

Consideration of the Gibbs Theory of Surface Tension

RICHARD C. TOLMAN

California Institute of Technology, Pasadena, California

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The Gibbs theory of surface tension is discussed. Detailed consideration is given to the structure of transition layers between phases. This provides theoretical information, as to the magnitude of surface tension and as to the location of the surface of tension, which can be used in making applications of the Gibbs theory.

I. DISCUSSION OF THE GIBBS THEORY

1. Introduction

IN his treatise on heterogeneous equilibrium,¹ Gibbs has developed a comprehensive and valid theory for treating the phenomena of surface tension by the methods of thermodynamics. Various applications of thermodynamics to particular problems in the field of surface phenomena can be made without employing the complete theory of Gibbs, and simplified theories can be developed for the thermodynamic treatment of plane surfaces. Nevertheless, to obtain the full results that can be expected from thermodynamics, especially in the case of curved surfaces, it is essential to employ the complete theory of Gibbs or its equivalent.

In Part I of this article we present a brief review which will assist in furnishing a clear appreciation of the nature and consequences of the Gibbs theory. This includes in Sections 2-5 a resume of fundamental notions, such as those of dividing surface, decomposition of quantities, surface of tension, etc., that are introduced in the Gibbs development. In Section 6 we then derive two well-known consequences of the Gibbs theory needed in Part II and in a proposed later application. In Section 7 we comment on certain aspects of the Gibbs theory that need emphasis in order to prevent misconceptions and secure full understanding. And, finally, in Section 8 we consider the status of certain simplified treatments of surface tension.

In Part II of the article we undertake a detailed treatment of transition layers in order to gain added insight into the mechanisms under-

lying surface phenomena, and to provide theoretical information as to the magnitude of surface tension and as to the location of the surface of tension. This information can be of value in making applications of the Gibbs theory and will be so employed in a proposed later application. We devote Sections 9-12 to the rather complicated deduction needed to obtain our two theoretical expressions (12.6) and (12.7) for the magnitude of surface tension and for the location of surface of tension. In Sections 13 and 14 we then show that these detailed expressions can themselves be used as the starting point to derive the two consequences of the Gibbs theory presented in Part I. In Section 15 we give general consideration to different kinds of possibilities for the detailed treatment of transition layers. And, finally, in Section 16 we discuss the extent to which we may ascribe validity to the particular detailed treatment that we have presented.

2. Introduction of Dividing Surface

We may begin our discussion of the Gibbs theory by giving attention to the fundamental notion of "dividing surface." For this purpose let us consider the conditions for equilibrium in systems consisting of two fluid phases which meet at a surface of discontinuity. In accordance with the known conditions for equilibrium within a single phase, and with the short range of molecular force, we can regard such a system as composed of two phases which have substantially uniform distributions of matter throughout their interiors but which meet in a thin layer of physical inhomogeneity where a transition takes place from the distribution in one phase to that in the other.

In order to obtain a simple treatment of the

¹J. W. Gibbs, *Collected Works* (Longmans Green and Company, New York, 1928), Vol. I, pp. 55-353.

thermodynamic properties of such a system, it is convenient to regard the system as precisely separated into two parts by the construction of an imaginary geometrical surface, which lies within the layer of physical inhomogeneity, and which passes through points in that layer which are similarly located with respect to the condition of neighboring matter. Such a surface, which gives a precise separation of the system into two parts, with the homogeneous portions of the two phases located on its opposite sides, was called by Gibbs a *dividing surface*.

It is evident that a variety of choices for such a dividing surface can be made, according as one or another condition of the neighboring matter is selected for the construction of the surface. It will be noted, however, that the different dividing surfaces which we might choose in any given case can be thought of as "parallel" to each other and to the tangible physical surface of discontinuity. Hence we can regard the properties of the whole transition layer as determined by the area and configuration of the particular dividing surface that we are using. (For further discussion see Section 7.)

3. Decomposition of Quantities Having Extensive Magnitude

Having made some particular choice for the dividing surface, the whole volume v occupied by a two-phase system may then be regarded as thereby precisely divided into two volumes v' and v'' , which have boundaries determined by the physical boundaries of the system itself and by the location of the dividing surface, and which have magnitudes exactly satisfying the equation

$$v = v' + v''. \quad (3.1)$$

As a consequence of this division it will be seen that v' will contain the matter in one of the homogeneous regions together with a part of the small amount of matter in the transition layer, and v'' will contain the matter in the other homogeneous region together with the rest of that in the transition layer.

In view of the nature of the contents of the two volumes v' and v'' , it then appears natural, and actually proves useful, to express the total energy E of the system as the sum of the energies E' and E'' which the two phases would have if

they remained strictly homogeneous right to the surface of separation, plus an additional term E^s which gives the necessary correction arising from the actual presence of the homogeneous transition layer. Thus for the total energy of the system we shall write

$$E = E' + E'' + E^s. \quad (3.2)$$

Similarly, for other quantities having extensive magnitude, we shall write for the total entropy of the system

$$S = S' + S'' + S^s, \quad (3.3)$$

and for the total amounts m_1, m_2, \dots, m_h , of the h different independent components of which the system is regarded as composed, we shall write

$$\begin{aligned} m_1 &= m_1' + m_1'' + m_1^s, \\ m_2 &= m_2' + m_2'' + m_2^s, \\ &\dots \dots \dots \dots \dots \dots \dots \\ m_h &= m_h' + m_h'' + m_h^s. \end{aligned} \quad (3.4)$$

The terms without superscript on the left-hand side of these equations give the actual total amounts of the quantities in question for the two-phase system as a whole. The terms with single and double accents give the amounts of those quantities, computed as though the two phases were strictly homogeneous right to the geometrical dividing surface, and the terms with the superscript S (not to be confused with an exponent) give the corrections, arising from the actual presence of a transition layer, that have to be introduced to make the equations true. Thus the above equations may be taken as defining those quantities, indicated by the superscript S , which we assign to the presence of the transition layer.

4. Variation of Energy for a System at Equilibrium

Let us now consider variations in the state of a two-phase system originally in a condition of equilibrium. We shall take the state of such a system, and hence its energy E , as determined by its entropy S , by the masses m_1, m_2, \dots, m_h of the various independent components which compose it, by the volumes v' and v'' which contain the two phases, and by the area s and principal curvatures c_1 and c_2 of the dividing surface

between the phases, where this is assumed sufficient in accordance with Section 2 to complete the determination of the state of the whole system.²

Considering a small variation in the state of the system, we may then evidently write for the variation in its energy

$$\delta E = T\delta S + \mu_1\delta m_1 + \mu_2\delta m_2 + \cdots - p'\delta v' - p''\delta v'' + \sigma\delta s + C_1\delta c_1 + C_2\delta c_2, \quad (4.1)$$

where in the first instance we regard the quantities T , μ_1 , μ_2 , \cdots , μ_h , p' , p'' , σ , C_1 , and C_2 merely as coefficients having values determined by the initial equilibrium state of the system.

Introducing our previous expressions (3.2-4), however, we may rewrite the above equation in the form

$$\begin{aligned} \delta E &= \delta E' + \delta E'' + \delta E^S \\ &= T\delta S' + \mu_1\delta m_1' + \mu_2\delta m_2' + \cdots - p'\delta v' \\ &\quad + T\delta S'' + \mu_1\delta m_1'' + \mu_2\delta m_2'' + \cdots - p''\delta v'' \\ &\quad + T\delta S^S + \mu_1\delta m_1^S + \mu_2\delta m_2^S + \cdots \\ &\quad + \sigma\delta s + C_1\delta c_1 + C_2\delta c_2. \end{aligned} \quad (4.2)$$

Furthermore, for any single homogeneous phase at equilibrium we have the known dependence (see reference 1, Eq. (12), p. 63) of energy on heat absorption, change in material contents, and work done,

$$\delta E = T\delta S + \mu_1\delta m_1 + \mu_2\delta m_2 + \cdots - p\delta v, \quad (4.3)$$

where T , μ_1 , μ_2 , \cdots , μ_h , and p have their usual significance. Hence comparing with (4.2), we now see that the coefficient T appearing therein may actually be taken as the temperature of the system having a value which can be determined by usual methods in either of the homogeneous

² This treats the dividing surface as having constant curvatures c_1 and c_2 throughout. The procedure actually adopted by Gibbs in this connection was somewhat more general. He starts by treating elements of the transition layer which are small enough so that the corresponding elements of dividing surface can be regarded as having uniform curvature throughout (see reference 1, p. 225). After showing the possibility of choosing the dividing surface for any such element in a manner to secure the desired simplification, corresponding to our later reduction from (5.1) to (5.3), he then introduces the idea that the dividing surface for the whole transition layer can be regarded as composed of elements of surface all consonant with the desired simplification (see reference 1, p. 227). It has not seemed desirable to introduce this increased generality into the exposition given in the text, partly since it would require considerable space to give a rigorous development, and partly since our contemplated later applications will be to spherical surfaces of uniform curvature throughout.

regions, that the coefficients μ_1 , μ_2 , \cdots , μ_h may be taken as the Gibbs potentials for the components of the system also having values determinable in the homogeneous parts of the system, and that the coefficients p' and p'' may be taken as the pressures in the homogeneous parts of the two phases. The coefficients σ , C_1 , and C_2 in Eqs. (4.1) and (4.2) are, however, new quantities to the consideration of which we must now turn.

5. Introduction of the Surface of Tension

In order to proceed, it will be advantageous to introduce a rearrangement of the last two terms in Eq. (4.1), and rewrite our expression for variation in energy of the system in a form

$$\delta E = T\delta S + \mu_1\delta m_1 + \mu_2\delta m_2 + \cdots - p'\delta v' - p''\delta v'' + \sigma\delta s + \frac{1}{2}(C_1 + C_2)\delta(c_1 + c_2) + \frac{1}{2}(C_1 - C_2)\delta(c_1 - c_2), \quad (5.1)$$

which will make it easier to analyze the effects of changes in curvature.

In accordance with this equation, we see that the last three terms of (5.1),

$$\sigma\delta s + \frac{1}{2}(C_1 + C_2)\delta(c_1 + c_2) + \frac{1}{2}(C_1 - C_2)\delta(c_1 - c_2), \quad (5.2)$$

give the variation in the energy of the system which would accompany a variation in the area and curvatures of the dividing surface, without absorption of heat, change in composition, or change in the volumes containing the two phases. It is evident that the sum of these three terms would have a value determined by the actual variation in the condition of the surface layer and independent of the choice of dividing surface, but that the values of the individual terms therein would be dependent on the particular choice made. Hence it now becomes natural to introduce any simplification that can be obtained by a special choice for the location of the dividing surface.

To obtain such a simplification we shall choose the location of the dividing surface in such a manner as to make the coefficient $\frac{1}{2}(C_1 + C_2)$ of the second term in (5.2) equal to zero. A special investigation to show the possibility of such a location for the dividing surface was made by Gibbs (see reference 1, pp. 226-227), and in Part II of this article we shall obtain a specific expression (12.7) determining this location in

terms of the distribution of fluid pressures in the layer. Moreover, since change in curvature of the dividing surface would lead to increase in the lamelliform distribution of matter on one side of the surface and decrease on the other, it would seem reasonable, in general, to expect that a location for the dividing surface could be found which would make $\frac{1}{2}(C_1+C_2)$ equal to zero through a balancing of the consequences of such opposing changes in distribution. Hence, we shall assume that we can indeed eliminate the second term in (5.2) by a suitable choice of our dividing surface.

Having made this simplification, let us now consider the third term in (5.2), which depends on the coefficient $\frac{1}{2}(C_1-C_2)$. We note at once that this coefficient would be equal to zero for a plane surface, because of the equality of C_1 and C_2 for that case. Hence, with Gibbs (see reference 1, p. 228) we may conclude that the third term can also be dropped, without danger of sensible error, whenever the curvature of the actual transition layer is small enough compared with its thickness so that we can regard it as composed of parts which are essentially plane. Furthermore, since in proposed applications we shall actually be interested in the treatment of spherical surfaces of small radius, we also note that the coefficient $\frac{1}{2}(C_1-C_2)$ would be precisely equal to zero for spherical surfaces in general.

In accordance with the preceding two paragraphs, we now see that, by a suitable choice of dividing surface, we can write our Eq. (5.1) for variation in energy in the simplified form

$$\delta E = T\delta S + \mu_1\delta m_1 + \mu_2\delta m_2 + \dots - p'\delta v' - p''\delta v'' + \sigma\delta s. \quad (5.3)$$

Furthermore, since the conditions for thermodynamic equilibrium require a minimum of energy, with a given entropy, composition, and total volume for the system as a whole, we see—making use of the restrictions on the volumes v' and v'' given by (3.1)—that equilibrium requires validity of the equation

$$(p' - p'')\delta v' = \sigma\delta s. \quad (5.4)$$

This, however, is the form of equation which would apply to a system of two homogeneous fluids at pressures p' and p'' , separated by a membrane without rigidity having a tension σ

uniform in all directions. Hence, we may now designate the particular dividing surface that we have chosen as *the surface of tension*, and may define σ as *the surface tension* thereof.

Introducing the Helmholtz expression defining the free energy of a system

$$A = E - TS, \quad (5.5)$$

we can also write (5.3) in the form

$$\delta A = -S\delta T + \mu_1\delta m_1 + \mu_2\delta m_2 + \dots - p'\delta v' - p''\delta v'' + \sigma\delta s. \quad (5.6)$$

In accordance with (5.3) and (5.6), we then see that we can regard the surface tension σ either as the rate of change of energy with surface area at constant entropy, constant composition, and constant volumes for the two phases measured to the surface of tension, or as the rate of change of free energy with surface area at constant temperature, composition, and volumes. In both cases it will be appreciated that the surface area to be considered is that for the surface of tension within the transition layer.

Introducing a thermodynamic potential defined by

$$F = E - TS + p'v' + p''v'', \quad (5.7)$$

it would also be possible to write

$$\delta F = -S\delta T + \mu_1\delta m_1 + \mu_2\delta m_2 + \dots + v'\delta p' + v''\delta p'' + \sigma\delta s. \quad (5.8)$$

Such an expression, however, was not employed by Gibbs, and we shall make use of it only for purpose of comparison with an equation given by Lewis and Randall. (See Section 9.)

6. Two Consequences of the Gibbs Theory

We may now complete this brief resumé of the Gibbs theory by considering the derivation of two well-known consequences of special interest.

The first consequence that we wish to consider can be immediately obtained by applying Eq. (5.4), connecting variations in volume and surface, to the special case of a uniform displacement of the surface of tension everywhere normal to itself. As can be readily seen (see reference 1, Eq. (500), p. 229), this at once leads to the familiar equation of Kelvin

$$p' - p'' = (c_1 + c_2)\sigma, \quad (6.1)$$

connecting the pressures p' and p'' in the two phases with surface tension σ and with the principal curvatures c_1 and c_2 of the surface of tension. With a spherical surface, having the curvature c and radius r , this reduces to the form

$$p' - p'' = 2c\sigma = 2\sigma/r. \quad (6.2)$$

With positive values for the surface tension as are experimentally found, the higher pressure p' occurs in the so-called interior phase on the concave side of the surface, and the lower pressure p'' in the exterior phase on the convex side. We shall adopt the general convention of using a single accent to denote quantities applying to the interior phase and a double accent to denote those applying to the exterior phase.

The Kelvin relation between the pressures in the two phases given by (6.1) may be regarded as replacing the familiar equilibrium condition of uniform pressure throughout a system which is obtained when surface effects are neglected. It will be noted that equal pressures will prevail in the two phases only when they are separated by a plane surface and, *vice versa*, that maintenance of equality between these pressures is the condition for maintenance of a plane surface of separation.

In obtaining the second consequence of the Gibbs theory that will interest us, we shall be concerned with reversible³ changes in the state of our two-phase system, rather than in arbitrary variations, and shall indicate this by replacing the sign of variation δ by the sign of differentiation d in Eq. (5.3). For the change in energy accompanying a reversible change from the original equilibrium state, we can then write in agreement with (5.3)

$$dE = TdS + \mu_1 dm_1 + \mu_2 dm_2 + \dots - p'dv' - p''dv'' + \sigma ds, \quad (6.3)$$

which, in accordance with the discussion of Section 3, can also be written in the more detailed form

$$\begin{aligned} dE &= dE' + dE'' + dE^S \\ &= TdS' + \mu_1 dm_1' + \mu_2 dm_2' + \dots - p'dv' \\ &\quad + TdS'' + \mu_1 dm_1'' + \mu_2 dm_2'' + \dots - p''dv'' \\ &\quad + TdS^S + \mu_1 dm_1^S + \mu_2 dm_2^S + \dots + \sigma ds, \end{aligned} \quad (6.4)$$

³ The term reversible is used here in the usual thermodynamic sense, rather than in the special sense employed by Gibbs (reference 1, p. 222).

which shows the distribution of changes in energy, entropy, etc., among the different parts of the system.

Let us now consider the application of this equation to a calculation of the energy increase which would be brought about by an increase in the area of the surface of tension, *without* changes in the volumes v' and v'' , or in the idealized homogeneous distributions of fluid in those volumes. Under such circumstances it is evident that the expression given by (6.4) would reduce to the form

$$dE^S = TdS^S + \mu_1 dm_1^S + \mu_2 dm_2^S + \dots + \sigma ds, \quad (6.5)$$

where dE^S is the increase in energy of the system, TdS^S is the heat that has to be absorbed, dm_1, dm_2, \dots, dm_h are the additions that have to be made to the h components of the system, and σds the work that has to be done to increase the surface by the amount ds , without affecting the homogeneous distributions in the volumes v' and v'' . Furthermore, since the coefficients $T, \mu_1, \mu_2, \dots, \mu_h$, and σ which appear in this equation would evidently maintain constant values if we make a finite change in area maintaining uniform properties throughout the extent of the surface, we see that we can now integrate (6.5) between $s=0$ and some finite value $s=s$, and obtain

$$E^S = TS^S + \mu_1 m_1^S + \mu_2 m_2^S + \dots + \sigma s, \quad (6.6)$$

as a correct expression for the total correction term E^S which has to be added to E' and E'' , as discussed in Section 3, to get the total energy of a system of two fluid phases separated by a surface of tension of finite area s .

This equation now makes it possible to obtain one of the most important consequences of the Gibbs theory. Since (6.6) gives an analytically correct expression for E^S , we may now differentiate it with respect to all the variables on the right-hand side, and by comparing with (6.5) readily obtain the relation

$$-sd\sigma = S^S dT + m_1^S d\mu_1 + m_2^S d\mu_2 + \dots \quad (6.7)$$

Or if for simplicity we define the *superficial densities* of entropy and matter by

$$S_S = S^S/s, \quad \Gamma_1 = m_1^S/s, \quad \Gamma_2 = m_2^S/s + \dots, \quad (6.8)$$

we can write the desired result

$$-d\sigma = S_S dT + \Gamma_1 d\mu_1 + \Gamma_2 d\mu_2 + \dots \quad (6.9)$$

This consequence of the Gibbs theory, which is now sometimes called the Gibbs adsorption equation, has the important function of expressing the dependence of surface tension on the temperature of our two-phase system and on the potential of the components of which it is composed. The analogy of (6.9) with the Gibbs expression (reference 1, Eq. (98), p. 88) for the dependence of pressure, in a single-phase system of volume v , on temperature and potentials,

$$dp = (S/v)dT + (m_1/v)d\mu_1 + (m_2/v)d\mu_2 + \dots, \quad (6.10)$$

will be appreciated.

7. Comments on Certain Aspects of the Gibbs Theory

The theory of surface tension given by Gibbs was developed with a minimum of hypothesis as to the detailed structure of the transition layer, this being reduced essentially to the assumption that all the properties of the layer can be regarded as determined by the area and curvature of some selected imaginary dividing surface. This procedure has the advantage of providing a very general theory, which is valid for a wide range of possible kinds of transition layer. The procedure also carries the consequence, however, that the theory will not itself provide information as to the detailed structure of transition layers. It is for this reason that we shall consider a more detailed treatment of transition layers in Part II.

The idea of using changes in the area and curvature of a single imaginary dividing surface to specify changes in the state of the whole transition layer may need elucidation. Any given dividing surface is defined by its passage through points within the transition layer where the fluid is locally in some given specified condition, the same for all points. Furthermore, the entire series of possible "parallel" dividing surfaces can be regarded as corresponding to the series of different values which can be assigned to the specified condition of the fluid. Hence, in a condition of equilibrium, the area and curvature of any one of the possible dividing surfaces may be regarded as determining the areas and curvatures of all the surfaces in the series, if we neglect edge effects in the case of transition layers of large extent, or take lateral boundaries normal to the dividing surfaces in the case of transition

layers of small extent and in the case of small portions of a large layer. (Compare reference 1, pp. 219–220.) Thus, a variation in the area and curvature of any one dividing surface may be regarded as "controlling" the variation in state of the whole transition layer. It is to be emphasized that the specification of state in terms of the area and curvature of a selected dividing surface is a somewhat abstract procedure, not to be confused with more concrete attempts to treat the transition layer as a separate entity having some definite small value ζ for its thickness.⁴

Having chosen some particular dividing surface, it becomes possible, as we have seen in Section 3, to express the total energy E of a two-phase system as the sum of the energies E' and E'' , which would be computed for the two phases if they remained strictly homogeneous right to the geometrical dividing surface, plus an additional correction term E^s resulting from the actual presence of the transition layer. And similar decompositions can be carried out for other quantities having extensive magnitudes such as entropy S , and the masses $m_1 \cdots m_h$ of the different components of the system. It is to be emphasized in this connection that the values of the correction terms, such as E^s , S^s , $m_1^s \cdots m_h^s$, which are introduced by this procedure will depend on the particular choice that is made for the location of the dividing surface. Indeed, it will be noted that the values of such terms may be positive or negative according as that choice leads to a deficiency or excess for the sum of the values computed for the two phases as compared with the actual value of the quantity in question for the system as a whole. It should be specially kept in mind that the quantities E^s , S^s , m_1^s , etc., are not the energy, entropy, mass, etc., for some specific thin layer of substance between the two phases, but are correction terms as defined.⁴

Although it is possible to choose one or another of many different possible dividing surfaces for

⁴ See remarks made in Section 15 with regard to the somewhat unsatisfactory treatment given by J. Rice to the question of the location of the Gibbs surface of tension. By picturing the transition layer as having a definite thickness with a uniform distribution of surface energy throughout, he introduces a conception of the transition layer that does not agree with the conception of Gibbs which he is trying to illuminate.

the specification of state, it is to be emphasized that the most general results obtained by Gibbs are all dependent on the actual choice of the surface of tension as the one employed. This choice is made in order to reduce the fundamental expression, for the variation in energy δE , as given by (5.1), to the much simpler form (5.3), on which all further deductions are based. Hence, it is always to be presumed that the values of quantities appearing in the equations of Gibbs are taken with reference to the surface of tension, unless an explicit statement is made to the contrary, as is meticulously carried out by Gibbs. As an example, it may be noted that the Kelvin relation (6.2), connecting pressure difference between the phases ($p' - p''$), with surface tension σ and radius of curvature r , can be taken as strictly correct only when we use the values of σ and r for the surface of tension, a matter of importance when the radius is small enough so that the exact location of the surface of tension has an appreciable effect. As another example, it is to be noted and emphasized that the dependence of surface tension on temperature and potentials given by (6.9) holds in general only when we use the values for the superficial densities of entropy and matter $S_s, \Gamma_1, \Gamma_2, \dots$ that are computed with reference to the surface of tension. It is very important not to misunderstand the essential role played by the surface of tension in the Gibbs development.

8. Possibilities for Simplified Treatments

As has just been emphasized, the general results of Gibbs are obtained with the help of the reduction of Eq. (5.1) to the simplified form (5.3) through the choice of the surface of tension as the dividing surface employed. It will be noted, however, that the same reduction of (5.1) to the form (5.3) would be automatically achieved, for any choice of dividing surface, so long as applications are restricted to the behavior of plane surfaces, since the last two terms in (5.1) become zero if the curvatures c_1 and c_2 are not allowed to vary from zero. It is for this reason that simplified treatments are possible for plane surfaces with other and sometimes more illuminating choices for dividing surface. For example, that surface may be given such a location as to make the

surface density of some particular component equal to zero, e.g., the main component of the liquid phase.

This possibility of giving specially adapted treatments in the case of plane surfaces of separation is important, since most experimental studies of surface tension have been made with surfaces which are essentially plane. In giving such treatments, however, it is appropriate, following Gibbs, to attach a special suffix to symbols for surface densities to indicate their computation with respect to some special dividing surface. It is also to be emphasized that we must still use the surface of tension even for plane surfaces when we wish to employ Eq. (6.9) to calculate changes in surface tension that involve changes in curvature.

Thermodynamic treatments of surface tension which do not emphasize the role of the surface of tension can be carried out. One such possibility was briefly discussed by Gibbs (reference 1, footnote on p. 267), and in two recent American texts, Epstein⁵ and Keenan⁶ have presented somewhat complete theories of surface phenomena without explicit introduction of the notion of surface of tension. Such treatments, however, as suggested by Gibbs (reference 1, footnote on p. 267), may not have sufficient generality for all purposes.

A simplified thermodynamic treatment of surface tension, which is useful for some purposes but not general enough for others, was given by Lewis and Randall.⁷ Using our notation, their development is based on a definition of surface tension σ , in terms of thermodynamic potential F and surface areas, given by

$$dF = \sigma ds, \quad (8.1)$$

where it becomes evident later that they regard F as a function of the quantities p, T, m_1, \dots, m_n , and s , with p the pressure of the system. Comparing with (5.8), however, it is clear that a general treatment could be obtained only by including the possibility for different pressures

⁵ P. S. Epstein, *Textbook of Thermodynamics* (John Wiley and Sons, Inc., New York, 1937), see Chapter XII.

⁶ J. H. Keenan, *Thermodynamics* (John Wiley and Sons, Inc., New York, 1941), see pp. 434-447, 479-484.

⁷ G. N. Lewis and M. Randall, *Thermodynamics* (McGraw-Hill Book Company, Inc., New York, 1923), see pp. 247-253.

p' and p'' in the two phases, and thus also including in accordance with the Kelvin relation (6.1) the possibility for curved as well as plane surfaces of separation. This explains the reason why O. K. Rice,⁸ using the theory of Lewis and Randall to treat the effect of pressure on surface tension, finds a breakdown when he considers a one-component system where change in pressure at a given temperature would have to be correlated with change in curvature.

Our own further work will always be carried out in the light of the complete Gibbs theory.

II. DETAILED TREATMENT OF TRANSITION LAYER

9. Geometry of Transition Layer

We shall now endeavor to supplement our understanding of the Gibbs theory by undertaking a more detailed consideration of the nature of the transition layer. In doing this we shall limit the treatment to transition layers having spherical form, with values of the principal curvatures of the surface of tension which are kept equal when changes in curvature are made. We introduce this limitation partly to simplify our treatment, partly since the Gibbs treatment, as noted in connection with the reduction in form from (5.1) to (5.3), retains strict validity for highly curved surfaces only when they are spherical, and partly because of contemplated later application to spherical surfaces of small radius. We shall also restrict the treatment in the next section to one-component systems.

We shall regard the character of a spherical transition layer as determined by the area s and curvature c for the surface of tension, and shall treat the properties of the fluid within the transition layer as functions of the distance x from that surface. We shall measure this distance normal to the surface of tension and treat x as a variable, having positive values which increase from zero on the convex side of the surface of tension, and having negative values which decrease from zero on the concave side.

Taking r as the radius of the surface of tension, and ω as the solid angle subtended by the transi-

tion layer around the center of curvature, we can then write

$$s = \omega r^2 \quad (9.1)$$

as an expression for the area of the surface of tension, and can write

$$s(x) = \omega(r+x)^2 \quad (9.2)$$

as an expression for the area of any concentric surface of interest located within the transition layer at a distance x from the dividing surface. We use the same value of ω in the two expressions, since we shall assume it appropriate to neglect edge effects in the case of transition layers of large extent, and shall prescribe lateral boundaries determined by a conical surface having its apex at the center of curvature in the case of application to layers of small extent. Combining (9.1) and (9.2), and making use of the relation $c=1/r$ between the curvature and radius of the surface of tension, we can then write

$$s(x) = s[(r+x)^2/r^2] = s(1+cx)^2 \quad (9.3)$$

as a convenient expression for the areas of concentric surfaces within the transition layer.

Since we take the distribution of fluid within the transition layer as a function of x , the above expression for area now makes it possible to treat the whole layer as composed of a succession of infinitesimal layers, of area $s(1+cx)^2$ and thickness dx , within each of which we can take the condition of the fluid as uniform. Furthermore, for the volumes v' and v'' of the two fluid phases measured to the surface of tension, it now becomes convenient to introduce expressions of the form

$$v' = v'_a + s \int_{-a}^0 (1+cx)^2 dx, \quad (9.4)$$

and

$$v'' = v''_b + s \int_0^b (1+cx)^2 dx,$$

where we take the limits of integration at $x = -a$ and $x = b$ on the two sides of the surface of tension as sufficiently distant from that surface so that we can regard the condition of the fluid at those points as substantially the same as for the corresponding homogeneous phases, and can regard the remaining parts v'_a and v''_b of the two volumes as filled with homogeneous distributions of fluid.

⁸ O. K. Rice, J. Chem. Phys. 15, 333 (1947).

10. Condition of Fluid within the Transition Layer

We must now inquire in more detail into conditions within the transition layer. In doing so, we shall treat the fluid within the layer by the usual methods of thermodynamics, and shall return briefly later to the question of the validity of giving thermodynamic treatment to the exceedingly small portions of non-homogeneous matter that will now concern us. (See Section 16.)

In making this application, we recognize that the behavior of the fluid at any point in the transition layer will be determined not only by effects resulting from the local condition of matter at that precise point, but also by effects arising from the non-homogeneous distribution of neighboring matter. To take account of this, we shall assume that we can treat the fluid, at any point in the layer, as subjected to an isotropic pressure corresponding to the local density and temperature, and also to a directed force associated with the external force field produced by the non-homogeneous distribution of neighboring matter.

In accordance with the usual methods of thermodynamics (reference 1, pp. 144-150), we may then require, as the condition for equilibrium, constancy throughout the layer for the *intrinsic* Gibbs potential for each component of the system, *augmented* by the external potential corresponding to the force field resulting from non-uniform distribution. Restricting the treatment for simplicity to one-component systems, we may then take the requirement for equilibrium throughout the system as given by

$$\mu_i + \phi = \text{const.}, \quad (10.1)$$

where μ_i is the intrinsic Gibbs potential for the fluid at any point in the system and ϕ is the external potential at that point corresponding to the externally produced force field. We shall find it most convenient to take these two potentials as reckoned per unit mass, e.g., per gram, of substance.

In accordance with the definition (reference 1, Eq. (104), p. 89) of the Gibbs potential as the differential rate of increase in the Helmholtz free energy of a system, per gram of substance added to a homogeneous phase at constant tempera-

ture, volume, and composition, we can take μ_i as given by

$$\mu_i = \psi + (p/\gamma), \quad (10.2)$$

where ψ is the Helmholtz free energy per gram, p the pressure, and γ the density of the fluid at the point considered. The appropriateness of this expression is evident since ψ is the free energy per gram of substance in a condition suitable for introduction into the system, and p/γ is the work needed per gram to carry out the introduction reversibly, at constant temperature and volume. Substituting (10.2) into (10.1), we may now write the condition for equilibrium in the more detailed form

$$\psi + (p/\gamma) + \phi = \text{const.}, \quad (10.3)$$

where the constancy applies to all points in the two phases and in the transition layer of the system that concerns us. Certain consequences that can be drawn from this equation will prove illuminating.

In the first place, it will be appreciated that the requirement stated by (10.3) is equivalent to the familiar criterion for equilibrium that the reversible, isothermal work needed for the transfer of an infinitesimal amount of substance from one point of a system to another should be equal to zero. It is immediately obvious that (10.3) will secure this result, since it permits us to assign the value zero,

$$\psi_2 - \psi_1 + (p_2/\gamma_2) - (p_1/\gamma_1) + \phi_2 - \phi_1 = 0, \quad (10.4)$$

to an evident expression for the work per gram needed for such a transfer from points (1) to (2) in the system.

In the second place, it will be of interest to note that the full requirement for equilibrium given by (10.3) contains within it the special requirement needed for mechanical equilibrium in the interior of the non-homogeneous layer. To show this we may differentiate (10.3) with respect to position x within the transition layer, and write

$$\frac{d\psi}{dx} - \frac{p}{\gamma^2} \frac{d\gamma}{dx} + \frac{1}{\gamma} \frac{dp}{dx} + \frac{d\phi}{dx} = 0 \quad (10.5)$$

as a necessary relation. We can evidently write, however,

$$d\psi = -pdv = (p/\gamma^2)d\gamma \quad (10.6)$$

for the dependence of the free energy of the fluid per gram on its specific volume v or density γ . Hence, on substituting in (10.5) we obtain a necessary condition for equilibrium, which can be written in the form

$$\frac{1}{\gamma} \frac{d\phi}{dx} + \frac{d\phi}{dx} = -\frac{1}{\gamma} \frac{d\phi}{dx} - f_x = 0, \quad (10.7)$$

where $f_x = -d\phi/dx$ is seen to be the external force per gram acting in the x direction on the fluid. We at once appreciate that this result secures mechanical equilibrium through a balancing action of pressure gradient against external force.

Finally, it will be noted that the full condition for equilibrium given by (10.3) will reduce, in the homogeneous portions of the system where no external field of force has to be considered, to the simpler form

$$\psi' + (p'/\gamma') = \psi'' + (p''/\gamma'') = \mu, \quad (10.8)$$

where the single and double accents refer to the two homogeneous phases of the system, and μ is seen to be the Gibbs potential for the fluid in those phases. This result is of interest since it reasserts the accepted equality for the Gibbs potential in two homogeneous phases which are in equilibrium, and gives us a specific value for the constant in Eq. (10.3) which now permits us to rewrite that equation in the more explicit form

$$\psi + (p/\gamma) + \phi = \mu, \quad (10.9)$$

where μ is the value of the Gibbs potential for the fluid in the homogeneous portions of the system.

11. Detailed Expressions for Changes in Mass and Free Energy

We are now ready to obtain detailed expressions for the changes in mass and in free energy which would accompany a particular, specified variation in the state of our system of two phases and transition layer. We shall need these expressions in the next section, where we shall derive the desired expressions for the magnitude of surface tension and for the location of the surface of tension.

We shall specify the particular variation in the state of the system to be treated by the requirement that we start from a state of equi-

librium and make arbitrary variations δs and δc in the area and curvature of the surface of tension, keeping the temperature T of the system and the volumes v' and v'' of its two phases constant, and also keeping the homogeneous distributions of fluid pertaining to these phases unaltered by introducing whatever change δm in the mass of fluid in the system that is needed to secure this result. We select this particular variation in the state of the system in order to simplify the further treatment.

Since the specified variation in the state of the system is to be made without changes in the volumes v' and v'' of the two phases, we may begin by using the expressions for these quantities given by (9.4) to provide the following restrictions on the character of the variation

$$\begin{aligned} \delta v' = \delta v'_a + \delta s \int_{-a}^0 (1+cx)^2 dx \\ + 2s\delta c \int_{-a}^0 (1+cx)x dx = 0, \end{aligned} \quad (11.1)$$

and

$$\begin{aligned} \delta v'' = \delta v''_b + \delta s \int_0^b (1+cx)^2 dx \\ + 2s\delta c \int_0^b (1+cx)x dx = 0. \end{aligned} \quad (11.2)$$

Furthermore, since the variation is to be made without change in the idealized homogeneous distributions of fluid assigned to the two phases, we can evidently write for the needed change in the mass of the system

$$\begin{aligned} \delta m = \gamma' \delta v'_a + \delta s \int_{-a}^0 \gamma(1+cx)^2 dx \\ + 2s\delta c \int_{-a}^0 \gamma(1+cx)x dx \\ + \gamma'' \delta v''_b + \delta s \int_0^b \gamma(1+cx)^2 dx \\ + 2s\delta c \int_0^b \gamma(1+cx)x dx, \end{aligned} \quad (11.3)$$

where γ' , γ'' , and γ denote the densities of fluid in the two phases and in the transition layer, respectively, and where we treat γ as an unaltered function of the distance x from the surface of tension. Multiplying Eq. (11.1) by γ' and Eq. (11.2) by γ'' and subtracting from (11.3),

we can rewrite this expression for δm in the desired form

$$\begin{aligned} \delta m = & \delta s \int_{-a}^0 (\gamma - \gamma')(1 + cx)^2 dx \\ & + 2s \delta c \int_{-a}^0 (\gamma - \gamma')(1 + cx) x dx \\ & + \delta s \int_0^b (\gamma - \gamma'')(1 + cx)^2 dx \\ & + 2s \delta c \int_0^b (\gamma - \gamma'')(1 + cx) x dx. \quad (11.4) \end{aligned}$$

Finally, since the total free energy of the system can be expressed in terms of the intrinsic free energy of the elements of fluid in the system, augmented when necessary by their potential energy in the field of force in the transition layer, we can evidently write for the change in free energy of the system

$$\begin{aligned} \delta A = & \gamma' \psi' \delta v_a' + \delta s \int_{-a}^0 \gamma(\psi + \phi)(1 + cx)^2 dx \\ & + 2s \delta c \int_{-a}^0 \gamma(\psi + \phi)(1 + cx) x dx \\ & + \gamma'' \psi'' \delta v_b'' + \delta s \int_0^b \gamma(\psi + \phi)(1 + cx)^2 dx \\ & + 2s \delta c \int_0^b \gamma(\psi + \phi)(1 + cx) x dx, \quad (11.5) \end{aligned}$$

where ψ' , ψ'' , and ψ denote the intrinsic free energy per gram of fluid in the two phases and in the transition layer, respectively, where ϕ denotes the potential energy per gram of fluid in the transition layer associated with the force field in that layer, and where we now regard ψ and ϕ , as well as γ , as unaltered functions of the distance x from the surface of tension. Multiplying Eq. (11.1) by $\gamma' \psi'$ and Eq. (11.2) by $\gamma'' \psi''$ and subtracting from (11.5), we can rewrite this expression for δA in the desired form

$$\begin{aligned} \delta A = & \delta s \int_{-a}^0 (\gamma \psi + \gamma \phi - \gamma' \psi')(1 + cx)^2 dx \\ & + 2s \delta c \int_{-a}^0 (\gamma \psi + \gamma \phi - \gamma' \psi')(1 + cx) x dx \\ & + \delta s \int_0^b (\gamma \psi + \gamma \phi - \gamma'' \psi'')(1 + cx)^2 dx \\ & + 2s \delta c \int_0^b (\gamma \psi + \gamma \phi - \gamma'' \psi'')(1 + cx) x dx. \quad (11.6) \end{aligned}$$

It will have been appreciated that the derivations given for (11.4) and (11.6) involve the assumption that we can treat γ , ψ , and ϕ as functions of x which are unaltered by the variation. As a basis for the validity, or approximate validity, of this assumption, it will be noted that the condition of the fluid remains by hypothesis unaltered at the limits $x = -a$ and $x = b$, and can be expected to depend on position x as we pass through the transition layer in a manner only secondarily affected by infinitesimal changes in area and curvature.⁹ The degree of approximate validity that might be found for the assumption, as we proceed from a treatment of the simple case of nearly plane surfaces to a treatment of the more complicated case of highly curved surfaces, remains to be investigated.

12. Detailed Expressions for Surface Tension and for the Location of the Surface of Tension

We are now ready to derive detailed expressions for surface tension and for a condition on the location of the surface of tension. This we shall do by comparing the consequences of the Gibbs treatment of the free energy of a two-phase system with the more detailed consequences of the treatment given in the preceding section.

On the one hand, in accordance with the general equation of Gibbs (5.6) giving the dependence of the free energy of such a system on the variables which determine its state, we see that we can write the simplified expression,

$$\delta A = \mu \delta m + \sigma \delta s, \quad (12.1)$$

for the change in free energy of a one-component, two-phase system, when we make variations in its fluid content and in its transition layer, keeping temperature and the volumes of the two phases constant. In applying this equation it will be appreciated that μ is the Gibbs potential for the fluid in the system, as could be calculated from the properties of either homogeneous phase with the help of Eq. (10.8), that σ is the surface tension as defined by Gibbs, and that there is no term dependent on change in curvature δc because of choice of the surface of tension as the dividing surface employed.

⁹ A similar assumption is made by Gibbs (reference 1, p. 226), when he treats the distance λ between two different possible dividing surfaces as being unaffected by a variation in curvature.

On the other hand, by combining the expressions for δm and δA provided by Eqs. (11.4) and (11.6) in the preceding section, we see that we can also write the more detailed expression,

$$\begin{aligned} \delta A = \mu \delta m & \\ + \delta s \left[\int_{-a}^0 (\gamma\psi + \gamma\phi - \gamma'\psi' - \mu\gamma + \mu\gamma')(1+cx)^2 dx \right. & \\ + \int_0^b (\gamma\psi + \gamma\phi - \gamma''\psi'' - \mu\gamma + \mu\gamma'')(1+cx)^2 dx & \\ \left. + 2s\delta c \left[\int_{-a}^0 (\gamma\psi + \gamma\phi - \gamma'\psi' - \mu\gamma + \mu\gamma')(1+cx)xdx \right. \right. & \\ \left. \left. + \int_0^b (\gamma\psi + \gamma\phi - \gamma''\psi'' - \mu\gamma + \mu\gamma'')(1+cx)xdx \right] \right] & \end{aligned} \tag{12.2}$$

for the change in free energy of the same system, when we make the variations in its fluid content and in its transition layer that were specified in Section 11, keeping temperature and the volumes of the two phases constant. And this expression can be considerably simplified, since with help of Eqs. (10.8) and (10.9) we see that we can introduce the substitutions

$$\begin{aligned} (\gamma\psi + \gamma\phi - \gamma'\psi' - \mu\gamma + \mu\gamma') & \\ = \gamma\psi + \gamma\phi - \gamma'\psi' - \gamma\psi' - \gamma(p'/\gamma) + \gamma'\psi' + p' & \\ = \gamma[\psi + \phi + (p/\gamma) - \psi' - (p'/\gamma)] - p + p' & \\ = p' - p, & \end{aligned} \tag{12.3}$$

and, similarly,

$$(\gamma\psi + \gamma\phi - \gamma''\psi'' - \mu\gamma + \mu\gamma'') = p'' - p. \tag{12.4}$$

This then permits us to rewrite Eq. (12.2) in the simpler and physically more transparent form

$$\begin{aligned} \delta A = \mu \delta m + \delta s \left[\int_{-a}^0 (p' - p)(1+cx)^2 dx \right. & \\ + \int_0^b (p'' - p)(1+cx)^2 dx & \\ \left. + 2s\delta c \left[\int_{-a}^0 (p' - p)(1+cx)xdx \right. \right. & \\ \left. \left. + \int_0^b (p'' - p)(1+cx)xdx \right] \right] & \end{aligned} \tag{12.5}$$

This result appears reasonable since we can regard the first term $\mu\delta m$ as expressing the increase in free energy associated with introduction of fluid to be used in the formation of increased transition layer, and can regard the remaining terms as expressing the mechanical work associated with increase in the volumes $s(1+cx)^2 dx$ of the differential layers under pressure p within the transition region, and with decrease in the volumes v_a' and v_b'' containing homogeneous distributions of fluid under pressures p' and p'' .

We may now compare the consequences of the Gibbs treatment and the more detailed treatment. Since Eqs. (12.1) and (12.5) can both be taken as applying to the same system and same variation in state, it is evident by identifying coefficients in the two expressions that we can now write

$$\begin{aligned} \sigma = \int_{-a}^0 (p' - p)(1+cx)^2 dx & \\ + \int_0^b (p'' - p)(1+cx)^2 dx, & \end{aligned} \tag{12.6}$$

and

$$\begin{aligned} 0 = \int_{-a}^0 (p' - p)(1+cx)xdx & \\ + \int_0^b (p'' - p)(1+cx)xdx. & \end{aligned} \tag{12.7}$$

The first of these Eqs. (12.6) gives a detailed expression for the surface tension σ in terms of the distribution of fluid pressures p' , p'' , and p in the two phases and in the transition layer. The second of the Eqs. (12.7) gives detailed expression to the consequences arising from the simplifications introduced by Gibbs through choice of the surface of tension as the particular dividing surface to be used. The development which we have given for Eq. (12.5) would be valid for any choice of dividing surface, provided s and c were taken as the area and curvature thereof. But, when we specify with Gibbs that the surface of tension is to be used, it is evident that this choice requires the value zero for the coefficient of δc in Eq. (12.5). The necessary condition for this is given by our Eq. (12.7), and, with any specific dependence of p on position in the transition layer, this equation pre-

scribes a specific location for the surface of tension within that layer.

We regard these two equations as important for increasing our insight into the mechanisms underlying surface phenomena, and for providing supplementary information useful in making applications of the Gibbs theory. With the help of Eq. (12.6), we can correlate actual values of surface tension with the pressures that exist in the transition layer, including the negative pressures that would prevail in regions filled with liquid of reduced density. And with the help of Eq. (12.7), we can make estimates as to the location of the surface of tension for use in cases where the actual consequences of the Gibbs theory depend thereon.

We shall now take these more detailed equations as the starting point for deducing two relations which have already been obtained by the treatment of Gibbs. This can serve to increase our confidence in the validity of the more detailed treatment.

13. Deduction of the Kelvin Relation

We may first use Eqs. (12.6) and (12.7) to obtain a deduction of the Kelvin relation connecting the pressures in the two homogeneous phases with surface tension and curvature. Multiplying (12.7) by c and subtracting from (12.6), we see that we can rewrite the expression for surface tension in the following forms.

$$\begin{aligned} \sigma &= \int_{-a}^0 (p' - p)(1 + cx) dx + \int_0^b (p'' - p)(1 + cx) dx \\ &= \int_{-a}^0 \frac{p' - p}{2c} d(1 + cx)^2 + \int_0^b \frac{p'' - p}{2c} d(1 + cx)^2 \\ &= \left| \frac{p' - p}{2c} (1 + cx)^2 \right|_{-a}^0 + \left| \frac{p'' - p}{2c} (1 + cx)^2 \right|_0^b \\ &\quad + \frac{1}{2c} \int_{-a}^b \frac{dp}{dx} (1 + cx)^2 dx \\ &= \frac{p' - p''}{2c} + \frac{1}{2c} \int_{-a}^b \frac{1}{\gamma} \frac{dp}{dx} \gamma (1 + cx)^2 dx \\ &= \frac{p' - p''}{2c} + \frac{1}{2c} \int_{-a}^b f_x \gamma (1 + cx)^2 dx, \end{aligned} \quad (13.1)$$

where, in agreement with Eq. (10.7), f_x is the external force per gram acting in the x direction on the fluid in the transition layer. We see, however, since the external force acting on any element of the fluid is due to attraction or repulsion from neighboring elements, that the total integral in (13.1) will have to be zero because of the equality of action and reaction. Hence, we may drop the last term from (13.1) and rewrite the result in the form

$$p' - p'' = 2c\sigma = 2\sigma/r, \quad (13.2)$$

already given for the Kelvin relation by Eq. (6.2).

14. Deduction of Gibbs Expression for Change in Surface Tension

a. Lemma on Changes in Pressure

We shall next wish to use our equations to derive the Gibbs relation connecting changes in surface tension with changes in temperature and potential. To do this we shall first need to prove a lemma on the changes in fluid pressure that would accompany changes in temperature and potential.

Let us take a system at equilibrium, consisting of two phases and a spherical transition layer, filled with a one-component fluid which is distributed at some given temperature T , in accordance with the condition on equilibrium (10.9) given by

$$\psi + \frac{p}{\gamma} + \phi = \mu, \quad (14.1)$$

where p and γ are the pressure and density of the fluid, and ψ and ϕ its free energy and potential per gram, at any distance x measured normal from the surface of tension, and where μ is the Gibbs potential of the fluid as determined in either homogeneous phase having a value independent of x . And let us consider the change to a slightly varied equilibrium distribution which would be brought about by small changes, dT and $d\mu$, in the temperature and Gibbs potential for the system.

To examine the detailed consequences of such a change, let us first fix our attention on a particular element of the fluid originally located at some point x in the system, and let us denote by

δx the displacement which it receives normal to the surface of tension as a consequence of the change to the varied equilibrium distribution. Using the symbol δ to designate differences which involve the change δx in position, and reserving the symbol d to designate differences which apply at a given position, we can then evidently write, correct to the first order,

$$\delta\psi = -S_m dT + (p/\gamma^2)\delta\gamma, \quad (14.2)$$

as an expression for the change in free energy per gram of fluid in the element (reference 1, Eq. (88)) where S_m is the entropy per gram, and can write

$$\delta p = (dp/dx)\delta x + dp, \quad (14.3)$$

as an expression for the change of fluid pressure in the element, where (dp/dx) is the rate of change of pressure with position in the original distribution, and dp is the difference between the varied and original fluid pressures at the point $x + \delta x$, and can write

$$\delta\phi = (d\phi/dx)\delta x, \quad (14.4)$$

as an expression for the change in the external potential of the element, where $(d\phi/dx)$ is the rate of change of potential with position in the original distribution, and we regard $\delta\phi$ as determined correctly to the first order by change of position in the unvaried field. Furthermore, in addition to such equations derived by considering changes in the displaced element of fluid, it is evident, from the general condition on equilibrium given by (14.1), that we can also write

$$\delta\psi - (p/\gamma^2)\delta\gamma + (\delta p/\gamma) + \delta\phi = d\mu, \quad (14.5)$$

since an equation of the same form as (14.1) will have to hold at all points in the varied system with the constant μ replaced by $\mu + d\mu$.

Substituting from (14.2-4) into (14.5), we now obtain the result

$$-S_m dT + \frac{1}{\gamma} dp + \frac{1}{\gamma} \frac{dp}{dx} \delta x + \frac{d\phi}{dx} \delta x = d\mu, \quad (14.6)$$

and noting that the last two terms on the left-hand side will cancel in accordance with the condition for mechanical equilibrium given by (10.7), we can rewrite this in the form

$$dp = S_v dT + \gamma d\mu, \quad (14.7)$$

where S_v is seen to be entropy per unit volume of the fluid at any point of interest. This is the desired lemma connecting the change in pressure at any point with changes in temperature and potential.

Equation (14.7) has the same form as is known to apply to a homogeneous phase in the absence of external field. (See 6.10.) The present equation, however, applies throughout our system at points of varying external potential, and the quantity μ in the equation is not the intrinsic Gibbs potential at the point in the system under consideration, but that applying to the homogeneous parts of the system. Hence, a special derivation of our lemma was necessary.

b. Deduction of Gibbs Expression

We are now ready to use our detailed equations (12.6) and (12.7) to derive the Gibbs expression for change in surface tension. Differentiating the expression for surface tension given by (12.6), we can begin by writing

$$\begin{aligned} d\sigma &= \int_{-a}^0 (dp' - dp)(1+cx)^2 dx \\ &+ \int_0^b (dp'' - dp)(1+cx)^2 dx \\ &+ 2dc \int_{-a}^0 (p' - p)(1+cx)xdx \\ &+ 2dc \int_0^b (p'' - p)(1+cx)xdx \\ &- 2cdx_t \int_{-a}^0 (p' - p)(1+cx)dx \\ &- 2cdx_t \int_0^b (p'' - p)(1+cx)dx \\ &+ p'dx_t - p''dx_t, \quad (14.8) \end{aligned}$$

where dx_t is the differential change in the position of the surface of tension in the positive x direction. We note however, that only the first two terms in this expression will survive, since the sum of the next two terms will be zero in accordance with (12.7), and the remaining terms will cancel in accordance with the expressions for σ given by the first line of (13.1) and by (13.2).

Hence, substituting the expression for dp , given by our lemma (14.7), we now obtain

$$d\sigma = \int_{-a}^0 [(S_v' - S_v)dT + (\gamma' - \gamma)d\mu](1+cx)^2 dx + \int_0^b [(S_v'' - S_v)dT + (\gamma'' - \gamma)d\mu](1+cx)^2 dx. \quad (14.9)$$

And, finally, noting the definition of surface densities given by (6.8) in terms of the differences between the actual values of quantities and those computed on the basis of completely homogeneous distributions, as discussed in Section 3, we now see that we can rewrite this equation in the form

$$-d\sigma = S_s dT + \Gamma d\mu, \quad (14.10)$$

which for a one-component system agrees with the Gibbs expression (6.9) connecting the changes in σ , T , and μ with the superficial densities S_s and Γ for entropy and mass of the single component, calculated for the surface of tension. This completes our illustration of the use of the more detailed treatment to derive, for the special case treated, important results which can also be derived by the certainly valid methods of Gibbs.

15. Possibilities for Detailed Treatments of Transition Layers

In bringing this article to its conclusion, two further points need discussion. In the present section we discuss the general possibilities for giving detailed treatment to transition layers. And in the following section we consider the validity of the particular treatment that we have given.

First of all it may again be emphasized as in Section 7 that the thermodynamic treatment of Gibbs was developed, presumably purposely, in such a manner as to reduce detailed consideration of the structure of the transition layer to the minimum essential for the treatment, namely, to the bare assumption that all the properties of the transition layer would be determined by the area and curvature of an idealized geometrical dividing surface. This has the advantage that the results of the treatment have a wide range of applicability without reference to the structure

of the transition layer. It also carries, however, the concomitant disadvantage that such a treatment provides less physical insight into underlying mechanisms, and less theoretical foundation for calculating the values of parameters needed for specific application than we might like to have and be able to procure. Hence, it is also appropriate to be interested in more detailed treatments.

For purposes of discussion, we may roughly distinguish three methods of giving more detailed treatment to transition layers: firstly by the application of simple mechanical principles to the behavior of particles in the neighborhood of a boundary between phases, secondly by the application of the usual principles of thermodynamics to the infinitesimal portions of fluid composing a transition layer as has been essayed in the foregoing, and thirdly by application of the full methods of modern statistical mechanics to a study of the average behavior of matter at points within the transition layer.

The application of simple mechanical principles to particles in the neighborhood of a boundary between phases has a long past history which includes the original theoretical work of Young, Laplace, Gauss, and Poisson and later work of more recent investigators. Their treatments were carried out on the assumption of the existence of short-range forces between neighboring particles, and led to the general idea of a resultant "surface tension," and to correct conclusions as to the constancy of angle of contact between solids and liquids, and as to the equilibrium shapes of boundary surfaces.

The application of thermodynamics to the infinitesimal portions of fluid composing a transition layer has not usually been carried out in the past in any systematic manner, but has consisted in the qualitative use of thermodynamic terms such as pressure, temperature, and energy density in giving a rough description of the internal character of the transition layer. As an example we may mention the treatment given by J. Rice¹⁰ in the well-known volume of commentaries on the work of Gibbs, to the question of the location of the surface of tension within the

¹⁰ See article *L* by J. Rice in *A Commentary on the Scientific Writings of J. Willard Gibbs* (Yale University Press, New Haven, 1936), Vol. I, pp. 529-533.

transition layer. By ascribing a definite thickness ζ to the transition layer, and assuming that σ represents a surface energy per unit area which is actually uniformly distributed throughout the layer so defined, he comes to the conclusion that the surface of tension would lie midway at the distance $\zeta/2$ from his two postulated boundaries. It is evident, however, that such an analysis is inadequate¹¹ and leads to a result not in agreement with our Eq. (12.7). It is hoped that the systematic thermodynamic analysis of the transition layer attempted in this article will prove a useful step in the understanding of surface phenomena.

The application of the full methods of modern statistical mechanics to a study of the transition layers between phases must be regarded as an ultimate goal of great importance. Indeed, as will be mentioned again later, detailed thermodynamic treatments of the transition layer, of the kind that we have given, can in some ways be regarded as temporary procedures which may receive further justification and extension from the later application of statistical methods. Nevertheless, it is apparent that many complexities and difficulties stand at present in the way of such a development. Some steps in the direction of applying statistical mechanics to the transition region have already been taken by Fowler and Guggenheim,¹² where the existence of difficulties is well illustrated by the many simplifying approximations which they have had to introduce, including, finally, the assumption that the molecular densities at the boundary between a liquid and vapor phase would have strictly constant values right up to a geometrical surface of sharp discontinuity.

16. Validity of Detailed Treatment

We must now inquire specially into the validity of applying usual thermodynamic methods in treating the distribution of fluid in a thin transition layer, as was done in developing the detailed treatment of Part II. This is important, since it is planned to make later use of the con-

sequences of the treatment as given by Eqs. (12.6) and (12.7).

We have ample empirical justification for applying the usual methods of thermodynamics to a distribution of fluid in an external field of force, when the distribution is sufficiently uniform and the external forces are of such an origin that we can treat the system as composed of substantially homogeneous macroscopic elements, having dimensions large enough to cover many intermolecular distances, but at the same time also small enough to make the internal condition of the fluid and the intensity of the external force acting on it sensibly constant throughout any element. It is natural to feel the need of further inquiry, however, when we apply these same methods to a situation where the average condition of the molecules composing the fluid must be regarded as changing by substantial amounts within distances of the order of the separation between molecules, and the average forces acting on them must be regarded as resulting from the short-range influence of neighboring molecules.

To make the problem specific, let us return to the fundamental equation (10.3) on which we have based our detailed treatment of the transition layer,

$$\psi + \frac{p}{\gamma} + \phi = \text{const.} \quad (16.1)$$

In the first place, we may then inquire what meaning can be ascribed to the macroscopic quantities, ψ , p , γ , and ϕ , occurring in this equation when we apply it to microscopic layers of fluid in the transition region which have a thickness only of the same order as that of the distance between molecules. In the second place, we may inquire what justification there is for regarding the equation as still valid when applied to such microscopic regions. We can only make a few remarks on these points.

With regard to the meaning of the quantities in (16.1), it is clear that such quantities find their first entrance into theory as macroscopic thermodynamic variables having values which can be directly determined by large-scale measurements. Nevertheless, since it is well known in the case of large-scale systems that the values of such macroscopic variables can be given

¹¹ Note remarks made in footnote 4 as to the unsatisfactory character of the treatment given by Rice.

¹² R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, Teddington, 1939), pp. 445-450.

a statistical mechanical interpretation as the average values of appropriate microscopic quantities of molecular character, it can be hoped that a similar interpretation will be possible in the case of microscopic portions of a system. Thus, it might be natural to begin by taking the quantity γ , at any point x in the transition layer, as the time average of the density of fluid at that point, and then proceed by assigning to p and ψ the values of pressure and of free energy per gram which would be exhibited by fluid in bulk at the density γ and at the temperature of interest. The interpretation of ϕ presents more difficulty, since it involves some kind of successful distinction between very short-range molecular forces which depend on the immediate local condition of the fluid and only slightly longer range molecular forces which depend on the change in condition with position. It would seem reasonable, however, to expect that ϕ could be interpreted as an appropriate average of that part of the energy per gram at any

point, which depends on the derivatives of γ with respect to x .

With regard to the validity of (16.1), it seems rational for the present to extend the application of this macroscopically verified equation to microscopic regions, and for the future to expect that such an extension will find added statistical mechanical support, substituting appropriate averages of the kind suggested above into the equation. In addition, we may again call attention to the successful use of the consequences of (16.1) to derive, at least for a special case, significant results which can also be derived by the method of Gibbs. This outcome can, of course, not be taken as a sufficient criterion for the validity of (16.1) but can nevertheless increase our confidence therein.

For the time being, it would seem a sensible procedure to make tentative use of the consequences of our detailed treatment when we need them to supplement the consequences of the less detailed treatment of Gibbs.

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Ionization Processes on Tungsten Filaments

I. The Electron Affinity of the Oxygen Atom*

MAX METLAY^{††} AND GEORGE E. KIMBALL

Department of Chemistry, Columbia University, New York, New York

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The electron affinity of the oxygen atom was determined to be 53.8 ± 0.8 kcal./mole by measuring the ratio of ions to electrons leaving a hot tungsten filament in contact with nitrous oxide gas at a low pressure. Previous investigations of this quantity yielded discordant results. A possible reason for this disagreement is set forth.

INTRODUCTION

DIRECT experimental determinations of the electron affinity of the oxygen atom have

been made by Vier and Mayer,¹ Lozier,² and Hanson.³ These workers obtained, respectively, values of 70.8 ± 2 , 51 ± 5 , and 46 ± 9 kcal./mole. This investigation was undertaken in an attempt to resolve these differences. The method used,

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^{††} Present address: Northwestern University, Evanston, Ill.

¹ D. T. Vier and J. E. Mayer, *J. Chem. Phys.* **12**, 28 (1944).

² W. Lozier, *Phys. Rev.* **46**, 268 (1934).

³ G. Hanson, *Phys. Rev.* **48**, 476 (1935).