteristics of osmotic pressure, let us now show that the free energy of the solvent of a solution (with respect to the pure solvent) is given by

$$\Delta f = -v\Delta P_O \quad (148)$$

where v is the specific volume of the solvent and ΔP_O is the osmotic pressure of the solution. For example, if the solvent is water, the free energy Δf of the solvent is numerically equal but opposite in sign to the osmotic pressure ΔP_O , since the specific volume of water is unity in the c.g.s. system. Here, as will be recalled, we always take the zero point of free energy as that of free, pure water.

In proving equation 148, let us assume, as before, that we have a solution in contact with the pure solvent through a semipermeable membrane (fig. 13). The absolute specific free energy and the vapor pressure of the pure solvent are f_0 and p_0 , respectively; those of the solvent of the solution, f and p , respectively. As before, let ΔP_O denote the osmotic pressure—that is, the hydrostatic pressure that must be placed upon the solution in order to raise the escaping tendency, vapor pressure, and absolute free energy of the solvent of the solution to that of the pure solvent in the side B . We shall determine the specific free energy Δf of the solution with respect to the pure solvent by calculating the amount of free energy required to raise the absolute free energy f of the solution to that of the pure solvent f_0 . That is, we shall calculate the change in the free energy of the solution caused by applying a pressure ΔP_O to the solution.

By equation 102 we can calculate the change in the absolute free energy produced by an increase of the hydrostatic pressure on the solution:

$$\Delta f = f_B - f_A = \int_{P_A}^{P_B} v dP. \quad (149)$$

In our present case the initial absolute free energy and hydrostatic pressure on the solution are f and zero, respectively. Thus, using our present notation in the equation above, $f_A = f$, and $P_A = 0$. In the final state the absolute free energy of the solvent and the pressure on the solution are f_0 and ΔP_O , respectively. Thus in the final state, $f_B = f_0$ and $P_B = \Delta P_O$.

Since the specific volume v of a liquid is practically independent of pressure, equation 149 then becomes

$$f_0 - f = \int_0^{\Delta P_0} v dP = v \Delta P_0. \quad (150)$$

The quantity $(f_0 - f)$ actually gives the free energy of the pure solvent with respect to the solution. We want, instead, the free energy Δf of the solution with respect to the pure solvent, which is the negative of $(f_0 - f)$.

This is

$$f - f_0 = \Delta f = -v \Delta P_0 \quad (151)$$

or, in differential form,

$$\left(\frac{\partial f}{\partial P_0} \right)_T = -v. \quad (152)$$

When equation 151, giving the dependence of the free energy on osmotic pressure, is compared with equation 156, giving the dependence of the free energy on hydrostatic pressure, the two are seen to have the same form except for the difference in sign.

25. The Effect of Pressure on the Free Energy of Liquids and Gases

Let us assume that we have 1 gram of a fluid contained in a volume v . We wish to determine the dependency of its free energy on the pressure applied to it. We shall assume that all changes are isothermal and that the only mechanical energy changes involved are those due to the expansion and contraction against the external pressure. These considerations will answer, for example, the question as to how the free energy of water due to hydrostatic pressure increases with depth in a reservoir; or how the free energy of soil moisture, due to hydrostatic pressure resulting from the adsorptive force field surrounding the soil particle, increases as the surface of the soil particle is approached.

For isothermal changes without the performance of work except for an expansion against the pressure P , we found (eq. 102)

$$\Delta f = f_B - f_A = \int_A^B v dP. \quad (153)$$

If, therefore, we are dealing with almost incompressible liquids for which the specific volume v is practically unaffected by changes of pressure, we have for the free-energy change Δf due to a change in hydrostatic pressure,

$$\Delta f = f_B - f_A = v \int_{P_A}^{P_B} dP \quad (154)$$

or

$$f_B = f_A + v \int_{P_A}^{P_B} dP. \quad (155)$$

That is, if water has a free energy f_A initially and the pressure is increased from P_A to P_B , the free energy becomes f_B (eq. 155). For finite changes, equation 154 also becomes

$$\Delta f = f_B - f_A = v\Delta P. \quad (156)$$

Digressing momentarily, we will note that equation 153 may be placed in the very useful form

$$\left(\frac{\partial f}{\partial P}\right)_T = v \quad (157)$$

where the subscript T indicates that the temperature is kept constant during the variation of pressure P . According to equation 157, the rate of change of the specific free energy of a liquid with respect to changes of pressure equals the specific volume of the liquid.

Returning again to equation 156, let us apply it to liquid water whose specific volume v in the c.g.s. system is equal to unity. We then have

$$\Delta f = \Delta P. \quad (158)$$

That is, for water the free-energy change Δf due to the change in hydrostatic pressure is numerically equal to the change in hydrostatic pressure ΔP . On the other hand, as will be shown later or can be seen from equation 151, the free energy of water due to the presence of dissolved material is numerically equal to the negative of the osmotic pressure. The two expressions, therefore, have the same form except for a minus sign.

We have just shown the dependence of the free energy on pressure for incompressible fluids—that is, liquids. Let us now consider the same dependence for gases, which are compressible. In the present case, the specific volume v is no longer constant but varies with the pressure. Let us here assume that we are dealing with gases which follow the ideal gas law so that $pv = RT$, according to equation 367. We then have (eq. 153)

$$\Delta f = f_B - f_A = \int_{p_A}^{p_B} v dp = RT \int_{p_A}^{p_B} \frac{dp}{p} = RT \ln \frac{p_B}{p_A}. \quad (159)$$

Equation 159 indicates that the free energy Δf of the gas increases as its pressure increases isothermally. If p_B is less than p_A , the logarithm is negative, which indicates that the free energy of the gas in the state B at the pressure p_B is less than in the state A at the pressure p_A .

Let us apply equation 159 in the evaluation of the free energy of soil moisture to illustrate its meaning and usefulness. By convention we have considered that our datum or zero point of reference for the free energy of soil moisture is that of free, pure water. As has previously been shown (art. 22), free energy always has the same value in all phases which are in

equilibrium with each other; that is, the free energy of the water vapor above free water must also equal that of free water itself. Thus if we wish to determine the free energy of soil moisture—often a very difficult thing to do directly—we have merely to deal with the vapor in equilibrium with it. The free energy of the soil moisture whose vapor pressure is p_B is then given by equation 159, where p_A is the vapor pressure of the datum—that is, of free, pure water at the same temperature.

At this point we shall digress for a moment and observe a relation existing between the work done during the isothermal expansion of an ideal gas and the change in its free energy. The most general change of the free energy Δf was given by equation 97, which may in this case (since there is here no distinction between p and P) be written

$$\Delta f = -s\Delta T + v\Delta p - \Delta w_m$$

where Δw_m included all the work performed by the system except that of expanding against an external pressure p . For an ideal gas we will show that the term $v\Delta p$ equals the work of expansion against the external pressure p . At present we are dealing merely with isothermal changes in volume of a gas under a variable external pressure p , so that both $\Delta T = 0$ and $\Delta w_m = 0$. We therefore have

$$\Delta f = v\Delta p. \quad (160)$$

We wish to show that the decrease in the free energy of the ideal gas upon expansion equals the work done by it during isothermal expansion against the variable pressure p . That is, the term $v\Delta p$ in equation 97 takes care of the work $p dv$ of isothermal expansion of a gas. In other words,

$$-\Delta f = -v\Delta p = p\Delta v. \quad (161)$$

Differentiating the ideal gas equation for isothermal changes of volume and pressure, we have

$$\Delta(pv) = p\Delta v + v\Delta p = \Delta(RT) = 0,$$

or

$$v\Delta p = -p\Delta v. \quad (162)$$

Combining this with equation 160, we finally obtain 161, showing that either the term $-v\Delta p$ or $p\Delta v$ represents the work done by the ideal gas during isothermal changes of volume under the variable external pressure. In other words, equation 97 when applied to an ideal gas is equivalent to

$$\Delta f = -s\Delta T - p\Delta v - \Delta w_m.$$

26. Effect of a Force Field on the Free Energy of Water

For the change in free energy Δf during any transformation, equation 97 gives

$$\Delta f = -s\Delta T + v\Delta P - \Delta w_m. \quad (163)$$

At present we want to derive an expression for the change in free energy Δf per unit mass experienced by the water particle P in moving it from B to A (fig. 14), for example, where these points are located in a force field.

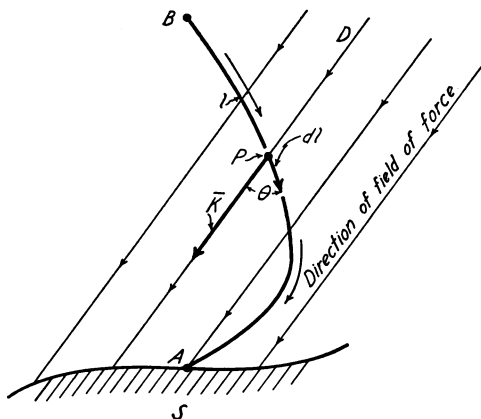


Fig. 14.—Relation between the direction of the force field acting on a body and its path of motion.

During this change neither the temperature nor the external pressure comes into consideration, since we shall regard both these as constant; and therefore both ΔT and ΔP are zero. Equation 163 then becomes

$$-\Delta f = \Delta w_m \quad (164)$$

which says that the work Δw_m per unit mass done by the particle of water on the surroundings in moving from B to A equals the decrease in its specific free energy ($-\Delta f$). According to our convention, a positive Δw_m indicates work done by the water particle (that is, the working substance) and a minus Δw_m indicates work done on the water particle by the surroundings. Of course, if the water moves in the opposite direction (that is, from A to B), work $-\Delta w_m$ will be done by the particle on the surroundings; and the increase in specific free energy of the particle is Δf . These changes are, of course, carried out reversibly, so that the work done by the particle is always equal to that done on the surroundings.

Obviously, this form of free energy is identical with the term “potential” as used throughout the domain of mechanics, electricity, and magnetism; potential is merely a special kind of the numerous forms of free

energy. The great generality and superiority, for some purposes, of the function called "free energy" thus become evident.

The work done per unit mass by a particle on the surroundings in going from a point B to a point A is defined according to mechanics by

$$\Delta w_m = \int_B^A \overline{K} \cdot \overline{dl} \quad (165)$$

where the vector \overline{K} represents both the magnitude and direction of the field of force at the element of the path \overline{dl} . The vector \overline{dl} represents the element of the path both in direction and magnitude, and the dot between the two vectors indicates that the product of the magnitude of the two vectors must be multiplied by the cosine of the angle between the two vectors; that is, $\overline{K} \cdot \overline{dl}$ is a scalar product. For those not acquainted with the vector notations, Δw_m may be expressed in a more common but often more cumbersome form:

$$\Delta w_m = \int_B^A K \, dl \cos \theta, \quad (166)$$

where K and dl are now scalar quantities.

The geometrical interpretation is clarified from a consideration of figure 14. As the particle of water P moves from a point B toward A along the path l , it does an amount of work Δw_m on the surroundings under the influence of the adsorptive force field of the soil particle S , for example. The direction of movement of the particle P makes an angle θ with the assumed direction of the force field, and the total work Δw_m done by the water particle on the surroundings in moving from B to A is given by the integral in equation 166. Of course, if the particle moves in the opposite direction (that is, from A to B) the work Δw_m changes its sign and becomes negative. We then have

$$\Delta w_m = \int_A^B K \, dl \cos \theta. \quad (167)$$

Although Δw_m appears positive according to equation 167 when the particle moves against the field of force, it is really not so, for the cosine of an obtuse angle is always negative. The disguised negative sign under the integral sign then makes Δw_m negative.

The expression for Δw_m takes on a particularly simple form if the line of action of the force is the same as that of the path of movement \overline{dl} . We have two cases. If the particle is moved in the direction of the force field (that is, from B to A) then $\cos \theta = 1$, and

$$\Delta w_m = \int_B^A K \, dl.$$

The particle thus releases energy to the surroundings, since Δw_m is positive. If, on the other hand, the particle is moved in a direction opposite to the field (that is, from A to B) the $\cos \theta = -1$, and we have

$$\Delta w_m = - \int_A^B K \, dl.$$

The water particle therefore gains energy from the surroundings, since Δw_m is negative; and work is done by the surroundings on the particle P to carry it from A to B .

Combining 164 with either 165 or 166, we have in vector notation

$$\Delta f = - \int_A^B \overline{K} \cdot \overline{dl}, \quad (168)$$

or in scalar notation

$$\Delta f = - \int_A^B K \cos \theta \, dl, \quad (169)$$

or in differential form

$$\frac{df}{dl} = -K \cos \theta.$$

As will be recalled from elementary physics, a scalar possesses only magnitude, whereas a vector possesses both magnitude and direction. Hence, as shown above, the rate of change of the free energy of the particle in any direction equals the negative of the component of the field in that direction.

In the special case where the path \overline{dl} coincides with the lines of force, $\cos \theta = +1$; or, if we consider the projection K of the resultant force \overline{K} on the path of integration according to figure 14, equation 169 becomes

$$\Delta f = - \int_A^B K \, dl; \quad (170)$$

or, in differential form,

$$\frac{df}{dl} = -K \quad (171)$$

where K is a scalar rather than a vector. Thus, as mentioned earlier, after equation 117, this form of free energy is analogous to potential as used in mechanics, electricity, and magnetism. We conclude, then, that the change in the specific free energy Δf of the particle of water entailed by its being moved from a point A to a point B in a field of force is given by either of the line integrals in equations 168 and 169 or, in the special case where the direction of the path and field coincide, by equation 170.

To illustrate the meaning of these relations between free energy and

field of force, let us consider a vertical column of liquid water at equilibrium. We wish to study the dependence of the free energy of a water particle on its height \bar{y} above the lower surface S of the column (fig. 15). The distance \bar{y} will be measured from the bottom up, in which case $\cos \theta$ is negative, since the positive direction of \bar{y} is opposite to the direction of the field. We suppose that the strength of the field is the same and equal to \bar{g} at all points above the water surface.

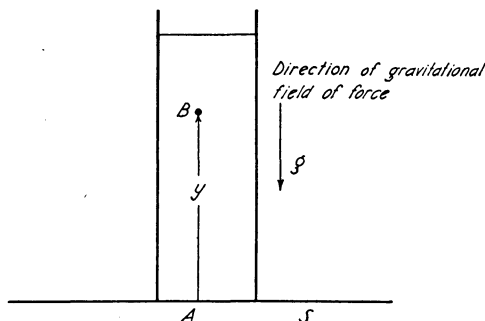


Fig. 15.—Column of water at equilibrium under a gravitational force field.

The total free energy Δf of the particle of water of unit mass at the point B is composed of two parts. One of these, Δf_P , is due to hydrostatic pressure; the other, Δf_F , is due to the position of the particle in the attractive force field. The first is given (eq. 153) by

$$\Delta f_P = \int_A^B v dP \quad (172)$$

and the second (eq. 169) by

$$\Delta f_F = \int_A^B g dy = g \int_A^B dy, \quad (173)$$

since the force $K = g$ is independent of the value of y and $\cos \theta = -1$. The total free energy Δf of the particle of water at the point B , with respect to that at A , is then

$$\Delta f = \Delta f_P + \Delta f_F = \int_A^B v dP + \int_A^B g dy.$$

Since the column of water is in equilibrium, the total free energy of the water must be the same throughout all parts (eq. 117). That is, $\Delta f = 0$. Hence

$$v dP + g dy = 0,$$

or

$$\frac{dP}{dy} = -\frac{g}{v} = -g\rho \quad (174)$$

since $v = \frac{1}{\rho}$ where ρ equals the density of the liquid. Equation 174 gives the well-known relation between the change of hydrostatic pressure and the change of height y in the column of water. It shows, in accordance with common experience, that as the height y increases, the hydrostatic pressure decreases.

THERMODYNAMIC INTERRELATIONS AMONG THE PROPERTIES OF SOIL MOISTURE

27. Relation between the Changes of Pressure ΔP and Temperature ΔT if Two Pure Phases Are to Remain in Equilibrium—Clausius-Clapeyron Equation

As will be recalled (art. 22), if two phases of a substance are in equilibrium with each other, their specific free energies must be the same. To fix our ideas, suppose the two phases are ice and water at 0°C and at 1 atmosphere. If now the pressure on the system is changed, the equilibrium is disturbed, and the free energies will no longer remain equal unless other changes are made in the system.

An increase of pressure, keeping the temperature unchanged, will cause the free energy of the ice to become greater than that of the water, because (eq. 157)

$$\left(\frac{\partial f}{\partial P}\right)_T = v. \quad (175)$$

Since for water, at 0°C , $v = 1.000 \text{ cc}$, the rate of increase of the free energy of water with respect to pressure is

$$\left(\frac{\partial f}{\partial P}\right)_T = 1.000. \quad (176)$$

And since for ice, at 0°C , $v = 1.090$, we have for ice

$$\left(\frac{\partial f}{\partial P}\right)_T = 1.090. \quad (177)$$

Evidently the free energy of the ice increases more than that of water for a given change of pressure. Thus the ice at 0°C will have a greater free energy at pressures higher than 1 atmosphere. As will be discussed later, the 1 atmosphere enters because of the peculiar definition of 0°C : 0°C is taken as the freezing point of water under a pressure of 1 atmosphere.

As will be recalled, free energy always decreases in a spontaneous change. Only when there is no possibility for the free energy to decrease will the system remain in equilibrium. From equations 176 and 177 we see that a given change in pressure causes a greater increase in the free energy of ice than it does in water. Consider ice and water at equilibrium under a given temperature and pressure. If now the pressure is raised, the free energy of the ice has a possibility of decreasing if it passes into the liquid state. All the ice accordingly melts. If, therefore, we have ice and water at equilibrium, an isothermal rise of pressure causes the ice to melt. By similar reasoning, since a given decrease in pressure causes a greater decrease of the free energy of ice than it does of water (eq. 176 and 177), it is clear that if ice and water are in equilibrium and the pressure is then decreased, all the water will pass into ice.

On the other hand, if we now keep the pressure constant and vary the temperature of the two phases originally in equilibrium, the specific free energies of the two phases will change differently according to equation 143, which is

$$\left(\frac{\partial f}{\partial T}\right)_P = -s. \quad (178)$$

According to equation 178, when the temperature is raised, the phase whose specific entropy s is the least will disappear completely, since its final free energy after the temperature change would be greatest. Likewise when the temperature is lowered, the phase whose specific entropy s is the greatest will disappear completely, since its final free energy after the temperature change would be greatest.

We have just considered how temperature and pressure affect the equilibrium of two phases originally in equilibrium with each other. One of the phases always disappears when either the temperature or pressure alone is changed from the equilibrium value. Let us now vary both temperature and pressure simultaneously in such a way that the amounts of the phases remain unchanged. We want to find the relation between the changes of the temperature ΔT and pressure ΔP that permit the phases to coexist. If f_1 , s_1 , and v_1 are the quantities associated with the first phase and if f_2 , s_2 , and v_2 are those of the second, and if the two phases are to be in equilibrium, we have (art. 22)

$$f_1 = f_2. \quad (179)$$

This means that when any change occurs in the system, the two free energies must change by an equal amount, namely,

$$df_1 = df_2. \quad (180)$$

Since only two variables such as P and T are required to fix the state of a substance, which we shall describe by the specific free energy f , and since the free energy is a perfect differential, we have (art. 2)

$$df_1 = \left(\frac{\partial f_1}{\partial P} \right)_T dP + \left(\frac{\partial f_1}{\partial T} \right)_P dT \quad (181)$$

and

$$df_2 = \left(\frac{\partial f_2}{\partial P} \right)_T dP + \left(\frac{\partial f_2}{\partial T} \right)_P dT. \quad (182)$$

Substituting 181 and 182 into 180 and recalling 143 and 157, we have

$$v_1 dP - s_1 dT = v_2 dP - s_2 dT. \quad (183)$$

This equation could, of course, have been obtained immediately from the generalized definition of the differential of the free energy given by equation 97, since no useful work dw_m is done. Rearranging 183 and collecting like terms, we have

$$\frac{dP}{dT} = \frac{s_2 - s_1}{v_2 - v_1}. \quad (184)$$

The quantity $(s_2 - s_1)$ gives the change in specific entropy in going from phase 1 to phase 2 without change of temperature and pressure. For example, if we were transforming ice to water, $(s_2 - s_1)$ would be the difference in entropy of the two phases. As before (eq. 84), we now also have

$$s_2 - s_1 = \frac{\Delta h}{T}$$

where Δh is the latent heat involved in changing a gram from the first phase to the second. If we are dealing with ice and water, Δh would be the well-known heat of fusion of ice l . The quantity $(v_2 - v_1) = \Delta v$ represents the increase in volume per gram of the substance in going from the first to the second phase. Equation 184 then becomes the well-known Clausius-Clapeyron equation and is

$$\left. \begin{aligned} \frac{dP}{dT} &= \frac{\Delta h}{T \Delta v}, \\ \text{or} \quad dP &= \frac{\Delta h dT}{T \Delta v}, \end{aligned} \right\} \quad (185)$$

or for water

$$\frac{dP}{dT} = \frac{l}{T \Delta v}. \quad (186)$$

Although equation 186 was applied above to the equilibrium between the two phases liquid and solid, it applies equally well to the equilibrium between any two phases. For example, when water passes from liquid to vapor, Δh or l and Δv are both positive. Equation 186 therefore predicts that an increase of pressure dP causes an increase dT of the boiling point.

When water passes from ice to liquid, Δh or l is positive and Δv is negative, since ice contracts upon melting. Equation 186 predicts, therefore, that an increase of pressure dP causes a decrease dT of the melting point of water. This is borne out by the common phenomenon of regelation, a special case of which is the flowing of glaciers. The ice melts at those points where pressure is applied and refreezes elsewhere. In particular, equation 186 gives, for finite changes, the effect of hydrostatic pressure on the freezing-point depression ΔT of a liquid as follows:

$$\Delta P = \frac{l\Delta T}{T\Delta v}. \quad (187)$$

If we are dealing with a solution, equation 187 applies quite independently of any dissolved material, the effect of which will be discussed in article 29.

The present article has taken up the treatment of the dependence of the freezing-point depression ΔT on the hydrostatic pressure ΔP when the latter has been kept the same on both phases. The treatment of the case where the pressure on one phase is different from that on the other is taken up in the more generalized treatment of article 30, and there is some plausible evidence that the freezing-point depression of relatively moist soils might fall under the latter case.

28. Dependence of the Free Energy of a Liquid Δf on the Hydrostatic Pressure ΔP as Measured by Its Freezing-Point Depression ΔT

As will be recalled from equation 156, the free energy Δf of a liquid under a hydrostatic pressure ΔP is given by

$$\Delta f = v\Delta P \quad (188)$$

where v denotes the specific volume of the liquid. Substituting equation 185 into 188, we have

$$\Delta f = \frac{v\Delta h}{T\Delta v} \Delta T \quad (189)$$

which expresses the free energy Δf of a liquid, due to hydrostatic pressure, in terms of its freezing-point depression ΔT . For water, $v = 1$ in the c.g.s. system, and $\Delta h = l$, so that

$$\Delta f = \frac{l\Delta T}{T\Delta v}. \quad (190)$$

29. Relation between the Changes of Pressure ΔP and Temperature ΔT for a Solution to Remain in Equilibrium with the Solid Phase of the Pure Solvent

The relation dealt with in this article might be considered as the Clausius-Clapeyron equation for solutions. The thermodynamic treatment will be remarkably similar to the case taken up in article 27, which was gone through in somewhat greater detail than will be undertaken here. To fix our ideas for the present, suppose we consider pure water and ice initially in equilibrium at 0°C . (The present treatment, however, applies to the equilibrium between two phases of any substance, one of the phases of which contains dissolved material.) Let f_1 represent the specific free energy of the ice, f_2 that of the liquid water. Since the ice and pure water are in equilibrium with each other at 0°C , we have

$$f_1 = f_2 .$$

Suppose we now add an amount of solute to the pure liquid water sufficient to raise its osmotic pressure from zero to ΔP_o . This disturbs the equilibrium between the two phases, and causes the specific free energy f_2 of the solvent to be decreased. Since the two parts of the system have now different specific free energies, a spontaneous change will occur according to inequality 116, tending to decrease the total free energy of the system. The ice, having a higher specific free energy f_1 , will therefore melt and become a liquid having a lower specific free energy f_2 . We see, therefore, that without change of temperature, the ice and water cannot be kept in equilibrium if the amount of solute (and consequently the osmotic pressure ΔP_o of the solvent) is changed. To keep the ice and solution in equilibrium and thus to prevent the disappearance of one of the phases, the temperature of the two phases as a whole must be changed by an amount ΔT . As is well known, the addition of salt to an ice-and-water mixture lowers its freezing point, which is the equilibrium temperature for the mixture of solution and pure ice.

We now wish to find the relation between the osmotic pressure ΔP_o of the solution and the necessary change in temperature ΔT in order that the ice and solution may remain in equilibrium. Assume that the temperature is changed from T to $T + \Delta T$. We must recall (from eq. 118) that in order to have equilibrium at the new temperature $T + \Delta T$ the new free energy of the ice f_1 must equal that of the solution f_2 . That is, both initially and finally we have

$$f_1 = f_2 ,$$

and therefore

$$df_1 = df_2 . \quad (191)$$

The specific free energy of the water in the form of ice depends here only upon the temperature and not explicitly on the pressure, since the system is assumed to be under atmospheric pressure at all times and therefore under a constant hydrostatic pressure. Hence (by eq. 3) we have

$$df_1 = \left(\frac{\partial f_1}{\partial T} \right) dT.$$

With equation 143 this becomes

$$df_1 = -s_1 dT. \quad (192)$$

The specific free energy of the water of the solution, on the other hand, depends not only upon the temperature change ΔT but also on the amount of solute present, which we shall here measure by the osmotic pressure of the solution ΔP_o . The change in the free energy of the solvent of the solution df_2 therefore depends upon two variables, and (by eq. 3) we have

$$df_2 = \left(\frac{\partial f_2}{\partial P_o} \right)_T dP_o + \left(\frac{\partial f_2}{\partial T} \right)_{P_o} dT.$$

With equations 152 and 143 this becomes

$$df_2 = -v_2 dP_o - s_2 dT. \quad (193)$$

Introducing 192 and 193 into 191 and remembering that v_2 is nothing more than v , the specific volume of the pure solvent, we have

$$-s_1 dT = -v dP_o - s_2 dT. \quad (194)$$

Rearranging 194, we have

$$\frac{dP_o}{dT} = - \frac{(s_2 - s_1)}{v}. \quad (195)$$

As in article 27, $(s_2 - s_1)$ gives the change in entropy of the solvent in going isothermally and isobarically from phase 1 to phase 2. We may now write (eq. 84)

$$s_2 - s_1 = \Delta s = \frac{\Delta h}{T} \quad (196)$$

where Δh is the latent heat that must be added per gram in going from the first to the second phase. When we are dealing with ice and water, Δh would be the well-known heat of fusion of ice l . Inserting 196 in 195 we have

$$\frac{dP_o}{dT} = - \frac{\Delta h}{vT} \quad \text{or} \quad dP_o = - \frac{\Delta h}{vT} dT. \quad (197)$$

In particular for water

$$\frac{dP_o}{dT} = -\frac{l}{vT} \quad \text{or} \quad dP_o = -\left(\frac{l}{vT}\right)dT. \quad (198)$$

For finite changes, 197 and 198 become

$$\Delta P_o = -\left(\frac{\Delta h}{vT}\right)\Delta T \quad (199)$$

and

$$\Delta P_o = -\left(\frac{l}{vT}\right)\Delta T. \quad (200)$$

All the quantities in the parentheses of equation 199 are positive. Whenever, therefore, soluble material, whose amount is measured by the osmotic pressure ΔP_o of the solution, is added to a solution, the freezing point of the solution is depressed by the amount $(-\Delta T)$.

Equation 199 is quite general and is not restricted to describing equilibria between ice and water. It will, for example, predict how the boiling point of water changes with changes in its content of dissolved material. As a measure of the amount of dissolved material, we can take the osmotic pressure ΔP_o of the solution according to equation 226.

By equation 199 we shall show that as the amount of dissolved material in the solution increases, the boiling point of the solution also increases. According to previous conventions, we must take the water vapor as phase 1. The second phase is therefore, as before, the solution. Consequently, Δh will represent the heat that must be added to the water vapor in order to condense it to the liquid phase. This is negative, since actually an amount of heat equal to the heat of vaporization of the water must be removed from the steam to condense it to water at 100° C; that is, $\Delta h = -540$ calories, or -2.27×10^{10} ergs per gram. The term v is the specific volume of the water at 100° C and therefore equals approximately unity in the c.g.s. system. Equation 199 then gives for the osmotic pressure

$$\Delta P_o = \frac{2.27 \times 10^{10}}{1 \times 373} \Delta T \text{ dynes per cm}^2$$

and enables one to calculate the rise in the boiling point of water ΔT attendant upon the addition of an amount of dissolved material producing the osmotic pressure ΔP_o .

Since by equation 226, the osmotic pressure can be calculated immediately for dilute solutions from the amount of dissolved material, we see that equation 199 at the same time predicts both a decrease of the freezing point and a rise of the boiling point of a solution with increase in the amount of dissolved material.

30. Generalized Treatment of the Effect of Pressure on the Freezing Point, and Its Application to Relatively Moist Soils—Generalized Clausius-Clapeyron Equation

Equation 186 gives the change in freezing point dT caused by a change in hydrostatic pressure dP on water. The hydrostatic pressure as well as any changes in its value was exerted uniformly on both the phases (ice and water). Under these conditions, the freezing point is lowered 0.00748°C per atmosphere increase of pressure, as is shown later in this article. This is only a special case of the following generalized treatment. We shall now consider the case where the hydrostatic pressure exerted uniformly on the ice differs from that exerted uniformly on the water. As another special case of this, we shall find that the freezing point of water is lowered 0.0899°C per atmosphere increase of pressure on the ice alone, the pressure on the water remaining unchanged. This depression is twelve times as great as that which is observed when the pressure is exerted uniformly on both the water and the ice.

In order to be specific, we derive the following expressions with respect to ice and water, but the results apply equally to the freezing point of any other substance.

Consider figure 16, in which P_I represents the pressure exerted uniformly on the ice by a piston that is permeable to water vapor only and P_W represents the pressure exerted uniformly on the water by a piston that is permeable to water vapor only, P_W and P_I being always so related that there is a common vapor pressure p throughout. This, of course, means that the three phases are always in equilibrium with each other. The total hydrostatic pressures in the water and in the ice are then

$$P_2 = p + P_W,$$

and

$$P_1 = p + P_I,$$

respectively, as indicated in the figure, since the vapor pressure is acting on both the ice and the water. Let T be the freezing point of the water under these conditions, that is, the temperature at which all three phases are in equilibrium with each other. In the following discussion, v_1 , s_1 , and

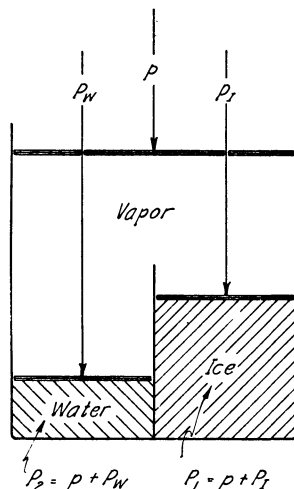


Fig. 16.—Equilibrium between the solid, liquid, and vapor, when the pressure exerted on each of the three phases may be different.

f_1 are quantities associated with the ice phase and v_2 , s_2 , and f_2 with the liquid phase.

With these pressures, we now seek an expression relating the change in freezing point dT to a change in any one or all of the pressures. Since we have postulated that the phases are to be in equilibrium, we have (art. 22)

$$f_1 = f_2.$$

This means that when any change occurs in the system, the two free energies must change by an equal amount, namely,

$$df_1 = df_2.$$

In the same manner as with equation 180, we substitute for df_1 and df_2 above and obtain

$$v_1 dP_1 - s_1 dT = v_2 dP_2 - s_2 dT$$

since dP_1 and dP_2 are the total changes in pressure on the ice and water, respectively. Unlike the previous case, these two pressures are in general not now equal to each other. The above equation could, of course, have been obtained immediately from the generalized definition of the differential of the free energy given by equation 97, since no appreciable useful work dw_m is done in changing the pressures on two such almost incompressible phases as ice and water. Substituting for dP_1 and dP_2 in the above, and dividing through by dT , we have

$$v_1 \left(\frac{dp}{dT} + \frac{dP_I}{dT} \right) - s_1 = v_2 \left(\frac{dp}{dT} + \frac{dP_W}{dT} \right) - s_2.$$

Rearranging, we have

$$\frac{v_2 dP_W}{dT} - v_1 \frac{dP_I}{dT} + \frac{dp}{dT} (v_2 - v_1) = (s_2 - s_1)$$

and exactly as in obtaining equation 186, we may set

$$s_2 - s_1 = \frac{l}{T},$$

where $s_2 - s_1$ is the difference in the specific entropies of the two phases in equilibrium with each other and l is the latent heat of fusion of ice and is positive. We have then

$$\frac{v_2 dP_W}{dT} - v_1 \frac{dP_I}{dT} + \frac{dp}{dT} (v_2 - v_1) = \frac{l}{T}. \quad (201)$$

This equation was first derived by Hudson (80) through an entirely different line of reasoning. He recognized the following four ways in which the freezing point is changed by changes of pressure.

Case 1. *The total change in pressure on the ice is always equal to the total change in pressure on the water.* Consequently, $dp + dP_w = dp + dP_I$. Let the total change equal dP . Equation 201 becomes then

$$\frac{dp + dP_w}{dT} = \frac{dp + dP_I}{dT} = \frac{dP}{dT} = \frac{l}{(v_2 - v_1)T}. \quad (202)$$

This is the special case taken up in article 27. Substitution of the proper values for the specific volume of water, v_2 , and ice, v_1 , and the latent heat of fusion l from ice to water (the latter is positive as brought out in art. 27), we find that a total increase in pressure dP equal to 1 atmosphere lowers the freezing temperature by the usual amount $dT = 0.00748^\circ \text{C}$.

Case 2. *The pressure on the water remains constant while the pressure on the ice is changed.* Consequently,

$$\frac{dP_w}{dT} = 0,$$

and equation 201 becomes, after dividing through by v_1 ,

$$\frac{dP_I}{dT} = -\frac{l}{Tv_1} - \frac{dp}{dT} \left(1 - \frac{v_2}{v_1}\right). \quad (203)$$

The first term on the right is many thousand times as large as the last term, as may be seen by substituting the proper values for the different terms; hence the last may be neglected, and we have

$$\frac{dP_I}{dT} = -\frac{l}{Tv_1}. \quad (204)$$

Substitution of the proper values in the right side of this shows that an increase in pressure, dP_I on the ice alone, equal to 1 atmosphere, *lowers* the freezing temperature by the amount $dT = 0.0899^\circ \text{C}$, a depression which is twelve times as great as that which is observed in case 1 when the pressure is exerted uniformly on the water and ice.

Case 3. *The pressure on the ice remains constant while the pressure on the water is changed.* Consequently,

$$\frac{dP_I}{dT} = 0,$$

and equation 201 becomes, after dividing through by v_2 ,

$$\frac{dP_w}{dT} = +\frac{l}{Tv_2} + \frac{dp}{dT} \left(\frac{v_1}{v_2} - 1\right);$$

and neglecting the small second term on the right, as was done in case 2, we have

$$\frac{dP_w}{dT} = + \frac{l}{Tv_2}. \quad (205)$$

Substitution of the proper values in the right side of this equation shows that an increase in pressure dP_w on the water alone, equal to 1 atmosphere, raises the freezing temperature by the amount $dT = 0.0824^\circ \text{C}$. This is in complete contrast to case 2.

Equation 205 might well describe, for relatively moist but not saturated soils, the relation between dP_w , the tension in soil moisture (as measured by a tensiometer for example) and dT , the corresponding freezing-point depression (as determined by the customary Beckmann method) if the soil moisture (under a state of tension depending upon the soil moisture content) is transformed to ice (under atmospheric pressure) upon freezing. This follows because if we have ice and water at equilibrium under atmospheric pressure, then the freezing point will be 0°C . Now if we change the pressure on the water alone, so that it is under the same tension dP_w as the soil moisture, then dT , the freezing-point depression of the system, should be given by equation 205. That the change in the freezing point dT is negative (indicating a freezing-point depression) is seen immediately from equation 205 when it is recalled that dP_w (the tension that must be put on the free water to place it in equilibrium with the soil moisture) is negative. A comparison of equation 198 with 205 shows that an osmotic pressure dP_o will cause the same freezing-point depression dT as a tension dP_w in the soil moisture, provided that when the soil moisture freezes to ice, the ice separates out from the soil moisture to a higher pressure of 1 atmosphere.

Schofield (138) gives an equation for calculating the freezing-point depression of soil moisture whose form may be transformed into that of equation 205 when certain suspected typographical errors in his published equation are corrected. He does not give any derivation for it, though, but mentions that the pF values, calculated from freezing-point depressions, he has plotted in his curve were calculated by means of it.

The total freezing-point depression of any relatively moist normal soil would in this case be the sum of (1) the effect of pressure given by equation 205 and (2) the effect of dissolved material in the soil solution given by equation 198.

Case 4. *The total changes in pressure on the ice and water are always so related that the freezing temperature remains constant.* Consequently, $dT = 0$ and equation 201 becomes, upon rearrangement,

$$\frac{(dP_I + dp)}{(dP_w + dp)} = \frac{d(P_I + p)}{d(P_w + p)} = \frac{dP_1}{dP_2} = \frac{v_2}{v_1}.$$

Thus if the changes in pressure on the water and ice are inversely proportional to the specific volumes, the freezing temperature will not change.

Let us now illustrate the application of the above four cases by a consideration of several specific examples. Let us first find the freezing temperature of water which is under a pressure of 10 atmospheres when upon freezing it is transformed into ice under a pressure of 16 atmospheres. According to case 1, ice and water are in equilibrium under a uniform pressure of 10 atmospheres at $-10(0.00748)^{\circ}\text{C}$. If a pressure of 6 additional atmospheres be applied to the ice alone, the freezing temperature will, according to case 2, fall an additional $6(0.0899)$ degrees. The resultant freezing temperature of the system is -0.614°C .

But suppose the uniform pressure on the water is 16 atmospheres when its ice is under a pressure of only 10 atmospheres. By case 1, ice and water are again in equilibrium under a uniform pressure of 10 atmospheres at $-10(0.00748)^{\circ}\text{C}$. If now, 6 additional atmospheres be applied to the water alone, the freezing temperature will, by case 3, rise $6(0.0824)$ degrees and will finally be 0.420°C above zero.

The use of the four cases may be also illustrated by showing that the lowering of the freezing point of solutions can be considered as the result of osmotic pressure acting as a negative pressure tending to expand the water. At first, this seems strange. It is known that ordinarily a positive pressure lowers the freezing temperature of water and a negative pressure raises the freezing temperature; therefore it might seem that solutions should freeze above 0°C rather than below, if the dissolved material produces a tension. As has been pointed out by Hudson (80), this reasoning is not correct, because the ice which freezes from a solution is under atmospheric pressure, not negative pressure; and only the solution may be properly regarded as being under a negative pressure, caused by the dissolved substance. Both the ice and solution are, of course, under atmospheric pressure, but in the case of the solution, the dissolved substance in effect contributes an additional negative pressure to the water. Let us assume that the dissolved material has the same tendency to expand that part of the solvent containing the dissolved material as the molecules of a perfect gas have to expand the volume they occupy. This might be thought of as causing a tension $-P_w$ in the water of the solution tending to pull it apart, and determined by $P_w v = x_2 RT$ where x_2 is the mol fraction of the solute in the solution. (This is recognized to be nothing more than the ideal gas law where R is the gas constant per gram.) Since this falls under case 3, let us substitute this expression for $-P_w$ for that in the expression under case 3 and obtain, after rearrangement,

$$dT = -\frac{RT^2}{l} dx_2 = -\frac{RT^2}{l} x_2,$$

since dx_2 is measured with respect to the pure solvent. This is the same as the well-known relation that van't Hoff obtained for the freezing-point depression, dT , produced by the addition of an amount of solute dx_2 , according to article 38. From the agreement of these two expressions for the molecular depression of the freezing temperatures, we must conclude that solutions may be regarded as being under a negative pressure, comparable with a positive mechanical tension, this negative pressure being caused by the dissolved substance and being numerically identical with the osmotic pressure of the solution.

Let us consider another illustration. As pointed out under case 4, it is possible to apply pressure to the ice and water in such a way as not to change the freezing point of the water. We had

$$\frac{dP_1}{dP_2} = \frac{v_2}{v_1}.$$

The specific volume of ice is $v_2 = 1.0909$, and of water, $v_1 = 1.0001$ cc per gram, respectively. Thus

$$\frac{dP_1}{dP_2} = 1.09,$$

so that the freezing temperature of the water will always remain the same no matter what pressure is applied to it so long as the pressure applied to it is 9 per cent greater than that simultaneously applied to the ice.

Finally, although it has never, so far as is known, been pointed out, it seems that freezing according to case 3 might occur in the freezing of soil moisture in the soil during winter. Of course, if as pointed out previously under case 3, the ice (freezing out from the relatively moist soil) separates out from the soil moisture to a pressure of 1 atmosphere, then this case must always occur. Suppose in a soil cavity some distance above a water table, we have an isolated particle of ice; and suppose also that below this cavity and extending down to the water table are capillary columns of water. Since the water in the capillaries is under tension, it will, at 0°C , have a lower vapor pressure than the particle of ice. Consequently, the moisture system in the cavity will not be at equilibrium at that temperature, and the ice will distill over to the water in the capillaries. The temperature of equilibrium may be calculated as follows: the water in the capillaries leading up to the cavity is under a tension that is less than atmospheric by an amount given by the height of the capillaries according to article 42. If, for the sake of our present argument, we assume that the water table is 76×13.6 centimeters below the cavity and that all the soil capillaries are small enough to raise the water this high, then the

hydrostatic pressure in the water at the upper end of the soil capillaries having their terminals in the cavity is -76×13.6 grams, or minus 1 atmosphere. At 0°C , if the water in the soil capillaries were not under tension, it would be in equilibrium with the isolated particle of ice in the cavity and would freeze at 0°C ; however, in our present case, we must consider the pressure on the particle of ice in the cavity as remaining constant, whereas the pressure on the capillary water adjacent to the cavity has been decreased by 1 atmosphere. Thus, according to case 3, the ice-particle-soil-moisture system in the cavity will be in equilibrium at -0.0824°C , at which temperature that part of the soil moisture adjacent to the cavity which is under a tension of 1 atmosphere will begin to freeze. That is, the freezing point of the soil moisture which is under a tension of 1 atmosphere is in the present case -0.0824°C , since the particle of ice is isolated from the water; and not $+0.00748^\circ \text{C}$, as might at first have been expected if case 1 had inadvertently been applied under the assumption that the ice was attached to the water and both were under the same pressure. In general, if the soil capillaries are small enough and the cavity containing the isolated particle of ice is h centimeters above the water table, the freezing temperature of the moisture adjacent to the soil cavity is

$$h \left(\frac{0.0824}{76 \times 13.6} \right) \text{degrees below } 0^\circ \text{C}.$$

Freezing according to case 3 might also occur in the freezing of soils when the Beckmann technique is used at relatively high soil moisture contents.

31. Dependence of the Free Energy of a Solvent Δf on the Amount of Dissolved Material as Measured by Its Freezing-Point Depression ΔT

As will be recalled (eq. 151), the free energy Δf of a liquid having an osmotic pressure ΔP_o is given by

$$\Delta f = -v\Delta P_o, \quad (206)$$

where v denotes the specific volume of the pure solvent. Substituting equation 199 into 206, we have

$$\Delta f = \frac{\Delta h}{T} \Delta T,$$

which expresses the free energy Δf of a solution with respect to that of the pure solvent due to the presence of dissolved material in it, in terms of its freezing-point depression ΔT . For water, let us use the more customary

symbol l in place of Δh for the latent heat of transition from one phase to the other; we then have

$$\Delta f = \frac{l}{T} \Delta T. \quad (207)$$

Although for concreteness in the derivation we have considered the transition between a water solution and ice, these equations are perfectly general and apply to any solution in equilibrium with another phase of one of its components in the pure state.

Equation 189 for the free energy due to hydrostatic pressure resembles 207 for the free energy due to osmotic pressure. Both express Δf in terms of the freezing-point depression ΔT ; but 189 contains Δv and v , the expansion of the liquid upon freezing and its specific volume respectively, whereas 207 contains neither.

32. Dependence of the Free Energy of a Liquid Surface Possessing a Surface Tension σ on Its Area A

As will be recalled from elementary physics, the surface tension σ of a liquid is defined as the tensional force in dynes per unit of length of the film measured, the tensional force being measured in a direction normal to the unit of length in the film. Thus if we increase the area of the film by an amount dA , the work done on the system composed of the vapor-liquid interface of area A will have been σdA . As will be noticed, surface tension can be expressed either as dynes per centimeter or as ergs per square centimeter. In either case, the dimensions of surface tension will be seen to be the same.

Now the mechanical work done on a system at constant temperature, excluding the work of expansion against a pressure P , has been found to equal the increase of the free energy of the system according to equation 99. Thus the increase in the total free energy of a liquid surface A when its area is increased by the amount ΔA is given by

$$\Delta F = \sigma \Delta A. \quad (208)$$

Since, however, by convention the free energy Δf should refer to the energy per gram of the water and since equation 208 as it stands refers to the total free energy ΔF of an element of surface ΔA , we must change the above equation. If we let τ represent the thickness of the surface layer of water in which the properties are different from the main body of the liquid, then the average of free energy per gram throughout the liquid surface layer may be represented by

$$\Delta f = \frac{\sigma}{\tau \rho}, \quad (209)$$

where ρ represents the average density of the water in the layer of thickness τ .

As will be shown (art. 46), the total specific surface energy is always greater than the surface tension σ or the total free energy ΔF per unit area as given by equation 208.

33. Dependence of the Free Energy of a Liquid on Its Surface Tension and Its Radius of Curvature

As will be shown (eq. 272), we have for the vapor pressure p over a curved vapor-liquid interface whose radius of curvature is r , where the vapor pressure over the free water is p_0 and where the surface tension is σ , the equation

$$\ln \frac{p}{p_0} = \frac{v}{RT} \frac{2\sigma}{r}. \quad (210)$$

From equation 159 we have then for the free energy of the vapor above, or of the liquid below the curved vapor-liquid interface

$$\Delta f = RT \ln \frac{p}{p_0} = \frac{2\sigma v}{r} \quad (211)$$

where v , the specific volume, is unity for water in the c.g.s. system and where the sign of r is negative if the vapor-water interface is concave to the vapor as is true for soil moisture. If we are dealing with water droplets, r is positive, and equation 210 predicts an increase in the vapor pressure p over that of the vapor pressure p_0 of the datum, which we have taken as free, pure water.

34. Dependence of the Free Energy of the Solvent of a Solution on the Amount of Dissolved Material Present

Raoult's law applies to the solvent in a dilute solution and states that its vapor pressure p is proportional to its mol fraction x . That is,

$$p = cx, \quad (212)$$

where c is the constant of proportionality. We wish to express 212 in terms of free energy f rather than of vapor pressure p .

Consider x and x_0 , two mol fractions of the solvent. These will determine two different equations of the type 212. Dividing one of these by the other and taking the logarithm of both sides, we have

$$\ln \frac{p}{p_0} = \ln \frac{x}{x_0}. \quad (213)$$

Multiplying both sides of equation 213 by RT , we have (eq. 159 and art. 22) for the free energy Δf of the solvent at one mol fraction x , expressed in terms of its value at the other mol fraction x_0 , the equation

$$\Delta f = (f - f_0) = RT \ln \frac{p}{p_0} = RT \ln \frac{x}{x_0}, \quad (214)$$

where it is assumed that the behavior of the vapor of the solvent approximates that of the ideal gas. Suppose that p_0 refers to the vapor pressure of the pure solvent. Then x_0 will be the mol fraction of the pure solvent. That is, by the usual definition of the mol fraction, $x_0 = 1$ exactly. From equation 214 we can then write

$$f = f_0 + RT \ln x, \quad (215)$$

where f_0 now equals the free energy of the free, pure solvent, which by our previous conventions is our datum, or zero point of free energy for a liquid. Since f_0 , the free energy of the datum, is a constant, equation 215 becomes by differentiation, where p and T are held constant,

$$\left(\frac{df}{dx} \right)_{pT} = \frac{RT}{x}. \quad (216)$$

As we shall wish to distinguish between the mol fraction of the solvent and of the solute in later discussions, we shall let x_1 represent the mol fraction of the solvent and x_2 that of the solute. Hence in the equation above, x will be changed into x_1 . Since, presumably, we are dealing with a dilute solution, the mol fraction x_1 of the solvent must be very close to unity. We see this because if m_1 is the number of mols of the solvent and m_2 the number of mols of the solute present in the solution, then the mol fraction x_1 of the solvent is defined by

$$x_1 = \frac{m_1}{m_1 + m_2} \quad (217)$$

If the concentration of the solution is low, m_2 must also be small in equation 217. The mol fraction x_1 of the solvent is therefore equal approximately to unity in a dilute solution. Such an approximation can be made in equation 216 without altering it appreciably; and 216 therefore becomes

$$\left(\frac{\partial f_1}{\partial x_1} \right)_{pT} = RT, \quad (218)$$

where the subscripts pT have been added merely as a reminder that the temperature and external pressure are to be kept constant during all changes of concentration in these solutions. Equation 218 gives the dependence of the free energy of the solvent f_1 on its mol fraction x_1 .

For future use, we shall also wish to express the changes in the free energy of the solvent f_1 in terms of changes in the mol fraction of the solute x_2 . To do this let us first recall that for a binary solution,

$$x_1 = \frac{m_1}{m_1 + m_2}$$

and

$$x_2 = \frac{m_2}{m_1 + m_2} ;$$

therefore

$$x_1 + x_2 = 1 . \quad (219)$$

Differentiating 219, we find

$$dx_1 = -dx_2 . \quad (220)$$

Inserting 220 into 218

$$\left(\frac{\partial f_1}{\partial x_2} \right)_{p,T} = -RT . \quad (221)$$

Equations 218 and 221 are merely two other ways of stating Raoult's law in terms of free energy rather than vapor pressure. Equation 221 states, by the way, that as the weight fraction x_2 of the solute increases (that is, as the solution becomes more concentrated) the free energy f_1 of the solvent decreases. Equation 218, on the other hand, states that as the proportion of solvent x_1 increases, the escaping tendency, or free energy f_1 , of the solvent increases. These two expressions will become useful in later considerations.

For finite changes equation 221 may be written

$$\Delta f_1 = -RTx_2 . \quad (222)$$

Equation 222 gives the free energy Δf_1 of the solvent of a solution with respect to that of the free, pure solvent, which we have taken as the datum or zero point of free energy. As the amount of dissolved material x_2 continues to increase, the free energy of the solvent Δf_1 continues to decrease.

35. Dependence of the Osmotic Pressure of a Solution on the Amount of Solute Present—Van't Hoff's Law of Osmotic Pressure

As has been shown (eq. 221), the absolute free energy f_1 of a solvent is always decreased by the addition of a solute at constant temperature and pressure. By the application of a pressure ΔP to the solution, however, the free energy of the solvent can be restored to its value in the pure state. The hydrostatic pressure ΔP that must be applied to the solution in order to place it in equilibrium with the pure solvent has been defined in article 24 as the osmotic pressure ΔP_o of the solution.

In general, since the absolute free energy f_1 of the solvent of a solution depends both on the hydrostatic pressure and on the mol fraction of solute present, and since df_1 is a perfect differential (art. 1), we have

$$df_1 = \left(\frac{\partial f_1}{\partial P} \right)_{x_2 T} dP + \left(\frac{\partial f_1}{\partial x_2} \right)_{PT} dx_2, \quad (223)$$

where the temperature is assumed to remain constant. Suppose that as the mol fraction of solute x_2 in the solution is varied, the hydrostatic pressure P on the solution is so adjusted as always to keep the absolute free energy f_1 of the solvent the same as that of the free, pure solvent. We then have $df_1 = 0$ in equation 223, which now becomes

$$\left(\frac{\partial f_1}{\partial P} \right)_{x_2 T} dP + \left(\frac{\partial f_1}{\partial x_2} \right)_{PT} dx_2 = 0. \quad (224)$$

Substituting equations 157 and 221 into 224, we have

$$v dP - RT dx_2 = 0,$$

or

$$\frac{dP}{dx_2} = \frac{RT}{v}. \quad (225)$$

If x_2 represents the total mol fraction of all dissolved material of the solute present, this equation becomes

$$\Delta P = \frac{RT}{v} x_2.$$

As was mentioned at the beginning of this article, the ΔP is equal to the osmotic pressure ΔP_o ; and we have, accordingly,

$$\Delta P_o = \frac{RT}{v} x_2. \quad (226)$$

This is a statement of van't Hoff's law. Equation 226 thus gives the osmotic pressure ΔP_o of a dilute solution in terms of the amount of solute present, expressed in terms of its mol fraction x_2 .

36. Dependence of the Vapor Pressure of the Solvent of a Solution on the Amount of Dissolved Material Present

Let us assume that we start out with a free, pure solvent whose vapor pressure is p_0 . If we add an amount of dissolved material whose value is given by the mol fraction x_2 , the vapor pressure of the solvent will be lowered to p . By equation 159 and article 22, the free energy of the solvent of the solution expressed in terms of the vapor pressures is given by

$$\Delta f_1 = RT \ln \frac{p}{p_0}; \quad (227)$$

and in terms of the mol fraction of dissolved material x_2 according to equation 222 it is

$$\Delta f_1 = -RT x_2. \quad (228)$$

Equating 227 and 228 and solving for the vapor pressure of the solvent of the solution, we have for dilute solutions

$$p = p_0 e^{-x_2} \quad (229)$$

showing the dependence of the vapor pressure p of the solvent of a dilute solution on the mol fraction of solute present x_2 when the vapor pressure of the pure solvent is p_0 .

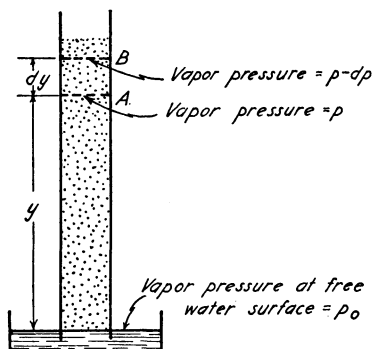


Fig. 17.—Column of vapor in an attractive force field.

37. Dependence of Atmospheric Pressure on Height

Consider a vertical column of air of unit cross-sectional area and unlimited height in the earth's gravitational field. We wish to find the relation between the height y and the gas pressure p in the chamber of figure 17. Sometimes this relation is called Laplace's law of atmospheric pressure. 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. We shall use the following notation:

p = pressure in dynes per square centimeter at a distance y above the reference point, for example, the surface of the earth or a free water surface

v = volume of the air

ρ = density of air in grams per cubic centimeter

g = 980 dynes per gram, the gravitational constant

R = gas constant per gram defined by the well-known gas law,

$$pv = RT$$

Transforming, we have

$$p = \rho RT,$$

and finally

$$\rho = \frac{p}{RT}. \quad (230)$$

The pressure at A is greater than that at B by an amount equal to the weight of the section dy of the column of gas or vapor $\rho g dy$. That is, in going from A to B , the pressure changes by the amount $-dp$. This is our basic assumption in deriving Laplace's pressure law and is quantitatively stated by

$$-dp = \rho g dy. \quad (231)$$

Eliminating ρ in equation 231 by means of equation 230 and rearranging, we have

$$-\frac{dp}{p} = \frac{g}{RT} dy.$$

Integrating from $y = 0$ at the surface of the free water, where $p = p_0$, to $y = y$, where $p = p$, we have

$$\begin{aligned} \ln p \Big|_{p_0}^p &= -\frac{g}{RT} y \Big|_0^y \\ \ln \frac{p}{p_0} &= -\frac{g}{RT} y. \end{aligned} \quad (232)$$

Thus if we know the vapor pressure p_0 at the free-water surface where $y = 0$, equation 232 determines the pressure p at a height y . Transforming 232 into a form that expresses p explicitly in terms of y and T , we have

$$p = p_0 e^{-\frac{gy}{RT}} \quad (233)$$

which is a statement of Laplace's law of atmospheric pressure.

38. Dependence of the Freezing Point of a Dilute Solution on the Mol Fraction of Solute Present

The free energy of the solvent of a dilute solution expressed in terms of the mol fraction of solute present x_2 is (eq. 222)

$$\Delta f_1 = -RT x_2; \quad (234)$$

and in terms of the change in freezing point of the solution ΔT , it is (eq. 207)

$$\Delta f_1 = \frac{l\Delta T}{T}. \quad (235)$$

Equating 234 to 235, we have

$$\Delta T = -\frac{RT^2}{l} x_2$$

showing that the freezing point of the solution is lowered by an amount $-\Delta T$ by the mol fraction of dissolved material x_2 .

39. A Datum for Free Energy and the Dependence of the Latter on Vapor Pressure

As will later be evident (art. 73), the absolute free energy f of soil moisture is not zero except at 0° A. Generally, however, it is convenient to choose a body of pure water outside the influence of any adsorptive field as the zero point of reference or datum with respect to which the free energy of other bodies of water are measured. Thus any water under the conditions corresponding to the datum is said to have its free energy Δf equal to zero although its absolute free energy f is by no means equal to zero.

Since we are interested in free-energy changes occurring at constant temperature, the temperature of the datum is usually taken to be the same as that of the soil moisture. Since the moisture is situated in a gravitational field, it has free energy due to its position. The free energy of any soil moisture due to its presence in the gravitational field is measured with respect to the level of the datum. Thus when the soil moisture is situated at the same level as the datum, its free energy due to its position in the gravitational field is zero.

Under usual conditions the atmosphere exerts on the soil moisture a pressure either greater or less than 1 standard atmosphere. This pressure contributes to the total free energy of the soil moisture (art. 25). Since this pressure, being exerted on both the datum and the unknown, is common to both, it is usually neglected. Thus we speak of the freezing point of pure water as 0° C with the understanding that it is under a pressure of 1 atmosphere. If we could reduce the pressure to zero, we should actually have a freezing point of $+0.0073^\circ$ C (art. 30 and eq. 378). All pressures on soil moisture are therefore measured with respect to the pressure on the datum. If, for example, the atmospheric pressure on the datum is 0.9 atmospheres and that on the soil moisture 1.1 atmospheres, the free energy Δf on the soil moisture due to hydrostatic pressure will be taken as that produced by only 0.2 of an atmosphere.

Thus we shall always associate arbitrarily the following conditions with our datum, or zero point, for the free energy of soil moisture:

1. It will usually have the same temperature as the water or soil moisture whose free energy we wish to determine.

2. Free energy of the datum due to its position in the gravitational field will be arbitrarily taken as zero, and the free energy of all other bodies due to their presence in a gravitational field will be measured with respect to the datum according to article 26.

3. If, as is usually the case, there is a pressure exerted on the datum, this value will be arbitrarily taken as the zero point of pressure in calculating the free energy due to pressure.

4. The datum is assumed to be free of all extraneous fields, such as adsorptive force fields surrounding soil particles, except gravitation, but is taken to include the usual surface forces next to a free flat water surface.

Under these conditions, water which is taken as the datum will for brevity be called merely "free water."

It frequently happens that we wish to determine the free energy of a substance in a particular state, such as solid or liquid, yet the conditions determining its free energy in the particular phase are so complicated that we cannot calculate its free energy directly. For example, the free energy of liquid soil moisture is, in general, determined by the amount of dissolved material, by the hydrostatic pressure in the soil moisture, and by the strength and distribution of the adsorptive force field that surrounds the elementary soil particles and acts on the soil moisture. Often it is impossible to calculate directly the contribution of each of these factors to the total free energy and, consequently, to calculate the total free energy of the soil moisture.

One way out of this difficulty is to use the results of article 22. We there found that when two or more phases of the same substance are in equilibrium with each other, then the specific free energies of all the phases are alike. Consequently, if we can find another phase whose free energy can be more easily calculated, and which is in equilibrium with the first phase, we can take the free energy of the second to be also that of the first. If, for example, we wish to ascertain the free energy of the soil moisture in a soil at a particular soil-moisture content, we have merely to determine the free energy of the vapor in equilibrium with it.

The total specific free energy Δf of the vapor, assuming that it behaves as an ideal gas, is given (eq. 159) by

$$\Delta f = RT \ln \frac{p}{p_0}, \quad (236)$$

where p denotes the vapor pressure of the soil moisture and p_0 denotes the vapor pressure of our datum, or zero point, which for soil moisture we usually take as free, pure water at the same temperature as the vapor whose free energy we wish to determine. Thus, from the simple measure-

ments of the vapor pressures, we can calculate by equation 236 the free energy of a complicated system of soil moisture, measured with respect to the free energy of free, pure water. This fact further emphasizes the general usefulness of the free-energy function in dealing with the energy states of soil moisture.

40. Relation between the Hydrostatic Pressure and Osmotic Pressure of a Pure Solvent and a Solution When the Two Are at Equilibrium

Suppose we have pure water in equilibrium with a soil solution through a semipermeable membrane. Because of the presence of dissolved material in the soil solution, its vapor pressure as well as its free energy will

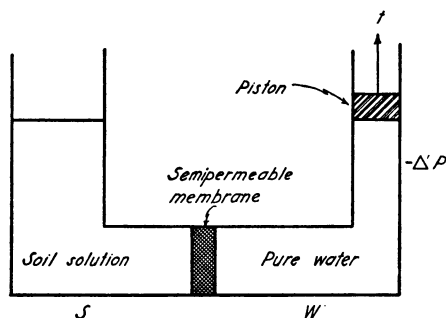


Fig. 18.—Equilibrium of a soil solution with pure water through a semipermeable membrane.

be less than that of the free, pure water. If the proper tension could be placed on the pure water, its vapor pressure as well as free energy would become equal to that of the soil solution. For example, a tension t might be placed upon the piston in figure 18, such that the vapor pressure and free energy of the pure water would be reduced to those of the soil solution.

In other words, the pure water on the side W under a hydrostatic pressure $-\Delta P$ can be in equilibrium through a semipermeable membrane with a solution on the side S having an osmotic pressure $+\Delta P$. For this reason, past measurements of what has been called the "capillary potential" of soil moisture, which depend upon balancing a column of pure water under tension against the pull of the soil moisture, are open to question. Sometimes, for example, a porous bulb connected to a manometer is immersed in a moist soil whose capillary potential is to be measured. The tension recorded by the manometer is then taken as the capillary potential of the soil moisture, which always contains varying amounts of dissolved material. The concentration of solutes inside the bulb at the

time of measurement is less than the concentration of the soil solution. One wonders whether the tension usually recorded is not, therefore, a combination of the true capillary potential plus the osmotic potential, rather than just the capillary potential alone. Only when the water in the porous bulb immersed in the moist soil and that in the manometer contain the same concentration of dissolved material as the soil solution could the tension indicated by the manometer be considered an accurate measure of the so-called capillary potential in the soil. The establishment of this equality of concentration takes a long time since diffusion of solutes through porous material is extremely slow. The discrepancy between the true capillary potential and what is actually measured decreases as the salinity of the soil solution decreases.

Let us now determine quantitatively the relation between the osmotic pressure ΔP_o of a solution in equilibrium with a body of pure water under a hydrostatic pressure ΔP_P . The hydrostatic pressure may be negative, in which case it is often called a "tension."

The free energy Δf_o of a solution measured with respect to free, pure water taken as the datum is (eq. 151)

$$\Delta f_o = -v\Delta P_o$$

where v is the specific volume of the solvent. The free energy due to hydrostatic pressure Δf_P , measured with respect to the same reference point or datum as for Δf_o , of a body of pure water under hydrostatic pressure ΔP_P is (eq. 156)

$$\Delta f_P = v \Delta P_P.$$

At equilibrium the free energies of the two bodies must be equal (art. 22); and we have

$$\Delta f_P = \Delta f_o;$$

therefore

$$\Delta P_P = -\Delta P_o. \quad (237)$$

Now, a minus ΔP_P is to be interpreted as a tension. When, therefore, pure water is in equilibrium with a free solution through a semipermeable membrane, the osmotic pressure of the solution ΔP_o is numerically equal to the tension ($-\Delta P_P$) in the pure water.

41. Dependence of the Vapor Pressure of a Liquid on the Hydrostatic Pressure in the Liquid

Frequently the vapor pressure of a liquid has been considered with the liquid in contact with the vapor, so that the hydrostatic pressure in the liquid is just equal to the vapor pressure. A solid or a liquid can, however,

exist under a hydrostatic pressure very different from its own vapor pressure. Water, for example, may be held in capillaries under a considerable negative hydrostatic pressure (that is, under tension); yet its vapor pressure is a finite positive quantity. Also water and its vapor may be enclosed in a chamber containing considerable quantities of some inert insoluble gas. The total hydrostatic pressure in the water is then the combined sum of its own vapor pressure and that of the inert gas. Certainly it would seem that the normal vapor pressure of the liquid would be changed by placing the liquid under a state of either tension or pressure. By the "normal vapor pressure of a liquid" we mean its value when we consider a large, free, isolated body of the liquid and its vapor, unaffected by extraneous forces.

We now wish to determine quantitatively how a change in vapor pressure Δp depends on the change of the hydrostatic pressure ΔP in the liquid. To fix our ideas, let us consider figure 19. Water at the point *A* in the capillary tube is under a tension or negative hydrostatic pressure determined by the height *h* of the meniscus above the water level in *C*. In equilibrium with the water at *A* is the water vapor enclosed in the chamber *V*. We wish to find how the vapor pressure in *V* is modified by changing the tension on the water at *A*—that is, by increasing or decreasing the length *h* of the capillary column.

Suppose the system comes to equilibrium at constant temperature. Then the vapor pressure *p* will differ from the hydrostatic pressure *P* at *A* except in the limit where *h* equals zero. If the hydrostatic pressure of the liquid at *A* is decreased by increasing *h*, the escaping tendency of the liquid is also decreased. To re-establish equilibrium, therefore, the escaping tendency from the vapor phase must also be decreased by a like amount until its escaping tendency is the same as that from the liquid.

The absolute free energy f_L of the liquid and f_V of the vapor are exact measures of their respective escaping tendencies. If the system is originally in equilibrium, then $f_L = f_V$ (art. 22). If the hydrostatic pressure *P* is changed by an amount ΔP and if the system is again allowed to come to equilibrium, the vapor pressure *p* will change by an amount Δp , and the free energies will spontaneously adjust themselves so that

$$\Delta f_V = \Delta f_L.$$

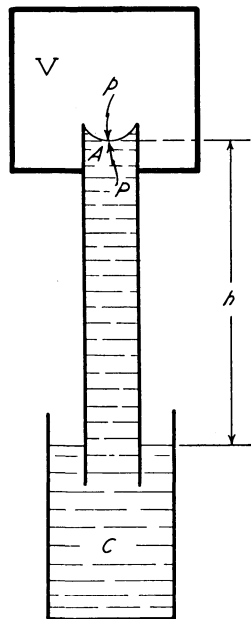


Fig. 19.—Equilibrium of a vapor with the liquid through a curved vapor-liquid interface.

Now (eq. 156)

$$\Delta f_V = v_V \Delta p$$

and likewise

$$\Delta f_L = v_L \Delta P,$$

where v_V and v_L are the specific volumes of the vapor and liquid respectively. Since the new state is also an equilibrium state, we may write in differential form

$$v_V dp = v_L dP$$

or

$$\frac{dp}{dP} = \frac{v_L}{v_V}. \quad (238)$$

Since the changes of pressure have been assumed to take place so that the initial and final temperatures are the same, we should write for 238

$$\left(\frac{dp}{dP}\right)_T = \frac{v_L}{v_V}. \quad (239)$$

The fraction $\frac{v_L}{v_V}$ is, in general, very small. For example, if we consider saturated water vapor and water at 0° C according to the critical tables, $\frac{v_L}{v_V} = 5 \times 10^{-6}$. Thus if the hydrostatic pressure on water at 0° C were

changed so that $\Delta P = 20$ atmospheres, equation 239 shows that the vapor pressure would change only by the amount $\Delta p = 10^{-4}$ atmospheres, approximately. We thus see that the effect of the hydrostatic pressure exerted by the vapor of a liquid on the liquid itself is negligible.

Equation 239 holds not only when the hydrostatic pressure is positive but also when it is negative. If, as in the original case, the liquid is placed under tension, dP is negative. This means that the change in vapor pressure dp must also be negative. Thus, increases of hydrostatic pressure dP cause increases of the vapor pressure dp , while decreases of hydrostatic pressure ($-dP$) cause decreases in the vapor pressure ($-dp$). As will be recalled, in studies of soil moisture the term "hydrostatic pressure" is not confined to positive pressures, as in engineering, but includes negative pressures also.

Suppose we wished to deal with the effect of very great changes of hydrostatic pressure ΔP on the changes of vapor pressure Δp or wished to determine the relation between p and P very accurately. Then, if we are dealing with water, for example, we may use Callendar's empirical equation of state for water vapor, which is

$$v_V = 4.548 \frac{T}{p} - 26.3 \left(\frac{373}{T}\right)^{\frac{10}{3}} + 1.0, \quad (240)$$

where p is the vapor pressure in atmospheres, T the absolute temperature, and v_v the specific volume of the vapor. For liquid water we have, likewise, the empirical equation

$$v_L = 1.002(1 - 4.0 \times 10^{-5} P) \quad (241)$$

where v_L is the specific volume of the liquid water and P is the hydrostatic pressure.

Of course equation 239 will give immediately the relation between changes of hydrostatic pressure ΔP and vapor pressure Δp , especially when the changes are small. It may be desirable, however, to deal with great changes of pressure—for example, several hundred atmospheres. In such a case one may modify the approach as follows by using the two equations 240 and 241 together with 239. We then have

$$\left\{ 4.548 \frac{T}{p} - 26.3 \left(\frac{373}{T} \right)^{\frac{10}{3}} + 1.0 \right\} dp = 1.002(1 - 4.0 \times 10^{-5} P) dP. \quad (242)$$

We shall assume that initially the vapor pressure is p_0 and that this causes a hydrostatic pressure, also p_0 , in the liquid. Finally, the hydrostatic pressure in the liquid is raised to an amount P , which is very great with respect to p_0 . We can therefore assume that the hydrostatic pressure finally is merely P . We shall then wish to calculate the resulting vapor pressure p caused by the hydrostatic pressure P according to equation 242 above. Integrating 242 above and substituting the limits, we have

$$4.548T \ln \frac{p}{p_0} + \left[1 - 26.3 \left(\frac{373}{T} \right)^{\frac{10}{3}} \right] (p - p_0) = 1.002P - 2.004 \times 10^{-5} P^2 \quad (243)$$

or, changing to common logarithms, we have

$$10.46T \log \frac{p}{p_0} + \left[1 - 26.3 \left(\frac{373}{T} \right)^{\frac{10}{3}} \right] (p - p_0) = 1.002P - 2.004 \times 10^{-5} P^2. \quad (244)$$

Equation 244 serves to determine the vapor pressure of water p for any hydrostatic pressure P , the normal vapor pressure p_0 of *free water* at the temperature T of course being known. For example, a solution of the equation above for $P = 300$ atmospheres and a temperature of 20°C gives an increase of the vapor pressure p , above its normal value over a free water surface, of only 20 per cent.

We may considerably simplify equation 243 by measuring p with respect to the normal vapor pressure p_0 , while sacrificing some accuracy.

Let us therefore express 243 in terms of Δp rather than p and p_0 . Let us place

$$p = p_0 + \Delta p. \quad (245)$$

The logarithmic term of equation 243 then becomes

$$\ln \left(\frac{p_0 + \Delta p}{p_0} \right) = \ln \left(1 + \frac{\Delta p}{p_0} \right). \quad (246)$$

The general series expansion of this logarithm, as obtained from any book of mathematical formulas, is

$$\ln (1 + x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4}$$

or

$$\ln \left(1 + \frac{\Delta p}{p_0} \right) = \left(\frac{\Delta p}{p_0} \right) - \frac{1}{2} \left(\frac{\Delta p}{p_0} \right)^2 + \frac{1}{3} \left(\frac{\Delta p}{p_0} \right)^3 - \dots$$

As previously indicated, even at such great hydrostatic pressures as 300 atmospheres Δp is only 20 per cent of p_0 . We are, therefore, in general, quite justified in dropping all but the first term in the series expansion above and accordingly have

$$\ln \left(1 + \frac{\Delta p}{p_0} \right) = \frac{\Delta p}{p_0}. \quad (247)$$

Introducing equation 247 into 243, recalling that $(p - p_0)$ equals Δp , and solving for Δp we have

$$\Delta p = \frac{1.002(P - 2 \times 10^{-5}P^2)}{\frac{4.548}{p_0} T + \left[1 - 26.3 \left(\frac{373}{T} \right)^{\frac{10}{3}} \right]}. \quad (248)$$

It is clear that the hydrostatic pressure P is applied to the liquid only, and not to the vapor.

This equation gives the increase in vapor pressure of water Δp , in atmospheres, corresponding to the application of a hydrostatic pressure of P atmospheres, the normal vapor pressure p_0 of free water at the temperature T of course being known. It shows the same relation between hydrostatic pressure and vapor pressure as the more general equation 239. Equation 248 is more useful for water, however, because the two specific volumes have been eliminated by expressing them in terms of the temperature and of the normal vapor pressure of water. Also, equation 248 is more accurate because it takes into account the variation in the

specific volumes with change of hydrostatic pressure. For great hydrostatic pressures it should be used; but for those usually encountered, equation 239 is probably preferable.

Assuming that $P = 20$ atmospheres and that $T = 27^\circ \text{C}$, which makes $p_0 = 0.035$ atmospheres, we have

$$\Delta p = \frac{1.002(20 - 2 \times 10^{-5} \times 20^2)}{\frac{4.548 \times 300}{0.035} + \left[1 - 26.3 \left(\frac{373}{300} \right)^{\frac{10}{3}} \right]} = \frac{1.002 \times 20}{89,600}$$

$$= 0.00051 \text{ atmospheres.}$$

By the application, therefore, of a hydrostatic pressure of 20 atmospheres to the water at 27°C , the vapor pressure of the water is increased from 0.035 to approximately 0.03551 atmospheres.

If, on the other hand, a tension of 20 atmospheres is placed on the water, the vapor pressure of the water will be decreased by 0.00051 atmospheres, so that the relative humidity will become 98.5 per cent with respect to a free water surface at the same temperature. This humidity is close to that corresponding to the permanent wilting percentage.

Let us now consider several illustrations of the general usefulness and wide applicability of equation 239. Let us first develop the relation between the free energy Δf_V of a vapor and its vapor pressure p as previously given (eq. 159). Equation 239 may be changed to

$$v_L dP = v_V dp. \quad (249)$$

The specific volume of a liquid v_L is in general approximately constant with change of pressure, but the specific volume v_V of a vapor changes and may be assumed to follow approximately the ideal gas law

$$pv_V = RT.$$

Equation 249 becomes then

$$v_L dP = RT \frac{dp}{p}. \quad (250)$$

Consider the change in going from one equilibrium state A to another equilibrium state B . Integrating equation 250 between the limits of hydrostatic pressure P_A and P_B and the vapor pressure between the limits p_A and p_B , and recalling that $v_L \Delta P$ (eq. 156) gives the change in free energy Δf of a liquid due to a change in hydrostatic pressure, we have

$$v_L(P_B - P_A) = v_L \Delta P = \Delta f = RT \ln \frac{p_B}{p_A}. \quad (251)$$

As the liquid and its vapor are assumed to be in equilibrium, their free energies must be the same (art. 22). Thus $\Delta f = RT \ln \frac{p_B}{p_A}$ gives the free energy of both a liquid or a vapor in the state B with respect to that in the state A , expressed in terms of the vapor pressure. This agrees with article 39.

Going further with equation 251, we can derive Laplace's law of atmospheric pressure, which gives the variation in pressure p of a gas with

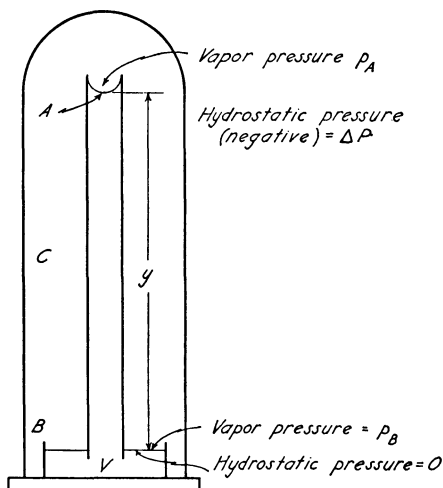


Fig. 20.—Equilibrium between vapor and liquid at different heights above a free water surface.

altitude y . The gas is to be situated in a uniform attractive force field of amount g dynes per gram. The law to be derived is

$$p_A = p_B e^{-\frac{gy}{RT}} \quad (252)$$

where p_B is the vapor pressure at the height $y = 0$, p_A that at the height y ; and where R is the gas constant per gram. From equation 251 we have

$$\Delta f = f_A - f_B = v_L \Delta P = RT \ln \frac{p_A}{p_B}. \quad (253)$$

Consider figure 20. The chamber C encloses a long capillary tube of length y dipping into the free, pure water in the vessel V . Equilibrium has been established so that the vapor and the water are in equilibrium at all heights. In particular, the water under the meniscus A at the height y is in equilibrium with the vapor there. Also at the bottom B , the water

in the dish is in equilibrium with the vapor. Applying equation 253, we have for the hydrostatic pressure ΔP , just below the meniscus at the height y ,

$$\Delta P = \frac{RT}{v_L} \ln \frac{p_A}{p_B}. \quad (254)$$

The hydrostatic pressure ΔP just below A , with reference to that at B taken as zero, is equal to

$$\Delta P = -y \rho g \quad (255)$$

(that is, the weight of a column of liquid of unit cross section, height y and density ρ). Combining equations 254 and 255, we have

$$\frac{RT}{v_L} \ln \frac{p_A}{p_B} = -y \rho g.$$

Since

$$\rho = \frac{1}{v_L},$$

then

$$\ln \frac{p_A}{p_B} = -\frac{gy}{RT}$$

or

$$p_A = p_B e^{-\frac{gy}{RT}},$$

which is recognized to be the same as equation 233 above and is therefore Laplace's law for the variation of vapor pressure with height in a uniform attractive field of force.

The general usefulness and applicability of equation 239 can be further illustrated by using it as the basis for deriving the relation between the osmotic pressure of a solution and its vapor pressure. As will be recalled (art. 24), the osmotic pressure is defined as the pressure that must be applied to a solution to place it in equilibrium with the pure solvent through a semipermeable membrane. From equation 239 we have

$$\frac{dP}{dp} = \frac{v_V}{v_L} \quad (256)$$

where now P will represent the osmotic pressure (that is, the hydrostatic pressure that must be applied to the solution to establish equilibrium with the pure solvent) and where p represents its associated vapor pressure. Equation 256 may be placed in the following form with the aid of the ideal gas law (art. 59):

$$dP = \frac{RT}{v_L} \frac{dp}{p}. \quad (257)$$

where v_L is practically constant. Choosing the upper limit of integration of dP so that it is equal to the osmotic pressure ΔP_O and consequently so that the vapor pressure of the solution has been raised from the normal value p to that of the pure solvent p_0 , we have

$$\Delta P_O = \frac{RT}{v_L} \ln \frac{p_0}{p}. \quad (258)$$

As this equation shows, the osmotic pressure ΔP_O is always positive, since p_0 of the pure solvent is always greater than p of the solution.

The free energy of a solution due to the presence of dissolved material may be expressed immediately in terms of its vapor pressure as follows, after recalling equation 151:

$$\Delta f_O = -v_L \Delta P_O = -RT \ln \frac{p_0}{p}. \quad (259)$$

As this equation shows, the free energy Δf_O of a solution due to the presence of dissolved material is always negative.

42. Dependence of the Hydrostatic Pressure in a Liquid on Its Surface Tension and Its Radius of Curvature

As will be recalled from equation 156, the change in the free energy Δf of a liquid caused by its being placed under a hydrostatic pressure ΔP is given by

$$\Delta f = v \Delta P.$$

Equation 211 expresses the same Δf in terms of the radius of curvature r and surface tension σ . Combining both, we have

$$\Delta P = \frac{2\sigma}{r}. \quad (260)$$

If the vapor-water interface is concave to the vapor, r is negative, and equation 260 predicts a state of tension in the water. This corresponds to the conditions in unsaturated soils and capillary tubes. If, on the other hand, the vapor-water interface is convex to the vapor, r is positive, and 260 predicts a state of compression in the water. This corresponds to the conditions found in droplets of liquid.

43. Effect of Surface Tension and Radius of Curvature of the Air-Water Interface on the Vapor Pressure of Soil Moisture

We wish to derive the expression

$$\ln \left(\frac{p}{p_0} \right) = \frac{v}{RT} \left[\frac{2\sigma}{r} + (p_0 - p) \right] \quad (261)$$

for the vapor pressure p of the vapor over a curved vapor-water interface, expressed in terms of the surface tension of the water σ , the radius of curvature r of the vapor-water interface, and the vapor pressure over a free, flat water surface p_0 . The terms R , T , and v have their usual meanings; and the radius of curvature r of the curved vapor-water interface is taken as positive when the interface is convex, towards the vapor phase.

In our present case, since the surface is concave towards the vapor

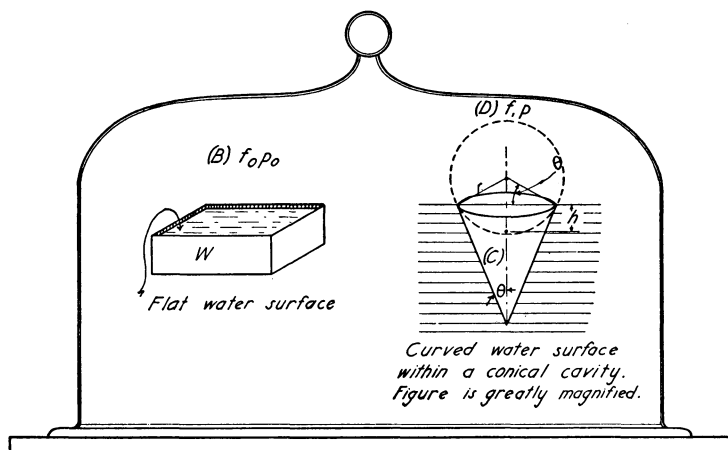


Fig. 21.—Flat water surface and a curved water surface in an enclosed chamber.

phase, we shall always substitute a negative value for r . In the succeeding development we shall also make use of the following terms:

$\theta = \frac{1}{2}$ the angle of the cone of water;

h = height of the zone forming the curved water surface;

$A = 2 \pi r h$ = area of zone forming the curved vapor-water interface;

f, f_0 = specific free energy of the vapor over the curved and free water surface, respectively.

To fix our ideas, consider figure 21, representing a wedge or cone of water whose vapor-water interface has a radius of curvature equal to r , and a vessel of free, pure water under its own vapor pressure, which we shall take to be the datum, or zero point, for free energy. The vapor pressure p_0 over the free, flat water surface at the temperature T will be assumed to have reached equilibrium with the free water surface. Also the vapor pressure p over the curved water surface at the temperature T will be assumed to have reached equilibrium with the liquid water below the curved vapor-water interface. The two systems in the chamber will of course not be in equilibrium with each other. It follows (art. 22) that

the free energy f_0 of the vapor at B equals the free energy of the water at W ; and the free energy f of the vapor at D equals that of the water at C . Hence the difference in the free energy between the vapor at D and B equals the difference in free energy between the liquids at C and W . In deriving equation 261 we shall therefore equate the difference or change in free energy between C and W to that between D and B .

The change in the free energy when dm grams of vapor are carried from B to D is (eq. 159)

$$(f - f_0) dm = RT \ln \left(\frac{p}{p_0} \right) dm. \quad (262)$$

Let us express dm in terms of the change in the radius of curvature dr of the interface. From any handbook of geometrical formulas giving the area of the zone of a sphere, we have for the area of the vapor-water interface

$$A = 2 \pi r h. \quad (263)$$

Also from the geometry of the figure, we have

$$\sin \theta = \frac{r - h}{r};$$

that is,

$$h = r(1 - \sin \theta). \quad (264)$$

Inserting equation 264 into 263, we have

$$A = 2 \pi r^2(1 - \sin \theta). \quad (265)$$

If dm grams of water are added to the curved surface of area A , a film of water of thickness dr is added to the curved surface. This corresponds to a volume

$$A dr = 2 \pi r^2(1 - \sin \theta) dr;$$

and remembering that v is the specific volume, we have

$$dm = \frac{A dr}{v} = \frac{2 \pi r^2(1 - \sin \theta)}{v} dr. \quad (266)$$

Inserting equation 266 into 262, we have, for the total amount of free energy required to transfer dm grams of vapor from B to D ,

$$(f - f_0) dm = \frac{2 \pi r^2 RT(1 - \sin \theta)}{v} \ln \frac{p}{p_0} dr. \quad (267)$$

Now let us also calculate the free energy required to carry dm grams of liquid from W to C . This, of course, equals $(f - f_0) dm$ (art. 22). To do this, let us recall the following fundamental relation between free energy and surface tension σ : the increase in the total free energy of a vapor-liquid interface when its surface area is increased by the amount dA is equal to σdA (eq. 208). Also let us recall the following fact: the increase in the free energy of a gram of water when the hydrostatic pressure on the water is changed from P_0 to P is given by $v(P - P_0)$ (eq. 156). Thus in carrying water from W to C , two forms of free energy are involved. One is due to the increase of a surface area having a surface tension σ , and the other is due to the change of hydrostatic pressure. The first form of free energy is given by

$$\sigma dA = \sigma 4 \pi r(1 - \sin \theta) dr \quad (268)$$

after differentiating A of equation 265 to get dA . The second form of free energy may be evaluated by carrying dm grams of water from W , where the hydrostatic pressure is p_0 (produced by the vapor over W), to C , where the hydrostatic pressure is p (produced by the vapor pressure p over C). This gives

$$v(p - p_0)dm = v(p - p_0) \frac{2 \pi r^2(1 - \sin \theta)}{v} dr, \quad (269)$$

making use of equations 156 and 266. The total change of free energy $(f - f_0) dm$ in carrying dm grams of water from W to C is therefore the sum of equations 268 and 269, or

$$(f - f_0)dm = 4 \pi r \sigma (1 - \sin \theta) dr + 2 \pi r^2 (p - p_0) (1 - \sin \theta) dr. \quad (270)$$

Equating 267 to 270 and rearranging, we have

$$\ln \left(\frac{p}{p_0} \right) = \frac{2 \sigma v}{r RT} + \frac{(p - p_0)v}{RT}$$

or

$$\ln \frac{p}{p_0} = \frac{v}{RT} \left[\frac{2 \sigma}{r} + (p - p_0) \right]. \quad (271)$$

Since the difference in vapor pressures $(p - p_0)$ is ordinarily so small with respect to $\frac{2 \sigma}{r}$, it is ordinarily neglected; and we obtain the common form

$$\ln \frac{p}{p_0} = \left(\frac{v}{RT} \right) \frac{2 \sigma}{r}. \quad (272)$$

Where r is negative, the logarithm must also be negative. We see, therefore, that the vapor pressure p over a concave surface is less than the vapor pressure p_0 over a free water surface. Equation 272 can also immediately be placed in the form

$$p = p_0 e^{\frac{2v}{RT} \frac{\sigma}{r}}.$$

Obviously, 272 also gives the vapor pressure outside of convex surfaces. In this case, r will be positive, because of our convention at the beginning as to the sign of r . In practice this might correspond to the determination of the vapor pressure in a closed vessel containing droplets of water of radius r . Equation 272 shows quantitatively how much greater the vapor pressure p , in equilibrium with the droplets, is than the vapor pressure p_0 over a free water surface. The importance of taking the proper sign for the radius of curvature is thus emphasized.

44. Comparison of Free Energy with Other Thermodynamic Functions Having Properties Similar to Free Energy

We shall begin by comparing the absolute free energy f with the thermodynamic function called "maximum work," which we shall symbolize by the letter a . Free energy is defined by

$$f = h - Ts = e - Ts + Pv. \quad (273)$$

Combining equations 48 and 70, we have

$$T ds = de + dw \quad (274)$$

where dw represents the total work done by the system, including any expansion against an external pressure P . Combining equations 274 and 273 after differentiation, we get

$$-df = s dT + dw - P dv - v dP.$$

If the temperature T is constant, this reduces to

$$-df = dw - P dv - v dP; \quad (275)$$

and if the pressure is also constant

$$-df = dw - P dv. \quad (276)$$

Let us, as in article 21, represent by dw_m all the work done by the system (this may include electrical and light energy) except any expansion

against an external pressure P . We then have $dw_m = dw - P dv$, and therefore equation 276 becomes

$$-df = dw_m. \quad (277)$$

That is, in any transformation of a system taking place at constant temperature and pressure, the decrease in the free energy of the system equals all the work done by the system such as that due to electrical- or light-energy changes; but it does not include work of expansion against the pressure P . When we are dealing with transformations of a substance from one phase to another at a constant temperature and pressure, the only mechanical work ordinarily done is that of expansion or contraction against the pressure P . Now dw_m does not include this work; hence, under these conditions, $dw_m = 0$, and therefore

$$-df = 0 \quad (278)$$

in any isothermal transformation of a substance at constant pressure from one phase to another. That is (art. 22), *all phases of a substance at the same temperature and pressure have the same free energy*. This fact is one chief justification for introducing the free-energy function in the study of soil moisture.

We shall find that the maximum-work function, a , is rather similar to f above. The main difference is that during any transformation of a substance from one phase to another at constant temperature and pressure, the change, da , is not zero, but equals the work of expansion or contraction against the external pressure P . Consequently, different phases of the same substance in equilibrium with each other do not have the same value for the maximum work a , as is true of the free energy f . In those cases where we wish to know the total work required to transform one phase of a substance into another, both in equilibrium with each other, we find that we should use the maximum-work function a .

The maximum work a is defined by

$$a = e - Ts. \quad (279)$$

Differentiating, we have

$$-da = -de + T ds + s dT,$$

and substituting for $T ds$ from equation 274,

$$-da = s dT + dw. \quad (280)$$

If the temperature remains constant during the transformation,

$$-da = dw. \quad (281)$$

That is, during any transformation of a system at constant temperature, the decrease of the maximum work ($-da$) equals all the work dw done by the system, including any expansion against an external pressure P . Now, as before, $dw = dw_m + P dv$; and we have

$$-da = dw_m + P dv.$$

If we are considering isothermal transformations of a substance from one phase to another, dw_m is ordinarily zero, as before, since there are no light- or electrical-energy changes accompanying phase transitions. Consequently,

$$-da = P dv. \quad (282)$$

As will be noticed, our so-called system is, in this case, 1 gram of the substance in one phase being transformed into 1 gram of another phase—for example, 1 gram of ice being transformed isothermally into 1 gram of water. Equation 282 shows, therefore, that two phases existing in equilibrium with each other do not have the same value for the maximum work a ; their values differ by the work of expansion or contraction $\int P dv$ against the external pressure P . The maximum-work function a , is therefore of great utility when we wish to calculate the total mechanical work required to transform isothermally a substance from one phase to another as, for example, in the transition of water from the liquid to the vapor state. The free-energy function f , on the other hand, has the advantage that when several phases are in equilibrium, they all have the same free energy; and the determination of the free energy in any one phase, such as the vapor phase, immediately gives the value of f for all the others.

Another advantage in using the free-energy function when dealing with such a substance as soil moisture is that free energy explicitly gives the amount of energy stored in the water because of hydrostatic pressure. This of course is not true for the maximum-work function. Since

$$dw_m = dw - Pdv,$$

we have, from equation 275,

$$-df = dw_m - vdP.$$

If the system performs no work other than that of expansion, dw_m will equal zero. Hence,

$$df = vdP;$$

and therefore an increase dP of the hydrostatic pressure in water, for example, will cause an increase in the free energy of the water equal to vdP , which is in agreement with equation 156.

A word of caution is perhaps appropriate here regarding the divergent terminology used by various authors in connection with such functions as free energy and maximum work.

Much confusion seems to have arisen since the thermodynamic functions f and a (or F and A , if one is dealing with 1 mol rather than 1 gram of the substance) were first proposed. According to Gibbs, what we now call the "free energy F " was originally called, by him, "thermodynamic potential" and symbolized by ζ . Many European and some American physicists still use this terminology. Others, such as Haas, have used the symbol ϕ . On the other hand, what we have here called the "maximum work A " was originally called by Helmholtz the "free energy" and by Gibbs in 1875 the "characteristic function ψ ." Most European and a few American physicists still use the symbol ψ ; but Haas, for example, still uses the letter F , calling it the "free energy" in agreement with the original work of Helmholtz. Since the original work by Helmholtz and Gibbs, some confusion has arisen among those working with the two functions: when supposedly dealing with what we now call the "maximum-work function," they have actually been dealing with what we now call the "free-energy function." This confusion probably arose because, in many calculations, the numerical values of ΔF and ΔA will be found to be identical or to differ very little. Since in practice, generally, the function

$$F = H - TS$$

is more important than the function

$$A = E - TS$$

the term "free energy" is now generally no longer associated with the latter function. Lewis and Randall use the terms "free energy F " and "maximum work A ," and we have followed this same terminology. They use the large letters F and A , because they are dealing with molal quantities; we use, however, the small letters f and a , since in studying soil moisture we always deal with specific quantities of the substance.

Still other functions similar to the free-energy function F have been used. Massieu in 1869 used, for deducing the thermodynamic properties of a fluid, functions that are actually the negative of our present functions F and A divided by T ; that is, $\left(-\frac{F}{T}\right)$ and $\left(-\frac{A}{T}\right)$.

Planck, in his treatise on thermodynamics, does the same, finding that $\left(-\frac{F}{T}\right)$ (which is what he calls the “characteristic function” ψ) is a much more convenient function than F itself for dealing in a generalized way with systems containing a number of independent constituents, when one wishes to study the dependency of the equilibrium upon the temperature, pressure, and masses of the independent constituents of the system. In agreement with the pioneer work by Helmholtz, Planck uses the term “free energy,” symbolized by F , to refer to the function we now call the “maximum work A .”

45. Thomson, or Gibbs-Helmholtz, Equation

We can now derive one of the more fundamental equations of thermodynamics, which was discovered by Thomson in 1855. Later Gibbs, Helmholtz, van't Hoff, Nernst, and many others made numerous applications. Often, therefore, it is called the “Gibbs-Helmholtz equation.” The maximum work a has been defined (eq. 279)

$$a = e - Ts.$$

From equations 280 and 93 we have

$$da = -s dT - dw = -sdT - Pdv - dw_m$$

so that if no work dw is done,

$$\left(\frac{\partial a}{\partial T}\right)_{v, w_m} = -s, \quad (283)$$

and therefore, by substituting this into the equation above, we obtain the Gibbs-Helmholtz equation,

$$a = e + T\left(\frac{\partial a}{\partial T}\right)_{v, w_m} \quad (284)$$

Often we deal with changes Δa and Δe in a process rather than with a and e themselves. It is desirable, therefore, to restate 284 in terms of Δa and Δe rather than of a and e . If any reaction or transformation of a system takes place in such a manner that the maximum work a and the internal energy e change by the amount Δa and Δe , respectively, we have from $a = e - Ts$,

$$\Delta a = \Delta e - T\Delta s \quad (285)$$

for a change taking place at a constant temperature. Now since equation

283 applies to the system both before and after the change in the system has taken place, we have

$$\left(\frac{\partial a_1}{\partial T}\right)_{v, w_m} = -s_1,$$

$$\left(\frac{\partial a_2}{\partial T}\right)_{v, w_m} = -s_2$$

where the subscripts 1 and 2 refer to the initial and final states, respectively, and therefore

$$\left[\frac{\partial(a_2 - a_1)}{\partial T}\right]_{v, w_m} = -(s_2 - s_1)$$

or

$$\left(\frac{\partial \Delta a}{\partial T}\right)_{v, w_m} = -\Delta s.$$

Substituting this into equation 285, we have

$$\Delta a = \Delta e + T \left(\frac{\partial \Delta a}{\partial T}\right)_{v, w_m}, \quad (286)$$

showing the relation between changes in the maximum work Δa and the internal energy Δe of a system during an isothermal change or transformation.

If, instead of dealing with the maximum work a , we deal with the free energy f , we obtain a set of equations similar to those above. Briefly, we have (eq. 92)

$$f = h - Ts.$$

From equation 97 we have the differential of the above

$$df = -s dT + v dP - dw_m$$

so that

$$\left(\frac{\partial f}{\partial T}\right)_{P, w_m} = -s. \quad (287)$$

Substituting this into equation 92, we have

$$f = h + T \left(\frac{\partial f}{\partial T}\right)_{P, w_m}, \quad (288)$$

which is similar in form to equation 284. Likewise, if we are dealing with changes Δf and Δh of f and h , we have for an isothermal change

$$\Delta f = \Delta h - T \Delta s. \quad (289)$$

And, as previously, since equation 287 applies to the system both before and after the change has taken place, we have

$$\left(\frac{\partial f_1}{\partial T}\right)_{P, w_m} = -s_1,$$

$$\left(\frac{\partial f_2}{\partial T}\right)_{P, w_m} = -s_2;$$

consequently

$$\left[\frac{\partial(f_2 - f_1)}{\partial T}\right]_{P, w_m} = -(s_2 - s_1)$$

or

$$\left(\frac{\partial \Delta f}{\partial T}\right)_{P, w_m} = -\Delta s.$$

Substituting this into equation 289, we have

$$\Delta f = \Delta h + T \left(\frac{\partial \Delta f}{\partial T}\right)_{P, w_m},$$

giving the relation between changes of f and h in a system undergoing an isothermal change. Here, of course, we are dealing with changes of the heat content Δh rather than of the internal energy Δe as in equation 286; here the partial differentiation is with the pressure rather than the volume constant, while w_m is held constant for both differentiations.

46. Relation between Surface Tension, Total Surface Energy per Unit Area, and Temperature

As a result of molecular attraction, the molecules of the surface of a liquid substance are acted upon by a force at right angles to the surface and directed toward the interior of the liquid. This force of attraction is produced by the molecules of the liquid adjacent to the surface and is also the source of the tangential tension over the vapor-liquid interface that we call "surface tension." When the area of such an interface is increased, additional molecules must be pulled from the interior of the liquid into the interface against the force of attraction of the molecules making up the body of the liquid. Work, consequently, must be expended to increase the area of the interface; and the behavior of the interface therefore somewhat resembles a stretched elastic membrane.

The velocities of the molecules are distributed among the different molecules of the liquid according to the Maxwell distribution law (art.

54). Thus the kinetic energies of the different molecules will vary widely. Some molecules will have sufficient kinetic energy to carry them beyond the range of the attractive force of the liquid and into the vapor phase, whereas others will be able to get only part way into the vapor phase. For this reason, there exists a transition layer between liquid and vapor, in which the density grades from that of the liquid to that of the vapor. The formation of this layer of intermediate densities furnishes the basis for explaining the fact that a cooling generally occurs when the area of the interface is increased. Clearly, an adiabatic expansion of the liquid against the force of molecular attraction takes place in the formation of

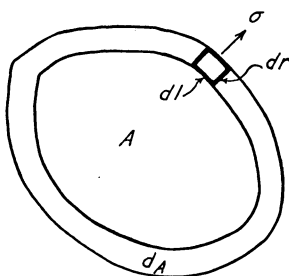


Fig. 22.—An expanding surface.

the transition layer, since part of the liquid moves into the transition layer where the density is lower. Thus, as with the adiabatic expansion of a gas when no external work is done, cooling occurs according to the Joule-Thomson effect, in addition to the slight amount of work done in the expansion against atmospheric pressure. To form a fresh surface isothermally, therefore, work must be done against surface tension, and heat must be added to prevent cooling.

Assume that an area A (fig. 22) is increased to $A + dA$. The quantity (σdA) of article 32 does not represent the total energy expended when a fresh interface of area dA is formed. When such an increase in area at the interface takes place adiabatically, it is shown below that a quantity of heat $\left(-T \frac{d\sigma}{dT}\right)$ per unit area is absorbed from the interior, which is therefore cooled.

Let us now derive the relation between this heat, the surface tension σ , and the total surface energy e_A per unit area, the energy e_A being localized in the surface layer of thickness τ taken up in article 32. The work done by the surroundings on the liquid at constant temperature because of surface tension is, according to equations 101 and 208,

$$-\Delta w_m = \int (\sigma dl) dr. \quad (290)$$

The negative sign indicates that work is actually done on the liquid by the surroundings in creating the element of surface ($dldr$). Since the temperature is constant (eq. 281), we may write

$$\Delta a = \int (\sigma dl) dr = \sigma \Delta A . \quad (291)$$

There is no appreciable expansion against atmospheric pressure in the formation of a new surface. It follows, therefore, that $\Delta a = \Delta f$ in this case since the term Pdv of equation 276 is approximately zero. That is,

$$\Delta a = \Delta f = \sigma \Delta A .$$

The term Δa will, however, be most convenient for the immediate purpose. (If we were to follow strictly the conventions of article 10 as to symbols, we should use capital letters here instead of f , w , a , and e . The use of capital letters here might lead to confusion because other meanings have already been assigned to such letters as A . If it be remembered that the symbols f , w , a , and e in this paragraph refer not to 1 gram of water but rather to unit area of the surface, the reasoning and conclusions will in no way be altered.) The increase in total surface energy is

$$\Delta e = e_A \Delta A , \quad (292)$$

where e_A is the total surface energy per unit area. As lately shown (art. 45), the Gibbs-Helmholtz equation (286) is

$$\Delta a = \Delta e + T \left(\frac{\partial \Delta a}{\partial T} \right)_{v, w_m} . \quad (293)$$

Inserting equations 291 and 292 into 293, we have

$$\sigma \Delta A = e_A \Delta A + T \left[\frac{\partial (\sigma \Delta A)}{\partial T} \right]_{v, w_m}$$

or

$$\sigma = e_A + T \left(\frac{\partial \sigma}{\partial T} \right)_{v, w_m} \quad (294)$$

or

$$e_A = \sigma - T \left(\frac{\partial \sigma}{\partial T} \right)_{v, w_m} . \quad (295)$$

Equation 295 relates the surface tension σ to the total surface energy per unit area e_A and the temperature of the surface T .

In using equation 295 it is necessary to evaluate $\left(\frac{\partial \sigma}{\partial T} \right)$. This has been

done by several investigators. The expressions obtained are largely empirical. For water, probably the most commonly accepted relation that may be used for evaluating the differential coefficient is the empirical relation given by equation 434. There is also the Ramsay-Shields equation:

$$\sigma(Mv)^{\frac{2}{3}} = k(T_c - 6 - T) \quad (296)$$

where M is the molecular weight, T_c the critical temperature of the liquid, T the temperature of the liquid surface, v the specific volume, and k a constant for the given liquid. The value of k is approximately the same for all

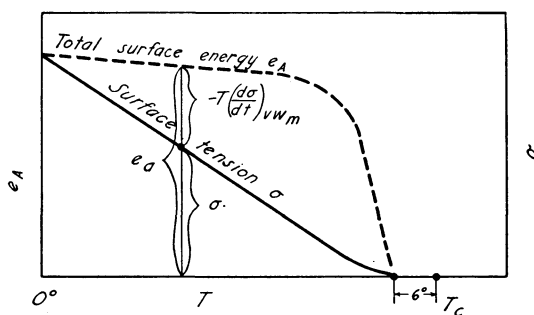


Fig. 23.—Relation between surface tension, surface energy, and temperature of a surface.

liquids that exist as simple undissociated molecules, such as benzene, carbon tetrachloride, and carbon disulfide. For these liquids, k is equal to approximately 2.12 when surface energy is expressed as ergs per square centimeter. For liquids whose molecules are associated in the liquid state into double or more complex molecules, such as water, methyl and ethyl alcohols, and acetic acid, k has a smaller value than 2.12 and varies with the liquid.

The general form of the linear decrease in the surface tension σ with rise in temperature T (eq. 434 and 296) is shown in figure 23. As the graph shows, σ approaches zero at a temperature approximately 6 degrees below the critical temperature. The critical temperature T_c for water, at which the liquid and vapor become identical, is 647° A.

According to equation 295, since $\left(\frac{\partial \sigma}{\partial T}\right)$ is negative, the curve representing e_A always falls above the curve representing σ . Also, since $\left(\frac{\partial \sigma}{\partial T}\right)$ is nearly constant, $\left[-T\left(\frac{\partial \sigma}{\partial T}\right)\right]$ is positive and of such a magnitude that it represents approximately the difference between σ at 0° A and σ at the

temperature in question. Thus when this value is added to σ to get e_A (eq. 295 and fig. 23), we find e_A remaining nearly constant with change of temperature until the critical temperature is neared, at which e_A becomes zero, since $\left(\frac{\partial \sigma}{\partial T}\right)$ and σ become zero there.

By comparing equation 295 and the statement of the First Law of thermodynamics (eq. 47), we note that $\left[-T\left(\frac{\partial \sigma}{\partial T}\right)\right]$ represents the heat Δq required for isothermal formation of unit surface area, since e_A corresponds to Δe and since $(-\sigma)$ corresponds to Δw . As will be recalled, Δw is the work done by the liquid surface on its surroundings during the isothermal formation of the liquid surface. Consequently, if the extension of the liquid surface were carried out adiabatically, a quantity of heat $\left[-T\left(\frac{\partial \sigma}{\partial T}\right)\right]$ would be absorbed from the interior of the liquid, whose temperature would consequently drop. When the new surface is created isothermally, this quantity of heat is added by the surroundings to the surface layer to compensate for the cooling effect; it may be called the latent heat of surface formation.

KINETIC THEORY OF SOIL MOISTURE

47. Dependence of the Properties of Soil Moisture on the Velocities and Energies of the Individual Molecules

In dealing with a substance such as soil moisture, we may generally assume that any one molecule has the same properties and is in the same condition as any one of those adjacent to it. We know that any single water molecule in soil moisture has the same structure as any other. Presumably, too, within any sufficiently small region of soil moisture, all the molecules are acted upon by the same forces, while the temperature and the hydrostatic pressure in the water are the same throughout.

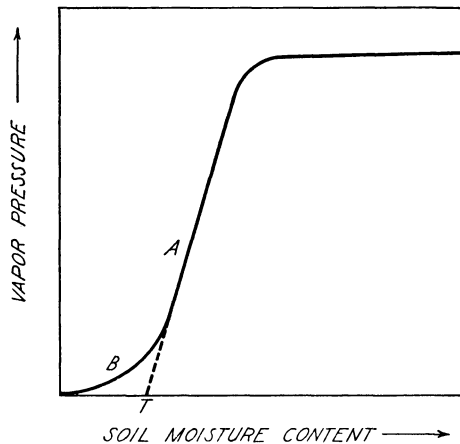


Fig. 24.—Dependence of the vapor pressure of soil moisture on the soil moisture content.

Likewise, in considering the vapor phase at equilibrium, we assume the vapor pressure and the temperature to be the same throughout.

Certain physical phenomena lead one, however, to suspect that although the elementary water molecules may be chemically alike, each one may carry properties or characteristics widely different from those of its neighbors. A single molecule in a large group possesses characteristics (such as velocity of translation, momentum, kinetic energy, and the energy of vibration of the atoms composing it, as well as their potential energy) widely different from the properties of the adjacent molecule.

Let us consider how these facts affect the explanation for the shape of the curve showing the relation between the soil moisture content and the vapor pressure of the soil moisture at low moisture contents. Experimentally (fig. 24) we know that as the soil moisture content is decreased, the vapor pressure decreases (part *A* of the curve). The vapor pressure is

never zero, no matter how small the moisture content, since the curve bends over along the part *B*. As has been shown by Kelley, Jenny, and Brown (95), the *B* part of the curve is irregular because of water of crystallization.

Actually, one would expect the vapor pressure of the soil moisture to become zero for some finite soil moisture content if all the water molecules had the same velocity and kinetic energy. Consider figure 25. As the soil moisture content decreases (in other words, as the interface *I* moves in towards the soil particle), the water molecules at the interface are more and more influenced by the adsorptive force of the soil particle. At the same time, consequently, more and more work is required to free a water

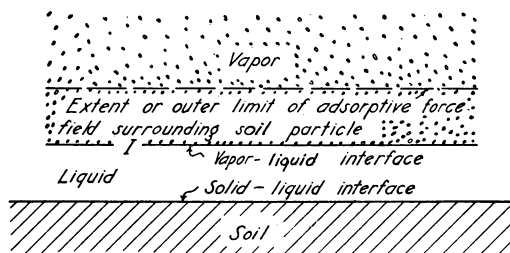


Fig. 25.—Thin layer of soil moisture in the adsorptive force field.

molecule completely from the liquid and to carry it into the free vapor state. A water molecule in the interface *I* will always be able to escape into the free-vapor state as long as the component of its velocity normal to the soil surface gives it a kinetic energy greater than the work required to carry the molecule out of the interface into the free vapor state as shown in article 55. As the soil moisture content decreases (and, therefore, as the work required for the removal of a water molecule into the vapor phase increases), we shall reach a point corresponding to a finite soil moisture content where the vertical component of the kinetic energy of the molecule can no longer carry the molecule out from the interface *I* into the free vapor state. At this moisture content and at all those less than this, the molecule will remain bound to the liquid layer. Evidently, then, if all the water molecules of a body of soil moisture had the same velocity and, therefore, the same kinetic energy, we should expect to find the vapor pressure of a moist soil zero over the lowermost range of soil moisture contents. Here there is a close analogy between the vertical component of the velocity that a rocket must have in order to escape permanently from the surface of the earth, and the velocity that a molecule in the soil moisture must have in order to escape permanently into the

vapor phase. If the rocket has not enough kinetic energy, it will not escape permanently.

If, on the other hand, the velocities of the different molecules varied widely, we should not expect the vapor pressure of the soil moisture to become zero abruptly at some finite soil moisture content. As the soil moisture content is decreased, the work required to remove a molecule from the soil moisture always increases, and consequently the minimum velocity that a molecule may have and still escape is also increased. As the soil moisture content is decreased, accordingly, more and more molecules find themselves bound because of insufficient velocity or kinetic energy. The fastest molecules always escape, but the number that can escape is diminished gradually as the soil moisture content is decreased. We should, therefore, expect to observe a gradual rather than an abrupt decrease of the vapor pressure with a decrease of soil moisture content if the velocities of the water molecules vary widely. Experimentally (2, 39, 42, 46, 153, 154) we always find a gradual decrease, never an abrupt decrease, of the vapor pressure with a decrease of soil moisture content.

The effect of increasing the temperature is always to increase the momentums and velocities of all the molecules and consequently their ability to escape. We therefore always find an increase of the vapor pressure of soil moisture with a rise of temperature.

Since, in the subject of soil moisture, the solution of many problems will, in the future, depend upon an accurate knowledge of how the individual molecules of a substance are distributed among the different possible velocity and kinetic-energy states, we shall now take up the basic theory for solving such problems. An analogy to the situation above, in which we considered the distribution of molecules among different velocity or energy states, is represented by the distribution of the population of a country according to yearly income. Some in the population have a very small income; some very large; but the majority are clustered about the "most probable income." The incomes (or velocities by analogy) vary from one individual to the next, and a distribution curve would show how the different individuals are distributed among the different intervals or brackets of income. The distribution of incomes among the different individuals is then bound by the condition that if one multiplies the number of individuals belonging to each interval, or "bracket," of income by the value of the income for that interval and then takes the sum of these products over all intervals, the result will give the total annual income of the population. The distribution is bound also by the condition that the total number of individuals of the population shall remain the same during the determination. In fact, the mathematical treatment is exactly like the one to be followed for molecules.

48. Meanings of Terms to Be Used in the Statistical Analysis of Molecular Velocities and Energies

Let us consider the meaning associated with several terms. We must distinguish between the macroscopic and microscopic states of a substance. A "macroscopic" state is one determined by quantities such as temperature and pressure, which can be measured by ordinary methods. For example, the macroscopic state of an ideal gas at equilibrium is entirely determined by only two variables, such as pressure and temperature. The "microscopic" state, on the other hand, requires, for its specification, that the position and motion of all parts of the substance be determined in detail. For example, the microscopic state of an ideal gas at equilibrium is not determined merely by two variables such as pressure and temperature; for its specification one must know the positions and velocities of all the molecules composing the gas. Relatively speaking, a knowledge of the macroscopic state of a substance at equilibrium is a rather superficial bird's-eye sort of information, whereas knowledge of the microscopic state of a substance is a complete and detailed description of the parts and their interrelations.

Evidently, then, for the same macroscopic state of a substance, there may be numerous microscopic states. Let us consider a volume of water vapor sufficient to hold 1 mol under standard conditions of temperature and pressure. Its macroscopic equilibrium state is determined by any two of such quantities as p , v , T , f , or s . Its momentary microscopic state, on the other hand, requires for its specification both the position and motion of each of the molecules in the vessel; and there are 6.06×10^{23} of them! The molecules all have different positions in the vessel, and their velocities vary widely. Suppose now we interchange two of them with respect to their instantaneous location. Obviously, the T , p , v , f , and so forth of the gas will not be affected; that is, the macroscopic state of the water vapor will remain the same. Its microscopic state, on the other hand, is not the same; instead, we have actually created a new microscopic state. The same holds true if we interchange the velocities associated with two different molecules. The macroscopic state remains the same, but the microscopic state is new. Such quantities as internal energy, temperature, pressure, and consequently the macroscopic state of the substance all remain the same in all interchanges of position and motion of the molecules. Meanwhile, the microscopic state does not remain the same; each interchange of the velocity or position of two molecules creates a new one. Since the volume of vapor we have been considering contains 6.06×10^{23} molecules, evidently we could create innumerable different microscopic states, corresponding to the one macroscopic state, by making all possible interchanges of the velocities and positions among the molecules.

Often in statistical mechanics, one encounters the term "complexion." This is completely synonymous with "microscopic state." Each new microscopic state corresponds to a different complexion; and for each macroscopic state there are many complexions. Since the two terms have the same meaning, we will use "complexion" in place of microscopic state to avoid an annoying similarity in spelling and pronunciation.

At equilibrium the molecules of water vapor are in continuous motion and are continually colliding, changing their positions and velocities. The complexion of the vapor is therefore continually changing with lapse of time, although the macroscopic state of the vapor and the quantities that determine it remain the same. The quantities determining the macroscopic state are averages over all the molecules in the given volume for a finite interval of time; they remain constant within the limits of sensitivity of our ordinary instruments of observation.

Why, then, one might ask, is the complexion of a substance at equilibrium always changing even though the macroscopic state remains apparently the same? The answer must be that all or most of the different complexions in which the substance exists from time to time, correspond to the same or nearly the same macroscopic quantities such as p , v , T , that define the equilibrium macroscopic state. Consequently, there must be extremely few and short-lived complexions of the substance whose macroscopic quantities differ widely from those of the average, normal, or most probable macroscopic state. Any that do arise disappear almost immediately. Thus the number of complexions associated with any macroscopic state appreciably different from the equilibrium macroscopic state must be negligible when compared with the entire number of possible complexions in which the substance may exist over a long period.

If the substance is not in equilibrium throughout, it will be in some nonequilibrium macroscopic state (depending upon the temperature and pressure throughout), with which are also associated several different complexions. But in this case the number of different possible complexions is relatively small as compared with the total number of different complexions by which the equilibrium macroscopic state can be realized. The equilibrium state of a substance corresponding to a given temperature and pressure is therefore that macroscopic state (of all those conceivable at the particular temperature and pressure) which has associated with it the greatest number of different complexions and can therefore be realized in the most ways. A substance not in equilibrium throughout is continually changing from a macroscopic state having few complexions to one having many. The equilibrium macroscopic state is, therefore, the one associated with a maximum number of complexions; that is, the equilibrium state is the most probable, since it can be realized in the most ways.

Our problem now, therefore, will be to obtain a quantitative expression for the probability of occurrence (that is, the total number of microscopic states) of a particular macroscopic state of a substance and to find out under what conditions the probability is a maximum. These conditions will then serve to describe completely the equilibrium state of the substance, since they define or determine the most probable state. Our problem for the present, accordingly, is mainly one of statistics.

49. Molecular Statistics

Consider, for example, an assembly of molecules having a mass of 1 gram. Suppose we wish to study and determine the speeds of each indi-

	$\overset{\cdot}{2} \overset{\cdot}{7} \overset{\cdot}{11}$		$\overset{\cdot}{4} \overset{\cdot}{5} \overset{\cdot}{6} \overset{\cdot}{9}$		$\overset{\cdot}{3} \overset{\cdot}{8} \overset{\cdot}{12}$	$\overset{\cdot}{10}$
Speed of molecule	du	$2du$	$3du$	$4du$	$5du$	$6du$
Interval number (n)	1	2	3	4	5	6
Number of molecules N_n lying in interval n . (Total number of molecules is $N = 12$)	$N_1 = 3$	$N_2 = 0$	$N_3 = 5$	$N_4 = 0$	$N_5 = 3$	$N_6 = 1$

Fig. 26.—Distribution of molecules in velocity space.

vidual molecule when the entire system is in a state of equilibrium. To do this let us divide the total range of possible speeds that a molecule might possess into a series of equal intervals of amount du . This gives us a plurality or series of different speed states in which a given molecule might exist and enables us to classify the different molecules on the basis of their speed.

We then ask how, under a given set of conditions, the different molecules are distributed among the different speed states. Take, for example, the hypothetical case of 12 molecules and divide the total range of possible speeds that a molecule might possess into six equal intervals of amount du (fig. 26). Any molecule happening to be in interval 3 has 3 du units of speed; in interval 5, 5 du units of speed, and so on. The figure shows one particular complexion of a definite macroscopic state in which 3 molecules are in the first and fifth interval, 5 in the third, and 1 in the sixth. By interchanging, for example, molecules 10 and 2, which are in different compartments, we obtain another complexion; but the macroscopic state remains unchanged. If, on the other hand, we interchange

two molecules in the same speed state, we change neither the macroscopic state nor the number of complexions. Different complexions are formed, therefore, only by interchanging molecules that are in different and distinct states or intervals. Evidently we can obtain many other complexions, all having the same macroscopic state, by interchanging different molecules between different states or intervals. Only by changing the total number of molecules in each compartment or interval can we change the macroscopic state.

As stated in the previous section, the equilibrium state of a substance, at a given temperature and pressure, is the most probable macroscopic state; it is the one, at the given temperature and pressure, out of which can be formed the greatest number of different possible complexions.

Let us define the "thermodynamic probability" W of a given macroscopic state as the number of different complexions that will produce that state. It cannot be too strongly emphasized that we use synonymously the three terms "thermodynamic probability" W , "number of microscopic states" W , and "number of complexions" W . The term "probability" originated in pure mathematics; the terms "complexion" and "microscopic state" in the field of physics. Figure 26 shows one complexion of a particular macroscopic state. Let us, for example, determine the total number of possible complexions which will produce the same macroscopic state shown in the figure—that is, in which any 3 molecules are in the first interval, 0 in the second, 5 in the third, 0 in the fourth, 3 in the fifth, and 1 in the sixth. The total number of possible complexions is given by the well-known permutation formula for a totality of N objects, which are divided into groups of N_1, N_2, N_3, \dots . The thermodynamic probability W is equal to the number of complexions corresponding to the *one* macroscopic state in which N_1 molecules have a speed du , N_2 a speed $2du$, and so on, up to the last velocity interval i in which N_i molecules each has a speed idu . Thus

$$W = \frac{N!}{N_1! N_2! \dots N_n! \dots N_i!} \quad (297)$$

This formula becomes self-evident if one considers that if all the N molecules possessed different speeds (that is, fell in different speed intervals so that there would be N different speed intervals), the number of different possible complexions would equal the number of permutations of the N different molecules, each permutation containing all the molecules; that is, $N! = (N) (N - 1) (N - 2) \dots (3) (2) (1)$ complexions. Now when N_1 of the N molecules are identical (that is, N_1 molecules fall in the same speed interval), let the number of different complexions or

permutations be Y . If, however, the N_1 identical molecules were each given a different speed, factorial N_1 ($N_1!$) different complexions or permutations could be formed from each of the Y complexions. Therefore

$$Y N_1! = N!$$

because of the well-known theorem that if one situation can happen in a ways and another in b ways, then the compound situation composed of both of them can happen in ab different ways. In like manner it is shown that when the molecules are divided into several groups containing N_1, N_2, N_3, \dots , identical molecules (the speed of each molecule in a given group being the same), the number of permutations or complexions corresponding to the given macroscopic state equals the expression for W given by equation 297.

To bring out more concretely the meaning of equation 297, let us apply it to the calculation of the total number of possible complexions corresponding to the macroscopic state shown. Recalling from elementary algebra that $0! = 1$, we have

$$W = \frac{12!}{3!0!5!0!3!1!} = 110,880 \text{ complexions.}$$

That is, the given macroscopic state can be realized in 110,880 different ways.

Let us digress for a moment to generalize this treatment so that it may be applied to an actual substance such as water vapor. Above, for purposes of illustration, we have considered essentially only a one-dimensional array of velocity states in which the representative point of any one molecule is given by but one value of velocity. We have thus, in the above, confined our attention to only one of the three components of velocity of a molecule. Actually a molecule has, in general, three components of translational velocity, u_x, u_y , and u_z , along three coördinate axes, associated with the three translational degrees of freedom. Besides the translational degrees of freedom, or movements, a polyatomic molecule may have rotational and internal movements or degrees of freedom that arise because of the relative motions of the atoms with respect to each other within the molecule. Each of these degrees of freedom will have energy associated with it.

In general, therefore, when we consider a substance such as water vapor, whose molecules are all alike, we shall assume that each molecule has d degrees of freedom, not merely 1, as in the elementary example used. The state of any one molecule is then defined at any moment by the d generalized coördinates of position of the molecule in space as well as the d generalized coördinates of velocity (associated with the d coördi-

nates of position) necessary to describe completely the whole movement of the molecule (both translational and interatomic). Thus $2d$ independent variables are required to specify the state of the molecule. This means that the state of a molecule is fixed only when both its position and movements are fixed. Let us use these $2d$ variables as coördinates in a $2d$ dimensional space that we shall call, for short, the "phase space" or "state space." The state of each molecule is then specified by a point (henceforth called the "representative point" of the molecule) in this space. There will be as many representative points in the space as molecules in the substance. Since the molecules are always moving, the representative points in the phase space will also be in continuous motion describing what may be called "phase paths." If the vapor, for example, is composed of N molecules, the instantaneous complexion of the substance is specified at any moment by the location of all the N representative points in the phase space.

Let us divide this $2d$ dimensional phase space into small compartments, boxes, or cells, all of equal size g . Then the instantaneous complexion of the substance is completely defined when we know in which cell each individual representative point lies, in the same manner as we previously knew the instantaneous state of our hypothetical vapor when we knew in which cell or interval of our one-dimensional velocity space each individual representative point fell.

Our definition of the term "complexion" also remains the same. When we interchange molecules between two different cells in the phase space, we keep the macroscopic state of the system the same but create a new complexion.

At first it may seem strange to speak of cells and compartments that have more than three dimensions. Although it seems impossible to visualize more than three, we are not handicapped by any such limitations in mathematics, where we can deal with a space of as many dimensions as we please. Since these multidimensional spaces have properties analogous to the three-dimensional spaces of ordinary experience, we often apply many of the terms associated with the latter to the former.

After this digression, we are now able to treat statistically the case of an actual substance and the behavior of its molecules.

We recall that since we are interested in the state of thermodynamic equilibrium, we are interested in that macroscopic state whose thermodynamic probability W is a maximum; that is, we want that distribution N_1, N_2, \dots, N_i of the molecules among the different compartments in phase space which will make W a maximum. Before we can determine this mathematically according to equation 297, we must simplify the expression for the statistical probability W to a form that may be handled more

easily. To do this, we must use an easily derivable mathematical formula of approximation for $N!$ given by equation 304. We shall derive this now. Making use of the identities,

$$\ln N! = \ln 1 + \ln 2 + \ln 3 + \dots + \ln N \quad (298)$$

and

$$\ln N^N = \ln N + \ln N + \ln N + \dots + \ln N. \quad (299)$$

Consequently, since the difference between the logarithms of two numbers is always equal to the logarithm of their quotient—that is

$$(\log a - \log b) = \log \frac{a}{b} \text{—we have (eq. 298 and 299)}$$

$$\ln \frac{N!}{N^N} = \ln \frac{1}{N} + \ln \frac{2}{N} + \dots + \ln \frac{N}{N}. \quad (300)$$

Equation 300 may be graphically represented by an area as in figure 27.

If we multiply equation 300 by $\frac{1}{N}$, a little consideration of the right side

of the equation will show that $\frac{1}{N} \log \frac{N!}{N^N}$ is equal to the area between the

curve and the vertical axis, between the limits $\frac{1}{N}$ and $\frac{N}{N}$. Strictly speak-

ing, the shaded areas should be included; but if N is large, as always when we are dealing with vapors, these may be neglected. To find this area and consequently the value of $\log \frac{N!}{N^N}$ let us set

$$dx = \frac{1}{N}.$$

Equation 300 then becomes, after multiplying both sides by $\frac{1}{N} = dx$,

$$\frac{1}{N} \ln \frac{N!}{N^N} = \ln (dx)dx + \ln (2dx)dx + \dots + \ln (N dx)dx. \quad (301)$$

From this equation and from the very definition of an integral, it follows that

$$\frac{1}{N} \ln \frac{N!}{N^N} = \int_0^1 \ln x \, dx, \quad (302)$$

where it is evident, as in figure 27, that the limits of integration of x are 0 and $+1$. Integrating, we have

$$\int_0^1 \ln x \, dx = \left[x \ln x - x \right]_0^1 = -1.$$

Consequently

$$\frac{1}{N} \ln \frac{N!}{N^N} = -1$$

or

$$\ln \frac{N!}{N^N} = -N. \quad (303)$$

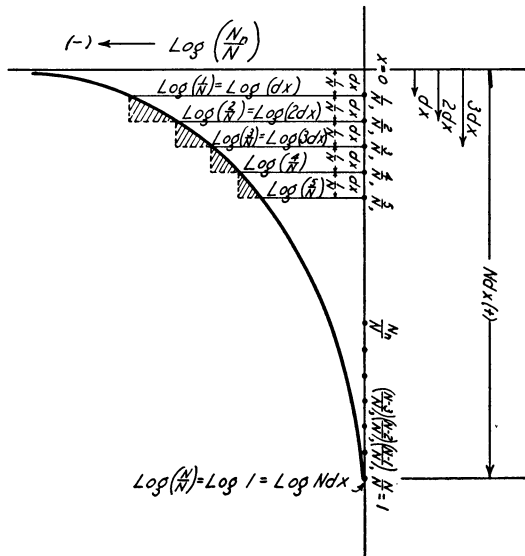


Fig. 27.— $\text{Log} \left(\frac{N_n}{N} \right)$ plotted as a function of $\left(\frac{N_n}{N} \right)$.

But according to the definition of the natural logarithm whose base is e, we have $\ln e^N = N$. Equation 303 then becomes

$$\ln \frac{N!}{N^N} = -\ln e^N.$$

Rearranging, we have

$$\ln (N!) - \ln N^N = -\ln e^N$$

or

$$\ln (N !)=\ln \frac{N^N}{e^N}=\ln \left(\frac{N}{e}\right)^N$$

so that

$$N! = \left(\frac{N}{e}\right)^N \quad (304)$$

enabling us to replace factorial N by the N th power of $\left(\frac{N}{e}\right)$.

Making use of equation 304, we may now simplify the expression for the thermodynamic probability W —that is, the number of different complexions corresponding to a given macroscopic state (eq. 297). We have

$$\begin{aligned} W &= \frac{\left(\frac{N}{e}\right)^N}{\left(\frac{N_1}{e}\right)^{N_1} \left(\frac{N_2}{e}\right)^{N_2} \left(\frac{N_3}{e}\right)^{N_3} \dots \left(\frac{N_n}{e}\right)^{N_n} \dots \left(\frac{N_i}{e}\right)^{N_i}} \\ &= \frac{N^N}{N_1^{N_1} N_2^{N_2} N_3^{N_3} \dots N_n^{N_n} \dots N_i^{N_i}} \end{aligned}$$

since $N = (N_1 + N_2 + \dots)$. Consequently

$$\begin{aligned} \ln W &= \ln N^N - \ln (N_1^{N_1} N_2^{N_2} N_3^{N_3} \dots N_n^{N_n} \dots N_i^{N_i}) \\ &= N \ln N - N_1 \ln N_1 - N_2 \ln N_2 - N_3 \ln N_3 - \dots - N_n \ln N_n \dots \\ &\quad - N_i \ln N_i \\ &= N \ln N - \sum_{n=1}^{n=i} N_n \ln N_n. \end{aligned} \quad (305)$$

Let us now put

$$w_1 = \frac{N_1}{N}, w_2 = \frac{N_2}{N}, \dots, w_n = \frac{N_n}{N}, \dots, w_i = \frac{N_i}{N} \quad (306)$$

and consequently

$$w_1 + w_2 + w_3 + \dots + w_n + \dots + w_i = 1 \quad (307)$$

since $N = (N_1 + N_2 + \dots + N_i)$. That is, w_n represents the fraction of the total number of molecules N whose representative points fall in the n th compartment or cell of phase space. All the molecules whose representative points fall in the same cell of phase space are in the same state in every respect, within the limits imposed by the finite but small dimensions of an individual cell. We will also call w_n the mathematical probability that a given molecule is in the state corresponding to the n th

compartment or cell in phase space. Applying equation 306 to 305, we have

$$\begin{aligned}\ln W &= N \ln N - Nw_1 \ln Nw_1 - Nw_2 \ln Nw_2 - \dots - Nw_i \ln Nw_i \\ &= N \ln N - \{ (Nw_1 \ln N + Nw_2 \ln N + \dots + Nw_i \ln N) \\ &\quad + (Nw_1 \ln w_1 + Nw_2 \ln w_2 + \dots + Nw_i \ln w_i) \} \\ &= N \ln N - \{ (w_1 + \dots + w_i) N \ln N + N(w_1 \ln w_1 + \dots + w_i \ln w_i) \}.\end{aligned}$$

With equation 307 this becomes

$$\begin{aligned}\ln W &= -N(w_1 \ln w_1 + w_2 \ln w_2 + \dots + w_i \ln w_i) \\ &= -N \sum_{n=1}^{n=i} w_n \ln w_n\end{aligned}\tag{308}$$

where the letter n denotes any of the numbers from 1 to i . Equation 308 gives the thermodynamic probability—that is, the number of different possible complexions W corresponding to the given macroscopic state in which a fraction w_1 of the N molecules have their representative points falling in the first compartment of phase space, a fraction w_2 have their representative points falling in the second compartment of phase space, and so on.

We now shall determine that distribution, w_1, w_2, \dots, w_i , of the representative points of the molecules among the different compartments of phase space that will make W a maximum. This will determine that macroscopic state having the greatest number of complexions and consequently having the maximum thermodynamic probability. It will therefore be the equilibrium state of the substance. Necessarily, when W is a maximum, $\delta W = 0$ for small changes of the variables ($w_1 \dots w_i$), in accordance with the mathematical principles pointed out in article 4. Since it is more convenient to calculate with the logarithm of W than with W itself, we shall express the condition for the maximum ($\delta W = 0$) by $\delta(\ln W) = 0$. Consequently (eq. 308), since N is a constant, we have

$$\delta(\ln W) = -N \sum_{n=1}^{n=i} \ln w_n \delta w_n - N \sum_{n=1}^{n=i} \delta w_n = 0.$$

Now by 307 the last sum vanishes; hence our condition becomes

$$\sum_{n=1}^{n=i} \ln w_n \delta w_n = 0.\tag{309}$$

Besides $\delta(\ln W) = 0$, we must introduce two other subordinate conditions for determining the equilibrium distribution of the molecules. The first is that the total number N of molecules in our system is to remain constant; that is, $\delta N = 0$. This may be placed in more usable form:

$$\delta N = \delta(N_1 + N_2 + \dots + N_i) = 0,$$

or

$$\delta\left(\frac{N_1}{N} + \frac{N_2}{N} + \dots + \frac{N_i}{N}\right) = 0$$

and

$$\delta(w_1 + w_2 + \dots + w_i) = 0$$

$$\delta w_1 + \delta w_2 + \dots + \delta w_i = 0.$$

Hence

$$\sum_{n=1}^{n=i} \delta w_n = 0. \quad (310)$$

The second subordinate condition is that the total internal energy e of the system is to remain constant. That is (art. 4) $\delta e = 0$ for any changes the system might be made to undergo. This may be placed in more usable form if one lets $\epsilon_1, \epsilon_2, \epsilon_3, \dots, \epsilon_i$ represent the total energy of each molecule in the $(1, 2, \dots, i)$ compartments in the phase space, respectively. The energy ϵ_n associated with a molecule in the n th phase cell is the sum of its kinetic energy of translation and the interatomic and subatomic energies of the molecule. If we are dealing with a monatomic substance, there will be no interatomic energies, and ϵ_n will represent the total kinetic energy of translation of the molecule. We have, then, for the total energy of all the molecules of our substance,

$$e = N_1 \epsilon_1 + N_2 \epsilon_2 + \dots + N_n \epsilon_n + \dots + N_i \epsilon_i$$

since the N 's represent the number of molecules in the corresponding cells of phase space. Dividing through by the total number of molecules N and recalling the definition of the w 's (eq. 306)

$$e = N(w_1 \epsilon_1 + w_2 \epsilon_2 + \dots + w_i \epsilon_i). \quad (311)$$

Recalling that N is a constant, our condition that $\delta e = 0$ becomes

$$\delta e = N(\epsilon_1 \delta w_1 + \epsilon_2 \delta w_2 + \dots + \epsilon_i \delta w_i) = 0.$$

Consequently our third condition becomes finally

$$\sum_{n=1}^{n=i} \epsilon_n \delta w_n = 0. \quad (312)$$

Our three conditions for determining equilibrium are then

$$\left. \begin{aligned} \sum_{n=1}^{n=i} \ln w_n \delta w_n &= 0 \\ \sum_{n=1}^{n=i} \epsilon_n \delta w_n &= 0 \\ \sum_{n=1}^{n=i} \delta w_n &= 0. \end{aligned} \right\} (313)$$

We shall now solve this set of three equations simultaneously for w_n by the method of Lagrange, whose proof and explanation are given in article 5, the standard way of solving such a set of equations. Multiply the second equation by the undetermined constant β and the third by λ . We have

$$\sum_{n=1}^{n=i} \ln w_n \delta w_n + \beta \sum_{n=1}^{n=i} \epsilon_n \delta w_n + \lambda \sum_{n=1}^{n=i} \delta w_n = 0.$$

Combining like terms, we have

$$\sum_{n=1}^{n=i} (\ln w_n + \beta \epsilon_n + \lambda) \delta w_n = 0. \quad (314)$$

By introducing the two undetermined multipliers β and λ , we have enabled all the variations δw_n to be carried out independently of each other in any arbitrary manner; the justification for this statement will be found in article 5. Since the variations δw_n can be carried out independently of each other in any arbitrary manner, the only way equation 314 can remain satisfied at all times and remain equal to zero is for the coefficient of each of the δw 's to vanish. We see, then, that in order to permit any arbitrary changes in the δw 's we must adjust the auxiliary variables β and λ so that the quantity in parentheses will vanish, and consequently equation 314 will remain satisfied at all times. That is,

$$\ln w_n + \beta \epsilon_n + \lambda = 0$$

or

$$w_n = e^{(-\beta \epsilon_n - \lambda)} = e^{-\lambda} e^{-\beta \epsilon_n}.$$

If the constant $e^{-\lambda}$ is simplified and set equal to a , we have

$$w_n = a e^{-\beta \epsilon_n}. \quad (315)$$

Both α and β are constants, obviously independent of n , and are therefore the same for all the values of $w_n = w_1, w_2, w_3, \dots$. They are constants to be determined by the conditions of the particular problem to which equation 315 is applied. If the constant β is positive, as will later be shown to be the case, equation 315 indicates that the fraction or the probability w_n (that the representative point of a molecule lies in a compartment of the phase space having a large energy ϵ_n) is less than the probability that the representative point lies in a compartment of the phase space having a small energy ϵ_n .

The equilibrium distribution of the molecules among the different possible molecular energy states ϵ_n is consequently determined by

$$w_n = \alpha e^{-\beta \epsilon_n} \quad (316)$$

with the subordinate condition according to equation 307 for the sum of all the w 's

$$\sum_{n=1}^{n=i} w_n = \alpha \sum_{n=1}^{n=i} e^{-\beta \epsilon_n} = 1 \quad (317)$$

and also with equation 311 for the total sum e of all the energies of the molecules,

$$e = N \sum_{n=1}^{n=i} \epsilon_n w_n = N \alpha \sum_{n=1}^{n=i} \epsilon_n e^{-\beta \epsilon_n} \quad (318)$$

since α is a constant for all the w 's.

From equation 318 by substituting for α from 317 we obtain, for the average energy $\frac{e}{N}$ per molecule, the following expression, which includes the interatomic, the subatomic, and the kinetic energy of translation:

$$\frac{e}{N} = \frac{\sum_{n=1}^{n=i} \epsilon_n e^{-\beta \epsilon_n}}{\sum_{n=1}^{n=i} e^{-\beta \epsilon_n}}. \quad (319)$$

Before we can determine quantitatively the velocities of the different molecules of a vapor in a state of equilibrium at a temperature T , we must ascertain the relation between the thermodynamic probability W (that is, the number of possible complexions W of the given state) and the entropy of the vapor s . By means of this relation we can evaluate the constants α and β of equation 316, both of which will be found to involve the temperature T .

50. Relation between the Entropy s and the Thermodynamic Probability W

We wish now to determine the relation between the entropy s of a given macroscopic state and the number of different complexions W associated with that state. According to the previous article, W is also referred to as the thermodynamic probability associated with the given macroscopic state.

From the point of view of probability, the state of equilibrium of a system is its most probable state; or it is that macroscopic state whose thermodynamic probability W is a maximum. Furthermore, when W is a maximum at a given temperature and pressure, the substance is in the macroscopic state that can be realized by the greatest number of different complexions.

From the point of view of thermodynamics, on the other hand, the state of equilibrium of a substance at a given temperature and pressure is the one whose entropy s has reached a maximum. Thus the entropy s is closely similar to the thermodynamic probability W . As a system approaches equilibrium, both the thermodynamic probability W and the entropy s approach a maximum. Consequently (art. 4), when s and W have reached a maximum, $\delta s = 0$ and $\delta W = 0$ for small changes in the variables determining the state of the system.

Let us next consider two different substances or independent systems having entropies s_1 , s_2 , and thermodynamic probabilities W_1 , W_2 , respectively. We wish to determine the relation between the total entropy s of the two combined systems and the total thermodynamic probability W of the combination. As will be recalled (art. 19), the total entropy of a system equals the sum of the entropies of its parts; hence

$$s = s_1 + s_2. \quad (320)$$

On the other hand, the total thermodynamic probability W of the simultaneous existence of specified macroscopic states of two different substances equals the product of the probabilities of the individual macroscopic states; that is,

$$W = W_1 W_2. \quad (321)$$

This is merely the statement of a well-known elementary theorem of probability, found in any college algebra text and given in a different form in article 49, which states that the total probability W (that both of two independent events will happen together) is the product of their separate probabilities W_1 and W_2 .

By taking the logarithm of both sides, we have

$$\ln W = \ln W_1 + \ln W_2. \quad (322)$$

Comparing equation 322 with 320 one sees that the entropies, as well as the logarithms of the thermodynamic probabilities of the separate systems, are additive. Also, as has been pointed out, both functions are a maximum when the systems are in equilibrium. Consequently, since the entropy s of a system is proportional to and behaves like the logarithm of thermodynamic probability W of the system, the following relation appears to exist between the entropy s of a single system in a particular macroscopic state and the thermodynamic probability W of that state:

$$s = k \ln W, \quad (323)$$

where k is a universal constant, later shown to be equal to the gas constant for one molecule.

A somewhat more rigorous derivation of the relation (eq. 323) between the entropy and the thermodynamic probability of any system composed of atoms or molecules may be made as follows. At the start we shall merely assume that the entropy s is some function $f(W)$ of the thermodynamic probability W . In other words, we assume only that there exists some relation between s and W . What it is, will be our problem to determine. We have then

$$s = f(W). \quad (324)$$

It must be noticed that f here denotes not free energy but rather some function $f(W)$ that depends on W . We wish now to determine the form of $f(W)$. Suppose we have two entirely independent and separate systems whose entropies are s_1 and s_2 and whose thermodynamic probabilities are W_1 and W_2 . It then follows for the first and second system, respectively, that

$$\left. \begin{aligned} s_1 &= f(W_1), \\ s_2 &= f(W_2). \end{aligned} \right\} \quad (325)$$

Let us now combine the two systems. The total thermodynamic probability W of the two systems taken together as a single unit is the product ($W_1 W_2$). This follows because to each of the W_1 complexions of the first system, there are W_2 of the second. Consequently, the total number of complexions of the two independent systems, taken together as one, must be ($W_1 W_2$). The same result follows from the theorem of probability just previously mentioned.

Now the total entropy s of the two systems combined equals the sum of the entropies s_1 and s_2 of the separate ones. From equations 320, 324, and 321, we have then

$$s = s_1 + s_2 = f(W) = f(W_1 W_2); \quad (326)$$

and from equations 325 and 326, using the second and fourth member of 326,

$$f(W_1) + f(W_2) = f(W_1W_2).$$

Differentiating this equation with respect to W_1 , we have

$$\frac{df(W_1)}{dW_1} + \frac{df(W_2)}{dW_1} = \frac{df(W_1W_2)}{dW_1}. \quad (327)$$

From a well-known theorem on differentiation, we may write for the last term of equation 327

$$\frac{df(W_1W_2)}{dW_1} = \frac{df(W_1W_2)}{d(W_1W_2)} \frac{d(W_1W_2)}{dW_1} = \frac{d(W_1W_2)}{dW_1} \frac{df(W_1W_2)}{d(W_1W_2)} = W_2 \frac{df(W_1W_2)}{d(W_1W_2)};$$

and since $f(W_2)$ is independent of W_1 , the first system being independent of the other, the second term of 327 is zero, so that equation 327 becomes with the above

$$\frac{df(W_1)}{dW_1} = W_2 \frac{df(W_1W_2)}{d(W_1W_2)}. \quad (328)$$

Differentiating the same equation in like manner, but with respect to W_2 , we have, corresponding to equation 328,

$$\frac{df(W_2)}{dW_2} = W_1 \frac{df(W_1W_2)}{d(W_1W_2)}. \quad (329)$$

Multiplying equations 328 and 329 by W_1 and W_2 , respectively, we find that their right-hand members are identical. Hence

$$W_1 \frac{df(W_1)}{dW_1} = W_2 \frac{df(W_2)}{dW_2} = W_1W_2 \frac{df(W_1W_2)}{d(W_1W_2)}. \quad (330)$$

Since the two systems were assumed to be entirely separate and independent of each other, any variation of W_1 can be carried out independently, with no relation to the changes in W_2 . Now the first member of equation 330 is a function of W_1 only and is therefore completely unaffected by changes of W_2 , whereas the second or middle member is a function of W_2 only and is completely unaffected by changes of W_1 . The only way for such a state of affairs to exist, where both members of the equation are always equal to each other yet depend on entirely different variables, is

for both members of the equation to equal one and the same constant, which we shall here call k . Thus

$$W_1 \frac{df(W_1)}{dW_1} = k,$$

and

$$W_2 \frac{df(W_2)}{dW_2} = k.$$

For the type of systems with which we are dealing, k is a universal constant, the same for all systems, no matter of what type. Obviously it is immaterial which of these equations we integrate. Both will yield an integral of the same final form. Let us therefore drop the subscripts 1 and 2. We have

$$df(W) = k \frac{dW}{W}.$$

Integrating, we now obtain the exact form of the originally unknown function $f(W)$. It is

$$f(W) = k \ln W + C. \quad (331)$$

Recalling from 324 that s was assumed to be a function of W , we find that equation 331 becomes

$$s = k \ln W + C. \quad (332)$$

To evaluate C let us note the conditions at absolute zero where there is no motion of the molecules and where all molecules are therefore in the same cell in the phase space where the energy of each molecule is zero. Then W , the number of complexions of the system, has a value of 1 at absolute zero, and therefore $\ln W = 0$ at absolute zero. Since (eq. 90) s is also zero at this temperature, C must be equal to zero; and therefore we may write

$$s = k \ln W. \quad (333)$$

This equation, the same we found previously by a less rigorous approach, determines the desired relation between the entropy s and the thermodynamic probability W , where k is a universal constant because it is the same for all systems. The only two assumptions made in obtaining 333 were, first, the idea that the total entropy s of a system was equal to the sum of the entropies s_1, s_2, \dots of its parts; and, second, the fundamental theorem of probability previously given in connection with equation 321. Both these assumptions are substantiated by all available evidence.

51. Relation between the Entropy s of a System at Equilibrium and the Internal Energy ϵ_n of the Different Molecules

We can now show how the entropy s of the system depends on the distribution w_n of the molecules among the different possible energy states ϵ_n in which a molecule of the system might find itself. From equation 308, we had

$$\ln W = -N \sum_{n=1}^{n=i} w_n \ln w_n + w_2 \ln w_2 + \dots = -N \sum_{n=1}^{n=i} w_n \ln w_n.$$

Inserting this in equation 333 above, we have

$$s = -kN \sum_{n=1}^{n=i} w_n \ln w_n. \quad (334)$$

But from equation 316

$$w_n = a e^{-\beta \epsilon_n};$$

hence

$$\ln w_n = (-\beta \epsilon_n + \ln a) = -(\beta \epsilon_n - \ln a).$$

Therefore 334 becomes

$$s = kN \sum_{n=1}^{n=i} w_n (\beta \epsilon_n - \ln a)$$

or

$$s = kN \sum_{n=1}^{n=i} (\beta w_n \epsilon_n - w_n \ln a).$$

Splitting this into the two series and recalling from the statements made in connection with equation 315 that β and a are constants independent of n ,

$$s = kN \beta \sum_{n=1}^{n=i} w_n \epsilon_n - kN \ln a \sum_{n=1}^{n=i} w_n.$$

From equations 307 and 311 we had, respectively, that

$$\sum_{n=1}^{n=i} w_n = 1,$$

and

$$N \sum_{n=1}^{n=i} w_n \epsilon_n = e$$

where e denotes the total internal energy of the system. Hence the expression for the entropy s becomes

$$s = k \beta e - kN \ln a.$$

Again from equation 317 we had

$$\alpha \sum_{n=1}^{n=i} e^{-\beta \epsilon_n} = 1,$$

or

$$\alpha = \frac{1}{\sum_{n=1}^{n=i} e^{-\beta \epsilon_n}}$$

so that

$$\ln \alpha = -\ln \sum_{n=1}^{n=i} e^{-\beta \epsilon_n}.$$

With this, the expression for s becomes

$$s = k \beta e + kN \ln \sum_{n=1}^{n=i} e^{-\beta \epsilon_n}. \quad (335)$$

52. Relation of the Temperature to the Distribution w_n of the Molecules among the Different Possible Energy States ϵ_n

A statement of the First Law of thermodynamics is given by equation 47 as

$$de = dq - dw. \quad (336)$$

Now if the only work w done is that of expansion against an external pressure, equation 336 becomes

$$de = dq - p dv. \quad (337)$$

For reversible processes the Second Law (eq. 70) permits us to write equation 337 in the following form:

$$de = T ds - p dv. \quad (338)$$

Solving equation 338 for ds , we have

$$ds = \left(\frac{1}{T}\right) de + \left(\frac{p}{T}\right) dv. \quad (339)$$

Let us now obtain another expression for ds . As already pointed out (art. 2), the state of a simple system is determined by two variables, and these might be any such pairs as either T and v , or e and v . Let us use

the pair e and v to describe the state of the system. Then the entropy s of the system is a function of these two variables. Purely as a mathematical consequence (art. 1 and 2), we have

$$ds = \left(\frac{\partial s}{\partial e} \right)_v de + \left(\frac{\partial s}{\partial v} \right)_e dv. \quad (340)$$

Equations 339 and 340 are merely two ways of stating the same dependence of ds upon de and dv . Hence, equating the coefficients of de and dv in equations 339 and 340, we have

$$\left. \begin{aligned} \left(\frac{\partial s}{\partial e} \right)_v &= \frac{1}{T} \\ \left(\frac{\partial s}{\partial v} \right)_e &= \frac{p}{T} \end{aligned} \right\} \quad (341)$$

and

We shall now use these general thermodynamic expressions for evaluating β in the distribution function w_n of equation 316; but first we must transform equation 335, which was

$$s = k \beta e + kN \ln \left(\sum_{n=1}^{n=i} e^{-\beta \epsilon_n} \right), \quad (342)$$

into a form such that we can substitute the result for $\frac{1}{T}$ in the first of equations 341. Remembering that k , N , and the energy ϵ_n associated with a molecule in the n th compartment of phase space are constants, independent of all changes made in the system itself so long as the total number of molecules N in the system remains the same; and remembering further that the internal energy e depends on β , according to equation 319, we find upon differentiating equation 342 with respect to β ,

$$\left(\frac{\partial s}{\partial \beta} \right)_v = ke + k\beta \left(\frac{\partial e}{\partial \beta} \right)_v - \frac{kN \sum_{n=1}^{n=i} \epsilon_n e^{-\beta \epsilon_n}}{\sum_{n=1}^{n=i} e^{-\beta \epsilon_n}}. \quad (343)$$

From equation 319 it will be recalled that

$$e = N \frac{\sum_{n=1}^{n=i} \epsilon_n e^{-\beta \epsilon_n}}{\sum_{n=1}^{n=i} e^{-\beta \epsilon_n}}.$$

Substituting this for the summation expressions in equation 343, we have

$$\left(\frac{\partial s}{\partial \beta}\right)_v = k\beta \left(\frac{\partial e}{\partial \beta}\right)_v. \quad (344)$$

Now, by a mathematical theorem on partial differentiation proved in article 6,

$$\left(\frac{\partial e}{\partial \beta}\right)_v = \frac{1}{\left(\frac{\partial \beta}{\partial e}\right)_v}.$$

Equation 344 therefore becomes

$$\left(\frac{\partial s}{\partial \beta}\right)_v \left(\frac{\partial \beta}{\partial e}\right)_v = k\beta.$$

It was shown (art. 7) that we may write

$$\left(\frac{\partial s}{\partial \beta}\right)_v \left(\frac{\partial \beta}{\partial e}\right)_v = \left(\frac{\partial s}{\partial e}\right)_v,$$

so that the preceding equation becomes

$$\left(\frac{\partial s}{\partial e}\right)_v = k\beta,$$

from which (by eq. 341) we get

$$k\beta = \frac{1}{T}, \quad \text{or} \quad \beta = \frac{1}{kT}. \quad (345)$$

We can now express the distribution function w_n of equation 316 in terms of the universal constant k , often called Boltzman's constant—that is, the gas constant per molecule (art. 59)—and of the temperature T . From equation 316 we had

$$w_n = ae^{-\beta \epsilon_n},$$

which now becomes

$$w_n = ae^{-\frac{\epsilon_n}{kT}}. \quad (346)$$

Equation 346 gives the fraction w_n of the total number of molecules N

of the system that have an energy ϵ_n when the whole system is at the uniform temperature T throughout. Thus, though the system is at the temperature T throughout, the energy of the individual molecules ϵ_n varies widely among the different molecules.

53. Relation of the Entropy s and the Maximum Work a , of the System, to the Energies ϵ_n of the Individual Molecules of the System

From equation 335 we have for the entropy s of the system

$$s = k \beta e + kN \ln \left(\sum_{n=1}^{n=i} e^{-\beta \epsilon_n} \right),$$

which by equation 345 becomes

$$s = \frac{e}{T} + kN \ln \left(\sum_{n=1}^{n=i} e^{-\frac{\epsilon_n}{kT}} \right) \quad (347)$$

and defines the specific entropy s of the system composed of N molecules in terms of the energies of the individual molecules ϵ_n , the total internal energy e , and the temperature T of the system.

As will be recalled (eq. 279), the maximum work, a , was defined by

$$a = e - Ts.$$

Introducing the value of s from this into equation 347, we find, upon solving for a ,

$$a = -kNT \ln \left(\sum_{n=1}^{n=i} e^{-\frac{\epsilon_n}{kT}} \right), \quad (348)$$

showing, in the same manner as equation 335 for the entropy, the dependence of the maximum work a on the energies ϵ_n of the individual molecules of the system.

Now, to demonstrate the consistency of the expressions developed in this section on kinetic theory, including the relation between s and W given by equation 333, we will show that the Gibbs-Helmholtz equation, a fundamental equation of thermodynamics, can be derived from equation 348 for the maximum work function a . The Gibbs-Helmholtz equation (eq. 284) is

$$e = a - T \left(\frac{\partial a}{\partial T} \right)_{v, w_m}.$$

Differentiating a in equation 348, while maintaining all the other variables except T constant, we have

$$\frac{\partial a}{\partial T} = -kN \ln \left(\sum_{n=1}^{n=i} e^{-\frac{\epsilon_n}{kT}} \right) - kNT \frac{\sum_{n=1}^{n=i} \left(\frac{\epsilon_n}{kT^2} \right) e^{-\frac{\epsilon_n}{kT}}}{\sum_{n=1}^{n=i} e^{-\frac{\epsilon_n}{kT}}}.$$

Simplifying the last term,

$$\frac{\partial a}{\partial T} = -kN \ln \left(\sum_{n=1}^{n=i} e^{-\frac{\epsilon_n}{kT}} \right) - \frac{N}{T} \frac{\sum_{n=1}^{n=i} \epsilon_n e^{-\frac{\epsilon_n}{kT}}}{\sum_{n=1}^{n=i} e^{-\frac{\epsilon_n}{kT}}}.$$

Multiplying through by T ,

$$T \frac{\partial a}{\partial T} = -kNT \ln \left(\sum_{n=1}^{n=i} e^{-\frac{\epsilon_n}{kT}} \right) - N \frac{\sum_{n=1}^{n=i} \epsilon_n e^{-\frac{\epsilon_n}{kT}}}{\sum_{n=1}^{n=i} e^{-\frac{\epsilon_n}{kT}}}.$$

The first term on the right side of the equation is immediately recognized to be nothing but the maximum work, a , according to equation 348; and the second is, according to equation 319 as modified by equation 345, the negative of the total internal energy e of the system. The whole then simplifies down to

$$T \frac{\partial a}{\partial T} = a - e,$$

which, rearranged, gives us directly the desired Gibbs-Helmholtz expression

$$e = a - T \frac{\partial a}{\partial T}. \quad (349)$$

54. Maxwell Distribution of Molecular Velocities

We shall use equation 315 in determining the speeds of translation possessed by the different molecules of a gas or vapor. Actually we shall determine the expression for the fraction w_n of the total number of molecules N having a given specified speed. This expression will be used later in discussing the speeds of the different molecules moving normally to the air-water interface of soil moisture.

Let us express the total energy ϵ_n of a molecule of an ideal gas as the

sum of its kinetic energy of translation ϵ_n' and its internal energy ϵ_n'' so that

$$\epsilon_n = \epsilon_n' + \epsilon_n''.$$

Then the fraction w_n of the total number of molecules whose representative points fall in the n th compartment or cell of the multidimensional phase space is given by equation 315, together with 345,

$$w_n = \alpha e^{-\frac{\epsilon_n'}{kT} - \frac{\epsilon_n''}{kT}}. \quad (350)$$

As pointed out earlier (art. 49), if the molecule has d degrees of freedom, the phase space has $2d$ dimensions. The first d dimensions describe the instantaneous position of the center of mass of the molecule, which we represent by x , y , and z , as well as the position of the parts of the molecule with respect to its center of mass, which we represent by x_1 , x_2 , x_3 , . . . x_{d-3} . The other d dimensions describe the velocity of translation of the center of mass, which we represent by u_x , u_y , and u_z , as well as the movements of the parts of the molecule with respect to its center of mass, which we represent by u_1 , u_2 , u_3 , . . . u_{d-3} . Let us divide the phase space into compartments, all of equal volume, whose amount we shall call g . We then have

$$g = (dx \, dy \, dz \, dx_1 \, dx_2 \, \dots \, dx_{d-3}) (du_x \, du_y \, du_z \, du_1 \, du_2 \, \dots \, du_{d-3}). \quad (351)$$

It may seem strange at first to speak of the multidimensional element g as an element of volume. Although ordinarily it seems impossible to visualize a volume of more than three dimensions, we are, as previously mentioned, not handicapped by any such limitation in mathematics, where we can deal with a space of as many dimensions as we please. Since these multidimensional spaces have properties analogous to the three-dimensional spaces of ordinary experience, we often apply many of the terms associated with the latter to the former.

Multiplying the denominator and numerator of equation 350 by g and its equivalent, respectively, according to equation 351, and recalling that the kinetic energy of translation is $\epsilon_n' = \frac{1}{2} m u^2$ where

$$u^2 = u_x^2 + u_y^2 + u_z^2,$$

we have

$$w_n = \frac{\alpha}{g} e^{-\frac{\epsilon_n'}{kT}} e^{-\frac{\epsilon_n''}{kT}} \frac{m u^2}{2kT} (dx \, dy \, dz \, dx_1 \, dx_2 \, \dots) (du_x \, du_y \, du_z \, du_1 \, du_2 \, \dots).$$

This equation may be restated as

$$w_n = \frac{\alpha}{g} e^{-\frac{\epsilon_n''}{kT}} (dx_1 \, dx_2 \, \dots \, du_1 \, du_2 \, \dots) (dx \, dy \, dz) e^{-\frac{m u^2}{2kT}} (du_x \, du_y \, du_z). \quad (352)$$

As already mentioned (eq. 306), w_n gives the fraction of the total number of molecules having an energy ϵ_n whose representative points fall in the n th compartment or cell of phase space having the volume g .

What we are now really seeking is an expression for the fraction w_n' , of the total number of molecules, having a translational velocity u , whose components lie between u_x and $u_x + du_x$, u_y and $u_y + du_y$, and u_z and $u_z + du_z$, no matter what their internal energies ϵ_n'' might be. Since the internal energies are entirely independent of the velocities of translation u_x , u_y , u_z , we may integrate or sum the first exponential of equation 352 (entirely independently of the second) over all dimensions in the phase space except those corresponding to u_x , u_y , u_z . We then obtain

$$w_n' = \left[\frac{a}{g} \int e^{-\frac{\epsilon_n''}{kT}} (dx_1 dx_2 \dots du_1 du_2 \dots) (dx dy dz) \right] e^{-\frac{mu^2}{2kT}} du_x du_y du_z.$$

Denoting the constant within the brackets, obtained after the integration, by a' and recalling that $u^2 = u_x^2 + u_y^2 + u_z^2$, we have

$$w_n' = a' e^{-\frac{m}{2kT}(u_x^2 + u_y^2 + u_z^2)} du_x du_y du_z. \quad (353)$$

We may determine a' by recalling (eq. 307) the condition that

$$\sum_{n=1}^{n=i} w_n' = 1.$$

We have

$$\sum_{n=1}^{n=i} w_n' = a' \int_{-\infty}^{\infty} e^{-\frac{mu_x^2}{2kT}} du_x \int_{-\infty}^{\infty} e^{-\frac{mu_y^2}{2kT}} du_y \int_{-\infty}^{\infty} e^{-\frac{mu_z^2}{2kT}} du_z = 1,$$

since components of velocity may be either positive or negative. Using the formula for the definite integral given by equation 37, this reduces after integration so that we have

$$a' \left(\frac{2kT\pi}{m} \right)^{\frac{3}{2}} = 1$$

and therefore

$$a' = \left(\frac{m}{2kT\pi} \right)^{\frac{3}{2}}.$$

Then, upon recalling the definition of w_n' , equation 353 becomes, with the above and equation 306,

$$w_n' = \frac{N_n}{N} = \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} e^{-\frac{mu^2}{2kT}} du_x du_y du_z.$$

From this we obtain immediately Maxwell's law giving the number of molecules N_n (which we shall now denote by dN) having components of velocity lying between u_x and $u_x + du_x$, u_y and $u_y + du_y$, u_z and $u_z + du_z$. Substituting dN for N_n in the equation above and solving for dN , we have

$$dN = N \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} e^{-\frac{m}{2kT} (u_x^2 + u_y^2 + u_z^2)} du_x du_y du_z. \quad (354)$$

Suppose we now consider only one of the components of velocity of the molecules, such as u_x along the x axis, and ask how dN depends on the velocity u_x . That is, we wish to find out how many molecules dN have

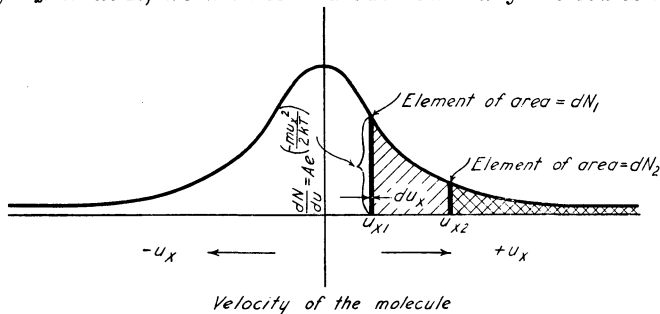


Fig. 28.—Distribution of the components of the velocities of the molecules along any one direction in space. Area under curve between any two abscissas u_{x1} and u_{x2} gives the number of molecules having velocities between u_{x1} and u_{x2} .

a value for the x component of their velocity falling between u_x and $u_x + du_x$. To answer this, we shall integrate equation 354 over all molecules with respect to u_y and u_z :

$$dN = A e^{-\frac{m}{2kT} u_x^2} du_x \quad (355)$$

where A is the constant obtained after the integration has been performed. If we plot the coefficient of du_x of equation 355 against u_x (fig. 28), we get the well-known Gaussian form of distribution curve. This is symmetrical; that is, as many molecules dN in the vapor have a given velocity $+u_x$ in one direction as have a velocity $-u_x$ in the opposite. Also, very few molecules have great velocity; and many have no x component of velocity at all. The expressions for the distribution of velocities along the y and z axes have the same form as equation 355.

55. Velocities of Molecules Normal to Vapor-Liquid Interface as Related to Vapor Pressure

Equation 355 applies directly to the problem, considered to some extent in article 47, of the outward emission of water molecules from the liquid films surrounding soil particles. In this case we are interested only

in half of the curve—that is, only in the molecules moving outward from the film. If no adsorptive forces surrounded the soil particle, all the molecules of the $(+u_x)$ part of the curve (fig. 28) would leave the moisture film. Since, however, there are adsorptive forces, the water molecules must possess a certain definite minimum kinetic energy in order to escape into the vapor phase. This will entail a minimum velocity u_{x1} . All molecules in the layer having a velocity less than u_{x1} will be held back in the liquid surface, but all those having a velocity greater will escape; that is, the faster molecules escape, while the slower ones are held behind.

As the moisture content of the soil is decreased, the vapor-liquid interface comes more and more under the influence of the adsorptive forces surrounding the soil particle, so that the molecule must possess more and more kinetic energy in order to escape. Consequently, the minimum velocity required will be increased to some other velocity (for example, u_{x2}); and only those molecules in the liquid layer having velocities greater than this will escape.

The curve (fig. 28) should be so constructed that the area under it between two velocities such as u_{x1} and u_{x2} gives the total number of molecules having velocities within the velocity interval $(u_{x2} - u_{x1})$. Also the area under the curve to the right of some velocity value such as u_{x1} and extending out to infinity gives the total number of molecules having a velocity greater than u_{x1} .

Figure 28, based on the Maxwell distribution law, is the basis for predicting how changes of moisture content will affect the vapor pressure of soil moisture. When the soil is saturated, all the molecules whose numbers are represented by the area of the positive half of the figure escape into the vapor phase, being beyond the influences of the soil forces. When the soil-moisture content is decreased from a state of saturation the molecules begin to require, in order to escape into the vapor phase, a certain minimum amount of kinetic energy which depends upon the moisture content. If the moisture content has been decreased so that an amount of kinetic energy $\frac{1}{2}mu_{x1}^2$ is necessary for escape, then all the molecules whose number is represented by the entire area under the curve to the right of u_{x1} will escape into the vapor phase, and all the rest will remain in the liquid. If the soil moisture content is further decreased so that at least an amount of kinetic energy $\frac{1}{2}mu_{x2}^2$ is required for the escape, then only those molecules whose number is represented by the entire area under the curve to the right of u_{x2} will escape into the vapor phase, and this area is seen to be less than that corresponding to a higher moisture content. Thus as the soil moisture content is decreased, more and more molecules having positive u_x components of velocity are held back in the liquid, and fewer and fewer can go into the vapor phase.

No matter how dry the soil or how tightly the soil moisture is bound to the soil particle, there will always be a few molecules with a high enough velocity and therefore with sufficient kinetic energy to escape. As the soil moisture content approaches zero, the vapor pressure of the soil moisture thus decreases gradually; but it cannot become zero until the soil moisture content is also zero.

The Maxwell distribution law also explains why a moist surface placed in an atmosphere whose humidity is below 100 per cent tends to cool off. Experimentally we find that the lower the humidity and the greater the wind movement, the greater is the cooling effect. The explanation is that

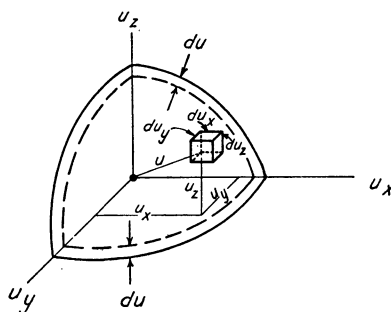


Fig. 29.—Element of volume in phase space.

the temperature of an object is determined entirely by the mean kinetic energy of all the molecules composing it. As this energy is decreased, the temperature also decreases. Now, as was just shown, only the fastest-moving molecules can escape from the liquid and be carried away by the air currents. Thus those remaining behind have a smaller average velocity, a smaller mean kinetic energy, and therefore a lower temperature. Hence evaporation from a moist surface tends to cool it off.

If the space above the liquid is saturated, just as many fast molecules move out of the liquid in a given time as move into it. In this latter case, accordingly, there is no cooling effect.

56. Number of Molecules Having Speeds within Certain Limits

In article 54 we considered the number of molecules dN having components of velocity u_x in any single direction within the velocity interval between u_x and $u_x + du_x$. We considered the same also for the y and z axes. Now, going a bit further, we shall determine the number of molecules dN having speeds within the interval between u and $u + du$ without regard to direction of movement of the molecule. Thus the three compo-

nents of velocity may vary in any arbitrary manner so long as they satisfy the equation

$$u^2 = u_x^2 + u_y^2 + u_z^2,$$

and u lies within the velocity interval between u and $u + du$. Thus the element of volume du_x, du_y, du_z in the velocity space as given by equation 354 may be replaced by the volume included between the two concentric spheres of radii u and $u + du$, an octant of which is shown in figure 29. This is possible, since all the molecules whose representative points fall within the same spherical shell have the same speed u and therefore the same value for the total kinetic energy $\frac{1}{2}mu^2$ in the exponential of the

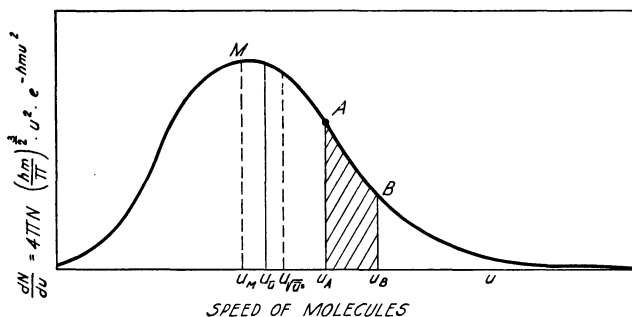


Fig. 30.—Speed distribution of molecules.

distribution function, even though their components of velocity u_x, u_y, u_z may be widely different. The volume of the spherical shell included between the concentric spheres of radii u and $u + du$ is immediately seen to be $4\pi u^2 du$. We shall therefore replace the cubical volume element of integration du_x, du_y, du_z by this spherical shell. Equation 354 then becomes

$$dN = 4\pi N \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} u^2 e^{-\frac{mu^2}{2kT}} du.$$

To simplify this, let us set $\frac{1}{2kT} = h$. Obviously, h is the same for all molecules and is independent of u . We have then

$$dN = 4\pi N \left(\frac{hm}{\pi} \right)^{\frac{3}{2}} u^2 e^{-hmu^2} du. \quad (356)$$

Let us plot the coefficient of du of equation 356 against u as shown in figure 30. The area under any segment of the curve equals the number of molecules having speeds whose values lie between those represented by

the abscissas of the limits of the segment. Thus, for example, the number of water-vapor molecules, in a container at a temperature T , whose speeds lie between u_A and u_B , is given by the shaded area under the segment AB . There is no negative half of the curve, since we are here interested only in the absolute magnitudes of the velocities, not in their direction. Also the distribution curve will be found to extend asymptotically out to $u = +\infty$; but since the area under the portion of the curve representing high velocities is negligible, the number of molecules having these high speeds must also be negligible. This curve for the distribution of speeds u contrasts greatly with figure 28, for the distribution of velocities of one of the three components of u . In figure 28 the curve is symmetrical with respect to the vertical axis; in figure 30, it is not.

57. Dependence of Temperature on the Root-Mean-Square Speeds of Molecules

As mentioned previously, the temperature of a substance is determined entirely by the kinetic energy of the molecules; and the kinetic energy of a molecule equals $\frac{1}{2}mu^2$. Since the molecules of a substance have widely different velocities, we see that in order to express the temperature or the internal energy of the gas in terms of the kinetic energy of the individual molecules we must find the *average* of the squares of the velocities (which we shall denote by $\overline{u^2}$) of all the molecules. The formula for the average of all the u^2 's associated with the different molecules is, according to the definition of $\overline{u^2}$,

$$\overline{u^2} = \frac{\int_0^{\infty} u^2 dN}{N},$$

which with equation 356 becomes

$$\overline{u^2} = 4\pi \left(\frac{h m}{\pi} \right)^{\frac{3}{2}} \int_0^{\infty} u^4 e^{-h m u^2} du.$$

Integrating this by means of the expression given for the definite integral in equation 40, we have for the average of the squares of the velocities of all the molecules

$$\overline{u^2} = \frac{3}{2 h m} = \frac{3 k T}{m},$$

since h was set equal to $\frac{1}{2 k T}$. From this we have for the average kinetic

energy of a molecule,

$$\frac{m \overline{u^2}}{2} = \frac{3}{2} k T. \quad (357)$$

This shows that as the average kinetic energy of the molecules of a substance increases, the temperature T of the substance must also increase, since k is a universal constant which, as will be shown (art. 59), is the well-known gas constant per molecule. The position of the root-mean-square speed $\sqrt{u^2}$ with respect to the maximum M of the distribution curve is shown in figure 30. As shown, the root-mean-square speed $\sqrt{u^2}$ is greater than the most probable velocity u_M .

58. Average Speed of Molecules

We have just been considering the root-mean-square speed of the molecules denoted by $\sqrt{u^2}$. We shall now determine their average speed, which we shall denote by \bar{u} . By definition it is

$$\bar{u} = \frac{\int_0^{\infty} u dN}{N}, \quad (358)$$

and with 356 it becomes

$$= \frac{4\pi N \left(\frac{h m}{\pi}\right)^{\frac{3}{2}} \int_0^{\infty} u^3 e^{-hmu^2} du}{N}$$

or

$$= 2\pi \left(\frac{h m}{\pi}\right)^{\frac{3}{2}} \int_0^{\infty} u^2 e^{-hmu^2} du^2,$$

putting $u^2 = x$ in order to transform it into the familiar integral form

$$= 2\pi \left(\frac{h m}{\pi}\right)^{\frac{3}{2}} \int_0^{\infty} x e^{-hmx} dx,$$

which can be found in any table of integrals and works out to be

$$\bar{u} = 2\pi \left(\frac{h m}{\pi}\right)^{\frac{3}{2}} \frac{1}{(h m)^2} = \frac{2}{\sqrt{\pi h m}} = 2\sqrt{\frac{2kT}{\pi m}}. \quad (359)$$

The position of the mean or average speed \bar{u} with respect to the root-mean-square $\sqrt{u^2}$ and the maximum M of the distribution curve is shown in figure 30.

59. Equation of State of an Ideal Gas and the Gas Constant k per Molecule

In the previous articles, on a purely statistical foundation based upon considerations of probability, we have arrived at several expressions describing the energy relations among the individuals of an assemblage of

molecules. No experimental data were used. On the basis of these expressions there was derived, in article 54, the Maxwell distribution law for molecular velocities, whose validity has been thoroughly substantiated by experiment. We shall now show that the ideal gas law also follows as a natural consequence from these statistical considerations. In so doing we shall make use of

$$p = - \left(\frac{\partial a}{\partial v} \right)_T, \quad (360)$$

which is obtained from equation 280 when the only work done is that of expansion against an external pressure, so that $dw = p dv$, and equation 348, which is

$$a = -kNT \ln \sum_{n=1}^{n=i} e^{-\frac{\epsilon_n}{kT}}. \quad (361)$$

Let us consider an ideal polyatomic gas. Each molecule will then possess not only three degrees of freedom in translation, but also certain others often called internal degrees of freedom, such as vibration and rotation of the parts of the molecule. Let ϵ_n' , as before, denote the kinetic energy of translation of a molecule whose representative point lies in the n th compartment of the phase space; and let ϵ_n'' be its corresponding internal energy. Then the total energy of the molecule, as pointed out previously, is

$$\epsilon_n = \epsilon_n' + \epsilon_n''. \quad (362)$$

As previously pointed out (art. 49), if the molecule has d degrees of freedom, the corresponding phase space will have $2d$ dimensions: one set of d dimensions describes the instantaneous position of the parts of the molecule, while the other set of d dimensions describes the movements of the corresponding parts. The phase space is then divided up into compartments, all of equal volume, whose amount we shall call g (eq. 351). If u_x, u_y, u_z represent the components of the velocity of translation of the molecule whose instantaneous coördinates of position are x, y, z and if u_1, u_2, \dots and x_1, x_2, \dots represent in like manner the movements and coördinates of position associated with the internal degrees of freedom of the molecule, we have, for the volume of each compartment or cell of phase space,

$$g = (du_x du_y du_z dx dy dz) (du_1 du_2 \dots; dx_1 dx_2 \dots).$$

There are, of course, d dimensions of the type $(u_x u_y u_z; u_1 u_2 \dots)$, and d of the type $(xyz; x_1 x_2 \dots)$, making $2d$ dimensions in all. The coördinates

$u_x u_y u_z; xyz$ determine ϵ_n' , and the coördinates $u_1 u_2 \dots; x_1 x_2 \dots$ determine ϵ_n'' .

Let us now proceed to evaluate the summation found in equation 361. According to 362 the summation becomes

$$\sum_{n=1}^{n=i} e^{-\frac{\epsilon_n'}{kT} - \frac{\epsilon_n''}{kT}}.$$

This summation is to be carried out over all the i cells or small compartments, whose volume is g , of phase space. The summation may most easily be carried out by converting it into an integration over all the i cells, as follows:

$$\sum_{n=1}^{n=i} e^{-\frac{\epsilon_n'}{kT} - \frac{\epsilon_n''}{kT}} = \frac{1}{g} \iiint \dots \int e^{-\frac{\epsilon_n'}{kT}} du_x du_y du_z dx dy dz \iiint \dots \int e^{-\frac{\epsilon_n''}{kT}} du_1 du_2 \dots dx_1 dx_2 \dots \quad (363)$$

We shall now evaluate the first integral. Since we are dealing with an ideal polyatomic gas in which there are no forces between the molecules, the translational energy ϵ_n' of a molecule may be represented by

$$\epsilon_n' = \frac{m}{2} (u_x^2 + u_y^2 + u_z^2),$$

so that

$$\begin{aligned} & \frac{1}{g} \iiint \dots \int e^{-\frac{\epsilon_n'}{kT}} du_x du_y du_z dx dy dz \\ &= \frac{1}{g} \int_{-\infty}^{\infty} e^{-\frac{m u_x^2}{2kT}} du_x \int_{-\infty}^{\infty} e^{-\frac{m u_y^2}{2kT}} du_y \int_{-\infty}^{\infty} e^{-\frac{m u_z^2}{2kT}} du_z \iiint dx dy dz. \end{aligned}$$

Integrating the first three integrals on the right-hand side by equation 37, it reduces to

$$\frac{1}{g} \left(\frac{2 \pi kT}{m} \right)^{\frac{3}{2}} \iiint dx dy dz.$$

The triple integral in the equation above is the total volume v occupied by all the molecules of the gas, since x, y, z extend over all the possible coördinates of position that a molecule might take on. Hence we find that the right side of the equation above further reduces to

$$\frac{v}{g} \left(\frac{2 \pi kT}{m} \right)^{\frac{3}{2}}. \quad (364)$$

Thus equation 363 becomes

$$\sum_{n=1}^{n=i} e^{\frac{\epsilon_n'}{kT} - \frac{\epsilon_n''}{kT}} = \frac{v}{g} \left(\frac{2\pi kT}{m} \right)^{\frac{3}{2}} \iint \dots \int e^{\frac{\epsilon_n''}{kT}} du_1 du_2 \dots; dx_1 dx_2 \dots \quad (365)$$

Inserting equation 365 in 361, we have

$$a = -kNT \ln \left\{ \frac{v}{g} \left(\frac{2\pi kT}{m} \right)^{\frac{3}{2}} \right\} - kNT \ln \left\{ \iint \dots \int e^{-\frac{\epsilon_n''}{kT}} du_1 du_2 \dots; dx_1 dx_2 \right\}. \quad (366)$$

The second term on the right is not a function of the volume v , since $x_1, x_2 \dots$ refer only to the coördinates of the internal degrees of freedom of a molecule measured with respect to a fixed point in that molecule. Consequently when we take the partial differential of equation 366 with respect to v , we have, according to equation 360,

$$p = - \left(\frac{\partial a}{\partial v} \right)_T = \frac{kNT}{v},$$

or

$$pv = kNT,$$

or

$$pv = RT,$$

$$\left. \vphantom{\begin{matrix} pv = kNT, \\ pv = RT, \end{matrix}} \right\} (367)$$

where R is set equal to kN .

Equations 367 are recognized immediately as the familiar ideal gas law. Since v and N refer to 1 gram of the substance, R is obviously the gas constant per gram, and k the gas constant per molecule. As will be recalled, k appeared first as a constant of proportionality in equation 332, relating entropy with the probability of the state of the system. No other physical significance was, at that time, attached to it.

A relation connecting the specific heat at constant volume c_v with the specific heat at constant pressure c_p will now be developed. Recalling equation 51,

$$de = c_v dT,$$

and equation 49,

$$dq = de + p dv,$$

we have

$$dq = c_v dT + p dv. \quad (368)$$

Now, differentiating equation 367 and dividing the result by equation 367, we have

$$\frac{dp}{p} + \frac{dv}{v} = \frac{dT}{T}. \quad (369)$$

Solving equation 369 for $p dv$ and substituting this into 368, we have

$$dq = c_v dT + p v \left(\frac{dT}{T} - \frac{dp}{p} \right).$$

Introducing R from equation 367, this becomes

$$dq = c_v dT + R dT - v dp.$$

If the pressure is kept constant, $dp = 0$; and we have

$$dq = c_v dT + R dT.$$

Since the pressure is constant, this last equation becomes (by eq. 52)

$$c_p dT = c_v dT + R dT$$

or

$$c_p - c_v = R. \tag{370}$$

As equation 370 shows, there is always a constant difference between the specific heat of a gas at constant pressure and at constant volume; and this difference is the familiar gas constant per gram R .

THE APPLICATION OF THERMODYNAMICS TO THE QUANTITATIVE DESCRIPTION OF THE STATE OF SOIL MOISTURE

60. Useful Concepts in the Interpretation of Soil-Moisture Phenomena

In some conceptions of the distribution of water in unsaturated soils, the water is thought of as spread over the soil-particle surface as films and water rings. Its behavior in the soil is accounted for solely on the basis that the water has surface tension, in virtue of which it distributes itself in a definite way throughout the soil, depending upon the shape of the pore space and upon the moisture content.

On the basis of this interplay of pore space, moisture content, and the surface-tension effects of water, explanations have been given for the experimental observations made in soil-moisture studies. Some apparent inconsistencies are revealed, however, by a review of the thermodynamic and hydrodynamic aspects of some of the studies made by vapor pressure, freezing point, dilatometer, centrifuge, and suction methods. By studying certain basic relations, we may uncover some of these difficulties.

The present equations in soil literature, relating vapor pressure over a water surface to the radius of curvature of that surface, are based on the assumption that the body of the liquid is outside the field of force exerted by the soil particles. This assumption is questionable at low moisture content, as is evident from the very fact that the presence of a field of force surrounding a solid surface must be assumed in explaining all capillary phenomena. Obviously, an attraction must exist between the solid material and the water in the region of the liquid-solid interface in order for the surface to be wetted and for the water to adhere to the solid surface; otherwise the vapor-water interface could not be concave to the vapor phase.

In addition, the literature shows that certain factors have not been included in dealing with the thermodynamics relating freezing-point depression of soil moisture to the free energy of the moisture. The treatment of the freezing-point depression of relatively moist soils has been partly taken up under case 3 of article 30; that of relatively dry soils, where the adsorptive force field comes into play, will be taken up in the following articles.

The latter treatment will incorporate the effect of the strong attractive forces exerted by the soil particles on the soil moisture in the region adjacent to the surfaces of the particles, as well as the osmotic effect of the solutes dissolved in the soil moisture. It will relate the freezing-point depression of soil moisture to its free energy and vapor pressure, with particular reference to measurements made by the dilatometer.

61. Need for Introducing the Concept of an Adsorptive Force Field in Dealing with Soil-Moisture Phenomena

The assumption of an adsorptive force in the region adjacent to the soil-particle surface is important in accounting for the behavior of moisture in soils. Without this assumption, the results observed are hard to explain, particularly for relatively dry soils. As was pointed out earlier, some of these difficulties become evident when we try to interpret the results of vapor-pressure studies. Further evidence for the necessity of introducing the concept of a force field surrounding the soil particle is furnished by studies of the freezing point of soil moisture.

Adsorptive-Force-Field Indications from Vapor-Pressure Studies.—Equation 271 indicates the relation between the soil moisture content and its associated vapor pressure if no adsorptive field is assumed. It is

$$\ln \frac{p}{p_0} = \frac{2\sigma}{r} \frac{v}{RT} + (p - p_0) \frac{v}{RT} \quad (371)$$

and purports to determine the vapor pressure p immediately above a water surface whose radius of curvature r is given. All the other quantities in the equation are constants and can be obtained from a set of physical tables.

We are thus led to conclude that this equation should describe the relation between vapor pressure and moisture content in a soil, since r is a measure of moisture content. When r is large, the moisture content of the soil is high; when it is small, the moisture content is also small. Hence if we wish to find the behavior, more or less qualitatively, of the vapor pressure p with respect to moisture content at low moisture contents, we have merely to study the variation of the vapor pressure p in this equation with respect to the radius of curvature r of the air-water interface.

As mentioned above, however, this relation was developed by using an assumption that seems unjustifiable at low soil moisture contents. In developing equation 371 it was assumed that the soil particles do not attract the water molecules lying in the vapor-liquid interface and therefore do not affect their vapor pressure outside the interface. Curiously enough, we apparently cannot get interfaces concave towards the vapor phase without assuming that water adheres to the surface of the solid. Necessarily, therefore, the soil must have an adsorptive force field that attracts the water molecules. At low moisture contents this adsorptive field surrounding the soil particle must affect the vapor pressure and cause a deviation from equation 371. The vapor pressure of water in small capillaries has been found to be much smaller (145) than equation 371 would predict.

The idea of an adsorptive force field surrounding solid surfaces is not radical, since practically all explanations of adsorptive phenomena use some such concept. It involves the idea of a force being transmitted through space. Such forces are also called "field forces," "body forces," and "adhesive, attractive, or repulsive forces." Reference to some considerations and results bearing on this point is of interest. A consideration, for example, of the shape of the experimental curve (fig. 31) showing

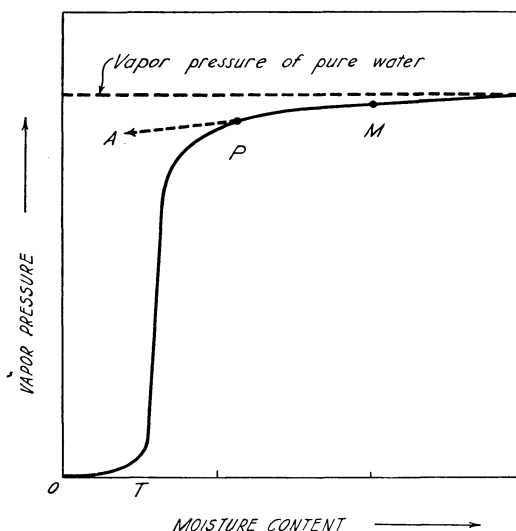


Fig. 31.—Vapor pressure of soil moisture as a function of moisture content.

the relation between vapor pressure and soil moisture content makes the introduction of the concept of an adsorptive field of force appear necessary.

If we postulate that the decrease of the vapor pressure of soil moisture, as the soil dries out, is caused entirely by the increase in the concentration of ionizable solutes in the soil solution, we should expect to have a greater slope of the curve between the moisture equivalent M and the permanent wilting percentage P than between the permanent wilting percentage P and the point T . In other words, for a given increase in concentration, we should expect a greater rate of decrease in vapor pressure at low concentrations (high soil moisture content) than at higher concentrations (lower soil moisture content), because the salt molecules are more dissociated at low concentrations. We should therefore expect the curve, as the soil is dried out, to continue in the direction A , whereas it actually turns sharply toward T . Some factors other than the presence of dis-

solved material seem therefore to come into play. One of these is the adsorptive force field surrounding the soil particle. It probably plays a minor role at the higher moisture contents. But this force becomes increasingly effective as the moisture content is decreased to the neighborhood of the permanent wilting percentage and increases very rapidly as the moisture content is further decreased.

We shall now point out the importance of the Maxwell distribution law at the lowermost soil moisture contents. The close approach of the curve (fig. 31) to the abscissa near T , at an appreciable moisture content, can be explained if we assume that this strong adsorptive field of force acts on the water molecules, inhibiting their outward movement into the vapor phase sufficiently to give a very small vapor pressure at appreciable soil moisture contents. That the curve does not actually strike the axis at T has been accounted for (art. 47 and 55) on the basis of the kinetic theory of matter, by the fact that molecules of the water film have widely different velocities. According to the Maxwell distribution law, some molecules move very rapidly, some move very slowly, but only the faster group can escape against the adsorptive force field. If all the molecules, on the other hand, had the same velocity, one would expect the vapor pressure to become zero at some appreciable moisture content T . At moisture contents below T none of the molecules would, on the basis of the latter assumption, have sufficient kinetic energy to pass beyond the adsorptive force field exerted by the soil particles; and we should have zero vapor pressure. Since, however, the water molecules have velocities as determined by the Maxwell distribution law, we may expect that no matter how strong the adsorptive field, some molecules will have energy enough to escape into the vapor phase and thus produce a small but appreciable vapor pressure.

The vapor-pressure curves reported by Edlefsen (46) and by Thomas (153) show this general trend, in that the vapor-pressure curves change their slope markedly at soil moisture contents where plants wilt; if the curve is extrapolated to zero vapor pressure, it intercepts the moisture-content axis at appreciable soil moisture contents. Apparently, therefore, the soil would have a zero vapor pressure at appreciable moisture contents if all molecules had the same speed. From his studies, Edlefsen concluded (42, 46) that adsorptive forces probably played an important role in soil moisture at moisture contents lower than the permanent wilting percentage.

In our considerations here, as in most soil-moisture literature, the state reached after prolonged drying of the soil at 110° C will be regarded as zero soil moisture content. As the temperature is raised to higher values, more water will of course be driven off; and, as pointed out by

Kelley, Jenny, and Brown (95), the steplike shape of their curves at extremely low moisture contents indicates that this moisture is chemically combined.

Adsorptive-Force-Field Indications from Plant Behavior and Freezing-Point Data.—As every student of soil moisture knows, the freezing point of soil moisture is less than 0°C ; the amount of the depression increases as the moisture content decreases. Though the theoretical interpretation of such data will be given later, it is now pertinent to recall some qualitative facts that seem to require the concept of a field of force.

One cannot get sufficient concentrations of salts in soil moisture, having the ordinary proportions of nutrient elements for plant growth, to account alone for the observed freezing-point depressions of soil moisture at moisture contents in the vicinity of the permanent wilting percentage. In the first place, some of the nutrients will precipitate long before sufficient concentration can be reached to account alone for the observed freezing-point depression in the neighborhood of the permanent wilting percentage. By the time such a concentration is reached, the proportions of the nutrients will be seriously unbalanced. If this precipitation of necessary nutrients took place one might expect to find plants showing certain nutritional deficiencies in the neighborhood of the permanent wilting percentage. Such nutritional deficiencies are seldom if ever evident.

In the second place, the soil solution would be highly toxic to plants if the concentration of the soil solution were sufficiently high to account alone for the observed freezing-point depression in the neighborhood of the permanent wilting percentage. But it is a well-demonstrated fact that plants grow normally for all moisture contents above the permanent wilting percentage. As the transpiration rate over this range of moisture content is practically independent of moisture content, concentration of solute in the soil solution plays only a minor role in affecting the availability of soil moisture to plants.

And in the third place the freezing-point depression of soil moisture at the permanent wilting percentage is many times what it is at field capacity. To explain this enormous change in the freezing-point depression (as the moisture content is progressively decreased) on the basis of concentration of dissolved materials alone, one must assume that the concentration of solutes in the soil solution has increased many times more rapidly than the moisture content has decreased. This seems inconceivable, however, for apparently the concentrations should, to a first approximation, vary inversely as the moisture content.

Another phenomenon difficult to explain without the introduction of an adsorptive force field is that at the permanent wilting percentage the

rate of transpiration decreases abruptly. If the change in the difficulty of removing water from soil as the moisture content is decreased were caused entirely by dissolved materials, one would expect this difficulty to increase gradually as the moisture content becomes smaller. There should therefore be no sudden increase in the difficulty of removing water from the soil in the neighborhood of the permanent wilting percentage. As Edlefsen (42) has pointed out, this abrupt increase in the difficulty experienced by plants in obtaining water at the permanent wilting percentage indicates that as the moisture films get thin, other forces acting on soil moisture are brought into play. Apparently, therefore, we can explain this abrupt change by assuming that an adsorptive force field surrounds the soil particles and that the magnitude of this field increases very rapidly as the soil-particle surface is approached.

These notions agree with those of Parker (115) when he says:

At moisture contents below the water-holding capacity of the soil, the water is held to the soil by an attractive force commonly called adhesion. As the moisture content of the soil gradually decreases, the force with which the remaining water is held continually increases. This causes an increase in the freezing-point depression of the soil water, a decrease in the rate of evaporation and a decrease in the vapor pressure of the soil water as the moisture content is reduced. This force is great enough to prevent part of the soil water from being frozen at low temperatures.

Some, including Parker (114), believe that aside from dissolved material present, colloidal material produces a freezing-point depression not because it is in solution, but because it is surrounded by an adsorptive force field that compresses the capillary water films and that therefore increases the freezing-point depression.

Apparently, then, there are several reasons why the vapor-pressure depression, the freezing-point depression of soil moisture, and the behavior of plants in extracting soil moisture, cannot be explained on the basis of dissolved materials alone and thus why it seems necessary to introduce the idea of an adsorptive force field surrounding the soil particles, which in turn, creates a hydrostatic pressure in the soil solution.

62. The Use of the Free-Energy Concept in Interpreting Soil-Moisture Phenomena

In past quantitative studies of the energy relations of a soil-moisture system, a mathematical function known as "capillary potential," "total potential," or merely "potential" has been used (20, 30, 45, 46, 55, 57, 58, 59, 81, 91, 103, 104, 111, 125, 126, 138, 153, 154, 159). The total potential of soil moisture has been defined as $\Phi = \psi + \omega + \lambda$. Here ψ is the capillary, or pressure, potential, existing because the water is under a tension or pressure; ω is the gravitational potential, as used in the past, but may include all potentials that exist by virtue of an adsorptive force

field acting on soil moisture (for example, the adsorptive field exerted by soil particles on moisture); and λ represents the osmotic potential that the moisture has by virtue of the material dissolved in it. The idea of potentials has also long been used in the study of electricity, magnetism, and mechanics. In thermodynamics and physical chemistry, an analogous function called "free energy" or "thermodynamic potential" has been introduced.

Just as one must, considering a gravitational field, refer the potential to some datum, often taken at sea level, so in dealing with soil-moisture energy relations one must also choose some datum, or reference point. This datum, for soil-moisture energy, was usually taken as free, pure water. Capillary potential, often called "pressure potential," is therefore defined by different investigators as the work done, per unit mass of water, against the capillary field forces in moving water from the free, pure water, the datum, to the point where the potential is to be evaluated.

Capillary potential as thus defined is a mechanical potential measuring the energy of compression or tension in the water. Gravitational as well as osmotic potentials are defined similarly, the free, pure water surface being always used as the datum of potential. Students of soil moisture have usually been interested only in the liquid state of water. They have defined the potential of soil moisture in such a way that its magnitude is calculated with respect to a datum at the same temperature. In other words, they have considered the soil moisture and the free, pure water (used as the datum) to be at the same temperature. In the past, they have not inquired whether or not the potential of the reference point changed with temperature.

As pointed out (art. 21), when one must consider all three phases of water existing in equilibrium with each other, together with the effects of adsorptive force fields and temperature on the energy relations of soil moisture, one may conveniently introduce a more comprehensive thermodynamic function called "free energy." This function, as already mentioned, has had its most extensive use in the field of physical chemistry, where the investigator is interested in all phases of a substance rather than in the liquid phase only. This quantity f , free energy, is defined according to article 21 by the equation

$$f = h - Ts, \quad (372)$$

where h represents the heat content, T the absolute temperature, and s the entropy of the system. At this point we are interested mainly in the characteristics of the function f . This, as well as the other terms appearing in equation 372, has been more completely discussed in previous

articles. As is usually pointed out in texts on thermodynamics, a change in free energy Δf of a system from one value to another represents the maximum useful work obtainable from the given process when it occurs at a constant temperature and pressure. Curiously enough, almost all the major changes in soil moisture take place under the conditions of constant temperature and pressure. This function seems, therefore, peculiarly adapted to soil-moisture studies. Free energy, because of the more generalized meaning given to it, is a more appropriate function for our purpose than is potential.

At this point we may well discuss certain characteristics of this function which are a consequence of the facts outlined in articles 21, 22, and 39 and which will be used in describing the energy states and energy changes of soil moisture. Where we speak of a change in free energy without any qualification, we assume that the process is carried out isothermally.

1. The absolute, or total, value of free energy as defined above cannot be measured. We must content ourselves with measuring changes in the function, just as in the case of the gravitational potential, where we always measure not the absolute value but rather its difference measured with respect to some datum, usually taken as sea level (art. 39).

2. When a substance exists in several different states in equilibrium with each other, the specific free energy of that substance is the same in all of the states (art. 22). For example, when water in a salt solution is in equilibrium with its vapor and ice, the specific free energy is the same in all three states—ice, water, and vapor.

3. The change of free energy in any transformation of a system in going from a state A to a state B equals (eq. 101) the mechanical work required to go from A to B at constant temperature, neglecting the work of expansion against constant pressure.

4. The increase in the total free energy of a system, where the surface area of the air-water interface is increased by an amount equal to dA , is equal to σdA , where σ equals the surface tension of water (eq. 208).

5. The increase in free energy of a system containing v cubic centimeters of water, where the pressure on the water is changed from P_1 to P_2 , equals $v(P_2 - P_1) = v \Delta P$ (eq. 156). This relation is the same as used by soil-moisture investigators to express changes in pressure or capillary potential ψ caused by changes in hydrostatic pressure.

6. The difference in specific free energy between vapor at a pressure p_2 and at p_1 (eq. 236) is $\Delta f = f_2 - f_1 = RT \ln \frac{p_2}{p_1}$, where R equals the gas con-

stant per gram and T equals the temperature of the vapor. A measure of the maximum capacity of the system for performing useful work is $-\Delta f$. This equation expressing changes of free energy in terms of changes in

vapor pressure of a liquid is identical with equations used by soil-moisture investigators for expressing the potential of water as a function of vapor pressure (20, 46, 104, 139, 154).

7. The thermodynamic relations are available for determining the dependence of free energy on temperature. These have been discussed in articles 21 and 23, and their application to soil moisture will be further considered in articles 72 to 81. The potentials as previously defined in soils did not lend themselves to such a determination, since the equations did not contain the temperature explicitly. The temperature was, of course, involved implicitly; but the mere knowledge of the potential at one temperature did not enable one to calculate it at some other temperature. In other words, it had to be determined by experiment at each temperature. Clearly, free energy defined by equation 372 as $f = h - Ts$ contains the temperature explicitly.

The choice of terms in this connection is not easy. "Free energy" would appear to be a more appropriate term than "potential" when one is dealing with systems that contain all three of the phases. The word is equivalent, furthermore, to "potential" as applied previously in the soil literature that deals with the liquid phase. For these reasons it has been adopted here. The term "molal free energy" appears often in the literature of physical chemistry. In the present discussion, however, we are not especially concerned with the molal free energy of water; rather, we are interested in the change in free energy per unit mass, or in the specific free energy. For the sake of brevity, however, we shall use the general term "free energy," with the understanding that it refers to the free energy per unit mass.

The specific quantities of a substance are obtained immediately from the molal by merely dividing the latter by the molecular weight of the substance. Obviously, according to the discussion above, the total potential, as used previously in literature on soil moisture, and the specific free energy, as here defined, are somewhat analogous functions both dimensionally and quantitatively except for the more generalized meaning associated with the latter. Since, as pointed out before, the total potential equals the sum of the osmotic pressure and the adsorptive-force-field potentials, then the specific free energy of the substance in any state also equals the sum of the osmotic pressure and the adsorptive-force-field potentials in the liquid state.

Other factors may contribute to the total free energy of the soil moisture. For example, the presence of the water molecule in the adsorptive force field surrounding the soil particles may give rise to an orientation of the molecules. This orientation is one form of potential energy that the water may possess.

63. The Role of the Adsorptive-Force-Field Concept in the Interpretation of Soil-Moisture Properties

To illustrate the usefulness of the function called "free energy" when applied to the description of the energy relations existing in soil moisture, and to show its relation to the other potentials found in the literature and just previously described, let us consider the system *A* shown in figure 32,

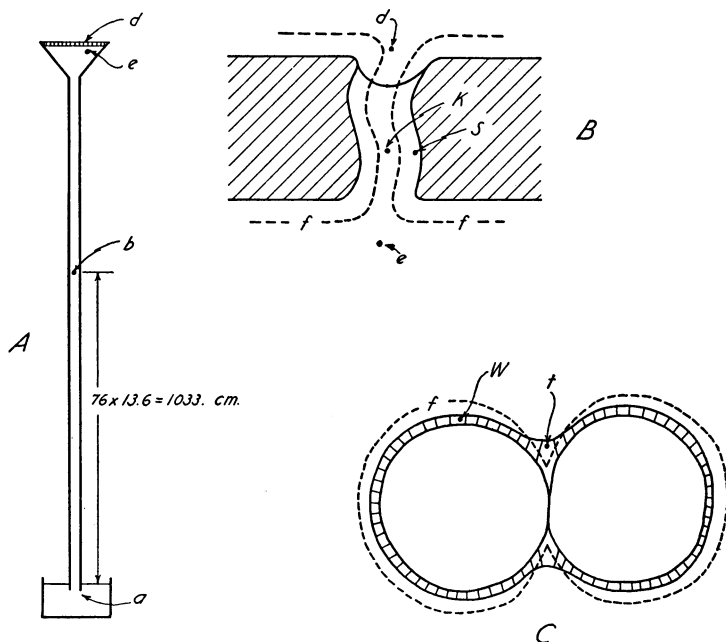


Fig. 32.—Hypothetical effect of an adsorptive force field.

consisting of a glass tube sealed at the top to the open end of an inverted porous vessel, here in the shape of a cone. The system is filled with pure water, the lower end of the tube being placed in the vessel at point *a*; and the entire system is exposed to atmospheric pressure. At point *a* we have free, pure water, which we shall use as our datum both for gravitational potential and for pressure potential. Assuming that we have pure water, the osmotic potential is zero throughout. It should be recalled that the total specific free energy equals the sum of all the potentials. When water in this system is in equilibrium, the specific free energy is the same throughout; and therefore no energy will be required to move water from *a* to any other point in the liquid. This follows from the second and third characteristics of free energy (art. 62).

The sum of the pressure, or capillary, potential and the gravitational potential is constant and equal to zero for all points in the liquid since the

total potential is zero at point *a*. At any point, therefore, the capillary potential and the gravitational potential are equal in magnitude but opposite in sign. At the point *b*, for example, $76 \times 13.6 = 1,033$ centimeters above *a*, the gravitational potential will have increased by an amount 1,033 gram-centimeters per gram, whereas the capillary or pressure potential will have decreased by the same amount, leaving the total potential or free energy unchanged. At a point to the right or left of *b*, for example, the water has a hydrostatic pressure of $-1,033$ grams per square centimeter with respect to point *a* except when it is close to the wall of the glass tube, where adsorptive forces become effective. These forces will now be discussed.

Consider in detail a pore (fig. 32, *B*) in the porous material at *d* of figure 32, *A*. Water at the point *k* in the center of the pore might actually be under tension, whereas water at *s* near the wall of the pore might be under compression because of an adsorptive force field surrounding the clay surface whose range of influence reaches out as far as the dotted lines *f*. Clearly, therefore, water under tension might be in equilibrium with water under pressure; that is, the water might have the same total potential or the same specific free energy throughout, although the partial potentials vary considerably under the widely different conditions of pressure and position found in the water mass.

Figure 32, *C*, shows a hypothetical picture of two soil particles surrounded by a film of water, held on by an adsorptive force field extending out from the particle as far as the dotted line *f*. The cross-hatched area represents the film of water. At a point *t* the water is under a negatively curved surface and might therefore be expected to be under a tension, whereas the water at *w* is under a positively curved surface as well as inside the adsorptive force field. Both these effects would tend to produce a positive pressure at *w*. Here, again, we have an example, comparing points *t* and *w*, of an equilibrium condition where water under pressure is in equilibrium with water under tension, since we know that water actually distributes itself approximately as shown in the figure when two soil particles are brought into contact and that there is no tendency for any preferential movement of the water when the equilibrium distribution of soil moisture has been established.

The fact that in the same mass of soil moisture, one region may be in a state of tension and another under great compression, although the whole mass of soil moisture is at equilibrium, is rather important in our interpretation of the so-called "capillary-potential measurements" frequently made on soil moisture. The capillary potential is usually determined by placing in the soil a porous clay bulb, filled with water and connected to a mercury manometer. The water in the manometer is adjusted until the

water in the porous bulb is in equilibrium with the soil moisture. That is, the water in the bulb and manometer is in such a state of tension that it balances the pull exerted by the moisture in the soil.

On the basis of such evidence, seeming to indicate a state of tension throughout the soil moisture, attempts are made to explain such properties of soil moisture as the variation of vapor-pressure depression with decrease in moisture content as well as the distribution of moisture within the soil, it being assumed that the water is held in the form of water wedges at the points of contact of soil particles.

Actually, even though the water in the manometer and bulb is in a state of tension, much of the water in the soil is probably far from being so, except at relatively high moisture contents. If a moisture film is acted upon by an adsorptive force field, it might be expected to be under positive hydrostatic pressure. If so, it can be in equilibrium with a body of pure water only if the latter is placed in the proper state of tension. This follows because an adsorptive force field reduces the escaping tendency of the water molecules of the soil moisture. This reduces the vapor pressure and consequently gives the soil moisture a negative value of free energy. For a body of pure water to be in equilibrium with the soil moisture, its free energy must also be lowered to the same negative value (art. 22). This can be accomplished by placing it under tension.

To attain vapor pressure and free energy corresponding to soil moisture at the permanent wilting percentage, the soil moisture would have to be under a tension of approximately 16 atmospheres. According to a well-known fact, only with special experimental precautions can water be made to withstand tensions much greater than 1 atmosphere, and this only after most of the dissolved air has been carefully removed. At the lower moisture contents, therefore, tension is unlikely to be an important contributing factor to the value of the free energy of soil moisture.

If free, pure water is to be in equilibrium with soil moisture, it must be placed under tension. This fact indicates that the moisture adjacent to the soil particle must be under the influence of an adsorptive force exerted by the soil particles. Otherwise, the soil moisture will not adhere to the soil particles when a tension exists at some other point in the soil moisture.

If an attractive force is exerted by the soil particles on the soil moisture, it must act through a finite distance. Thus a positive hydrostatic pressure is produced. Consequently, the water molecules contained within a layer adjacent to the soil-particle surface will be attracted towards the surface. The molecules farthest away will be attracted and will press on the adjacent ones closer to the soil surface, which will, in turn, press on those still closer to the soil-particle surface. Thus a hydrostatic pressure

is built up in the layer adjacent to the soil-particle surface, increasing as the soil surface is approached. A rough analogy is found in the increase of hydrostatic pressure in a reservoir of water as one descends towards the bottom. In both cases an adsorptive force field acts on the water producing the pressure. In the former case, the force is probably electrical; in the latter, gravitational.

Thus, judging from the factors that determine equilibrium of soil moisture and from the properties of the thermodynamic function called "free energy," an appreciable amount of the soil moisture is not under tension even at the high moisture contents. Rather, it is under an adsorptive force field surrounding the soil particle, which entails a hydrostatic pressure increasing as the surface of the soil particle is approached. Dissolved material, which doubtlessly increases in concentration as the surface of the soil particles is approached, further augments the effects produced by the adsorptive field. At higher moisture contents, some of the soil moisture is under tension because of the negative curvature of the air-water interface, and the effect of this might well be, according to case 3 of article 30, to lower the freezing point of the soil moisture. This freezing-point depression would be in addition to that caused by osmotic pressure.

Let us now consider briefly the effects of the positive hydrostatic pressure on the freezing point of soil moisture in the vicinity of the soil-particle surface. Also, we shall assume that the ice separating out, as more and more of the soil moisture is frozen, continues to be attracted towards the soil-particle surface, in contrast to what was considered under case 3 of article 30.

To learn how pressure and tension affect the freezing point of soil moisture, we may refer, first, to Le Châtelier's theorem which states that when any isolated system is acted upon by an influence, a change will occur within the system, making the effect of the influence less than if the change had not occurred.

To understand the consequence of this theorem when applied to the problem of the change in freezing point of soil moisture, consider a system composed of pure water and ice at 0°C in a closed system. According to the theorem, if pressure is applied to this system, the volume will decrease and will thereby tend to relieve the applied pressure. Obviously, the only way this can occur is for ice to melt, since the volume of water is less than the volume of ice. Conversely, if a tension is applied to the water (that is, if the pressure is decreased) a volume change will occur that will tend to relieve the tension. This, obviously, can happen only if the volume increases, which means that some of the water will change to ice. Clearly, therefore, pressure decreases the freezing point of water, whereas tension tends to increase it.

Le Châtelier's theorem is useful in reasoning qualitatively on various phenomena. It does not, however, enable us to get quantitative results. For this purpose, as applied to the problem at hand, we must resort to the thermodynamic relation known as the Clausius-Clapeyron equation (eq. 186). This will be recognized as case 1 of article 30.

A consideration of this equation, when applied to such a system as that above, leads one to inquire why, if soil moisture is under tension, we do not observe a freezing point in it higher than 0° C. The Clausius-Clapeyron equation is

$$\frac{\Delta P}{\Delta T} = \frac{l}{T \Delta v}.$$

Here Δv equals the volume contraction of ice per unit mass upon melting; l is the heat absorbed by ice upon melting and is really a positive quantity in this particular case since heat is actually absorbed when ice melts; and T is the absolute temperature at which the transformation occurs. Thus, if we place water under tension, ΔP is negative. The right-hand member of the equation is already negative because l is of opposite sign from Δv . Hence ΔT must be positive. By placing water under tension we are therefore led to the conclusion that we raise its freezing point.

So far as we are aware, no one has ever observed the freezing point of soil moisture to be higher than 0° C. And yet, as mentioned before, water in soils is sometimes thought to be in a state of tension. There are three reasons why we probably do not observe any elevation of the freezing point above 0° C as would be predicted from our previous considerations. First, the Clausius-Clapeyron equation shows that the freezing point changes very slowly with changes in pressure; one could probably never get water in soils under sufficient tension to raise its freezing point a measurable amount, since (according to the Clausius-Clapeyron equation) a tension of 133 atmospheres is required to increase the freezing point 1 degree. Second, there are always salts present that tend to depress the freezing point in soils. Third, when the water content of the soil has been reduced until the water should actually be under an appreciable tension, due to film curvature according to article 42, the water films are thin enough so that they are probably under the influence of an adsorptive force field exerted by the soil particles themselves, which tends to compress the water and thus lower its freezing point.

To show more clearly how the adsorptive force surrounding the soil particles affects the properties of soil moisture, let us consider an analogous situation more familiar than that found in soils. Consider an adsorptive force field acting on pure water. If we have a column of water in a vertical position on the earth's surface, every particle of water through-

out will be acted upon by the earth's gravitational field, and a definite pressure will be produced at the bottom of the column. If the height is doubled, the hydrostatic pressure will be doubled. Also, measurement of the hydrostatic pressure at different distances below the upper surface of the water will show that the pressure increases at a constant rate with respect to changes in height. Obviously, neither this doubling of the hydrostatic pressure by doubling the height of the column, nor the uniformity in the rate of increase of pressure as one descends in the column, would hold true if the length of the column were of the same order of

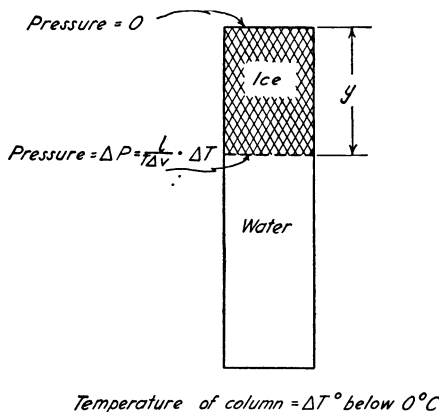


Fig. 33.—Position of water-ice interface at depth y below the surface when the column is subjected to ΔT degrees below 0°C .

magnitude as the radius of the earth, since the gravitational field of force is known to obey the inverse square law. In other words, the weight of unit mass of water varies inversely as the square of its distance from the center of the earth. If, therefore, we were dealing with a water column of a height comparable with the radius of the earth, we should find a significant increase in the weight (gravitational constant) of unit mass of water as we descend in the column. Thus hydrostatic pressure, in such a case, is not proportional to the depth below the free water surface, but instead increases much more rapidly as determined according to Newton's inverse-square law. On the other hand, in a reservoir whose depth is small as compared with the earth's radius, the weight of a unit mass of water at the top and bottom is practically the same, and consequently the hydrostatic pressure is nearly proportional to the depth.

Let us now consider how freezing temperatures affect this column of water. If we choose some hydrostatic pressure ΔP corresponding to that at some depth y of figure 33 in the column and if we lower the entire

column to a temperature ΔT degrees below 0° C such that ΔP and ΔT are related by the Clausius-Clapeyron equation,

$$\frac{\Delta P}{\Delta T} = \frac{l}{T \Delta v},$$

all the water above the depth y will be frozen; that below, unfrozen. The temperature of the column ΔT degrees below 0° C, and the hydrostatic pressure ΔP at the water-ice interface will always be related according to the equation above. Thus the thickness of the ice on a pond would depend only on the temperature if there were no convection and if sufficient time and heat were available to establish equilibrium conditions.

64. Effect of an Adsorptive Force Field Surrounding Soil Particles on the Freezing Point of Soil Moisture

The situation described above, relating the adsorptive force acting on the soil moisture to its freezing-point depression and to the amount of water frozen out, seems analogous to that found in the soil-moisture film surrounding and immediately adjacent to a soil particle, the additive effect of surface tension and osmotic pressure being neglected for the present.

Since the postulated fields of force are assumed by various investigators to be anywhere from the inverse-square law to an inverse fifth law, clearly the force of attraction on a particle of water increases very rapidly as it approaches the soil-particle surface. The hydrostatic pressure in water, therefore, increases very rapidly as the surface of a soil particle is approached. As was mentioned earlier, a measurement of the hydrostatic pressure enables one to calculate easily the partial free energy due to hydrostatic pressure, since the latter is numerically equal to the hydrostatic pressure in the c.g.s. system. This follows according to equation 156 because the free energy

$$\Delta f = \frac{\Delta P}{\rho} = v \Delta P_P$$

where ρ and v are the density and specific volume of water respectively, and where each is approximately equal to unity. Here ΔP_P represents the hydrostatic pressure.

Now consider figure 34, *B*, which consists of a layer of soil covered with a layer of pure water over which is a layer of ice, both the ice and the water being acted upon by an attractive force that increases in magnitude very rapidly as one approaches the soil-particle surface. The figure represents a small radial section through the soil particle; since we are

considering only a small element of soil-water interface, it can be represented by a straight line. (The following considerations would not be altered if the section of the surface were curved.) Figure 34, *A*, drawn to the same scale as 34, *B*, represents the trend, within the water and ice layers, of the hydrostatic pressure resulting from the adsorptive forces exerted by the soil particle.

The water-ice interface is the locus of points where the two phases, ice and water, are at equilibrium under the existing temperature and hydrostatic pressure. Points above this locus have too low a pressure for

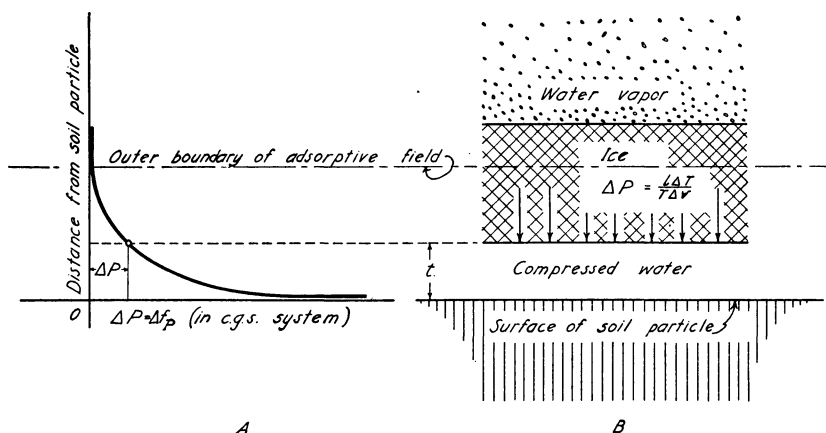


Fig. 34.—Relation of the adsorptive force field to the amount of frozen and unfrozen water in soils at a given temperature below zero where Δf_p is the partial free energy due to pressure; l is the thickness of the unfrozen layer of water; l is the specific heat of fusion; Δv is the change in specific volume when water freezes; T is the temperature of soil moisture; ΔT is the number of degrees below 0°C , of the soil moisture; and ΔP is the hydrostatic pressure at the water-ice interface by virtue of the soil adsorptive force field.

water to exist at the given temperature, whereas points below have too high a pressure for ice to exist. At the interface, therefore, the hydrostatic pressure must be ΔP (as determined by the Clausius-Clapeyron equation) if the whole system is subjected to a temperature ΔT degrees below 0°C , since both phases are in equilibrium at the interface.

In every respect, the present case of a partially frozen soil-moisture film is analogous to the case of a partially frozen reservoir of water considered in the previous article. By means of the Clausius-Clapeyron equation of article 27 or of case 1 in article 30, the pressure and therefore the free energy at the water-ice interface can be calculated for any freezing-point depression ΔT degrees. Here, of course, we are dealing only with the contribution of the hydrostatic pressure to the free energy of soil mois-

ture. The hydrostatic pressure, in this case, exists because of the field or adsorptive forces that the soil particles exert on the water.

Measurements of the amount of unfrozen water remaining at different freezing-point depressions, where different amounts of ice are frozen out, together with a knowledge of the total area of the water-soil interface, would furnish sufficient information to construct the curve shown in figure 34, A, showing how the free energy due to hydrostatic pressure in the soil moisture at a given point is related to the distance of that point from the soil surface. The amount of unfrozen water divided by the area of the interface gives the average thickness of the film of unfrozen water.

In constructing such a curve, one should remember that the total free energy, which is the same throughout the soil moisture, is equal at any given point to the sum of the partial free energy due to hydrostatic pressure and that due to the adsorptive force field at that point. The total free energy may also be obtained (eq. 236) from such measurements as vapor pressure. The partial free energy due to the field is found, therefore, immediately from the difference between the total free energy and the partial free energy due to hydrostatic pressure. It is the gradient of this partial free energy, due to the adsorptive field at any point, which gives the magnitude of the force exerted by the soil on a water particle located at that point.

Clearly, then, the presence of an adsorptive force surrounding the soil particles increases the magnitude of the component of the free energy due to hydrostatic pressure as well as the freezing-point depression of soil moisture.

This effect of the adsorptive force field in producing hydrostatic pressure and therefore changing the free energy of the soil moisture is distinct from, and should not be confused with, the change in the free energy of the soil moisture caused by the mere presence of the soil moisture in the adsorptive force field surrounding the soil particle (art. 26). In the presence of an adsorptive force field, the partial free energy of the moisture (due to the position of the moisture in the field) decreases as the partial free energy (due to the hydrostatic pressure caused by the field) increases. A detailed consideration of these relations is taken up in article 69.

65. Effect of Dissolved Material and Hydrostatic Pressure on the Freezing Point and the Free Energy of Soil Moisture

Considerations of the effect of dissolved material and hydrostatic pressure on the freezing point and the free energy apply especially to soil moisture in the vicinity of the soil-particle surface. Let us first consider how dissolved material contributes to the freezing-point depression of soil moisture. This effect of dissolved material is superimposed upon the

effect of the adsorptive force field discussed in the previous article. The condition we wish to discuss is represented in figure 35 as part of a radial section of a soil particle covered by a layer of soil solution over which is a layer of pure ice. As the temperature is lowered, the water-ice interface moves in toward the soil solution, concentrating it. The free energy of the water just inside the water-ice interface, expressed in terms of the osmotic pressure ΔP_o , can be calculated by the well-known equation 148

$$\Delta f = -v\Delta P_o.$$

According to equation 187, an increase in the hydrostatic pressure, as

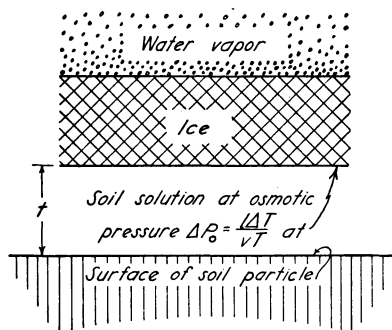


Fig. 35.—Part of a radial section through a soil particle covered by a layer of soil solution over which is a layer of pure ice; here t is the thickness of the unfrozen layer of water containing dissolved salt; l is the latent heat of fusion; v is the specific volume of water; T is the temperature of soil moisture; ΔT is the number of degrees the whole system is below 0°C ; Δf_o is the free energy due to osmotic pressure of soil solution at the liquid-ice interface; and ΔP_o is the osmotic pressure of the soil solution at the liquid-ice interface. Since $\Delta f_o = -v\Delta P_o = -\Delta P_o$ and $v = 1$ in the c. g. s. system, we have

$$\Delta f_o = -\Delta P_o = \frac{l\Delta T}{vT},$$

according to article 29.

well as an increase in the osmotic pressure or salt concentration (eq. 200), lowers the freezing point of water. Since both these factors are present in soil moisture in the vicinity of the soil-particle surface, the total freezing-point depression is the sum of the depressions produced by each factor separately. Stated quantitatively,

$$\Delta T = \Delta T_P + \Delta T_o. \quad (373)$$

Here ΔT_P represents the depression of the freezing point due to hydrostatic pressure, ΔT_o represents the freezing-point depression due to dissolved material, and ΔT represents the total observed depression. But

increases in hydrostatic pressure cause increases in free energy (eq. 156), whereas increases in concentration of dissolved material cause decreases in free energy of the water (eq. 151 and 222). These facts will be amplified in the following discussion.

As shown in article 25, the Δf_P due to the presence of hydrostatic pressure is given by $\Delta f_P = v \Delta P_P$, where the subscript P connotes hydrostatic pressure. Also, according to article 24, Δf_o due to the presence of dissolved material causing the osmotic pressure ΔP_o is given by $\Delta f_o = -v \Delta P_o$, where the subscript connotes osmotic pressure. Clearly, therefore, the total change in free energy Δf due to combined changes in concentration of dissolved material, as well as hydrostatic pressure, is given by the equation

$$\Delta f = \Delta f_P + \Delta f_o = v \Delta P_P - v \Delta P_o. \quad (374)$$

Experimentally it is often hard to measure ΔP_P and ΔP_o . It is therefore convenient to substitute, for these terms, quantities more easily determined experimentally. We can do this by referring to equation 187, from which we see that

$$\Delta P_P = \frac{l \Delta T_P}{T \Delta v}.$$

Here, it will be recalled, Δv is always negative, since ice contracts upon melting. By referring to equation 200, we see that

$$\Delta P_o = - \frac{l \Delta T_o}{T v}.$$

Substituting these in equation 374, we have

$$\Delta f = \frac{v l \Delta T_P}{T \Delta v} + \frac{l \Delta T_o}{T}. \quad (375)$$

Here Δf has been expressed in terms of ΔT_P and ΔT_o and other quantities that can be obtained from any table of physical constants. The first term on the right of equation 375 is inherently positive when the hydrostatic pressure is increased, since both the freezing-point change ΔT_P and the change of volume Δv are negative. The second term, on the other hand, is inherently negative, since the change in the freezing point ΔT_o of the solution is negative when soluble material is added. Thus the two terms on the right of equation 375 are of opposite sign.

It is sometimes thought that because both positive hydrostatic pressure and

dissolved material decrease the freezing point of a solution, these two factors should be additive in producing changes in the total specific free energy of the solution. As can be seen from both equations 374 and 375, however, this is not the case, since the changes in the free energy produced by hydrostatic pressure and osmotic pressure are of opposite sign.

Thus, for example, the concentration and hydrostatic pressure in the soil solution might be such that ΔT_P and ΔT_O would be so related that the total change in specific free energy Δf in equation 375 would be zero. In this case, the partial specific free energies produced by hydrostatic pressure and dissolved material are equal in magnitude but of opposite sign.

Clearly, then, one of the most important problems related to the analysis of freezing-point data on soils involves the separation of the observed freezing-point depression into its two components—namely, that due to dissolved material and that due to hydrostatic pressure.

The free energy of moist soil is then the sum of the free energies due to osmotic pressure and hydrostatic pressure, as well as the free energy due to the presence of the water in the adsorptive force field surrounding the soil particle. The latter has been considered in detail (art. 26) and will be considered later (art. 68 and 69). Only the former two factors would be expected to produce a freezing-point depression of soil moisture.

A quantitative thermodynamic treatment will be given in article 69 incorporating the factors mentioned above, for determining the free energy of soil moisture from measurements made with the dilatometer.

66. Methods of Making Freezing-Point Measurements on Soils

Two methods are commonly used in making cryoscopical measurements on soils or other materials. In one (often called the Beckmann technique, since the procedure followed is largely that used by Beckmann in determining the freezing points of solutions) the soil sample is prepared at a certain moisture content and is placed in a vessel in which is inserted a sensitive thermometer or other temperature-measuring device. Then the temperature of the moist sample of soil is lowered until freezing of the moist soil is just initiated. This temperature is then noted. A series of such measurements of the freezing point made on several separate soil samples, each at a different moisture content, furnishes the data necessary to construct a curve showing the dependence of the freezing point of soil moisture on the soil moisture content.

In the other (often called the dilatometer method) whose thermodynamic treatment will be taken up in article 69, the sample of soil to be studied is placed in a closed vessel on top of which is attached a long vertical capillary tube. More than enough water is added to saturate the

soil, the amount of which is carefully determined. On top of the saturated soil is added some light oil (for example, kerosene) to fill completely all remaining space in the vessel, as well as a small part of the lower end of the capillary tube. The temperature of the vessel and of its contents is lowered until ice is formed within the saturated soil. A change from water to ice causes the contents of the vessel to expand. This expansion, due to the formation of ice, forces the oil up the capillary tube, which is calibrated so that the exact amount of expansion can be calculated and therefore the amount of water changed to ice. Knowing the amount of ice formed, one can calculate the amount of water remaining unfrozen, since the total amount of water in the soil is known. Thus by determining the amount of unfrozen moisture in the more-than-saturated soil sample, for a series of temperatures below 0°C , we can, as with the Beckmann method, plot a curve showing the dependence of the amount of unfrozen moisture in the soil on the corresponding soil temperature. In contrast to the Beckmann method, we here obtain the entire curve from but one soil sample.

67. Previous Quantitative Interpretation of Freezing-Point Data

Data are available on the freezing point of moist soils (23, 24, 52, 77, 114). Some authors have made no attempt to interpret their findings in terms of thermodynamic equations. Although certain others have considered this aspect of the problem, further analysis appears necessary.

The effects of hydrostatic and osmotic pressure of the solution on the depression of the freezing point have been discussed earlier. In analyzing freezing-point data, no one seems to have made any quantitative use of the hydrostatic pressure caused by the presence of an adsorptive field surrounding soil particles, although Bouyoucos (23) considered it qualitatively and concluded that it did not play a role in what he called "free water." Bouyoucos' work on the freezing point of soil solutions seems to indicate that he was convinced that the freezing point was largely determined by the concentration of dissolved material; for he said, "All evidences, both direct and indirect, point overwhelmingly to the fact that these high depressions of the freezing point are produced by, and represent actual concentrations." He apparently had certain doubts, nevertheless, for he made the following statement: "The foregoing hypothesis, however, does not explain why the lowering of the freezing point increases in a geometric progression while the moisture content decreases in an arithmetical progression, and [does] not follow a direct inverse proportionality ratio (approximately) as might be expected." As if he felt called upon to introduce another hypothesis, he remarked, "The hypothesis is also offered that some of the water contained by the soil

might be either loosely chemically combined or physically adsorbed, or both”

Schofield (138) interprets the freezing-point data secured with the Beckmann method on unsaturated soils by means of an equation, presumably meant to be equivalent to equation 200, giving the relation between the freezing-point depression and the osmotic pressure of the soil moisture. Although he does not specifically make the statement, we may logically conclude, in view of this similarity in the equations after suspected typographical errors are corrected, that he attributed the depression of the freezing point of soil solution entirely to dissolved material. On the other hand, since his expression is similar to equation 205 obtained under case 3 of the generalized Clausius-Clapeyron equation, it may be that he assumed the water, at the water-ice interface, to be under a different pressure from that in the ice. That is, as the water under tension freezes out, it separates out to the higher pressure of one atmosphere. This inequality of hydrostatic pressures at the water-ice interface, when the soil moisture is under tension, seems plausible, but more experimental work is necessary to substantiate it.

A quantitative interpretation of the behavior of the freezing-point depression of saturated soils is given in articles 64, 65, and 69.

68. Effect of an Adsorptive Force Field on the Freezing Point of Soil Moisture as Measured by the Beckmann Method

When the freezing point of soil moisture is being determined by the Beckmann technique, the soil might be far from saturated, and very little if any of the water would then be expected to be under tension, so that case 3 of article 29 probably does not apply. In consequence, the adsorptive force field surrounding the soil particle will extend beyond the vapor-liquid interface of the moisture films. Figure 36, *A*, represents a radial section through the water-soil interface. The adsorptive force field is assumed to extend out to the dotted line *F*. Figure 36, *B*, shows a similar section through a body of free water unaffected by any soil particle or other extraneous force field except that due to the body of water.

Consider the surface layer of water of thickness Δt_1 , which is part of the whole water film of thickness t_1 on the soil particle. Let us inquire how the average hydrostatic pressure in Δt_1 compares with that in a similar layer Δt_2 on free water, and how this difference in hydrostatic pressure influences their respective freezing points. If the average hydrostatic pressure in Δt_1 is greater than in Δt_2 , the freezing point of Δt_1 should be expected to be the lower, according to the Clausius-Clapeyron equation, 187. It will be noticed that we are assuming that the hydrostatic pressure at the liquid-ice interface is the same in both phases and that, there-

fore, the type of freezing considered by case 1 of article 30 applies. Since Δt_1 is within the sphere of influence of the adsorptive force field surrounding the soil particle, its hydrostatic pressure will be greater and will increase progressively as the surface of the soil particle is approached (art. 63) and thus will have a finite freezing-point depression by virtue of the hydrostatic pressure arising from the presence of an adsorptive force field. This is, of course, in addition to the usual freezing-point depression caused by dissolved material, which we are, for the present, neglecting. The freezing-point depression should also be expected to increase as more

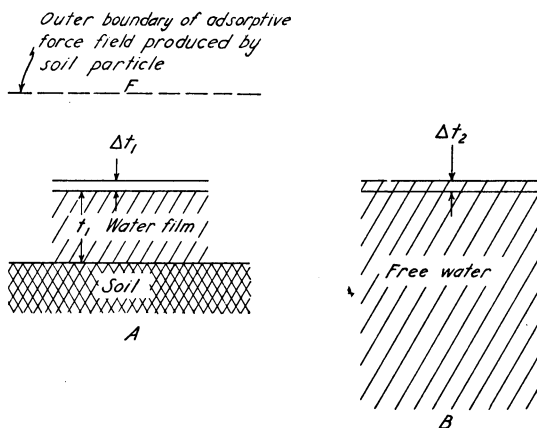


Fig. 36.—*A*, A radial section through a water-soil interface; *B*, a radial section through free, pure water.

and more soil moisture is frozen, because the hydrostatic pressure at the liquid-ice interface increases as the interface moves closer to the soil particle. This agrees qualitatively with the usual observations made in determining the freezing point of moist soil by the Beckmann method.

One might increase the hydrostatic pressure in Δt_2 (by a piston, for example, or by any other external means) to the value found in Δt_1 and consequently secure the same freezing-point depression for the two layers. Despite this equality of freezing-point depressions, the vapor pressures over the two layers would be quite different. The hydrostatic pressure produced by the piston on Δt_2 will increase the vapor pressure (art. 41), which originally was already greater than that over Δt_1 because of the presence of the adsorptive field surrounding the soil particle. Thus two layers of ice, Δt_1 and Δt_2 , may have the same freezing-point depression and yet possess widely different vapor pressures and consequently widely different free energies. The presence of the adsorptive force field surrounding the soil particle seems to account for this discrepancy of the

vapor pressures, although the freezing point of the water is the same in the two cases.

Because of the presence of the adsorptive force field, the escaping tendency of the water molecules from the soil moisture is reduced; consequently more work is required to carry a water molecule outward into the vapor phase against the adsorptive field of the soil, which is stronger than that of the free water. The velocities of the water molecules are distributed among the molecules according to the Maxwell distribution law (art. 54 and 55). Because of the adsorptive force field, those molecules having their velocities in the lower range of the Maxwell distribution are prevented from escaping into the vapor phase. The stronger the adsorptive force field, the larger the proportion of the slower molecules that are prevented from escaping. Not only will fewer molecules of the soil moisture be able to make the trip into the vapor phase, but those that do will be more inclined to return to the soil moisture because of the greater attractive influence exerted on them than when they are over free water. Thus, at equilibrium, there will be a smaller density of molecules over the moist soil than over the free-water surface. Since the average velocity is determined by temperature, which is the same for both Δt_1 and Δt_2 , then the vapor pressure will be higher over the free-water layer Δt_2 .

We are led in consequence to the following considerations of the Beckmann method when used in determining the freezing point of soil moisture at relatively low moisture contents where there is relatively little water under tension.

The thicker the layer Δt of soil moisture we freeze out, the greater the hydrostatic pressure at the liquid-ice interface and consequently the greater the observed freezing-point depression (art. 63). When we determine the freezing point of soil moisture by the Beckmann method, we therefore should try to freeze as thin a layer of soil moisture Δt as possible, for we wish to find the freezing point of the moisture that is most loosely bound. It is the freezing point of the *outermost layer of infinitesimal thickness* that we are seeking when we wish to determine the freezing point of a body of soil moisture by the Beckmann method. It is always the first layer to freeze. We should therefore supercool the soil moisture only as much as is absolutely necessary before freezing is initiated; otherwise we shall obtain an erroneous value for the freezing-point depression, which is too low in proportion to the thickness of the layer frozen out. The freezing-point depression caused by the dissolved material is, of course, superimposed upon the depression just discussed.

At least three serious difficulties arise when one uses the Beckmann method for determining the freezing point of soil moisture at low moisture contents. Since the total thickness of the moisture film is small at the

lower moisture contents, the minimum thickness of the layer that can be frozen out in determining the freezing point of the soil moisture must be a large fraction of the total thickness of the layer of soil moisture. Thus the measured freezing-point depression is proportionately greater than that of the true value and really corresponds to a proportionately lower soil-moisture content than the true one. The discrepancies are further magnified because the intensity of the adsorptive force field increases very rapidly as the surface of the soil particle is approached, which causes very significant changes in the hydrostatic pressure within thin moisture films when their thickness is changed but slightly. Attempts, of course, are made to correct for the amount of ice frozen out. The corrections usually applied are probably inadequate, since they do not consider the effect of the ice on the hydrostatic pressure in the liquid next to the soil particle. The presence of the ice layer (art. 63) would be expected to lower the freezing point of the remaining unfrozen liquid below what it would be for the same amount of liquid if the ice were not present.

A second difficulty at the lower moisture contents arises because the freezing out of the thin layer of water Δt reduces the amount of solvent liquid water to a relatively great extent and therefore concentrates the soil-moisture solutes in the same proportion, so that the observed freezing-point depression becomes still lower than the true value.

The third difficulty with the Beckmann method at the lower moisture contents is that when we supercool the soil moisture as little as possible in order subsequently to freeze out as thin a layer of ice Δt as possible, the total latent heat of fusion required to melt the thin layer of ice is very small; and the soil moisture consequently may not hold the equilibrium temperature long enough to permit a dependable reading of the thermometer.

69. Calculation of the Free Energy of Soil Moisture with Special Reference to the Interpretation of Dilatometer Measurements

There are several ways of measuring the free energy of soil moisture in relation to water retentiveness. The dilatometer method, however, seems to lend itself to a detailed analysis of the factors contributing to the total free energy of soil moisture, since we have developed a theory that enables us to consider the effect of each separate factor, such as dissolved material, adsorptive force field, and hydrostatic pressure.

As there is always an excess of water in the dilatometer, the freezing-point measurements made under these saturated conditions (where none of the water is under tension) must be interpreted in terms of the actual conditions found in the field or laboratory, where the soil is unsaturated. For this purpose, reference is made to figure 37. Part *A* of figure 37

represents a moist soil at some particular moisture content where the average thickness of the water film is t . We shall deal with a small enough radial section of moist soil so that the surface of the soil particle may be considered as flat. The figure at the right represents the same soil particle when placed in the dilatometer under conditions such that there is more than enough water to saturate the soil. The horizontal dotted line b

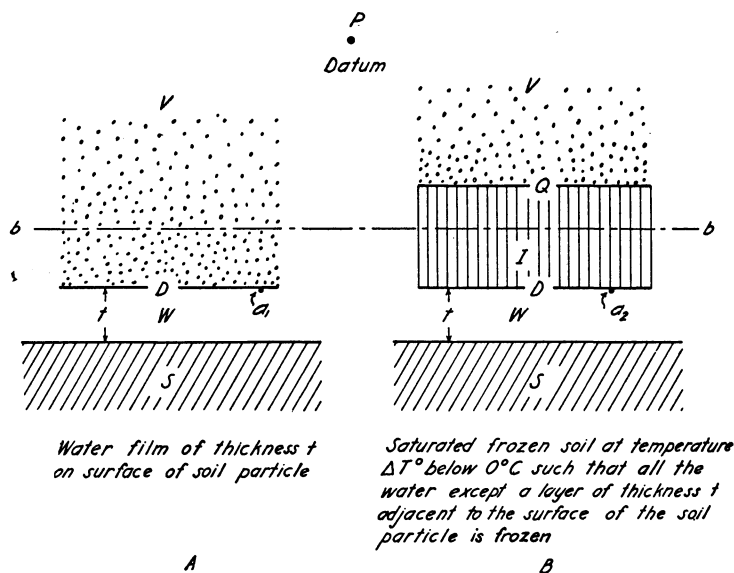


Fig. 37.—Comparison of conditions in moist soil outside and inside the dilatometer when the amount of unfrozen water in the dilatometer is the same as the actual soil moisture content in the soil outside the dilatometer.

crossing both figures represents schematically the outer boundary of the adsorptive force field, which, we postulate, surrounds the soil particles. We are here assuming that the temperature of the dilatometer containing the saturated soil (fig. 37, B) is at such a temperature ΔT° degrees below 0°C that the amount of water remaining unfrozen just equals the moisture content of the moist soil represented in figure 37, A. In other words, the thickness t of the liquid water film covering the soil surface is the same in the two diagrams.

The customary standard of zero soil moisture content (which is usually regarded as the state of the soil reached after prolonged drying at 110°C) should probably not be used here in determining the amount of water in the film. It is found that as the temperature is raised to higher values than 110°C (95) more adsorbed water is driven off. Here, we are concerned with all of the adsorbed water.

We seek now to represent the free energy of the soil moisture shown in figure 37, *A*, in terms of measurements of the total free energy of the unfrozen water in the dilatometer (fig. 37, *B*). To do this we shall first express the free energy Δf_s of the soil moisture in figure 37, *A*, in terms of its component free energies. We shall then represent the free energy Δf_D of the unfrozen water in figure 37, *B*, also in terms of its component free energies. Finally, we shall combine these two equations in such a way as to express the free energy of the soil moisture Δf_s in terms of the equivalent amount of unfrozen water and its freezing point in the dilatometer. We shall, in the future, represent this freezing point as ΔT degrees below 0°C . Often the freezing-point depression ΔT is spoken of as the freezing point ΔT .

Free Energy Δf_s of Soil Moisture in Terms of Its Components.—Starting now by considering figure 37, *A*, let Δf_s represent the total specific free energy of water. This is the same and a constant throughout both phases when the soil-moisture system has been allowed to reach equilibrium. Expressed in terms of vapor pressure, Δf_s may be represented (art. 39) by

$$\Delta f_s = RT \ln \frac{p_s}{p_0}. \quad (376)$$

This gives the free energy of the water in the soil-moisture system with reference to free, pure water at the same level as the moist soil, where p_s is the vapor pressure of the soil moisture, and p_0 is the vapor pressure over a free water surface used as the datum. In other words, Δf_s , as expressed above, represents the work per gram of water that must be expended in a reversible process by some exterior agency in carrying a particle of water from free, pure water (the datum) whose vapor pressure is p_0 to the moisture in the soil whose vapor pressure is p_s .

If Δf_s proves to be negative, energy or work is released to the exterior agency in the process of carrying water from free, pure water to any point in the soil moisture. That is, a gram of water as soil moisture would possess less energy than a gram of free, pure water, and therefore the free, pure water would spontaneously tend to pass into or flow into the moist soil.

The total free energy Δf_s of the soil moisture at any point in the liquid or vapor phase may be considered as a sum of several component free energies. Even though the soil moisture is in equilibrium and Δf_s is a constant throughout, the components of Δf_s may vary enormously from point to point in the soil moisture. Let us consider, for example, what these components of the free energy might be at the point a_1 , immediately below the vapor-water interface (fig. 37, *A*). Three components must be considered.

A. Soil moisture has free energy Δf_{PS} due to the hydrostatic pressure exerted on it by the combined action of the atmosphere and any other external forces that might be transmitted to the air-water interface. The value of this pressure will be constant throughout the fluid, since such a pressure is transmitted uniformly throughout a liquid according to Pascal's law. In addition, the soil moisture at any point may have hydrostatic pressure because of the adsorptive field surrounding the soil particles. The field pulls the superincumbent water lying above the point in question towards the soil surface, and thereby produces a pressure similar to the hydrostatic pressure created in a body of water on the surface of the earth by the presence of the earth's gravitational field. At the point a_1 under consideration (fig. 37, A), the compression produced by the field will be assumed to be zero, since there is no liquid farther out from the soil S to press against the liquid layer W and compress it.

The water at the air-water interface at the point a_1 , for example, is under a hydrostatic pressure ΔP_{PS} because of the pressure exerted by the atmosphere. The value of the free energy Δf_{PS} due to this pressure is given by $\Delta f_{PS} = v \Delta P_{PS}$ (eq. 156), where v equals the specific volume of water (which in the c.g.s. system equals unity approximately) and where ΔP_{PS} equals the total pressure acting on the water at the point in question. We then have

$$\Delta f_{PS} = 1 \times \Delta P_{PS} . \quad (377)$$

That is, the component of the free energy due to pressure is numerically equal to the hydrostatic pressure.

At the point a_1 under consideration, ΔP_{PS} is only 1 atmosphere, and no other external forces are acting upon the interface. If there were any, Δf_{PS} would be augmented by the additional amount. When, therefore, the soil moisture exists under the usual conditions, the pressure ΔP_{PS} exerted on the water surface D is 1 atmosphere, and consequently

$$\Delta P_{PS} = 0.1 \times 10^7 \text{ dynes per sq. cm.}$$

So that

$$\Delta f_{PS} = 1 \times \Delta P_{PS} = 0.1 \times 10^7 \text{ ergs per gram of water.}$$

But according to the conventions presented in article 39, we must take

$$\Delta f_{PS} = 0 , \quad (378)$$

since only 1 atmosphere is acting on the air-water interface of the moist soil. This follows because of the peculiar conditions involved in the cus-

tomary definition of the freezing point of pure water and what we have taken as our datum (art. 39). To support this statement, we must recall that one external condition defining the freezing point of pure water, 0°C , is that the water is at a pressure of 1 atmosphere while freezing. Actually, if pure water could be frozen without any external force or pressure acting on it, its freezing point would be $+0.0073^{\circ}\text{C}$, according to equation 187.

B. The free energy of soil moisture has another component, Δf_{os} , because it contains dissolved material. This component has, in previous literature (20, 103, 104), been called the "osmotic potential"; but for reasons mentioned earlier, the term "free energy" will be adhered to in this discussion.

If the osmotic pressure is ΔP_{os} at a_1 (fig. 37, A), then (art. 24)

$$\Delta f_{os} = -v\Delta P_{os}.$$

In the c.g.s. system the specific volume of water v is approximately equal to unity, and therefore

$$\Delta f_{os} = -1 \times \Delta P_{os}.$$

We notice that the zero point of the osmotic component of the specific free energy is taken as pure water, containing no dissolved material. Under this condition the osmotic pressure ΔP_o equals zero. Also, we notice that unlike a positive hydrostatic pressure ΔP_p (which increases the free energy of water), an osmotic pressure ΔP_o decreases the potential of the water, as is indicated by the minus sign in the equation above, as well as by article 65. That is, dissolved material decreases, whereas positive hydrostatic pressure increases, the specific free energy of soil moisture.

The osmotic component of the free energy Δf_{os} of the water at the point a_1 , which later will be shown to equal that at a_2 , may be expressed in terms of the freezing-point depression ΔT_{os} produced by the dissolved material, the osmotic pressure of which is ΔP_{os} . By equation 200,

$$\Delta P_{os} = -\frac{l\Delta T_{os}}{vT} = -\frac{l\Delta T_{os}}{T}, \quad (379)$$

since $v = 1$, approximately, for water. Therefore (eq. 148), the osmotic component

$$\Delta f_{os} = +\frac{l\Delta T_{os}}{T}.$$

Thus if the freezing-point depression of a soil solution ΔT_{os} due to osmotic pressure or dissolved material is determined, the osmotic component of the specific free energy of the soil moisture Δf_{os} can be found immediately.

C. Soil moisture possesses free energy also because it is situated in a field of force. The component of the free energy due to this cause will be designated by Δf_{FS} and will be called the component of the free energy due to the force field.

The component Δf_{FS} (art. 26), is roughly analogous to the gravitational potential of a particle above the earth's surface. As the particle is moved upwards against the earth's gravitational field, its gravitational potential increases. Upon its return to its original position, its potential energy is released. If it is allowed to fall freely, its gravitational potential will be transformed into kinetic energy; if suddenly stopped, it will be transformed into heat. The symbols Δf_{FS} represent the component of the free energy possessed, for example, by water at a_1 (fig. 37, A) by virtue of its position in the force field surrounding the soil particle. This might be due to any force field which may surround the soil particle and which acts on the water molecules, such as electric, magnetic, or gravitational. This would include any free energy due to orientation which the water molecules surrounding the soil particle may have.

For soil moisture we shall take, as in the past, for the datum of the free energy due to the field, any point P in free, pure water beyond the influence of the force field surrounding the soil particle. The outer range of influence of the force field surrounding the soil particle is schematically represented by the line bb in figure 37. The free energy of the soil moisture Δf_{FS} at the point a_1 is then the work required per gram to carry water from free, pure water to a_1 . Because the water particles tend to move towards the soil surface and because mechanical energy is released in doing so, Δf_{FS} is always negative for soils except at the datum, where it is zero.

We have considered in detail three of the most important components of free energy Δf_s of soil moisture. Let us now combine them so as to obtain the resultant. The free energy Δf_s of the soil moisture is the sum of the component free energies

$$\Delta f_s = \Delta f_{FS} + \Delta f_{os} + \Delta f_{FS}. \quad (380)$$

Since the soil moisture is in equilibrium, Δf_s is a constant and the same at all points throughout the liquid and vapor phases (art. 22) as long as the moisture content remains the same, which in figure 37, A, means that the thickness t of the liquid layer remains constant. This follows

directly from the thermodynamic properties of free energy (art. 22). On the other hand, the three partial or component free energies may change enormously from point to point in the soil moisture. For example, if we assume that Δf_{OS} is constant throughout the soil moisture, the component of the free energy due to the field Δf_{FS} will decrease as the soil surface is approached, while the component of the free energy due to hydrostatic pressure Δf_{PS} will increase in such a way as to keep the total free energy Δf_S constant. We shall wish to evaluate the total free energy Δf_S in terms of its partial or component free energies at the point a_1 just under the vapor-water interface.

Our object is now to determine the total free energy Δf_S of soil moisture at a given moisture content in terms of the total free energy of the soil moisture in the dilatometer Δf_D (which in turn is expressed in terms of the three following partial free energies: that due to the hydrostatic pressure Δf_{PD} , that due to the osmotic pressure Δf_{OD} , and that due to the adsorptive force field Δf_{FD}), obtained from freezing-point measurements made with the dilatometer on a saturated sample of the soil. This determination can, as we shall see, be made, provided we know the freezing point ΔT at which the amount of unfrozen moisture remaining in the dilatometer (fig. 37, *B*) equals the moisture content of the soil in question (fig. 37, *A*). In other words, we require the freezing-point depression ΔT in order that the thickness t of the unfrozen water (fig. 37, *B*) may be equal to the thickness of the soil-moisture film (fig. 37, *A*). The reason for making the amount of unfrozen water equal in the two parallel cases will become apparent later.

Free Energy Δf_D of the Unfrozen Water in the Dilatometer Expressed in Terms of Its Components.—Before we can express Δf_S of the moist soil in terms of data obtained from the dilatometer, we shall obtain an expression for the total free energy Δf_D of the soil moisture in the dilatometer, in terms of its component free energies. This will require a detailed consideration of the component free energies of Δf_D .

Figure 37, *B*, represents a small portion of a radial section of a soil particle with a liquid layer of thickness t overlain by an ice layer I and by water vapor V . The outer boundary of the influence of the adsorptive force field surrounding the soil particle is schematically represented by the line bb . Any water lying beyond this line is free from the body forces exerted by the soil particle. Since the point a_2 (fig. 37, *B*) is within bb , it will be affected by the attractive force surrounding the soil particle.

Let us express Δf_D , the total free energy of water in any of the three phases, in terms of its components at the point a_2 in the liquid adjacent to the water-ice interface D . Let Δf_D equal the total free energy of the water in figure 37, *B*, under the conditions assumed in figure 37, *A*. The

value of Δf_D is a constant and the same throughout all the three phases (liquid, ice, and vapor) when the system is at equilibrium, because of the thermodynamic properties of free energy (art. 22). Expressed in terms of the vapor pressure of the vapor phase, Δf_D may (art. 22 and 39) be represented by

$$\Delta f_D = RT \ln \frac{p_D}{p_0}. \quad (381)$$

Like Δf_S , Δf_D is measured with respect to the point P in free, pure water, which is our datum; p_D denotes the vapor pressure of the ice at the temperature T_D of the partially frozen soil moisture in the dilatometer, and p_0 denotes the vapor pressure of the pure, supercooled water at the same temperature T_D .

We shall now consider in detail (fig. 37, *B*) the three component free energies that go to make up Δf_D at the point a_2 in the water layer adjacent to the water-ice interface.

A. Let Δf_{PD} represent the component free energy due to hydrostatic pressure exerted on the unfrozen water layer of thickness t . This component is due to two factors. One of these is the force or "weight" of the superincumbent ice between D and bb which lies within the influence of the adsorptive force field and which presses against the liquid water layer of thickness t (art. 64). This hydrostatic pressure in the soil moisture is analogous mechanically to the hydrostatic pressure found below the surface of a body of water in a reservoir. In the water of the reservoir, the hydrostatic pressure is produced by the weight of the overlying water arising from the presence of the earth's gravitational field. In soil moisture, the hydrostatic pressure arises from the presence of an adsorptive force field surrounding the soil particle. The other factor that contributes to Δf_{PD} is the atmospheric pressure exerted on the air-ice interface and communicated, in turn, to the water-ice interface.

The combined hydrostatic pressure ΔP_{PD} due to both of the pressures mentioned above produces a freezing-point depression ΔT_P of the soil moisture at the water-ice interface, in accordance with the Clausius-Clapeyron equation (art. 27)

$$\Delta P = \frac{l\Delta T_P}{T\Delta v}.$$

We find (eq. 156) that

$$\Delta f_{PD} = v\Delta P = v \frac{l\Delta T_P}{T\Delta v} = \frac{l\Delta T_P}{T\Delta v} \times 1, \quad (382)$$

since $v = 1$, approximately, in the c.g.s. system. Thus a determination of the freezing-point depression ΔT_P due to the hydrostatic pressure of the

water at a_2 lying in the water-ice interface (fig. 37, *B*) will immediately determine the component free energy Δf_{PD} of the water at the water-ice interface, since all the other quantities in equation 382 are well-known constants.

If dissolved salts are present in the liquid water layer of thickness t (fig. 37, *B*), the total freezing-point depression ΔT of the water at a_2 adjacent to the water-ice interface in the dilatometer will have two components: ΔT_P , due to hydrostatic pressure just discussed; and ΔT_O , due to the osmotic pressure of the dissolved material within the unfrozen water layer to be considered below. As will be recalled (art. 65), although hydrostatic pressure and dissolved material both produce freezing-point depressions of the soil water, whose combined freezing-point depression is the arithmetical sum of both, positive hydrostatic pressure gives soil moisture a positive component free energy, whereas dissolved material gives water a negative component free energy. Thus the component freezing-point depressions ΔT_P and ΔT_O are additive; but the component free energies Δf_P and Δf_O are subtractive, tending to neutralize each other (art. 65).

B. Let Δf_{OD} represent the component free energy of the water at a_2 of figure 37, *B*, possessed because of the dissolved material. The same considerations apply to Δf_{OD} as were made for Δf_{OS} . Therefore $\Delta f_{OD} = + \frac{l \Delta T_{OD}}{T}$

where ΔT_{OD} represents the component freezing-point depression of the water at a_2 in the water-ice interface because of the dissolved material.

Suppose a very small layer of water at the interface *D* (small as compared with the total thickness of the water film) is frozen and removed from solution. This procedure will concentrate the solute in the remaining liquid soil moisture, increasing its osmotic pressure ΔP_{OD} as well as its freezing-point depression ΔT_{OD} . Assuming for the present that the solutes are uniformly distributed throughout the liquid soil moisture, then if half the liquid layer is frozen, the osmotic pressure ΔP_{OD} as well as the freezing-point depression ΔT_{OD} of the remaining liquid will be doubled. Thus the relation between the volume of the unfrozen moisture and its osmotic pressure will follow van't Hoff's law (eq. 226). Because of the hypothesis above, as more of the soil moisture is frozen, the osmotic pressure ΔP_{OD} , together with the freezing-point depression ΔT_{OD} of the unfrozen moisture, should be expected to increase approximately in accordance with the following equations:

$$\begin{aligned} &(\text{amount of soil moisture still unfrozen}) \times (\text{osmotic pressure } \Delta P_{OD}) \\ &= (\text{a constant at a specific temperature}) \end{aligned}$$

$$\begin{aligned} &(\text{amount of soil moisture still unfrozen}) \times (\text{freezing-point depression } \Delta T_{OD}) \\ &= (\text{a constant at a specific temperature}). \end{aligned}$$

It is generally conceded, however, that the solute concentration increases as one approaches the soil-particle surface. Therefore, as the amount of solvent or liquid water is decreased by the gradual freezing out of soil moisture, one might expect the osmotic pressure ΔP_{OD} as well as the freezing-point depression ΔT_{OD} to increase more rapidly than is predicted by the equations above. To a first approximation, however, we shall assume the above equations. Further work with the dilatometer should shed more light on their validity.

Thus if the temperature of the saturated soil in the dilatometer is lowered so as to freeze part of the soil moisture, the part of the freezing-point depression due to dissolved material, ΔT_{OD} , determines the osmotic pressure ΔP_{OD} (eq. 200) and therefore the osmotic component of the free energy Δf_{OD} of the soil solution at the water-ice interface D of figure 37, B , in accordance with equation 148.

Since we have postulated that the thickness t of the unfrozen or liquid water layer surrounding the soil particle in the dilatometer (fig. 37, B) is the same as the thickness of the moisture layer surrounding the soil particle outside (fig. 37, A), we should expect that

$$\Delta f_{OS} = \Delta f_{OD} \quad (383)$$

since there is, to a first approximation, the same amount of liquid water as well as dissolved material present in the two cases.

C. Let Δf_{FD} represent the component free energy possessed by the water at a_2 (fig. 37, B), arising because it is situated within the adsorptive force field surrounding the soil particle (art. 26 and 64). Comparing Δf_{FD} and Δf_{PD} above, one may say that Δf_{FD} is the component free energy possessed by water at a_2 by virtue of its *position* in the adsorptive force field, whereas Δf_{PD} is the component possessed by water at a_2 by virtue of the *hydrostatic pressure* there, arising in part from the presence of the force field surrounding the soil particle and acting on the superincumbent ice layer, and in part from external agencies such as atmospheric pressure. As was mentioned for Δf_{FS} , the free energy Δf_{FD} due to the adsorptive force field is roughly analogous to the gravitational potential possessed by a mass in the earth's gravitational field. All the considerations mentioned in connection with Δf_{FS} apply here to Δf_{FD} . But in addition, Δf_{FD} includes any effect of the adsorptive field surrounding the ice, which effect we shall represent by K . Since the points a_1 and a_2 are at the same distance t from the surface of the soil particles, we may, for reasons that will follow, write

$$\Delta f_{FD} = \Delta f_{FS} + K. \quad (384)$$

Since K will enter into the final expression for the total specific free energy of the soil moisture Δf_s , we had better consider its meaning in more detail and evaluate it. Consider again figure 37. As will be recalled, the datum for the free energy is taken as any point (here schematically represented by the point P) in free, pure water outside the influence of the adsorptive force field. The total free energy Δf_{FS} at a_1 in the soil moisture represents the work per gram of water required to carry water from the point P to a_1 against the force of the adsorptive field surrounding the soil particle. Since water is attracted toward a_1 , mechanical energy is released by the water in moving it from P to a_1 . Consequently Δf_{FS} , the component of the free energy due to the adsorptive force field, will be inherently negative (eq. 168).

Let us now evaluate the component of the free energy Δf_{FD} at the point a_2 in the water of the water-ice interface of the dilatometer. It will be shown, as stated by equation 384, that Δf_{FD} may be considered as made up of two parts, one of which is Δf_{FS} . In A of figure 37, Δf_{FS} represents the component free energy produced by the adsorptive force field surrounding the soil particle. In B of figure 37, Δf_{FS} is only part of Δf_{FD} . The other part, K , of Δf_{FD} arises from the presence of the adsorptive force field produced by the superincumbent ice layer that acts upon the water at a_2 . The term Δf_{FS} is therefore the work per gram required to carry water from the point P to the point a_1 or from P to the point a_2 against the adsorptive force field produced only by the soil particle, neglecting the effect of the ice layer at a_2 . This follows because a_1 and a_2 were assumed to be the same distance t from the soil-particle surface.

The second part of Δf_{FD} , which we shall call K , is therefore the work per gram of water required to carry the water from the point P to the point a_2 through the adsorptive force field produced by the ice layer only. In other words, the force field at a_2 differs from that at a_1 only in that a_2 is acted upon by the additional adsorptive force field produced by the ice layer. Since the soil in the dilatometer is always saturated, the ice layer will, in general, be so thick that K is independent of the amount of unfrozen water and ice present. Only when the thickness of the ice layer becomes such that its outer boundary Q falls inside the range of influence bb of the force field surrounding a soil particle will K change—that is, begin to decrease. One may then consider K as a constant representing the work per gram of water required in carrying water from the point P , through the adsorptive force field produced only by the ice, to the surface of the ice layer. Since it is a general characteristic of free energy that the total free energy at a point equals the sum of the components, we have immediately

$$\Delta f_{FD} = \Delta f_{FS} + K.$$

This follows because, although superimposed force fields are added vectorially, the associated free energies are added as scalars. Thus the total free energy due to the force field Δf_{FD} at a_2 has been split up into two parts: (1) the work per gram Δf_{FS} required to carry water from the point P to a_2 through the adsorptive force field produced only by the soil particle, and (2) the work per gram of water K required to carry water from P to a_2 through the adsorptive force field produced only by the superincumbent ice layer. Since the thickness of the liquid layer is the same in the case of both A and B of figure 37, any effect of Δf_{FS} will be found to cancel out in the end. It might at first have seemed strange to split Δf_{FD} into two parts, one of which is Δf_{FS} ; but it was merely a mathematical artifice permitting us to reduce the number of unknown variables. If we know Δf_{FS} , we can now determine Δf_{FD} immediately, except for the universal constant K .

The free energy Δf_D of the moisture in the dilatometer is then the sum of three component free energies just considered in detail:

$$\Delta f_D = \Delta f_{PD} + \Delta f_{OD} + \Delta f_{FD}. \quad (385)$$

Since we have assumed that the soil moisture in the dilatometer is in equilibrium, the total free energy Δf_D must be a constant having the same value at all points throughout the liquid, ice, and vapor phases so long as the thickness t of the liquid layer remains the same. This is true even though the three component free energies may change enormously from one point to another in the soil moisture or in going from one phase to the other. No matter how they vary among themselves, their sum, under equilibrium conditions of the soil moisture, is a constant. This follows immediately from a consideration of the thermodynamic properties of the free-energy function (art. 22).

By using equations 380 and 385, we can now express the total free energy Δf_S of the moist soil at a given moisture content in terms of a freezing-point measurement made on a similar sample of saturated soil placed in the dilatometer.

Referring again to figure 37, A , we have (as has previously been shown at the point a_1 in the moist soil)

$$\Delta f_S = \Delta f_{PS} + \Delta f_{OS} + \Delta f_{FS}. \quad (386)$$

At a like position a_2 in the saturated soil (fig. 37, B) in the dilatometer,

$$\Delta f_D = \Delta f_{PD} + \Delta f_{OD} + \Delta f_{FD}. \quad (387)$$

Also, since we have the same amount of liquid water surrounding the soil particles in the two cases (permitting the reasonable assumption that the concentrations are the same in both cases, as previously mentioned) and since a_1 and a_2 are at the same distance from the surface of the soil particles, we have equations 383 and 384 giving the free energy due to the osmotic pressure and the field, respectively:

$$\Delta f_{OD} = \Delta f_{OS}; \quad (388)$$

$$\Delta f_{FD} = \Delta f_{FS} + K. \quad (389)$$

With the aid of these two equations, equation 387 becomes

$$\Delta f_D = \Delta f_{PD} + \Delta f_{OS} + \Delta f_{FS} + K. \quad (390)$$

Therefore, combining equations 386 and 390 by equating $(\Delta f_{OS} + \Delta f_{FS})$ of the former to $(\Delta f_{OS} + \Delta f_{FS})$ of the latter, we have

$$\Delta f_S = \Delta f_D - \Delta f_{PD} + \Delta f_{PS} - K. \quad (391)$$

In our present case, $\Delta f_{PS} = 0$ (eq. 378). This follows (as was explained before where Δf_{PS} was considered in detail) because of the peculiar conditions involved in the customary definition of the freezing point of pure water as well as the definition of 0° C and because the only pressure acting on the soil moisture at the air-water interface is 1 atmosphere. The free energy of the soil moisture then becomes

$$\Delta f_S = \Delta f_D - \Delta f_{PD} - K. \quad (392)$$

Also, because of our method of defining 0° C, the hydrostatic pressure to be used in evaluating Δf_{PD} at any point in the dilatometer is the total hydrostatic pressure at that point minus 1 atmosphere. If, then, the dilatometer contents are open to a pressure of 1 atmosphere, as is usually the case, then Δf_{PD} is due entirely to the hydrostatic pressure caused by the adsorptive field surrounding the soil particle.

The terms Δf_D and Δf_{PD} (eq. 392) can be expressed in terms of measurable quantities such as temperature and pressure, as was shown earlier in this article when Δf_D and Δf_{PD} were considered in detail. We have then

$$\Delta f_S = RT \ln \frac{p_D}{p_0} - \frac{l \Delta T_P}{T \Delta v} - K \quad (393)$$

where ΔT_P is the freezing-point depression due only to hydrostatic pres-

sure in the soil moisture. This, of course, represents the difference between the total freezing-point depression ΔT and that due to the presence of dissolved material ΔT_O (art. 65).

We now wish to evaluate K . The term K is a constant and, as previously pointed out, is in general independent of the amount of unfrozen water in the dilatometer. Thus, whether one evaluates Δf_s for small or great amounts of unfrozen water, K should remain unchanged. If, then, K can be evaluated at some particular value of ΔT_P in the equation above corresponding to a given amount of unfrozen moisture, it will have been determined for all others. We shall proceed to evaluate it in equation 393 at such a freezing-point depression ΔT_P that the water-ice interface is beyond the influence of the adsorptive force field surrounding the soil particle—that is, beyond bb of figure 37, B .

Suppose Δf_s is evaluated for a moisture content (fig. 37, A) such that the thickness t of the unfrozen water layer is greater than the range of influence bb of the adsorptive force field exerted by the soil particle. We shall distinguish Δf_s under these conditions by $\Delta f_s'$. In this upper range of moisture contents, the freezing-point depression due to hydrostatic pressure ΔT_P must equal zero, since the adsorptive force field surrounding the soil particle does not in this case extend out far enough to produce any hydrostatic pressure at the water-ice interface. Thus in this particular case the third term in equation 393 drops out, and we have

$$\Delta f_s' = RT \ln \frac{p_D}{p_0} - K. \quad (394)$$

Since, in order to evaluate K , we are considering a very wet soil (fig. 37, A) where t is very great, then the vapor pressure p_s of the soil moisture equals the vapor pressure P_D of the parallel case of the unfrozen water in the dilatometer (art. 22) when the interface D (fig. 37, B) lies above the plane bb . In other words, t extends beyond the adsorptive force field of the soil particle. Equation 394 then becomes

$$\Delta f_s' = RT \ln \frac{p_s}{p_0} - K. \quad (395)$$

The term $\Delta f_s'$ of the reduced equation 395 can readily be evaluated. Since the point a_2 (fig. 37, B) is now assumed beyond the adsorptive force field, the only significant factor contributing to the free energy $\Delta f_s'$ of the soil moisture is the osmotic pressure of the dissolved material in the soil solution. Hence, under these special conditions, the total freezing-point depression ΔT must be the same at the air-water interface of the

moist soil as at the water-ice interface in the dilatometer. Thus since $\Delta f_s'$ is produced entirely by dissolved material, we may (eq. 207) express $\Delta f_s'$ in still another way:

$$\Delta f_s' = \frac{l \Delta T}{T}. \quad (396)$$

Combining equations 395 and 396 we get:

$$\frac{l \Delta T}{T} = RT \ln \frac{p_s}{p_0} - K. \quad (397)$$

But

$$RT \ln \frac{p_s}{p_0} = + \frac{l \Delta T}{T} \quad (398)$$

since (eq. 236 and 207) the two members of equation 398 are merely two ways of expressing the free energy of the same solution due to the presence of dissolved material and since the concentrations of the soil solutions of both *A* and *B* of figure 37 are the same to a first approximation. The first member expresses the free energy of the solution in terms of its vapor pressure; the second, in terms of its freezing-point depression. Thus (eq. 398) the two terms of equation 397 cancel out, and we find

$$K = 0.$$

The free energy (eq. 393) of soil moisture at a particular soil moisture content, as determined from freezing-point measurements carried out with the dilatometer, takes on the final form

$$\Delta f_s = RT \ln \frac{p_D}{p_0} - \frac{l \Delta T_P}{T \Delta v}. \quad (399)$$

Here it is recalled that:

T = temperature of the dilatometer corresponding to the total freezing-point depression ΔT necessary to freeze out all but an amount of moisture equal to the soil moisture content whose free energy is desired (fig. 37).

ΔT_P = the part of the total freezing-point depression ΔT in the dilatometer due to hydrostatic pressure alone; since this is a depression, it will be substituted as a negative quantity numerically. The value of ΔT_P is determined from the total freezing-point depression measured with the dilatometer by subtracting from the latter the freezing-point depression produced by the

dissolved material. The latter is readily determined at each temperature from a knowledge of the freezing-point depression of the unfrozen soil solution in the dilatometer and the amount of unfrozen water shown by the dilatometer at each temperature.

p_D = the vapor pressure of the ice in the dilatometer at the temperature T .

p_0 = the vapor pressure of supercooled water at the temperature T .

R = gas constant per gram of water.

l = heat of fusion of water which must be taken as negative if Δv is taken as positive.

Δv = volume change when 1 gram of water changes to ice; since water expands on freezing, Δv will be positive.

As will be recalled (following eq. 186), the ratio $\frac{l}{\Delta v}$ is always negative;

and since the freezing point T of soil moisture is always less than 0°C , ΔT_P is also always negative. The quantity Δf_s (eq. 399) is therefore composed of two negative terms.

This equation permits us to evaluate the free energy Δf_s of soil moisture, at a particular moisture content, from freezing-point measurements made with a dilatometer. A series of such evaluations will be reported by the authors in a separate publication.

70. Heat of Wetting and Swelling of Soils

When any dry substance, such as a soil, containing colloidal material is wetted, several phenomena are observed. There is usually a change in color, an increase in volume, and an increase in temperature. Since heat is developed at the same time that a change in volume takes place, physical chemists and botanists have devoted considerable attention to what has been called "heat of swelling." The differential heat of swelling

$\left(\frac{\partial q}{\partial V}\right)_T$ is the heat developed ∂q when the volume of the material wetted by the liquid changes by an amount ∂V . The subscript T is added to indicate that the initial and final temperature must be the same during the determination of ∂q . The differential heat of swelling increases rapidly as the moisture content of the substance being wetted decreases.

The differential heat of swelling $\left(\frac{\partial q}{\partial V}\right)_T$ is closely related to the differential heat of wetting $\left(\frac{\partial q}{\partial m}\right)_T$. This relation will be discussed later. The differential heat of wetting of a soil at a particular moisture content may

be defined as the ratio of the heat developed ∂q to the mass of water ∂m , added uniformly throughout to a large amount of the moist soil already at the moisture content m . We note that enough soil is taken so that the amount of water ∂m added to the moist soil does not change the soil moisture content appreciably. If we take a very large amount of soil, the differential quotient is the heat developed when 1 gram of water is added and distributed uniformly throughout the large mass of soil.

The differential heat of wetting $\left(\frac{\partial q}{\partial m}\right)_T$ may be measured in three

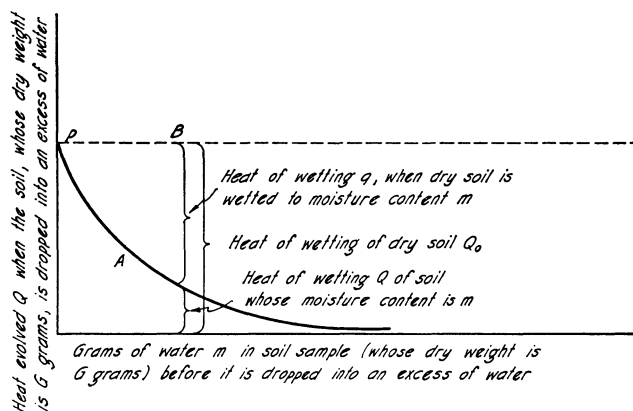


Fig. 38.—Integral heat of wetting of soils as a function of moisture content.

ways. In the first method, the material is wetted by adding a small increment of water Δm and measuring the quantity of heat Δq developed by the increment of moisture. This method, however, presents serious experimental difficulties: *It is impossible to make moisture distribute itself uniformly throughout a soil within a reasonable period at any moisture content below the moisture equivalent of the soil (157, 158, 163);* and it happens that the moisture equivalent always falls in the wet range of soil moisture contents, where the heat of wetting is practically zero. Such measurements, therefore, cannot well be made with reasonable accuracy at the moisture contents usually found in soils where plants are growing.

In the second method we prepare the soil sample at the desired moisture content in any of the standard ways. For example, we might spray a fine fog of water vapor over the dry soil and then enclose it in an airtight vessel until an equilibrium distribution of soil moisture is established. After the soil sample has reached equilibrium, suppose we drop it into a calorimeter containing an excess of water and measure the amount of heat Q , often called the *integral heat of wetting*, evolved by the soil sam-

ple, whose dry weight is G and which originally contained m grams of water. We can repeat the same procedure for a series of soil samples of varying moisture content m , and plot the results as shown by curve A (fig. 38). The vertical distance from the origin to the point P (where the point P is the intersection of curve A with the vertical axis) represents the amount of heat Q_0 liberated when enough water is added to the dry soil to saturate it. The difference between Q_0 and any other Q , associated with a particular moisture content m , represents the heat q liberated when dry soil is wetted uniformly to the particular moisture content m .

The slope $\left(\frac{\partial q}{\partial m}\right)_T$ of this curve is the magnitude of the differential heat of wetting. The reason is readily seen if we draw a horizontal line B from P . We see from the curve that the more water m we add to the originally dry soil sample, the greater is the amount of heat q evolved.

The third method, which is indirect, uses the Clausius-Clapeyron equation:

$$l = T \left(\frac{dp}{dT} \right) (v_V - v_L), \quad (400)$$

as derived in article 27, where l represents the heat required to vaporize 1 gram of water (that is, the latent heat of vaporization) and where v_L and v_V are the specific volumes of liquid and vapor, respectively, at the vapor pressure p . Here $(v_V - v_L) = \Delta v$ is the change in volume accompanying the change in phase from liquid to vapor. If v_L may be neglected in comparison with v_V , as is usually the case, we may write 400 in the form

$$l = T v_V \left(\frac{dp}{dT} \right). \quad (401)$$

If we may assume that the vapor obeys the perfect gas law, we may express v_V in terms of p ; and 401 becomes

$$l = \frac{RT^2}{p} \frac{dp}{dT} = RT^2 \frac{d \ln p}{dT}. \quad (402)$$

The latent heat of evaporation l is the negative of the heat of condensation or adsorption, which we shall denote by λ ; that is $l = -\lambda$. The heat of condensation λ is therefore the amount of heat liberated per gram of water vapor when the vapor condenses completely to the liquid state.

Expressed in terms of λ , equation 402 becomes

$$\lambda = -RT^2 \frac{d \ln p}{dT}.$$

We shall denote by λ_0 the heat liberated per gram when water vapor condenses to the free, pure liquid state; and by λ the heat liberated per gram when water vapor condenses uniformly onto a large amount of soil already at a definite moisture content. We have, then, from the above, both

$$\lambda_0 = -RT^2 \frac{d \ln p_0}{dT} \quad \text{and} \quad \lambda = -RT^2 \frac{d \ln p}{dT}, \quad (403)$$

where p denotes the vapor pressure of the moist soil and p_0 that of the free, pure water at the same temperature, T .

The heat of condensation or adsorption λ of soil moisture may be thought of as composed of two parts: (1) the heat liberated λ_0 when 1 gram of water is condensed from the saturated vapor of the free liquid state; (2) the heat liberated when the same gram of water is taken from free, pure water and evenly distributed throughout a large mass of the soil at the moisture content at which we wish to determine the differential heat of wetting. To be strictly correct we should take so large an amount of soil that the addition of the gram of water will not alter the moisture content appreciably. The second part of the above is recognized immediately to be the differential heat of wetting $\left(\frac{\partial q}{\partial m}\right)_T$. Therefore

$$\lambda = \lambda_0 + \left(\frac{\partial q}{\partial m}\right)_T$$

or

$$\left(\frac{\partial q}{\partial m}\right)_T = \lambda - \lambda_0,$$

which with 403 becomes

$$\begin{aligned} \left(\frac{\partial q}{\partial m}\right)_T &= -RT^2 \frac{d \ln p}{dT} + RT^2 \frac{d \ln p_0}{dT} \\ &= RT^2 \frac{d(\ln p_0 - \ln p)}{dT} = RT^2 \frac{d \ln \left(\frac{p_0}{p}\right)}{dT} \end{aligned}$$

or, for small finite changes,

$$\left(\frac{\partial q}{\partial m}\right)_T = RT^2 \frac{\Delta \ln \left(\frac{p_0}{p}\right)}{\Delta T}. \quad (404)$$

Here the differential heat of wetting $\left(\frac{\partial q}{\partial m}\right)_T$ denotes the heat liberated per gram of water added when pure water whose vapor pressure is p_0 at

the temperature T is added to moist soil whose vapor pressure is p at the temperature T .

Equation 404 may, by a slight transformation, be adapted to the evaluation of the differential heat of wetting from measurements of vapor pressure of soil moisture at two different temperatures. If, therefore, the vapor pressures p_0 and p of the free water and the moist soil, respectively, are measured at two different temperatures, T_1 and T_2 , we may write

$$\left(\frac{\partial q}{\partial m}\right)_T = \frac{RT_1T_2 \left[\ln \left(\frac{p_{02}}{p_2} \right) - \ln \left(\frac{p_{01}}{p_1} \right) \right]}{T_2 - T_1} \quad (405)$$

as representing a close approximation to the truth. Here we have resorted to the approximation of replacing the infinitesimal change of the logarithm of the pressures as well as the temperature by finite changes. This implies that the ratio of the finite changes is practically equal to the ratio of infinitesimal changes. At the same time, we have replaced T^2 by $T_1 T_2$ as being a very good average of T^2 over the range for which the ratio is being determined. Thus, by measuring the vapor pressures p_1 and p_2 of the moist soil as well as the vapor pressures p_{01} and p_{02} of a free body of water at two different temperatures T_1 and T_2 , we can evaluate the differential heat of wetting $\left(\frac{\partial q}{\partial m}\right)_T$. Since the determination of the differential heat of wetting of a soil at a particular moisture content depends upon the measurement of the relative vapor pressure of a free body of water p_0 with respect to that of the soil moisture p , evidently equation 405 is most useful in that range where p_0 differs appreciably from p —that is, for relatively dry soils.

Finally, it is interesting to observe the close relation existing between the differential heat of wetting $\left(\frac{\partial q}{\partial m}\right)_T$ and the differential heat of swelling $\left(\frac{\partial q}{\partial V}\right)_T$. As was proved in article 7, we may write

$$\left(\frac{\partial q}{\partial V}\right)_T = \left(\frac{\partial q}{\partial m}\right)_T \left(\frac{\partial m}{\partial V}\right)_T.$$

And according to article 6, the second term on the right may be transformed into its reciprocal, which is more readily visualized, giving

$$\left(\frac{\partial q}{\partial V}\right)_T = \frac{\left(\frac{\partial q}{\partial m}\right)_T}{\left(\frac{\partial V}{\partial m}\right)_T} \quad (406)$$

where $\left(\frac{\partial V}{\partial m}\right)_T$ is the total increase of volume of our moist soil per unit mass of water added at a particular soil moisture content m , when the initial and final temperature during the process are kept the same, and a large enough amount of soil is taken so that the moisture content of the soil is not changed appreciably by the addition of the moisture. The volume here considered is the actual volume occupied by both soil and water *but does not include the volume occupied by air*.

If, as is frequently the case, no great change occurs in the total volume of the water and soil when water is added to the soil and if we use the c.g.s. system, we may set $\left(\frac{\partial V}{\partial m}\right)_T = 1$. Under these conditions, the heat of wetting would be numerically equal to the heat of swelling according to equation 406, which becomes

$$\left(\frac{\partial q}{\partial V}\right)_T = \left(\frac{\partial q}{\partial m}\right)_T. \quad (407)$$

We have then for the heat of swelling, according to 405 and 406,

$$\left(\frac{\partial q}{\partial V}\right)_T = \frac{RT_1T_2 \left[\ln \left(\frac{p_{02}}{p_2} \right) - \ln \left(\frac{p_{01}}{p_1} \right) \right]}{(T_2 - T_1)} \left(\frac{\partial V}{\partial m}\right)_T. \quad (408)$$

And as mentioned above, if $\left(\frac{\partial V}{\partial m}\right)_T = 1$, approximately, in the c.g.s. system, equation 408 becomes

$$\left(\frac{\partial q}{\partial V}\right)_T = \frac{RT_1T_2 \left[\ln \left(\frac{p_{02}}{p_2} \right) - \ln \left(\frac{p_{01}}{p_1} \right) \right]}{(T_2 - T_1)}, \quad (409)$$

enabling one to determine the heat of swelling of soil in terms of its vapor pressure at any two different temperatures, T_1 and T_2 . Equation 408 or 409 can be used easily only for comparatively dry soils, for the reasons given in connection with equation 405.

Incidentally, $\left(\frac{\partial V}{\partial m}\right)_T$ is not exactly equal to 1, but departs from it slightly in drier soils.

71. Free Energy and Vapor Pressure of Soil Moisture in Relation to the Swelling Pressure of Soils

As will be recalled, the osmotic pressure of a solution is defined as the hydrostatic pressure ΔP that must be placed on the solution to establish equilibrium between it and the pure solvent, through a semipermeable membrane—that is, to raise the vapor pressure or free energy of the solvent of the solution to that of the pure solvent. The swelling pressure of a colloid is defined in exactly the same way: it is the hydrostatic pressure ΔP that must be applied to the water films surrounding the colloidal

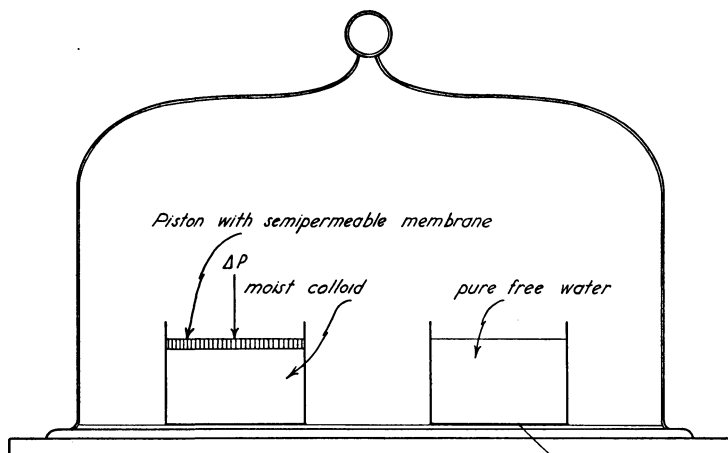


Fig. 39.—Moist colloid under the hydrostatic pressure necessary to make it in equilibrium with free, pure water.

particles in order to raise the vapor pressure of the colloid moisture to that of free, pure water at the same temperature.

One might even speak of the osmotic pressure of a colloid in analogy with that of a solution, as far as external appearances are concerned. Internally we should find the kinetic picture somewhat different. The vapor pressure of a solution is reduced by the solute particles in proportion to the ratio of the relative number of solute particles to solvent particles; that of a moist colloid, by the adsorptive forces surrounding the colloidal particles as well as by any solute that might be present in the colloid moisture.

Suppose the moisture in a colloid is at equilibrium with its vapor in a closed chamber (fig. 39). If a vessel of free water is brought into the chamber, the equilibrium will be disturbed, and the free water will distil onto the colloid because the vapor pressure or free energy of the free, pure water is greater than that of the colloid moisture. To restore equi-

librium in the chamber, we need only apply a hydrostatic pressure ΔP to the colloid moisture (by means of a piston, permeable to vapor but not to liquid water) sufficient to raise its free energy and consequently its vapor pressure by the amount Δp , making the vapor pressure of the colloid moisture equal to that of the free, pure water. This particular change of the hydrostatic pressure ΔP has been defined as the "swelling pressure."

As was shown in connection with equation 238 with the aid of equation 156 and article 22, the increase of the free energy Δf of a liquid as well as of its vapor (which, in the present case, is the colloid moisture) due to a hydrostatic pressure ΔP on the liquid is given by

$$\Delta f = v_L \Delta P = v_V \Delta p. \quad (410)$$

Thus to increase the free energy of colloid moisture by the amount Δf to that of free, pure water we must exert a pressure ΔP on the colloid moisture, which raises its vapor pressure by the amount Δp . Let ΔP_C denote the hydrostatic pressure necessary to raise the vapor pressure p of the colloid moisture to that of free water p_0 , in analogy with ΔP_O for osmotic pressure.

The free energy of the colloid moisture, which we shall represent by Δf_C , is therefore a negative quantity equal to $-\Delta f$ of equation 410, since we always measure free energies with respect to free, pure water. That is,

$$\Delta f_C = -\Delta f = -v_L \Delta P_C = -v_V \Delta p. \quad (411)$$

Thus if the swelling pressure in the colloid is ΔP_C , the free energy Δf_C of the colloid moisture is $-v_L \Delta P_C$. Equation 411, by the way, has the same form as equation 151 for the free energy due to osmotic pressure.

We wish now to express the swelling pressure ΔP_C in terms of the vapor pressure p of the colloid. From equation 411 we may write, for infinitesimal changes,

$$v_L dP_C = v_V dp.$$

Assuming that the vapor obeys the ideal gas law (eq. 367), we have

$$v_L \int_0^{\Delta P_C} dP_C = RT \int_p^{p_0} \frac{dp}{p}.$$

Integrating, we have

$$\Delta P_C = \frac{RT}{v_L} \ln \frac{p_0}{p};$$

or, by inverting the ratio $\frac{p_0}{p}$, we get

$$\Delta P_C = -\frac{RT}{v_L} \ln \frac{p}{p_0}. \quad (412)$$

It will be remembered that when we are dealing with water in the c.g.s. system, $v_L = 1$.

This, it might be noted, is identical in form with equation 251, giving the relation between hydrostatic pressure and vapor pressure, and particularly with the following equation, giving the relation between osmotic pressure and vapor pressure:

$$\Delta P_o = -1 \times \frac{RT}{v_L} \ln \frac{p}{p_0}.$$

The latter was obtained by combining equations 148 and 227.

Caution must be exercised in attempting to apply equation 412 experimentally to unsaturated soils where a force is applied to squeeze out water. In this case, part of the force applied to the soil mass may be transmitted through the solid particles by direct mechanical contact between them. Such a force contributes no hydrostatic pressure to the colloid moisture and should not be included with ΔP_c , since it merely tends to break down the granules. The other part, representing the actual increase of hydrostatic pressure in the colloid moisture, represents the swelling pressure ΔP_c . Only when all the pores of the colloid are completely filled with water can we be certain that the hydrostatic pressure necessary to just begin to squeeze out water from the colloid is equal to the swelling pressure ΔP_c of the colloid, unless the pressure is applied by means of some inert fluid filling the space not occupied by moisture. Thus we see that if we are not careful, the hydrostatic pressure of the colloid moisture may have no relation to the force applied to the colloid externally, unless that force is applied through an inert fluid which fills up all the voids and transmits the pressure directly to the soil moisture.

To illustrate the application of these ideas, we might consider a concrete highway underlain by a very heavy clay soil into which moisture would tend to seep. Suppose some free water comes in contact with the clay subsoil. We might ask how great a pressure would be exerted upward on the pavement because of the tendency of the free water to move into the clay. We should find that the upward pressure is just the swelling pressure ΔP_c we have been considering, and that p is the vapor pressure of the clay subsoil at the time the swelling pressure ΔP_c is being determined.

THEORY UNDERLYING THE CALCULATION OF THE ABSOLUTE VALUE OF THE FREE ENERGY f OF SOIL MOISTURE AT ANY TEMPERATURE

72. General Treatment of the Dependence of Free-Energy Relations of Soil Moisture on Temperature

In all our foregoing considerations of the free energy Δf_s of soil moisture, we have been dealing with the difference between two absolute values of free energy f and f_0 such that $\Delta f_s = (f - f_0)$. Here f_0 equals the absolute value of the specific free energy of our datum, which is usually taken as free, pure water; and f represents the absolute value of the specific free energy of the soil moisture. In other words, Δf_s represents the energy, aside from the work of expansion against atmospheric pressure, that must be given to each gram of water to change it from its state in the soil moisture to that in free, pure water.

Parenthetically we may add that the datum need not be a free, pure body of water. Actually the water may be in any desired state. With few exceptions, however, free, pure water will be found to be the most convenient and desirable datum. Unless otherwise mentioned, f_0 will therefore refer to the absolute value of the specific free energy of free, pure water.

It will be recalled that the specific free energy Δf_s is measured with both the datum and the soil moisture at the same temperature. Until now, nothing has been explicitly stated regarding the effect of a change of temperature either on the absolute specific free energies f and f_0 or on Δf_s itself. It is important and interesting to determine this dependency. For example, Δf_s may be determined from freezing-point measurements on soil moisture, at a temperature near 0°C . It may, however, actually be desirable to know the specific free energy Δf_s of the soil moisture at some higher temperature in order, for example, to determine the amount of energy a plant must expend to extract water from the soil at a given moisture content. The question then is, how are we to find the specific free energy Δf_s at any temperature T when we have determined it once at some particular temperature T_0 ? A satisfactory answer to this should greatly increase the range of usefulness of our known values of Δf_s . It will enable us to calculate Δf_s at any temperature T in terms of a single determination at some temperature T_0 .

In order to fix in mind the relation between the absolute value of the specific free energy f and the specific free energy Δf_s and their dependency on temperature, let us consider with reference to a moist soil the schematic diagram shown in figure 40. The curve f_0 indicates the variation of the absolute value of the specific free energy of free, pure water, our da-

tum, as the temperature is changed; f indicates the change of the absolute value of the specific free energy of soil moisture as the temperature is changed. The specific free energy Δf_{ST_1} of the soil moisture at the temperature T_1 is given by the difference in ordinate between the curves at T_1 ; that is, $(f - f_0) = \Delta f_{ST_1}$. The shape and values for the free-energy curves will of course depend upon the particular problem. As we proceed to a different temperature T_2 of our soil moisture, both f_0 and f_1 change; and consequently the specific free energy changes to a new value, Δf_{ST_2} . We thus observe that in general Δf_s changes with the temperature.

As will be recalled (art. 62 and the latter part of art. 21) the specific

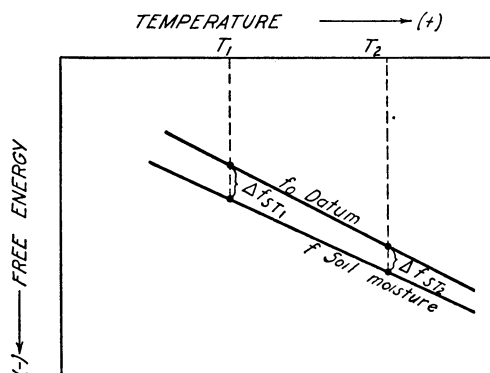


Fig. 40.—The change in free energy Δf_s with temperature.

free energy Δf has distinct advantages over the quantities total potential and capillary potential used previously in soil literature in describing the energy relations of soil moisture. Our present case is another excellent illustration of this fact. The quantities capillary potential and total potential were not defined in such a way as to show explicitly the dependence of these functions on temperature. The definition of free energy, on the other hand, involves the temperature explicitly (eq. 92). If we have determined the total or capillary potential of our soil-moisture system at one temperature, for example, the definition of these terms does not permit us conveniently to calculate the magnitude of these functions at any other temperature. We shall find, though, that the manner in which the term "free energy" has been defined enables us directly to show how the energy of soil moisture depends on the temperature.

Our problem in the articles to follow is therefore to calculate, on the basis of thermodynamics, the specific free energy Δf_{ST_2} of our soil moisture at any temperature T_2 from a known value Δf_{ST_1} at a particular temperature T_1 .

73. Dependence of the Absolute Value of the Free Energy f of Soil Moisture on the Temperature

In this article we shall derive by two different methods an expression showing how the absolute value of the free energy f of water varies with changes in temperature. Then, in later articles, we shall show how the difference $(f_1 - f_0) = \Delta f_s$, the free energy of soil moisture, varies with temperature. Thus the dependence of these functions of soil moisture on temperature will have been indicated.

Method I.—As already shown (art. 21), the free energy f is defined basically by

$$f = h - Ts. \quad (413)$$

From equation 91, the heat content h may be expressed by

$$h = \int_0^T c_p dT \quad (414)$$

where c_p denotes the specific heat at constant pressure and the integration is carried out from 0° A to T° A. The entropy s (eq. 86), may be expressed by

$$s = \int_0^T \frac{c_p dT}{T}. \quad (415)$$

Thus equation 413 becomes

$$f = \int_0^T c_p dT - T \int_0^T \frac{c_p dT}{T}. \quad (416)$$

For our present purpose, let us evaluate f at the two temperatures T_1 and T_2 . As will be seen later, T_1 will be taken as 273° A. At T_1 , equation 416 takes on the following form:

$$f_1 = \int_0^{T_1} c_p dT - T_1 \int_0^{T_1} \frac{c_p dT}{T}; \quad (417)$$

and at T_2

$$f_2 = \int_0^{T_2} c_p dT - T_2 \int_0^{T_2} \frac{c_p dT}{T}. \quad (418)$$

The integration of equation 418 from 0° A to T_2 may be divided into two steps: an integration from 0° A to T_1 , and then from T_1 to T_2 , giving

$$f_2 = \int_0^{T_1} c_p dT + \int_{T_1}^{T_2} c_p dT - T_2 \int_0^{T_1} \frac{c_p dT}{T} - T_2 \int_{T_1}^{T_2} \frac{c_p dT}{T}. \quad (419)$$

Subtracting equation 417 from 419, we have

$$f_2 - f_1 = \int_{T_1}^{T_2} c_p dT - T_2 \int_0^{T_1} \frac{c_p dT}{T} + T_1 \int_0^{T_1} \frac{c_p dT}{T} - T_2 \int_{T_1}^{T_2} \frac{c_p dT}{T}. \quad (420)$$

As shown by Nernst and others, the specific heat at constant pressure c_p decreases considerably as one approaches 0°A ; but in the neighborhood of $T_1 = 273^\circ \text{A}$, it is practically constant for water in the liquid phase (art. 20). Therefore c_p can be taken outside the integral sign of the first and last terms of the right-hand side of equation 420 since c_p is approximately constant within the limits of temperature determined by T_1 and T_2 ; and, as will be recalled (eq. 415), the integrals of the second and third terms above are $T_2 s_1$ and $T_1 s_1$, respectively. Equation 420 accordingly becomes

$$f_2 - f_1 = c_p(T_2 - T_1) - s_1(T_2 - T_1) - T_2 c_p \int_{T_1}^{T_2} \frac{dT}{T}; \quad (421)$$

and therefore

$$f_2 - f_1 = c_p(T_2 - T_1) - s_1(T_2 - T_1) - T_2 c_p \ln \frac{T_2}{T_1}$$

and

$$\begin{aligned} f_2 &= f_1 + c_p(T_2 - T_1) - s_1(T_2 - T_1) - T_2 c_p \ln \frac{T_2}{T_1} \\ &= f_1 + (T_2 - T_1)(c_p - s_1) - T_2 c_p \ln \frac{T_2}{T_1}. \end{aligned} \quad (422)$$

This equation shows directly the dependence of the absolute value of the specific free energy of soil moisture on temperature. Knowing the absolute value of the free energy, specific heat, and entropy at one temperature T_1 , we can calculate the absolute value of the free energy f_2 of moisture at any other temperature T_2 . As T_2 approaches T_1 , f_2 approaches f_1 , a situation that is to be expected.

Method II.—To support the validity of equation 422 and to illustrate different possible general methods of applying thermodynamics to soil moisture, let us consider another approach to equation 422.

As shown in equation 143,

$$\left(\frac{\partial f}{\partial T} \right)_P = -s. \quad (423)$$

Now the specific entropy s (eq. 85) may be represented by

$$s = s_1 + \int_{T_1}^T \frac{c_p dT}{T}. \quad (424)$$

Here s_1 is the absolute value of the entropy at the temperature T_1 , which we shall put equal to 273° A. Since c_p is essentially constant (art. 20) with respect to changes of temperature in the vicinity of 273° A, we can take c_p outside of the integral sign; and therefore

$$s = s_1 + c_p \int_{T_1}^T \frac{dT}{T}. \quad (425)$$

Integrating, we have

$$s = s_1 + c_p \ln \frac{T}{T_1}. \quad (426)$$

Substituting s from equation 426 into equation 423, we get

$$\left(\frac{\partial f}{\partial T}\right)_P = -s = -s_1 - c_p \ln \frac{T}{T_1} = -s_1 - c_p \ln T + c_p \ln T_1. \quad (427)$$

Since we wish to deal with a definite integral from which the integration constant falls out, we may change the partial derivatives to total derivatives without altering the result, and obtain

$$df = -s_1 dT - c_p \ln T dT + c_p \ln T_1 dT. \quad (428)$$

Integrating 428, between T_1 and T_2 , we find

$$\begin{aligned} f_2 - f_1 &= -s_1 \int_{T_1}^{T_2} dT - c_p \int_{T_1}^{T_2} \ln T dT + c_p \ln T_1 \int_{T_1}^{T_2} dT \quad (429) \\ &= -s_1(T_2 - T_1) - c_p \left[T \ln T - T \right]_{T_1}^{T_2} + c_p(T_2 - T_1) \ln T_1 \\ &= -s_1(T_2 - T_1) - c_p T_2 \ln T_2 + c_p T_2 + c_p T_1 \ln T_1 - c_p T_1 \\ &\quad + c_p(T_2 - T_1) \ln T_1. \end{aligned}$$

Cancelling out and combining terms,

$$\begin{aligned} f_2 - f_1 &= -s_1(T_2 - T_1) - c_p T_2 \ln \frac{T_2}{T_1} + c_p(T_2 - T_1) \quad (430) \\ &= (T_2 - T_1)(c_p - s_1) - c_p T_2 \ln \frac{T_2}{T_1} \end{aligned}$$

and

$$f_2 = f_1 + (T_2 - T_1)(c_p - s_1) - c_p T_2 \ln \frac{T_2}{T_1}, \quad (431)$$

which is the same equation as arrived at by method I.

To bring out one way in which equations 422 and 431 might be used for calculating the change in the absolute value of the free energy of moisture in going from one temperature, T_1 , to another, T_2 , let us assume, for example, that $T_1 = 0^\circ \text{C}$, and $T_2 = 25^\circ \text{C}$, and calculate the change in the absolute value of the specific free energy of free, pure water which we have taken as the datum (art. 39). From the *International Critical Tables* for pure water we find that at 0°C

$$\begin{aligned} f_1 &= -1.5985 \times 10^{11} \text{ ergs per gram;} \\ s_1 &= 2.11 \times 10^7 \text{ ergs per degree per gram;} \\ c_p &= 4.18 \times 10^7 \text{ ergs per gram.} \end{aligned}$$

Substituting these in equation 431 in order to calculate f_2 at 25°C , we have

$$\begin{aligned} f_2 &= -1.5985 \times 10^{11} + (298 - 273) (4.18 \times 10^7 - 2.11 \times 10^7) \\ &\quad - 4.18 \times 10^7 \times 298 \times 2.3 \log \frac{298}{273} \\ &= -1.5985 \times 10^{11} + 0.517 \times 10^9 - 1.092 \times 10^9 \\ &= -1.6043 \times 10^{11} \text{ ergs per gram.} \end{aligned}$$

The *International Critical Tables* give as the free energy of water at 25°C

$$f_2 = -1.6060 \times 10^{11} \text{ ergs per gram.}$$

The calculated value of f_2 at 25°C is reasonably close to the one given by the *International Critical Tables*, which was determined experimentally.

It is interesting to calculate the total *change* in the absolute value of the free energy in going, for example, from $T_1 = 0^\circ \text{C}$ to $T_2 = 25^\circ \text{C}$. From the values of f_2 and f_1 above we have

$$\begin{aligned} f_2 - f_1 &= (-1.6043 \times 10^{11}) - (-1.5985 \times 10^{11}) \\ &= -58 \times 10^7 \text{ ergs per gram.} \end{aligned}$$

Thus the absolute free energy is decreased by 58×10^7 ergs as the free, pure water goes from 0°C to 25°C . Suppose that the free energy Δf_s of soil moisture at the permanent wilting percentage is approximately -8×10^7 ergs per gram in the neighborhood of 0°C .

These relations are schematically illustrated by figure 41, which, for clarity, is drawn to a distorted scale. The top curve represents the variation of the absolute value of free energy with temperature for free, pure water in ergs per gram. When the temperature of the free, pure water is

changed from 273°A to 298°A , the absolute value of the free energy of the free, pure water drops from A to B , which entails a drop of 58×10^7 ergs per gram.

The variation, with changes in temperature, of the absolute value of the free energy f of soil moisture at a particular soil moisture content is represented by a curve such as CD . If CD corresponds to the moisture content at the permanent wilting percentage, then the curve for all moisture contents greater than this, such as the *moisture equivalent* or *field*

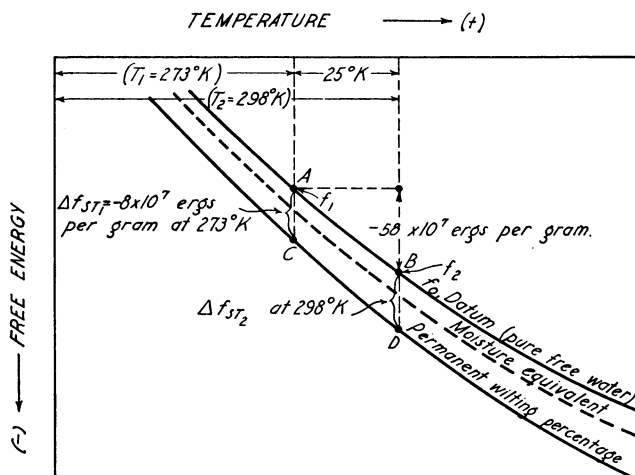


Fig. 41.—The variation of the free energy of soil moisture with temperature at the moisture equivalent and permanent wilting percentage.

capacity, will lie between CD and AB . If the soil is drier than the permanent wilting percentage, then the corresponding curve will lie below CD . Thus the absolute value of the specific free energy f of soil moisture for a given soil at different moisture contents is represented by a family of curves. Each member corresponds to a single value of the soil moisture content and shows the variation of the free energy f of the soil moisture with temperature.

The vertical distance between any two curves or members of the family, at a particular temperature, represents the difference in the absolute value of the free energy of the soil moisture at the two moisture contents. If one of the curves is that corresponding to free, pure water such as AB in the diagram, the vertical distance Δf_s , with respect to AB , is what we have previously called the "specific free energy" or just the "free energy" of the soil moisture. The assumed free energy Δf_{ST_1} at the temperature T_1 of the soil moisture at the permanent wilting percentage

is represented by the distance AC , or -8×10^7 ergs per gram. As will be noticed from the discussion above, a change of 25 centigrade degrees causes a change in the absolute value of the free energy of the datum of -58×10^7 ergs per gram, whereas the difference in the absolute value of the free energy between the datum and soil moisture at the permanent wilting percentage at a constant temperature ($T_1 = 273^\circ \text{A}$) is only -8×10^7 ergs per gram.

As the diagram indicates, the absolute free energy f changes rapidly with temperature. We have not yet shown quantitatively how Δf_s changes with temperature. If free energy of soil moisture Δf_s were independent of temperature, the two curves AB and CD , as well as all the other members of the family of curves, would be parallel to each other. This is not, in general, true, as will be discussed later. If, then, we have a sample of soil at a particular moisture content, the amount of work or effort a plant or any other mechanism must exert to remove water from the moist soil will in general vary with the temperature of removal.

THEORY UNDERLYING THE CALCULATION OF THE FREE ENERGY Δf_s OF SOIL MOISTURE AT ANY TEMPERATURE UNDER DIFFERENT CONDITIONS

74. Dependence of the Free Energy Δf_s of Soil Moisture on Temperature, the Effect of Surface Tension σ Only Being Considered

In the last article we considered the changes in the absolute value of the free energy f_0 of our datum, with respect to variations of temperature. We found it to be appreciable. In fact, a change from 0°C to 25°C entailed a drop in the absolute value of the free energy of about 58×10^7 ergs per gram.

We shall now consider the variation of the free energy Δf_s of soil moisture at a particular soil moisture content with variations of temperature. That is, we wish to study how the vertical distance between two curves such as AB and CD in figure 45 (p. 263) varies as we go from one temperature to another.

The determination of the dependency of Δf_s on temperature is extremely important. For example, as mentioned previously, our method of determining Δf_s at a particular soil moisture content may require us to determine it in the neighborhood of 0°C . Yet we might, for practical purposes, wish to use the value of Δf_s at 25°C —the temperature at which plant may be growing. Without knowing how Δf_s depends upon temperature, we should have to determine Δf_s experimentally at each temperature at which it is to be used.

We shall now turn to the case of a relatively moist soil where the effect on the air-water interface of the adsorptive force field surrounding the soil particle is negligible. The effect of dissolved material will be taken up later. The present treatment applies to determinations of the capillary potential made in the past by a porous bulb atmometer on soils whose moisture content falls in the vicinity of the field capacity or the moisture equivalent. Under the conditions here postulated, the capillary potential is practically synonymous with free energy, since the component of the free energy due to the adsorptive field is here negligible. The final mathematical expression we shall obtain for Δf_s will enable us to calculate Δf_s at any temperature from a single determination of Δf_s made at a particular temperature.

Let us assume that the free energy Δf_{sT_1} has been determined at a single temperature T_1 , and endeavor to express the free energy Δf_s at any other temperature T in terms of Δf_{sT_1} . Under the conditions postulated, the variation of Δf_s with temperature is caused by the variation of the surface tension σ with temperature. Since the surface tension σ decreases with increase of the temperature T , we might expect the free energy

Δf_s to decrease as the temperature T is raised. Quantitatively this is shown as follows:

From equation 211 we have the following relation connecting the surface tension σ , the free energy Δf_{ST} , and the radius of curvature r of the air-water interface of a capillary body of water at the temperature T :

$$\Delta f_{ST} = RT \ln \frac{p}{p_0} = \frac{2v \sigma_T}{r}. \quad (432)$$

Here p refers to the vapor pressure of the moist soil, p_0 to that of free, pure water, both at the same temperature, T . Neither v nor r would be expected to change appreciably as the temperature of the moist soil changes, since the soil moisture content is kept constant throughout all changes of temperature in the present treatment. Of course, if the moisture content is not kept constant when the temperature is changed, there are other complications, not treated here. Since the magnitude of the radius of curvature r of the air-water interface of soil moisture is hard to determine directly, we shall eliminate it from equation 432.

Let us assume that at another temperature T_1 the surface tension of water is σ_{T_1} and also that the free energy of the soil moisture has been determined and found to be Δf_{ST_1} . We then have (eq. 432)

$$\Delta f_{ST_1} = \frac{2v}{r} \sigma_{T_1}$$

so that

$$\frac{2v}{r} = \frac{\Delta f_{ST_1}}{\sigma_{T_1}}.$$

Hence equation 432 becomes

$$\Delta f_{ST} = RT \ln \frac{p}{p_0} = \left(\frac{\Delta f_{ST_1}}{\sigma_{T_1}} \right) \sigma_T. \quad (433)$$

Since we wish to express Δf_{ST} in terms of the temperature T , the surface tension σ_T must also be expressed in terms of T . The dependence of the surface tension σ_T on the temperature is given by figure 42, plotted from data taken from the *International Critical Tables*. From these data the following relation was derived:

$$\sigma_T = 117 - 0.152T \quad (434)$$

where the surface tension σ_T is expressed in dynes per centimeter, and the temperature T in degrees absolute.

Inserting σ_T of equation 434 in 433, we have

$$\Delta f_{ST} = RT \ln \frac{p}{p_0} = \left(\frac{\Delta f_{ST_1}}{\sigma_{T_1}} \right) (117 - 0.152T). \quad (435)$$

Equation 435 enables us to calculate the free energy Δf_{ST} at any temperature T in terms of a single determination of the free energy Δf_{ST_1} of the soil moisture, made at the temperature T_1 according to

$$\Delta f_{ST} = \frac{\Delta f_{ST_1}}{\sigma_{T_1}} (117 - 0.152T) . \quad (436)$$

The surface tension σ_{T_1} can, of course, be obtained from equation 434 or directly from a set of physical tables.

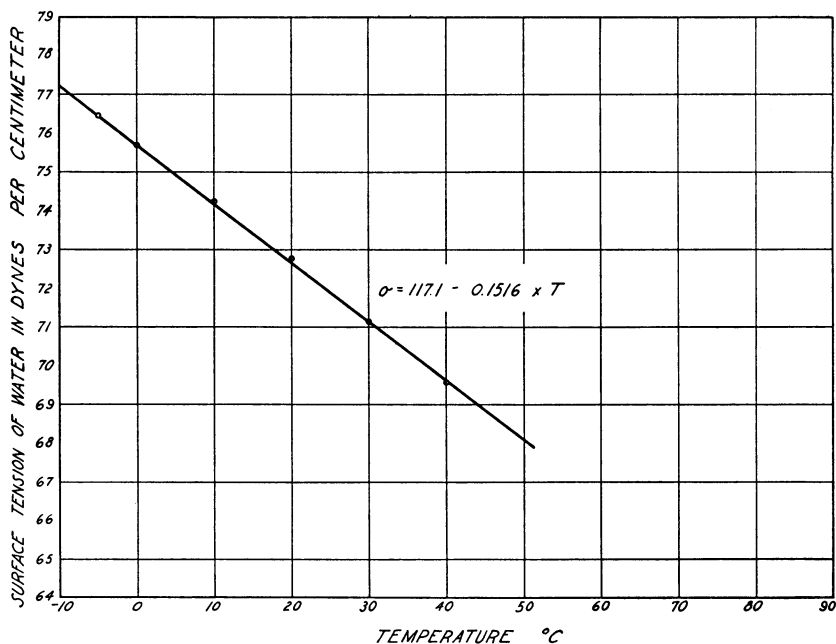


Fig. 42.—Variation of surface tension with temperature.

Similarly by equation 435 one can compute the vapor pressure of a relatively moist soil at any temperature T if the free energy Δf_{ST_1} or the vapor pressure p of the moist soil has been determined at some temperature T_1 . This is clear from a further consideration of equation 435.

$$RT \ln \frac{p}{p_0} = \frac{\Delta f_{ST_1}}{\sigma_{T_1}} (117 - 0.152T)$$

or

$$\ln \frac{p}{p_0} = \frac{\Delta f_{ST_1} (117 - 0.152T)}{\sigma_{T_1} RT}$$

so that

$$p = p_0 e^{\left(\frac{\Delta f_{ST_1}}{R \sigma_{T_1}} \right) \left(\frac{117}{T} - 0.152 \right)} . \quad (437)$$

According to this equation, if we know Δf_{ST_1} of a relatively moist soil at a particular moisture content and temperature T_1 , we can compute the vapor pressure p of this same sample of soil at any other temperature T , where p_0 is the vapor pressure of free, pure water at the temperature T . All the other quantities such as R and σ_T can be obtained from a set of physical tables.

Note again that equation 435 holds only for a relatively moist soil where the adsorptive force field surrounding the soil particle is negligible at the air-water interface.

Equation 437 might give the impression that the vapor pressure of soil moisture should decrease with increase of temperature, since the absolute value of the exponent decreases with temperature. It must be recalled (eq. 121), however, that the numerical value of the free energy Δf_{ST_1} has always been found negative for unsaturated soil moisture. Thus the vapor pressure p will increase with a rise in the soil-moisture temperature T . Clearly, judging from the form of the equation, as the temperature T increases, the vapor pressure of the soil moisture p will approach that of the free water p_0 . As the critical temperature of water is approached, its surface tension approaches zero; and consequently the factor in the exponent of equation 437 reduces to zero at this temperature, making the exponential unity and p equal to p_0 .

75. Dependence of the Variation in Height of a Water Table on the Variation in Temperature of the Soil Moisture

Equation 436 may be used as the basis to account for the diurnal variation in height of a water table close to the surface of the ground. As all soil workers have observed, a water table close to the surface of the ground gradually rises from dawn till about sunset and then begins to fall, continuing to fall throughout the night. The whole process is repeated the next day. The amplitude of the variation in height of the water table is found to increase with an increase in the amplitude of variation of the soil temperature between the day and the night.

Superimposed upon these fluctuations there will be a gradual and progressive lowering of the water table if the root hairs of actively transpiring vegetation are present and if the water table is close enough to the soil surface to make upward capillary movement appreciable. Sometimes, where the water table is close to the surface and plants are growing, the water table drops during the day because of transpiration. We are here concerned with none of these. What we are interested in is only a fluctuation in the height of the water table, without any total loss (through plants) of water from the whole soil-moisture system composed of the water table plus the overlying moist soil.

To illustrate the application of equation 436 to the explanation of the variation in height of a water table with temperature, let us consider the simplest case of the variation in height of a column of water in a vertical capillary tube dipping into a free water surface. Figure 43 shows a capillary tube of radius r having its lower end in a vessel of water. At the temperature T_1 the height is h_{T_1} ; at a higher temperature T , for example, the column will have dropped to h_T . For the present we are neglecting the effect of such minor influences as the slight change in the density ρ of water caused by changes of its temperature.

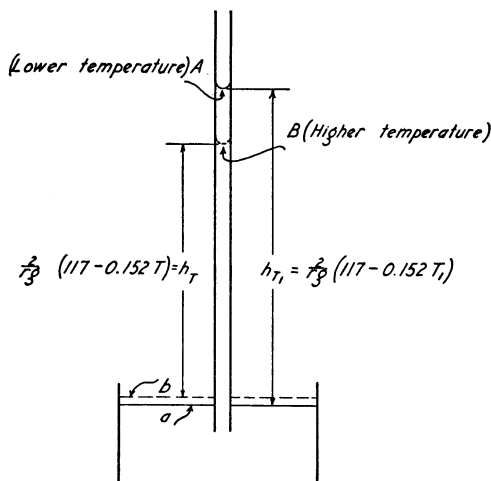


Fig. 43.—Illustration of change in water table with temperature.

If at the temperature T_1 the free energy is Δf_{T_1} just below the meniscus at A , and if at the temperature T it is Δf_T just below the new position of the meniscus at B , we have (eq. 436)

$$\Delta f_T = \frac{\Delta f_{T_1}}{\sigma_{T_1}} (117 - 0.152T). \quad (438)$$

This equation applies to any relatively moist soil, no matter how saline. From equation 211 we have

$$\Delta f_{T_1} = \frac{2\sigma_{T_1} v}{r}. \quad (439)$$

Here, as will be recalled, r is negative when the vapor-water interface is concave to the vapor phase. Inserting equation 439 into 438,

$$\Delta f_T = \frac{2v}{r} (117 - 0.152T). \quad (440)$$

Let us now express the height of the capillary column h in terms of the temperature T of the capillary column. From equation 156 we have, for the free energy due to hydrostatic pressure immediately below the water meniscus,

$$\Delta f_T = v \Delta P. \quad (441)$$

Since ΔP immediately below the meniscus equals the weight of the column of water (of length h and unit cross section) under the meniscus, we have $\Delta P = -h \rho g$. We insert the negative sign because ΔP here represents a state of tension or negative hydrostatic pressure with respect to our datum. Equation 441 then becomes

$$\Delta f_T = -h \rho g \quad (442)$$

where $g = 980$ dynes per gram.

Inserting Δf_T of 442 into 440 and solving for h , we have

$$h = -\frac{2}{gr} (117 - 0.152T), \quad (443)$$

where ρ and v have been omitted because the density ρ and the specific volume v of water are approximately unity in the c.g.s. system, and where the radius of curvature r is substituted as a negative value according to our previous convention.

According to equation 443, the height h of the capillary column rises as the temperature decreases and falls as the temperature rises. Thus, considering figure 43, we find equation 443 predicting that with rise of temperature the water table will rise from a to b as the capillary column drops from A to B . The amount of the rise ab of the water table can, of course, easily be calculated from a knowledge of the diameters of the capillary tube and the vessel.

This case of the simple capillary tube and the variation in height of its water table with changes of temperature is analogous to the actual situation found in a moist soil with a high water table. When equilibrium of the soil moisture has been established at a temperature T_1 in a soil column in contact with a body of water (fig. 44, A), the relation between the free energy Δf_{T_1} of the soil moisture at a height h (on the one hand) and the height h (on the other) may be schematically represented by the straight line Δf_{T_1} of figure 44, B . This, as well as the following statements, is entirely justified by the next article, which should be read in connection with the present one. Under equilibrium conditions of soil moisture, the

rate of change of the free energy Δf_{T_1} with respect to the height h (eq. 442) must be equal but opposite in sign to g , the gravitational force. That is,

$$\frac{d(\Delta f_{T_1})}{dh} = -g, \quad (444)$$

since $\rho = 1$. At the water table, $\Delta f_{T_1} = 0$, while at the top of the soil column, the free energy of the soil moisture Δf_{T_1} has reached its maximum negative value. The soil moisture contents C_{T_1} throughout the soil col-

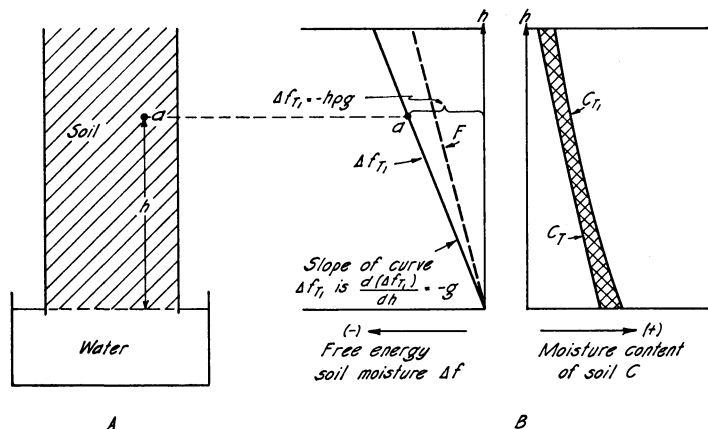


Fig. 44.—Variation of soil moisture with height above a water table because of variation of its free energy with temperature.

umn, corresponding to the free energy Δf_{T_1} at different heights h , are given by curve C_{T_1} also placed in figure 44, B. The highest moisture contents are, of course, at the bottom of the soil column.

Suppose we now raise the temperature of the entire soil-moisture system from T_1 to T and inquire what will happen to the free energy Δf of the soil moisture throughout the soil column, as well as to the moisture content C . From what has gone before, based upon equations 440 and 443, we should expect the free-energy curve Δf to drop temporarily to some such position as F . In other words, the free energy Δf of every element of moisture throughout the soil column at different heights h above the water table will have decreased numerically.

The free energy throughout the soil column cannot remain at equilibrium in the state represented by F , since under these conditions the gradient of the free energy is not equal to minus g (eq. 444). This relation represents the rate of change of the free energy in any soil column at any temperature at equilibrium.

Changes will therefore be set up throughout the soil column, no matter what the temperature change happens to have been, tending to restore Δf throughout the soil column to the values represented by curve Δf_{T_1} so that the gradient of the free energy $\frac{d(\Delta f)}{dh}$ at the new temperature T is restored to the same value, minus g . These readjustments will involve a progressive change of moisture contents throughout the soil column from C_{T_1} to those represented by the curve C_T when the temperature is raised. In other words, if the temperature is raised, water will flow out of the soil and into the water table, which will raise the height of the water table. (Likewise if the temperature of the soil column is lowered, water will move into the soil, and the water table will be lowered. The curves corresponding to the lowering of the temperature are not shown in the graph, but would be displaced in the direction opposite to C_T .) The equilibrium moisture distribution represented by the curve C_T is such that equations 444 and 442 are satisfied. At equilibrium the free-energy curve Δf_T at the higher temperature T , corresponding to C_T , therefore coincides with Δf_{T_1} . The reasons for this fact, besides those already given, follow immediately.

According to equation 442, the free energy Δf of the moisture in a soil column in contact with a water table under equilibrium conditions depends only on its height h above the water table. No matter what the temperature T happens to be, the free energy Δf at equilibrium is given by

$$\Delta f = -h \rho g.$$

Any variation of ρ , the density of water, with changes of temperature is a second-order effect and is therefore negligible. The question then is, how can the soil column at the higher temperature T maintain the same free energy throughout as represented by the curve Δf_{T_1} , when equation 440 seems to predict that the free energy Δf_T of the soil column will rise (become less negative) with rise in temperature to some such curve as F in figure 44, B ?

This difficulty is immediately cleared up when we recall the following experimental facts: (1) when the temperature is raised, water moves down in the soil and runs out of the bottom of the column, the soil moisture content thus being decreased; (2) as the soil moisture content is decreased, the free energy Δf of soil moisture decreases—becomes more negative.

As the temperature of the soil column is raised, the free-energy curve Δf_{T_1} will therefore temporarily tend to move to the position F , corresponding to a greater positive free energy at a height h . While this is going on, however, water will drain out of the bottom of the soil column

into the water table, which will cause the free energy at a given height h to become more negative and simultaneously counteract the change of Δf caused by the rise of temperature, until finally the free energy represented by curve Δf_{T_1} is reestablished throughout the soil column and the free-energy curve Δf_T at the higher temperature T coincides in position with f_{T_1} . The net result of the rise in temperature of the soil column is, then, the downward movement into the water table of the amount of soil moisture represented by the shaded area between the curves C_{T_1} and C_T . The water table accordingly rises with a rise in temperature, and no change finally occurs in the free energy Δf throughout the soil column caused by a change in temperature.

The reverse of the results obtained above would, naturally, have occurred if the temperature of the soil column had been lowered.

Carrying the analyses further, we should be able to calculate quantitatively the amount of water that would move into or out of a soil column and into the water table, with changes of temperature, merely by using equations 438 and 442 and by knowing the dependence of the free energy Δf_T of the soil moisture, at but a single temperature T , on the soil moisture content.

If the soil is relatively dry, equation 438 should be replaced by the more comprehensive equation 477 or 484 and by the treatment of articles 80 and 81.

76. Dependence of the Free Energy on Height h above a Free, Pure Water Surface Used as the Datum

In article 75 (eq. 442) it was shown that the free energy of water just under the meniscus, in a capillary tube (fig. 43), at the height h above the free water surface is given by

$$\Delta f = -h \rho g$$

where ρ is the density of water in grams per cc and $g = 980$ dynes. In this article, we shall show, as a corollary to the previous one, that *under equilibrium conditions* equation 442 gives the free energy Δf of water at a height h above free, pure water, no matter whether the water at the height h is in a capillary tube (as in the present case), or is soil moisture in a column of soil at a height h above the water table, or is vapor at a height h above a free water surface (art. 37).

The truth of this statement is seen immediately when one considers a soil column and a capillary tube both dipping down into a vessel of free, pure water used as the datum, the whole being contained in a closed chamber such as a large bell jar. When equilibrium has been established,

the liquid and vapor phases will be in equilibrium throughout the whole system, composed of the soil column and capillary tubes, all dipping down into the body of free water, surrounded by water vapor. Thus if the meniscus in the capillary tube comes to equilibrium at the height h , it will be in equilibrium with the vapor at that level. Likewise the soil moisture at the height h in the soil column will also be in equilibrium with the vapor at the height h . If they are not at equilibrium, a readjustment will take place until they are.

We see (art. 22) that the free energy of the water in the soil column, in the capillary tube, and in the vapor phase are the same at the same height h , when equilibrium has been established. Thus, no matter in what state water happens to be (whether as water in a capillary tube, soil moisture, or vapor) at a height h above the free water surface (when each of them is in equilibrium with the free water surface used as the datum), the free energy of the water, expressed in terms of that in the capillary at the height h , is given by $\Delta f = -h \rho g$. Expressed in terms of the vapor pressure p at the height h above the free water surface, it is (eq. 159 and 236)

$\Delta f = RT \ln \frac{p}{p_0}$ where p_0 is the vapor pressure at the free water surface used as the datum.

The equation $\Delta f = -h \rho g$ presents one method (similar to the one previously used by many soil workers—20, 56, 81—for determining the capillary potential of soil moisture at different soil moisture contents) for determining the free energy of soil moisture at different moisture contents. The soil moisture in a long soil column dipping down into free, pure water is allowed to come to equilibrium throughout with the surface of free, pure water taken as the water table. When equilibrium has been established, the moisture content in the soil column will vary uniformly from saturation, at the lower end next to the free water surface, to relative dryness at the upper end of the soil column. The soil column is then taken down, broken up into small sections, and the moisture contents at the different heights h determined. The free energy corresponding to each different soil moisture content (associated with a definite value of the height h above the water table) is computed immediately from $\Delta f = -h \rho g$. Thus a curve can be plotted showing the dependence of the free energy Δf of the soil moisture on the moisture content, just as has been done in the past for the capillary potential of soil moisture.

This method of determining the relation between soil moisture content and its free energy, although sound theoretically, is somewhat impractical because years are required for the soil moisture in a soil column to come to complete equilibrium with a water table, and because the temperature of the soil must be maintained constant throughout this time interval.

77. Dependence of the Free Energy Δf_s of Soil Moisture on Changes in Temperature
When the Ratio of the Vapor Pressures $\frac{p}{p_0}$ Remains Constant

The following treatment will be particularly applicable to very saline moist soils where, as will be shown later (art. 78), the ratio of the vapor pressure p of the solution to that of pure water p_0 remains practically unchanged with changes of temperature. It will also apply directly to any other cases where future experiments show that the ratio $\frac{p}{p_0}$ is relatively constant.

We shall proceed immediately to show how Δf_s , at a particular soil moisture content, might be calculated at any desired temperature when Δf_s has been experimentally determined at but one temperature, T_1 . As mentioned before, this calculation has not been possible with the quantities called capillary potential and total potential used in the past for describing the energy relations of soil moisture.

Equation 146, the basis for our development, is

$$\left(\frac{d(\Delta f_s)}{dT} \right)_p = -\Delta s. \quad (445)$$

Before using this expression, let us understand the meanings attached to the symbols d and Δ in our present problem. Figure 45 has been considerably distorted to bring out the meanings of the symbols Δ and d (differential).

To avoid confusion, we must recognize clearly that we are dealing in equation 445 with two types of changes in the value of the absolute free energy f . One change symbolized by Δ , as Δf , indicates the difference between the value of the absolute free energy of the soil moisture and the value of the absolute free energy of pure water in the standard state, both states being considered at the same temperature. A change in Δf , called the free energy of the soil moisture, is produced entirely by a change of soil moisture content, the temperature remaining constant. For example, at A in figure 45 this change or difference is represented by Δf_{ST_1} ; at B by Δf_{ST_2} . The other change, symbolized by d , as $d(\Delta f)$, arises from a variation of temperature, all other variables such as soil moisture content remaining constant. At the temperature T_1 , for instance, the free energy of the soil moisture is Δf_{ST_1} . If now the temperature is raised by an amount dT , the free energy Δf_{ST_1} is further increased by an amount $d(\Delta f_{ST_1})$ so that the free energy of the soil moisture at T_2 , Δf_{ST_2} , now equals the sum $\Delta f_{ST_1} + d(\Delta f_{ST_1})$. The quantity Δs (eq. 445), since it involves the symbol Δ , refers to the change in entropy per gram of water in going from the state of pure water f_0 to the soil moisture in the state f , both states being at the same temperature.

Summarizing, therefore, we can say that according to equation 445, the rate of change, $\left(\frac{d(\Delta f_s)}{dT}\right)_p$, of the free energy Δf_s of soil moisture with respect to temperature equals the negative of the specific entropy Δs of the soil moisture, with respect to free, pure water, the soil moisture and free, pure water being at the same temperature when Δs is computed. Clearly, the vapor pressure of soil moisture differs from that of pure water at the same temperature, and the subscript p indicates that the vapor pressure

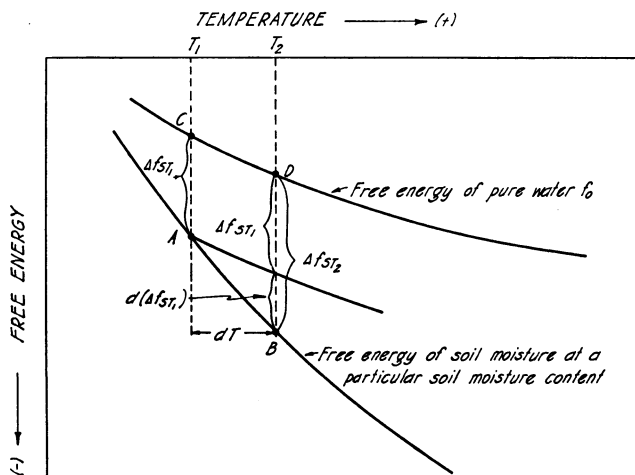


Fig. 45.—Illustration of two different types of changes in free energy of soil moisture at a given moisture content due to change in temperature.

of pure water as well as the vapor pressure of soil moisture must be regarded as constant during variations of temperature.

The evaluation of the free energy Δf_s will be performed in two steps. The first step will consist in an integration of equation 445, which will give the change in free energy $\Delta f_s'$ in going from one temperature T_1 to another temperature T , assuming that the vapor pressures do not change with temperature. The latter state, of course, is a hypothetical condition not found in nature. The second step will consist of showing that the difference in free energy between this hypothetical state and that actually experienced in nature is negligible. Thus we shall have determined the actual free energy of the soil moisture at the higher temperature.

To proceed with the first step, let us recall (art. 22) that the free energy is the same in all phases of a given substance when at equilibrium. Consequently, the free energy $\Delta f_s'$ of the vapor phase always equals the free energy of the liquid phase of the soil moisture. If, therefore, we calculate

the changes in free energy of the vapor phase caused by changing the temperature of the soil moisture, we have also calculated the change in the free energy of the soil moisture. In the present case, as in numerous others, it is much easier (art. 39) to deal with the vapor phase. We shall therefore carry out the following analysis with respect to the vapor phase.

Returning to equation 445 and using the notation Δf_s to represent the free energy of soil moisture, we have

$$d(\Delta f_s') = -\Delta s dT. \quad (446)$$

Integrating between the temperature T_1 and T ,

$$\Delta f_{sT'} - \Delta f_{sT_1} = -\int_{T_1}^T \Delta s dT. \quad (447)$$

Here $\Delta f_{sT'}$ represents, as before, the value of the specific free energy of soil moisture in the hypothetical state at any temperature T , and Δf_{sT_1} that at T_1 , the initial state.

To evaluate the integral, we may conveniently express Δs in terms of variables such as p , v , or T , which can be measured. From equation 16 we have

$$\Delta s = -\int_{p_{01}}^{p_1} \left(\frac{\partial v}{\partial T} \right)_p dp. \quad (448)$$

Here p_{01} refers to the vapor pressure of free, pure water at the standard state, and p_1 to the vapor pressure of the soil moisture, both at the same temperature T_1 . To evaluate $\left(\frac{\partial v}{\partial T} \right)_p$ let us assume that the water vapor surrounding the soil moisture obeys the ideal gas law as stated in equation 367 by

$$v = \frac{RT}{p}.$$

Differentiating v with respect to T ,

$$\left(\frac{\partial v}{\partial T} \right)_p = \frac{R}{p}. \quad (449)$$

Thus equation 448 becomes, by substituting from 449,

$$\Delta s = -R \int_{p_{01}}^{p_1} \frac{dp}{p}. \quad (450)$$

Integrating equation 450 to determine the change in entropy of the soil moisture in taking it from the standard state, corresponding to the vapor pressure p_{01} , to the state corresponding to the vapor pressure p_1 , we have

$$\Delta s = -R \ln \frac{p_1}{p_{01}}. \quad (451)$$

Substituting the value of Δs (eq. 451) into equation 447, we have

$$\Delta f_{ST'} = \Delta f_{ST_1} + R \int_{T_1}^T \ln \frac{p_1}{p_{01}} dT. \quad (452)$$

As will be recalled, p_1 and p_{01} above refer to the vapor pressure over the moist soil and free, pure water, respectively, at the temperature T_1 , the moisture content of the soil remaining the same throughout the temperature changes involved in the integration above.

Equation 452 is based, of course, on equation 446, in which the vapor pressure of the soil moisture as well as that of the free, pure water was assumed to remain unchanged with changes of temperature. The term $\Delta f_{ST'}$ of 452 therefore gives the free energy of the soil moisture in the hypothetical state at the temperature T , under the assumption that the vapor pressures p_1 of soil moisture and p_{01} of pure water do not change with temperature.

Now, proceeding to the second step, we shall show that the free energy $\Delta f_{ST'}$ of the soil moisture given by equation 452 in the hypothetical state is practically equal to the free energy Δf_{ST} actually found by experiment at the temperature T . To do this, let us reduce equation 452. Since the logarithmic term in the hypothetical state is independent of temperature because the vapor pressures p_1 and p_{01} were assumed to be unchanged in going from T_1 to T , equation 452 may be placed in the following form:

$$\Delta f_{ST'} = \Delta f_{ST_1} + R \ln \frac{p_1}{p_{01}} \int_{T_1}^T dT. \quad (453)$$

Substituting for the free energy Δf_{ST_1} of soil moisture at the temperature T_1 from equation 236 and integrating, we have

$$\begin{aligned} \Delta f_{ST'} &= RT_1 \ln \frac{p_1}{p_{01}} + R(T - T_1) \ln \frac{p_1}{p_{01}} \\ &= RT \ln \frac{p_1}{p_{01}}. \end{aligned} \quad (454)$$

Here the vapor pressures not only are those found experimentally for the

soil moisture at the initial temperature T_1 but are also those of the hypothetical state, since we assumed the vapor pressures to be unchanged by temperature in going to the hypothetical state. Since the vapor pressures were assumed to be constant in the derivation of equation 454, then the ratio $\frac{p_1}{p_{01}}$ is also independent of temperature and is the same at the temperature T (eq. 454) as at T_1 .

According to an experimental fact (as is shown in the next article), the ratio of the vapor pressure of a solution to that of free, pure water is practically independent of temperature, although the vapor pressures themselves change quite markedly with temperature. Thus the ratio of the vapor pressures $\frac{p}{p_0}$ actually found experimentally at the temperature T will prove experimentally to be the same as the ratio $\frac{p_1}{p_{01}}$ of the hypothetical vapor pressures at T . The pressures p_1 and p_{01} are, of course, the actual pressures found at the temperature T_1 . Since the free energy of the solvent of a solution depends only on the ratio of the vapor pressures (eq. 227), we may write, for the true experimental value of the free energy Δf_{ST} of the soil moisture at the temperature T ,

$$\Delta f_{ST} = RT \ln \frac{p}{p_0}. \quad (455)$$

Obviously, the right-hand side of equation 454, giving the free energy $\Delta f_{ST'}$ of the soil moisture in the hypothetical state to the temperature T , is equal numerically to the right-hand side of equation 455, giving the actual free energy Δf_{ST} of the soil moisture in the real state at the temperature T , since the two vapor-pressure ratios $\left(\frac{p_1}{p_{01}}\right)$ at the temperature T_1 and $\frac{p}{p_0}$ at the temperature T were originally assumed to be the same.

Thus we have shown that the actual free energy Δf_{ST} of soil moisture at the temperature T is equal numerically to the free energy $\Delta f_{ST'}$ of the hypothetical state and is given by equation 453 or 454. We then have

$$\Delta f_{ST} = \Delta f_{ST_1} + R(T - T_1) \ln \frac{p}{p_0}, \quad (456)$$

where the pressures p and p_0 are those at any temperature between T and T_1 , since the ratio is independent of temperature.

Thus, knowing the free energy of the soil moisture of a very saline moist soil at but one temperature T_1 , we can immediately by equation 456 calculate the free energy Δf_{ST} of the soil moisture at any other temperature T .

78. Dependence of the Free Energy Δf_{ST} on the Temperature, the Presence of Dissolved Material Only Being Considered

The treatment in the present article, using the results of the previous article, applies particularly to a very saline moist soil, and possibly to other cases in soils if future experimental work shows the ratio of the vapor pressures $\frac{p}{p_0}$ to be independent of changes in temperature. Let us examine whether experimental evidence now available will support our

TABLE 1
DEPENDENCE OF VAPOR PRESSURE OF SOLUTION ON TEMPERATURE

Temperature	Vapor pressure			Ratio, $\frac{p}{p_0}$	
	Of H_2O , p_0	Of 2.5 per cent solution of $NaCl$, p_{NaCl}	Of 5.0 per cent solution of Na_2CO_3 , $p_{Na_2CO_3}$	$\frac{p_{NaCl}}{p_0}$	$\frac{p_{Na_2CO_3}}{p_0}$
$^{\circ}C$	<i>mm</i>	<i>mm</i>	<i>mm</i>	<i>ratio</i>	<i>ratio</i>
0.....	4.58	4.5	4.5	0.982	0.982
10.....	9.21	9.1	9.0	.989	.978
20.....	17.5	17.3	17.2	.989	.983
30.....	31.8	31.4	31.2	.987	.981
40.....	55.3	54.5	54.2	.986	.980
50.....	92.5	91.2	90.7	.986	.981
60.....	149.3	147.2	146.5	0.986	0.981

assumption that the ratio $\frac{p}{p_0}$ is independent of temperature for a saline solution.

Table 1, taken from the *International Critical Tables*, gives the aqueous vapor pressures of pure water, of sodium chloride solution, and of sodium carbonate solution at different temperatures. From the vapor pressures, the last two columns have been computed. Evidently, the ratio of the vapor pressure p over the solution to that over the free, pure water surface p_0 is essentially independent of temperature over the temperature range considered. We should also note that the two solutions taken represent more extreme conditions, with respect to vapor-pressure depression caused by dissolved material, than are customarily found in soils.

Having shown above that $\ln \frac{p}{p_0}$ remains approximately constant as the temperature T of the solution is changed, we are justified in using equation 456 in calculating the dependence of the free energy Δf_{ST} on temperature:

$$\Delta f_{ST} = \Delta f_{ST_1} + R(T - T_1) \ln \frac{p}{p_0}. \quad (457)$$

Figure 46 should clarify the meaning of equation 457, which gives the free energy Δf_{ST} of a sample of soil moisture at any temperature T in terms of a known value of the free energy Δf_{ST_1} . Since the ratio $\frac{p}{p_0}$ is independent of temperature, it can be expressed in terms of Δf_{ST_1} . Figure 46 shows that in taking the sample of moist soil from the temperature T_1 at which we know the free energy Δf_{ST_1} and the vapor pressure p , to any other temperature T , the free energy of the soil moisture changes to Δf_{ST} (eq. 457). This relation enables one to calculate Δf_{ST} at any tem-

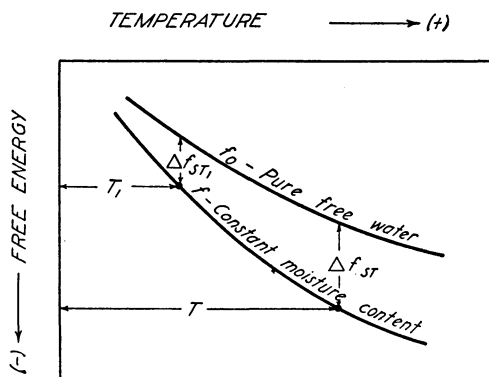


Fig. 46.—Change of free energy of soil moisture with temperature at a given moisture content.

perature T for a particular moisture content provided Δf_{ST} is known at some one temperature.

A more useful expression can be obtained if we further transform equation 457. As will be recalled (art. 39), the free energy of soil moisture Δf_{ST_1} may be expressed in terms of the vapor pressure of the soil moisture as follows:

$$\Delta f_{ST_1} = RT_1 \ln \frac{p}{p_0}. \quad (458)$$

Introducing 458 into equation 457, we have

$$\Delta f_{ST} = RT_1 \ln \frac{p}{p_0} + R(T - T_1) \ln \frac{p}{p_0}. \quad (459)$$

Expanding the last member of this equation and cancelling out like terms, we have

$$\Delta f_{ST} = RT \ln \frac{p}{p_0}. \quad (460)$$

To transform this equation into a more useful form, let us multiply the numerator and denominator of the right-hand side by T_1 , the temperature corresponding to the known value of the free energy Δf_{ST_1} , and recall 458. Equation 460 becomes

$$\Delta f_{ST} = \frac{T}{T_1} \Delta f_{ST_1}. \quad (461)$$

If we know, therefore, the free energy Δf_{ST_1} of the soil moisture of a saline soil at any particular moisture content and temperature T_1 , we may readily calculate the free energy Δf_{ST} at some other temperature T , but at the same moisture content. This equation may be applied to any soil moisture whose free energy is due mainly to the presence of dissolved material.

Thus one can calculate the free energies Δf_{ST} for a series of moisture contents at any temperature T if the free energies Δf_{ST_1} , at some one temperature T_1 , are known for the same series of moisture contents. Equation 461 shows, for a very saline soil, that the free energy Δf_{ST} of soil moisture decreases as the temperature of the moist soil is raised.

Equation 461 may be derived with much less effort by another method if we recall the experimental observation, from table 1, that the ratio of the vapor pressure p of a solution to that of pure water p_0 at a given temperature is a constant independent of temperature over the range of concentrations shown.

The free energy Δf_{OT} of a solution due to osmotic pressure has been defined (eq. 227) by

$$\Delta f_{OT} = RT \ln \frac{p}{p_0}. \quad (462)$$

When applied to solutions, Δf_{OT} has the same significance that Δf_{ST} does when applied to very moist saline soils. We may therefore write this equation in the following form for our present use:

$$\Delta f_{ST} = RT \ln \frac{p}{p_0}. \quad (463)$$

Let us assume that Δf_{ST} has been determined at some particular temperature T_1 and found to be

$$\Delta f_{ST_1} = RT_1 \ln \frac{p}{p_0}. \quad (464)$$

Dividing equation 463 by 464 and recalling the constancy of the ratio

$\frac{p}{p_0}$ of the vapor pressure of a solution to that of free water despite variations of temperature, we have

$$\frac{\Delta f_{ST}}{\Delta f_{ST_1}} = \frac{T}{T_1}$$

or

$$\Delta f_{ST} = \frac{T}{T_1} \Delta f_{ST_1}, \quad (465)$$

which is the same as equation 461.

79. Dependence of the Free Energy Δf_{ST} of Soil Moisture on the Temperature, the Effect of the Adsorptive Field Only Being Considered

The dependence of the free energy on the adsorptive field alone probably corresponds to no actual condition found with soil moisture. It approximates most closely the conditions to be expected in a relatively dry soil if very little dissolved material were present in the soil moisture. As the moisture film surrounding the soil particles becomes thinner, the air-water interface of the film comes increasingly under the influence of the adsorptive force surrounding the soil particles. The chief reason for introducing a treatment of this case is to complete the basic considerations necessary for the treatment of the generalized case to follow, which considers all the principal factors contributing to the free energy Δf_{ST} of soil moisture.

The free energy Δf_{ST} is given, as before, by

$$\Delta f_{ST} = RT \ln \frac{p}{p_0}.$$

It is a well-known fact that the electrostatic field surrounding a charged particle is not appreciably affected by temperature changes. Since the adsorptive field surrounding the soil particles arises from the unsatisfied electrostatic forces of the surface molecules of the soil particles, we shall assume, to a first approximation, that the adsorptive field as well as its resultant effects are not much modified by changes of temperature. The quantity of water adsorbed on soils of course decreases with increase in temperature; but this decrease occurs because the kinetic energy of the adsorbed molecules is higher at the higher temperatures rather than because the field changes with temperature. The sum, therefore, of the component of the free energy of water Δf_{FS} due to its presence within the adsorptive field surrounding the soil particle, as well as the component of the free energy of the moisture due to the hydrostatic pressure Δf_{PS} caused by the pull of the adsorptive force on the superincumbent layer of

moisture (art. 64), is a constant K with respect to changes of temperature. That is,

$$\Delta f_{ST} = \Delta f_{FS} + \Delta f_{PS} = K. \quad (466)$$

Thus in the next article we shall consider the total change in the free energy ($\Delta f_{FS} + \Delta f_{PS}$) of soil moisture, caused by the presence of the adsorptive field, to be independent of temperature so long as the soil moisture content remains constant throughout the temperature change. Although not considered in the discussion above, the free energy Δf_{PS} due to hydrostatic pressure clearly may be due in part to pressure transmitted from external sources such as atmospheric pressure. Any external pressure not influenced by temperature changes will, of course, be merely superimposed upon Δf_{PS} above; and the form of equation 466 will remain unchanged.

80. Dependence of the Free Energy Δf_{ST} of Soil Moisture on Its Temperature T , All Known Factors Affecting the Free Energy of Soil Moisture Being Considered

Having just taken up separately for extreme cases the various factors affecting the free energy Δf_{ST} of soil moisture as the temperature is changed, let us now consider the most general case, where all these factors enter simultaneously.

In the present instance, four component free energies will go to make up the total value of the free energy Δf_{ST} of soil moisture,

$$\Delta f_{ST} = RT \ln \frac{p}{p_0} = \Delta f_{\sigma S} + \Delta f_{PS} + \Delta f_{OS} + \Delta f_{FS}. \quad (467)$$

As before, $\Delta f_{\sigma S}$ denotes the component of the free energy due to surface tension and radius of curvature of the water-air interface; Δf_{PS} , that due to the hydrostatic pressure of the moisture adjacent to the soil-particle surface caused by the adsorptive forces surrounding the soil particle (but excluding that due to the surface tension and radius of curvature of the water-air interface), as well as due to any pressure transmitted from external sources; Δf_{OS} , that due to the osmotic pressure of the dissolved material; and Δf_{FS} , the free energy possessed by water by virtue of its position in the adsorptive field surrounding the soil particle as well as in the earth's gravitational field. The present generalized treatment is unlike the previous special cases where we had to determine Δf_{ST} experimentally at but a single temperature in order to calculate Δf_{ST} at any other; we must here experimentally determine Δf_{ST} at two temperatures.

Before evaluating Δf_{ST} we must properly express each of the four component free energies in terms of temperature.

Consider first the evaluation of $\Delta f_{\sigma S}$ as a function of temperature. According to equations 211 and 434,

$$\Delta f_{\sigma S} = 2(117 - 0.152T) \frac{v}{r}. \quad (468)$$

Equation 468 can be placed in the following form, where k_1 and k_2 are constants independent of temperature:

$$\Delta f_{\sigma S} = k_1 + k_2 T. \quad (469)$$

Next let us evaluate Δf_{oS} as a function of temperature. It was previously shown that the ratio of the vapor pressure p of a solution to that of pure water p_0 at a given temperature is a constant, independent of temperature. Therefore if k_3 is such a constant that

$$R \ln \frac{p}{p_0} = k_3, \quad (470)$$

we have

$$\Delta f_{oS} = RT \ln \frac{p}{p_0} = k_3 T. \quad (471)$$

Finally, as was brought out in the preceding article, the two component free energies Δf_{FS} and Δf_{PS} arising from the existence of the adsorptive field surrounding the soil particle are constants independent of temperature. Therefore we have

$$\Delta f_{FS} + \Delta f_{PS} = k_4, \quad (472)$$

k_4 being another constant independent of temperature.

We can now determine in a generalized way the total free energy Δf_{ST} of a moist soil at any temperature, the soil moisture content remaining constant. Substituting equations 469, 471, and 472 into 467, we have

$$\Delta f_{ST} = k_1 + k_2 T + k_3 T + k_4; \quad (473)$$

and upon further combining the terms on the right side, we may write

$$\Delta f_{ST} = C_1 + C_2 T, \quad (474)$$

where C_1 and C_2 are still other constants independent of T .

Since equation 474 contains two unknowns, C_1 and C_2 , we must determine Δf_{ST} experimentally at any two different temperatures T_1 and T_2 before we can calculate C_1 and C_2 and consequently before calculating

Δf_{ST} at any desired temperature T . Let us assume that Δf_{ST} has been determined experimentally and found to be Δf_{ST_1} at the temperature T_1 and Δf_{ST_2} at the temperature T_2 . We then have

$$\Delta f_{ST_1} = C_1 + C_2 T_1$$

and

$$\Delta f_{ST_2} = C_1 + C_2 T_2.$$

The unknowns C_1 and C_2 are determined immediately if we solve the set of linear simultaneous equations above, with two unknowns, for C_1 and C_2 . We then have

$$C_1 = \frac{T_1 \Delta f_{ST_2} - T_2 \Delta f_{ST_1}}{T_1 - T_2} \quad (475)$$

and

$$C_2 = \frac{\Delta f_{ST_1} - \Delta f_{ST_2}}{T_1 - T_2}. \quad (476)$$

Inserting C_1 and C_2 of equations 475 and 476 into equation 474, we have the free energy Δf_{ST} of soil moisture at any temperature T in terms of its value at but two temperatures, T_1 and T_2 . Then

$$\Delta f_{ST} = \left(\frac{T_1 \Delta f_{ST_2} - T_2 \Delta f_{ST_1}}{T_1 - T_2} \right) + \left(\frac{\Delta f_{ST_1} - \Delta f_{ST_2}}{T_1 - T_2} \right) T. \quad (477)$$

This equation is the result of the most general treatment in which all the factors known at present (for example, surface tension, osmotic pressure, hydrostatic pressure, and the adsorptive forces surrounding the soil particle) are considered.

Equation 477 in contrast to equations 436, 465, and 466 requires a determination of Δf_{ST} at two temperatures, T_1 and T_2 .

When, therefore, the conditions of the soil moisture happen to agree approximately with those conditions assumed in deriving the simpler equations 436, 465, or 466, it is advisable to use them. Equation 477 is a general one applicable under all conditions of soil moisture, of which 436, 465, and 466 are merely special cases.

To fix our ideas as to the use of equation 477, let us assume the following set of data: At the temperature $T_1 = 280^\circ \text{A}$, Δf_{ST_1} of a moist soil at a particular soil moisture content was found equal to -3×10^7 ergs per gram; at $T_2 = 300^\circ \text{K}$, for the same soil moisture content, $\Delta f_{ST_2} = -2 \times 10^7$ ergs per gram. Therefore

$$\begin{aligned} \Delta f_{ST} &= \frac{280 \times (-2 \times 10^7) - 300(-3 \times 10^7)}{280 - 300} + \frac{(-3 \times 10^7) - (-2 \times 10^7)}{280 - 300} \times T \\ &= -17 \times 10^7 + 5 \times 10^5 \times T. \end{aligned} \quad (478)$$

Let us now, by equation 478, calculate the free energy Δf_{ST} of our sample of soil moisture at 273° A.

$$\Delta f_{S\ 273} = -17 \times 10^7 + 5 \times 10^5 \times 273 = -3.35 \times 10^7 \text{ ergs per gram.}$$

81. Dependence of the Free Energy of Soil Moisture on Temperature, Expressed in Terms of the Differential Heat of Wetting

We shall approach the subject of the variation of the free energy of soil moisture with temperature by a method somewhat less empirical than that used in the previous article. We may, for example, wish to know the free energy Δf_{ST} of soil moisture at some temperature T but instead find it more convenient to measure its heat of wetting, from which the free energy Δf_{ST} may be computed. The following discussion will show how the free energy Δf_{ST} may be calculated from experimental results on the differential heat of wetting.

We have seen from equation 404 that

$$\left(\frac{\partial q}{\partial m}\right)_T = \frac{RT^2 d \ln \left(\frac{p_0}{p}\right)}{dT} \quad (479)$$

and from equation 236 that a change in the free energy Δf_{ST} in going from free water at a vapor pressure p_0 to the soil moisture at the vapor pressure p may be expressed by

$$\Delta f_{ST} = RT \ln \left(\frac{p}{p_0}\right)$$

or

$$\frac{\Delta f_{ST}}{RT} = -\ln \frac{p_0}{p}. \quad (480)$$

Substituting equation 480 into 479, we have

$$\left(\frac{\partial q}{\partial m}\right)_T = - \frac{RT^2 d \left(\frac{\Delta f_{ST}}{RT}\right)}{dT}$$

or

$$d \left(\frac{\Delta f_{ST}}{T}\right) = - \left(\frac{\partial q}{\partial m}\right)_T \frac{dT}{T^2}. \quad (481)$$

The value of $\left(\frac{\partial q}{\partial m}\right)_T$ depends, in general, on the temperature and moisture content. Suppose, now, we keep the moisture content of the material constant and determine experimentally the differential heat of wetting

of the material $\left(\frac{\partial q}{\partial m}\right)_T$ as some function $\Phi(T)$ of the temperature T , enabling us to write the identity

$$\left(\frac{\partial q}{\partial m}\right)_T \equiv \Phi(T). \quad (482)$$

If this function is substituted in equation 481, we have

$$d\left(\frac{\Delta f_{ST}}{T}\right) = -\Phi(T) \frac{dT}{T^2}.$$

Then, integrating between any two temperatures T_1 and T , we have

$$\int_{T_1}^T d\left(\frac{\Delta f_{ST}}{T}\right) = -\int_{T_1}^T \Phi(T) \frac{dT}{T^2}$$

or

$$\frac{\Delta f_{ST}}{T} - \frac{\Delta f_{ST_1}}{T_1} = -\int_{T_1}^T \Phi(T) \frac{dT}{T^2}. \quad (483)$$

Here Δf_{ST} and Δf_{ST_1} correspond to the free energy of the soil moisture with respect to that of free water at the temperatures T and T_1 , respectively. Rearranging equation 483, we have

$$\Delta f_{ST} = -T \int_{T_1}^T \Phi(T) \frac{dT}{T^2} + \left(\frac{\Delta f_{ST_1}}{T_1}\right)T. \quad (484)$$

This equation furnishes a rigorous method in addition to those given in articles 74, 78, 79, and 80 for determining the free energy Δf_{ST} of soil moisture as a function of the temperature T , regardless of whether the differential heat of wetting is due to solution effects or to adsorption of moisture. It requires an experimental determination of the differential heat of wetting $\Phi(T)$ of the soil sample as a function of temperature between T_1 and T , as well as a single determination of the free energy Δf_{ST_1} of the soil sample at some one temperature T_1 . Although we may not be able to make all the determinations on only one soil sample, we can make the determinations on different samples, all at the same moisture content.

As equation 484 shows, we can determine the free energy Δf_{ST} of soil moisture at any temperature T from the differential heat of wetting $\left(\frac{\partial q}{\partial m}\right)_T$ or, what is the same thing, ΦT (eq. 482), provided we know the free energy Δf_{ST_1} at some one temperature T_1 . Equation 484 is most useful in determining the dependence of the free energy of soil moisture on variations of temperature for comparatively dry soils where the

differential heat of wetting $\left(\frac{\partial q}{\partial m}\right)_T$ is appreciable. Because of the very minute heats of wetting of relatively moist soils, we cannot, with the present development of calorimetric technique, secure dependable results with this equation at high soil moisture contents. More usable approaches at such contents are discussed in articles 74, 77, and 80.

In contrast to the previous methods of determining the dependence of the free energy of soil moisture on temperature, where we considered the various mechanisms involved such as surface tension and salt concentration, equation 484 does not necessitate the assumption of specific mechanisms. Only measurable thermodynamic quantities such as differential heat of wetting and temperature are involved explicitly.

MOVEMENT OF SOIL MOISTURE

82. Importance of Free Energy Δf_s in Studies of the Movement and the Equilibrium of Soil Moisture

Because of the thermodynamic properties of the free energy Δf_s , two bodies of moist soil, A and B , at the same temperature will be in equilibrium if their values of Δf_s are the same (art. 21 and 22). The *temperature*, as well as the free energies, at A and B *must* be the same if equilibrium is to exist; for the free energies may well be the same at the two points A and B , since we may have

$$\Delta f_s = RT_A \ln \frac{p_A}{p_{OA}} = RT_B \ln \frac{p_B}{p_{OB}},$$

and yet equilibrium will not exist if the temperatures are different. If, however, Δf_s of B is less than that of A , there will (eq. 115) be a tendency for moisture to move from A to B because moisture will always move from points of higher Δf_s to points of lower Δf_s . It will continue to move until the final value of Δf_s at A is the same as the final value at B . The value of the free energy at A will then have decreased, whereas that at B will have increased. Incidentally, when equilibrium has thus been established, there will have been a net decrease of the total free energy of the system (art. 21).

The different values of Δf_s for different interconnected regions of moisture all tend to approach the same value. If the interconnections are through the vapor rather than the liquid phase, selective distillation will continue until enough moisture has moved from regions of high Δf_s to regions of low Δf_s to make the value of Δf_s uniform throughout. No matter whether the water is liquid, ice, or vapor, moisture will always move from regions of high Δf_s to regions of low Δf_s until the value of Δf_s is uniform throughout.

In perfect analogy with the idea of potential as used in electricity, magnetism, or soil-moisture studies, the gradient of the total specific free energy Δf_s in the soil is the negative of the force per gram acting on the water particle. Also the component of the force acting on a water particle per gram in any direction is the negative of the derivative of the total potential in that direction. All the vector properties usually associated with the gradient of a potential should be associated with the gradient of the free energy Δf_s .

We often hear that the gradient of the capillary or pressure potential at some point equals the negative of the resultant force per gram acting on the water at that point. This statement is not always true. The pressure or capillary potential, as customarily used in the past, seems not to con-

sider the effect of the variation in concentration of dissolved material in producing water movement. The capillary or pressure potential explicitly deals only with the energy in the soil moisture arising from the mechanical tension or pressure existing in the soil moisture.

The free energy Δf_s is a more generalized quantity than any of the others previously used for describing the energy content of water and includes them as special cases only. The free energy Δf_s (art. 60) includes the energy due to the adsorptive field surrounding the soil particle and that due to dissolved material, as well as that due to hydrostatic pressure. It includes any other terms that might be appreciable under certain conditions, such as the kinetic energy of water (taken up at the end of this article) and the energy due to the possible orientation of the water molecules in the vicinity of the water-soil interface. In the present treatment the latter contributions to the free energy Δf_s have been regarded as negligible.

It is self-evident that the adsorptive field surrounding the soil particle can cause differences in hydrostatic pressure and hence in moisture movement. On the other hand, let us show in a preliminary way that dissolved material will also cause movement. Referring to article 40, we see that if a solution is placed in contact through a semipermeable membrane with pure water in a capillary tube, water will, in general, move either into or out of the capillary tube. Let us gradually increase the tension on the pure water in the capillary tube. Water will flow into the solution until the hydrostatic tension $-\Delta P_P$ in the pure water of the capillary tube numerically equals the osmotic pressure ΔP_O of the solution. In other words (art. 24 and 40) when the free energy $v(-\Delta P_P)$ due to hydrostatic pressure on one side of the semipermeable membrane equals the free energy $-v\Delta P_O$ due to osmotic pressure on the other side of the membrane, no further movement takes place. If the tension $-\Delta P_P$ on the pure water is increased until its magnitude is numerically greater than the osmotic pressure ΔP_O , water will move from the solution into the pure water in the capillary tube. Thus we see that pure hydrostatic pressure or tension may not be the only cause of capillary movement of soil moisture.

Let us consider the two following hypothetical cases in soils in order to bring out the generalized usefulness of the free energy Δf_s in predicting, under given conditions, the tendency of moisture to move in a soil as well as to show that the capillary, or pressure, potential alone does not determine the movement of moisture in the soil.

Case I (fig. 47) represents a soil column whose capillary or pressure potential (equivalent throughout to Δf_P) is uniform throughout. In other words, the tension in the moisture, as measured by a porous bulb atmometer immersed in the soil for a long period until equilibrium has been

established, is the same throughout. This involves the assumption that the solution has the same concentration inside the porous bulb as in the soil moisture immediately outside the bulb. That is, the capillary potential at *A* equals that at *B*. A gradual increase of salinity occurs, however,

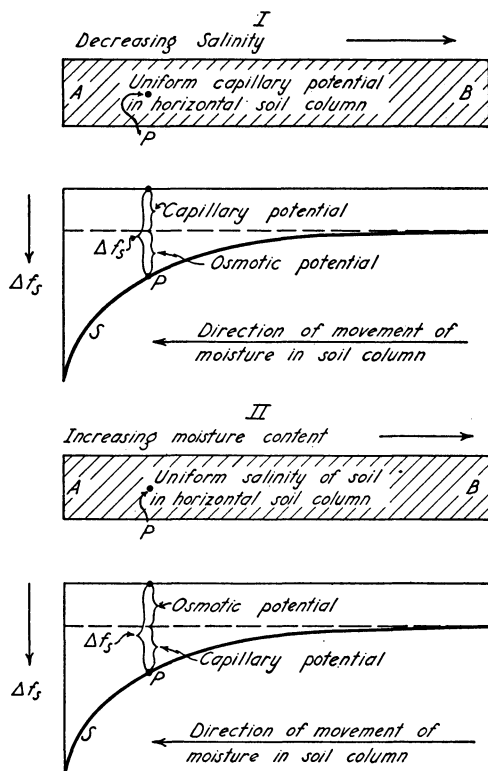


Fig. 47.—A given free-energy gradient produced (I) by varying salinity and uniform capillary potential, and (II) by uniform salinity and varying capillary potential.

in going along the soil column from *B* to *A*. This gives rise to a gradient of the osmotic potential (equivalent to the gradient of Δf_o) and consequently of the free energy Δf_s of the soil moisture. The gradient or force per gram acting on soil moisture at some point *P* and tending to cause movement in the direction *A* is given by the slope of the curve *S* at the point *P*. There is, in other words, a uniform tendency of moisture to move in the direction from *B* to *A*, although the capillary or pressure potential is the same throughout.

Case II somewhat resembles case I in that the free energy Δf_s at cor-

responding points in the two soil columns have the same values as shown by the graphs. In case II, however, the salinity or osmotic potential (equivalent throughout to Δf_o) is uniform throughout the soil column; but the soil moisture content is so adjusted along the soil column that the capillary or pressure potential will vary in such a way that corresponding points in the two soil columns have the same value for the total free energy Δf_s . The gradient of the free energy and, in consequence, the force acting on the soil moisture is the same at corresponding points in the two cases. The tendency of soil moisture to move from *B* to *A* in case I is therefore the same as in case II even though the factors giving rise to the movement are entirely different. It does not follow, of course, that the flow density will be the same in the two cases since the moisture contents are not the same.

To be sure, the variation in salinity in the soil column of case I will eventually decrease to zero, while the salt concentration will become uniform throughout by diffusion. No tendency towards movement of moisture will then exist. These considerations lead one to conclude that the porous bulb as generally used for measuring the capillary or pressure potential of soil moisture does not measure the capillary potential, the total potential, or the free energy. It would measure capillary potential only when sufficient time had elapsed to obtain equality in concentration of dissolved material between the soil solution and the water inside the atmometer. It would measure total potential or free energy only if one could get an equilibrium reading before any dissolved salts of the soil solution had moved into the inside of the atmometer. This is impossible because considerable time is required for pressure equilibrium to be established. In practice the porous-bulb technique usually gives a value somewhere between the capillary potential and the total potential, or free energy. For most soils, which are not very saline, this measured value is probably not far from the capillary potential, or the total potential, or the total free energy.

If we are to determine the total energy required to remove water from soil as well as its tendency to move from one point to another, we should, it seems, determine the total free energy Δf_s . The error caused by the diffusion of soil solutes made in measurements of the capillary or pressure potential by the porous-bulb technique will of course depend upon the circumstances, and in some cases will be negligible.

In the discussion above, we have considered the effect of dissolved substances on the osmotic pressure only, and therefore on the free energy Δf_s . Dissolved material affects Δf_s in still another way in that it changes the surface tension of water. Practically all salts cause a slight increase, and many organic substances a considerable decrease, of surface tension.

Such changes of the surface tension will affect the component of the free energy due to hydrostatic pressure. Since the salts as found in soil solutions change the surface tension by a very small percentage, the effect of changes in surface tension caused by dissolved material has been neglected in the foregoing treatment.

As mentioned above, the total free energy Δf_s plays, in a more comprehensive way, the same role in soil-moisture movement as has the potential in many former treatments of the subject (20, 30, 45, 55, 57, 58, 59, 81, 111, 125, 126). It is worth while, therefore, at this point, to restate some of the hydrodynamic equations of soil moisture in terms of free energy Δf_s . In such slow motion as that of water in soils, there is considerable evidence to justify the assumption that the frictional forces are proportional to the velocity. This may be expressed mathematically by

$$V = KF, \quad (485)$$

where V represents the mean velocity of the soil moisture; K the proportionality factor, whose magnitude depends on the frictional forces set up by the soil; and F the driving force on the moisture per unit mass of moisture.

Since, as pointed out earlier in this article, the force F equals the negative of the gradient of the free energy Δf_s , we may write (eq. 467)

$$F = -\nabla(\Delta f_s) = -\nabla(\Delta f_{\sigma s} + \Delta f_{ps} + \Delta f_{os} + \Delta f_{fs}), \quad (486)$$

where

$$\nabla \equiv i \frac{\partial}{\partial x} + j \frac{\partial}{\partial y} + k \frac{\partial}{\partial z},$$

i , j , and k being unit vectors in the positive direction of the x , y , and z axes. Here the component free energies have the same meaning as in equation 467.

Substituting F from equation 486 into 485, we have

$$V = -K\nabla(\Delta f_s) = -K\nabla(\Delta f_{\sigma s} + \Delta f_{ps}) + \Delta f_{os} + \Delta f_{fs}. \quad (487)$$

The factor K may be regarded as a transmission function. Equation 487 is simply Darcy's law and states that the force acting on soil moisture and, consequently, the velocity of movement of the soil moisture at a given point are proportional (at a given moisture content) to the greatest space rate of change of the four component free energies and have a direction proportional to the greatest space rate of change of the four component free energies.

Now the equation of continuity, which is simply a statement of the law of conservation of mass, is

$$\frac{\partial \rho}{\partial t} = \nabla \cdot (\rho V), \quad (488)$$

where the dot indicates the scalar product of the vector operator ∇ and the vector (ρV) and where ρ is the moisture density in grams per cubic centimeter at any point in the soil. Since we wish to express at any point the rate of change of the moisture density with time $\frac{\partial \rho}{\partial t}$, in terms of the free energy at that point, let us substitute equation 487 into 488, from which we get

$$\frac{\partial \rho}{\partial t} = \nabla \cdot [\rho K \nabla (\Delta f_s)]. \quad (489)$$

The transmission function K depends on the moisture density ρ , on the viscosity of the water (which depends on the temperature), and on the nature of the soil. For a given soil at a given temperature, we may therefore write

$$\rho K = \rho F'(\rho) = F(\rho), \quad (490)$$

where $F(\rho)$ denotes a function of the moisture density ρ . Equation 489 may therefore be written

$$\frac{\partial \rho}{\partial t} = \nabla \cdot [F(\rho) \nabla (\Delta f_s)]. \quad (491)$$

A solution of this equation obviously gives the moisture density as a function of time and position in the soil mass.

Under steady conditions of flow, including zero flow, we have

$$0 = \nabla \cdot [F(\rho) \nabla (\Delta f_s)]. \quad (492)$$

A solution of equation 492 gives the distribution of moisture as a function of position under the conditions of steady flow, including zero flow. It gives, for example, the moisture density as a function of height above a water table when equilibrium has been established between the upward movement from the water table and the evaporation from the surface of the ground.

The foregoing discussion in this article has been made on the assumption that the kinetic energy of the water is negligible. Where this is not the case, it must be included as another component of the total free

energy. If it is remembered that the total specific free energy represents the maximum amount of useful work possessed by, or obtainable from a substance at constant temperature and external pressure, it is obvious that the kinetic energy term should be included in Δf_s .

In view of the above, let us consider Bernoulli's theorem, which is of great importance in hydrodynamics. To our knowledge, this has never been discussed in terms of free energy. When dealing with incompressible liquids in steady streamline flow, the theorem may be stated as follows:

$$\frac{P}{\rho} + \frac{V^2}{2} + gZ = K = \Delta f. \quad (493)$$

The first term represents the component of the free energy due to pressure, as can be shown from equation 156, since P here equals ΔP and $\frac{1}{\rho}$ equals v ; the second, that due to the kinetic energy of the water; the third, that due to its position in the gravitational field (art. 26); and K is a constant (since we are considering a tube of flow in which the amount of water passing through any cross section in the tube of flow is always the same) equal to the free energy Δf . The equation merely states that at any point along a streamline of flow, the sum of the three component free energies is constant, although the component free energies may vary considerably among themselves.

Suppose we are considering a reservoir from which water is flowing out through an orifice. At the bottom of the reservoir in the orifice, the component free energy due to kinetic energy is a maximum, and that due to position in the earth's gravitational field, a minimum according to equation 493 above; at the top of the reservoir, the component free energy due to kinetic energy is zero, whereas that due to the gravitational field is a maximum; finally, at the bottom of the reservoir far back from the orifice where the water is at rest, we find both the component free energy due to kinetic energy and that due to position in the earth's gravitational field equal to zero, leaving the entire free energy equal to the term

$$\Delta f = K = \frac{P}{\rho}.$$

We thus notice that even for dynamic systems for which Bernoulli's theorem is applicable, where we are dealing with an incompressible liquid under steady flow, the free energy of the liquid is constant throughout a tube of flow, just as was shown to be the case for static systems in equilibrium in article 22.

DEFINITION OF PRINCIPAL SYMBOLS USED

In the definitions of the following series of terms, some will be found to have several meanings. The context in the articles will indicate which is to be used. A few terms have been omitted from this list since they are used so seldom in the articles and are defined at the place where they are used.

a	maximum work per gram (specific)
A	surface area
c	specific heat; in Raoult's Law, the constant of proportionality
c_p	specific heat at constant pressure
c_v	specific heat at constant volume
C	moisture content in soil
d	differential
e	base of natural logarithms
e	internal energy per gram
e_f	efficiency
E	total internal energy; total energy
f	function
f	absolute value of the free energy per gram (absolute specific free energy)
F	total free energy of a system; force per gram acting on soil moisture
Δf	specific free energy with respect to a datum
Δf_D	total specific free energy of saturated soil in the dilatometer with respect to the datum
Δf_{FD}	component specific free energy of soil moisture in the dilatometer due to its presence in the adsorptive force field surrounding the soil particle
Δf_{OD}	component specific free energy of soil moisture in the dilatometer due to the presence of dissolved material which creates an osmotic pressure
Δf_{PD}	component specific free energy of soil moisture in the dilatometer due to the hydrostatic pressure in the soil moisture
Δf_S	total specific free energy of soil moisture in the normal state with respect to the datum
Δf_{FS}	component specific free energy of soil moisture in the normal state due to its presence in the adsorptive force field surrounding the soil particle
Δf_{OS}	component specific free energy of soil moisture in the normal state due to the presence of dissolved material which creates an osmotic pressure

Δf_{PS}	component specific free energy of soil moisture in the normal state due to the hydrostatic pressure in the soil moisture
$\Delta f_{\sigma S}$	component specific free energy of soil moisture in the normal state due to the surface-tension effects in the soil moisture
Δf_{ST}	total specific free energy of soil moisture at the temperature T
g	acceleration due to gravity; also gravitational force
g	volume of individual compartments of phase space
G	dry weight of soil in grams
h	heat content per gram = $e + pv$ (in some literature, notably that of mechanical engineering, the term "enthalpy" is sometimes used in place of what we here call "heat content"); a constant in the Maxwell distribution equation = $\frac{1}{2kT}$; height
H	total amount of heat
k	molecular gas constant, that is, Boltzman's gas constant
K	degrees Kelvin or degrees Absolute
\bar{K}	force vector
K	component of a force
l	heat of transition from one phase to another; distance or path of integration in a field of force
\ln	natural logarithm
m	mass of a molecule; total mass; number of mols; mass (in grams) of water in soil
m_i	number of mols of i th constituent in a solution
M	molecular weight; weight of a mass
n_i	weight in grams of i th component of a solution
N	total number of molecules; number of molecules per gram (Loschmidt's number)
N_i	number of molecules lying in the i th cell, interval, or compartment of phase space
p	vapor pressure, or gas pressure
p_0	vapor pressure of datum
P	hydrostatic pressure (may include vapor pressure in general equation)
$\Delta P_P, \Delta P_O$	hydrostatic pressure, osmotic pressure, respectively, with reference to some datum
$\Delta P_{OS}, \Delta P_{OD}$	osmotic pressure of soil moisture in the normal state and in the dilatometer, respectively
$\Delta P_{PS}, \Delta P_{PD}$	hydrostatic pressure in soil moisture in the normal state and in the dilatometer, respectively
q	heat energy per gram

q	heat of wetting when dry soil is wetted to moisture content m
Q	heat evolved when the soil, whose dry weight is G grams, is dropped into an excess of water
r	radius of curvature
R	gas constant per gram
s	entropy per gram (specific entropy)
S	total entropy of system
t	time; total thickness of water film
Δt	thickness of a liquid surface layer whose total thickness is t
T	temperature
$\Delta T_o, \Delta T_P$	freezing-point depression due to osmotic pressure and hydrostatic pressure, respectively
u	velocity of molecule
v	specific volume
\bar{v}	partial specific volume
v_L, v_V	specific volume of liquid and of vapor, respectively
V	total volume; velocity of flow
w	work performed by a system or working substance
w_i	fraction of the total number of molecules N whose representative points fall in the i th compartment or cell in phase space
W	thermodynamic probability of a given macroscopic state
x_1, x_2, x_3	positional coördinates in phase space
x_i	mol fraction of i th constituent in a solution
X_i	weight fraction of the i th component of a solution
y	height
δ	mathematical symbol for a variation
Δ	symbol for a small part or element of a quantity; symbol for a finite change
ϵ_n	total energy of a molecule in the n th state, compartment, or cell of phase space
θ	angular measure in degrees; also, in some parts of the discussion, multiple-valued function
λ	heat of condensation; osmotic potential
ρ	density of moisture in the soil, in grams per cubic centimeter of soil; density of air in grams per cubic centimeter; density of water
σ	surface tension
τ	thickness of the surface layer of water in which properties are different from main body of the liquid
Φ	total potential of soil moisture
ψ	pressure potential of soil moisture

ω gravitational potential

$\nabla \equiv i \frac{\partial}{\partial x} + j \frac{\partial}{\partial y} + k \frac{\partial}{\partial z}$ operator gradient (i , j , and k being unit vectors in the x , y , and z directions, respectively)

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