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<thead>
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<th>Title</th>
<th>On the equilibrium of heterogeneous substances / by J. Willard Gibbs ; abstract by the author.</th>
</tr>
</thead>
<tbody>
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ON THE EQUILIBRIUM OF HETEROGENEOUS SUBSTANCES

By J. Willard Gibbs.* Abstract by the author.

It is an inference naturally suggested by the general increase of entropy which accompanies the changes occurring in any isolated material system that when the entropy of the system has reached a maximum, the system will be in a state of equilibrium. Although this principle has by no means escaped the attention of physicists, its importance does not appear to have been duly appreciated. Little has been done to develop the principle as a foundation for the general theory of thermodynamic equilibrium.

The principle may be formulated as follows, constituting a criterion of equilibrium:

I. For the equilibrium of any isolated system it is necessary and sufficient that in all possible variations of the state of the system which do not alter its energy, the variation of its entropy shall either vanish or be negative.

The following form, which is easily shown to be equivalent to the preceding, is often more convenient in application:

II. For the equilibrium of any isolated system it is necessary and sufficient that in all possible variations of the state of the system which do not alter its entropy, the variation of its energy shall either vanish or be positive.

If we denote the energy and entropy of the system by \( \varepsilon \) and \( \eta \) respectively, the criterion of equilibrium may be expressed by either of the formulas

\[
\begin{align*}
(\delta \eta)_\varepsilon & \leq 0, \\
(\delta \varepsilon)_\eta & \geq 0.
\end{align*}
\]

Again, if we assume that the temperature of the system is uniform, and denote its absolute temperature by \( t \), and set

\[ \phi = \varepsilon - t \eta, \]

the remaining conditions of equilibrium may be expressed by the formula

\[
(\delta \phi)_t \geq 0,
\]

the suffixed letter, as in the preceding cases, indicating that the quantity which it represents is constant. This condition, in connection with that of uniform temperature, may be shown to be equivalent to (1) or (2). The difference of the values of \( \phi \) for two different states of the system which have the same temperature represents the work which would be expended in bringing the system from one state to the other by a reversible process and without change of temperature.

The system is incapable of thermal changes, like the systems considered in theoretical mechanics, we may regard the entropy as having the constant value zero. Conditions (3) and (4) may then be written
\[ \delta S = 0, \quad \delta \phi = 0. \]
and are obviously identical in significance, since in this case \( \phi = z. \)

Conditions (2) and (4), as criteria of equilibrium, may therefore both be regarded as extensions of the criteria employed in ordinary states to the more general case of a thermodynamic system. In fact, each of the quantities \( a = - \partial S/\partial q \) (relating to a system without sensible motion) may be regarded as a kind of force-function for the system—\( z, \) the larger as the force-function for constant entropy, \( n, \) when only such states of the system are considered, have the same entropy, and the latter as the force-function for constant temperature, \( n, \) when only such states of the system are considered, have the same uniform temperature.

In the deduction of the particular conditions of equilibrium for any system, the general formula (4) has an evident advantage over (1) or (2) in respect to the brevity of the processes of reduction, since the limitation of constant temperature applies to every part of the system taken separately, and diminishes by one the number of independent variations in the state of those parts which we have to consider. Moreover, the transition from the systems considered in ordinary mechanics to thermodynamic systems is most naturally made by this formula, since it has always been customary to apply the principles of theoretical mechanics to real systems on the assumption (more or less distinctly conceived and expressed) that the temperature of the system remains constant, the mechanical properties of a thermodynamic system maintained at a constant temperature being such as might be imagined to belong to a purely mechanical system, and admitting of representation by a force-function, as follows directly from the fundamental laws of thermodynamics.

Note: Understanding these considerations, the author has preferred in general to use condition (2) as the criterion of equilibrium, believing that it would be useful to exhibit the conditions of equilibrium of thermodynamic systems in connection with those quantities which are most simple and most general in their definitions, and which appear most important in the general theory of such systems. The slightly different form in which the subject would develop itself, if condition (4) had been chosen as a point of departure instead of (2), is occasionally indicated.

Equilibrium of masses in contact.—The first problem to which the criterion is applied is the determination of the conditions of equilibrium for different masses in contact, when influenced by gravity, electricity, distortion of the solid masses, or capillary tensions. The statement of the result is facilitated by the following definition.

If to any homogeneous mass in a state of hydrostatic stress we suppose an infinitesimal quantity of any substance to be added, the mass remaining homogeneous and its entropy and volume remaining unchanged, the increase of the energy of the mass divided by the quantity of the substance added is the potential for that substance in the mass considered.

In addition to equality of temperature and pressure in the masses in contact, it is necessary for equilibrium that the potential for every substance which is an independently variable component of any of the different masses shall have the same value in all of which it is such a component, so far as they are in contact with one another. But if a substance, without being an actual component of a certain mass in the given state of the system, is capable of being absorbed by it, it is sufficient if the value of the potential for that substance in that mass is not less than in any contiguous mass of which the substance is an actual component. We may regard these conditions as sufficient for equilibrium with respect to infinitesimal variations in the composition and thermodynamic state of the different masses in contact. There are certain other conditions which relate to the possible formation of masses entirely different in composition or state from any initially existing. These conditions are best regarded as determining the stability of the system, and will be mentioned under that head.

Anything which restrains the free movement of the component substances, or of the masses as such, may diminish the number of conditions which are necessary for equilibrium.

Equilibrium of static forces.—If we suppose two fluid masses to be separated by a diaphragm which is permeable to some of the component substances and not others, of the conditions of equilibrium which have just been mentioned, those will still subsist which relate to temperature and the potentials for the substance in which the diaphragm is permeable, but those relating to the potentials for the substance to which the diaphragm is impervious will no longer be necessary. Whether the pressure must be the same in the two fluids will depend upon the rigidity of the diaphragm. Even when the diaphragm is permeable to all the components without restriction, equality of pressure in the two fluids is not always necessary for equilibrium.
Effect of gravity.—In a system subject to the action of gravity, the potential for each substance, instead of having a uniform value throughout the system, as far as the substance actually occurs as an independently variable component, will decrease uniformly with increasing height, the difference of its values at different levels being equal to the difference of level multiplied by the force of gravity.

Fundamental equations.—Let \( \xi, \eta, \theta, \pi \) and \( \mu \) denote respectively the energy, entropy, volume, absolute temperature, and pressure of a homogeneous mass which may be either fluid or solid, provided that it is subject only to hydrostatic pressure, and let \( m, m_2, \ldots, m_m \) denote the quantities of the independently variable components, and \( \mu_m, \mu_{m_2}, \ldots, \mu_m \) the potentials for these components. It is easily shown that \( \mu \) is a function of \( m, m_2, \ldots, m_m \) and that the complete value of \( \mu \) is given by the equation

\[
\mu = \xi - \eta = \eta + \mu_m + \mu_{m_2} + \ldots + \mu_m m_m
\]

(6)

Now if \( \xi \) is known in terms of \( \xi, m, m_2, \ldots, m_m \) we can obtain by differentiation \( \xi = \mu, \mu_2, \ldots, \mu_m \) in terms of the same variables. This will make \( \xi + 3 \) independent known relations between the \( 2n + 3 \) variables \( \xi, \eta, \mu, \mu_2, \ldots, \mu_m \). These are all that exist, for of these variables \( n + 2 \) are evidently independent. Now upon these relations depend a very large class of the properties of the compound considered,—we may say in general, all its thermal, chemical, and physical properties, so far as active tendencies are concerned, in case in which the form of the mass does not require consideration. A single equation from which all these relations may be deduced may be called a fundamental equation. An equation between \( \xi, \eta, m, m_2, \ldots, m_m \) is a fundamental equation. But there are other equations which possess the same property.

If we suppose the quantity \( \xi \) to be determined for such a mass as we are considering by equation (6), we may obtain by differentiation and comparison with (5)

\[
\eta = -\eta + \pi + \mu + \mu_m + \mu_{m_2} + \ldots + \mu_m m_m
\]

(8)

If then, \( \xi \) is known as a function of \( \xi, \rho, \eta, \mu, \mu_2, \ldots, \mu_m \) we can find \( \xi, \mu, \mu_2, \ldots, \mu_m \) in terms of the same variables.

If we then substitute for \( \xi \) in our original equation its value which takes from equation (6) we shall have again \( n + 3 \) independent relations between the same \( 2n + 3 \) variables as before.

Let

\[
\xi = \eta + \pi + \mu m_m
\]

(7)

then, by (6),

\[
\eta = -\eta + \pi + \mu m_m + \mu_{m_2} + \ldots + \mu_m m_m
\]

(9)

If, then, \( \xi \) is known as a function of \( \xi, \mu, \mu_2, \ldots, \mu_m \) we can find \( \xi, \mu, \mu_2, \ldots, \mu_m \) in terms of the same variables. By eliminating \( \xi \), we may obtain again \( n + 3 \) independent relations between the same \( 2n + 3 \) variables as at first.

If we integrate (5), (6) and (8), supposing the quantity of the compound substance considered to vary from zero to any finite value, its nature and state remaining unchanged, we obtain

\[
\xi = \xi + \pi + \mu m_m + \mu_{m_2} + \ldots + \mu_m m_m
\]

(9)

\[
\eta = \eta + \pi + \mu m_m + \mu_{m_2} + \ldots + \mu_m m_m
\]

(10)

\[
\mu = \mu + \mu m_m + \mu_{m_2} + \ldots + \mu_m m_m
\]

(11)

If we differentiate (9) in the most general manner, and compare with (10), we obtain

\[
\eta = \eta + \pi + \mu m_m + \mu_{m_2} + \ldots + \mu m_m
\]

(12)

or

\[
\eta = \eta + \pi + \mu m_m + \mu_{m_2} + \ldots + \mu m_m
\]

(13)

Hence, there is a relation between the \( n + 3 \) quantities \( \xi, \pi, \mu, \mu_2, \ldots, \mu_m \), which, if known, will enable us to find in terms of these quantities all the mass of the \( n + 2 \) quantities \( \xi, \pi, \mu, \mu_2, \ldots, \mu_m \). With (9), this will make \( n + 3 \) independent relations between the same \( 2n + 3 \) variables as at first.

Any equation, therefore, between the quantities

\[
\xi, \pi, \mu, \mu_2, \ldots, \mu_m
\]

or

\[
\xi, \xi, \eta, \mu, \mu_2, \ldots, \mu_m
\]

or

\[
\xi, \eta, \xi, \mu, \mu_2, \ldots, \mu_m
\]

or

\[
\xi, \eta, \xi, \mu, \mu_2, \ldots, \mu_m
\]

is a fundamental equation, and any such is entirely equivalent to any other.

Dissociated phase.—In considering the different homogeneous bodies which can be formed out of any set of component substances, it is convenient to have a term which shall refer solely to the composition and thermodynamic state of any such body without regard to its size or form. The word phase has been chosen for this purpose. Such bodies as differ in composition or state are called different phases of the matter considered, all

The properties of the quantities \( \rho, \pi, \mu, \mu_2, \ldots, \mu_m \) regarded as functions of the temperature and volume, and temperature and pressure, respectively, the composition of the body being regarded as inviolate, have been discussed by W. Thompson in a paper entitled "On the forces which sustain the structure and motion of the earth and its revenues" (Ann. Soc. Sci. Bruxelles, l. c.) in a brief sketch of his method as it is generally adopted to be given in Courbet's "Math. d'Astronm. et de Géod. des Flux Qu'ors par les fluxors," (Ann. Soc. Sci. Bruxelles, l. c.)
bodies which differ only in size and form being regarded as different examples of the same phase. Phases which can exist together, the dividing surface being plain, in an equilibrium which does not depend upon passive resistances to change, are called coexisting.

The number of independent variations of which a system of coexistent phases is capable is \( n + 2 - r \), where \( r \) denotes the number of phases, and \( n \) the number of independently variable components in the whole system. For the system of phases is completely specified by the temperatures, the pressure, and the \( n \) potentials, and between these \( n + 2 \) quantities there are \( n \) independent relations (one for each phase), which characterize the system of phases.

When the number of phases exceeds the number of components by unity, the system is capable of a single variation of phase. The pressure and all the potentials may be regarded as functions of the temperature. The determination of these functions depends upon the elimination of the proper quantities from the fundamental equations in \( p, T, \mu, \phi \), etc., for the several members of the system. But without a knowledge of these fundamental equations, the values of the differential co-efficients such as \( \frac{dp}{dT} \) may be expressed in terms of the entropies and volumes of the different bodies and the quantities of their several components. For this end we have only to eliminate the differentials of the potentials from the differential equations of the form (13) relating to the different bodies. In the simplest case, where there is but one component, we obtain the well-known formula

\[
\frac{d\phi}{dT} = \frac{\phi^2}{\phi_1^2} - \frac{p^2}{p_1^2}
\]

in which \( \phi^n, \phi^n, \phi^n, \phi^n \) denote the volumes and entropies of a given quantity of the substance in the two phases, and \( Q \) the heat which it absorbs in passing from one phase to the other.

It is easily shown that if the temperature of two coexistent phases of two components is maintained constant, the pressure is in general a maximum or minimum when the composition of the phases is identical. In like manner, if the pressure of the phases is maintained constant, the temperature is in general a maximum or minimum when the composition of the phases is identical. The series of simultaneous values of \( I \) and \( p \) for which the composition of two coexistent phases is identical are possible from those for which the composition of three coexistent phases is possible from those for which there are two pairs of coexistent phases.

If the temperature of three coexistent phases of three com-
eties which prevent the commencement of discontinuous changes. But a phase which is unstable with respect to continuous changes is evidently incapable of permanent existence on a large scale except in consequence of passive resistances to change. To obtain the conditions of stability with respect to continuous changes, we have only to limit the application of the variables in (14) to phases adjacent to the given phase. We obtain results of the following nature.

The stability of any phase with respect to continuous changes depends upon the same conditions with respect to the second and higher differential coefficients of the density of energy regarded as a function of the density of entropy and the densities of the several components, which would make the density of energy a minimum, if the necessary conditions with respect to the first differential coefficients were fulfilled.

Again, it is necessary and sufficient for the stability with respect to continuous changes of all the phases within any given limits, that within those limits the same conditions should be fulfilled with respect to the second and higher differential coefficients of the pressures regarded as a function of the temperature and the several potentials, which would make the pressure a minimum, if the necessary conditions with respect to the first differential coefficients were fulfilled.

The equation of the limits of stability with respect to continuous changes may be written:

\[
\begin{align*}
\left( \frac{d^2 p}{d \rho_1 d \rho_2} \right)_{\rho_3 \ldots \rho_n} &= 0, \quad \text{or} \quad \left( \frac{d^2 p}{d \rho_1 d \rho_2} \right)_{\rho_3 \ldots \rho_n} = 0, \quad (15)
\end{align*}
\]

where \( \rho_n \) denotes the density of the component specified or \( \rho_n = \rho \), It is in general immaterial to what component the suffix \( n \) is regarded as relating.

**Critical phase.**—The various phases of two coexistent phases are sometimes limited by the vanishing of the difference between them. Phases at which this occurs are called critical phases. A critical phase, like any other, is capable of \( n+1 \) independent variations, \( \rho \), \( \theta \), \( \phi \), the number of independently variable components. But when subject to the condition of remaining a critical phase, it is capable of only \( n \) independent variations. There are therefore two independent equations which characterize critical phases. These may be written:

\[
\begin{align*}
\left( \frac{d^2 \rho}{d \rho_1 d \rho_2} \right)_{\rho_3 \ldots \rho_n} &= 0, \quad \left( \frac{d^2 \rho}{d \rho_1 d \rho_2} \right)_{\rho_3 \ldots \rho_n} = 0, \quad (16)
\end{align*}
\]

It will be observed that the first of these equations is identical with the equation of the limit of stability with respect to continuous changes. In fact, stable critical phases are situated at that limit. They are also situated at the limit of stability with respect to discontinuous changes. These limits are in general distinct, but touch each other at critical phases.

**Geometrical illustration.**—In an earlier paper* the author has described a method of representing the thermodynamic properties of substances of invariable composition by means of surfaces. The volume, entropy, and energy of a constant quantity of the substance are represented by rectangular coordinates. This method corresponds to the first kind of fundamental equation described above. Any other kind of fundamental equation for a substance of invariable composition will suggest an analogous geometrical method. In the present paper, the method in which the coordinates represent temperature, pressure, and the potential, is briefly considered. But when the composition of the body is variable, the fundamental equations cannot be completely represented by any surface or finite number of surfaces. In the case of three components, if we regard the temperature and pressure as constant, as well as the total quantity of matter, the relations between \( z, m_1, m_2, m_3 \) may be represented by a surface in which the distance of a point from the plane sides of a triangular prism represents the quantities \( m_1, m_2, m_3 \), and the distance of the point from the base of the prism represents the quantity \( z \). In the case of two components, analogous relations may be represented by a plane curve. Such methods are especially useful for illustrating the combinations and separations of the components, and the changes in states of aggregation, which take place when the substances are exposed in varying proportions to the temperature and pressure considered.

**Fundamental equations of ideal gases and gas mixtures.**—From the physical properties which we attribute to ideal gases, it is easy to deduce their fundamental equations. The fundamental equation in \( x, p, v, \text{and} m \) is

\[
\frac{e^{\log \frac{c_0}{c_m}}}{c_m} = \frac{n}{m} - \frac{m}{n} + \log \frac{m}{n}
\]

that in \( x, p, v, \text{and} m \) is

\[
\phi = \log e + \log \left( \frac{e - 2 + \log c_0 + \log m} {c_0 - 2 + \log c_0 + \log m} \right)
\]

that in \( x, p, v, \text{and} m \) is

\[
\psi = \frac{m}{e} \left( \frac{e - 2 + \log c_0 + \log m} {c_0 - 2 + \log c_0 + \log m} \right)
\]

where \( e \) denotes the base of the Napierian system of logarithms. As for the other constants, \( e \) denotes the specific heat of the

gas at constant volume, a denotes the constant value of \( \frac{p}{v} \cdot \text{atm} \), \( R \) and \( \text{H} \) depend upon the nature of energy and entropy. The two last equations may be abbreviated by the use of different constants. The properties of fundamental equations mentioned above may result be verified in such case by differentiation.

The law of Dalton supposing a mixture of different gases affords a point of departure for the discussion of such mixtures and the establishment of their fundamental equations. It is found convenient to give the law the following form:

The pressure in a mixture of different gases is equal to the sum of the pressures of the different gases as existing with each of the same temperature and with the same volume of its potential.

A mixture of ideal gases which satisfies this law is called an ideal gas-mixture. Its fundamental equation in \( p, V, n, M, \) etc. is evidently of the form

\[
p = \sum \frac{N_i}{V_i} \quad (200)
\]

where \( \sum \) denotes addition with respect to the different components of the mixture. From this may be deduced other fundamental equations for ideal gas-mixtures. Thus in \( \phi, V, \varepsilon, m_i, \nu_i \)

\[
\phi = \sum \left( \frac{m_i}{V_i} + \frac{\varepsilon}{n_i} \right)
\]

The phase of dissipated energy of an ideal gas-mixture. When the components of a gas-mixture are so related that some of them can be formed out of others, although not necessarily in the gas-mixture itself at the temperature considered, there are certain phases of the gas-mixture which deserve special attention. These are the phases of dissipated energy, i.e., those phases in which the energy of the mass has the least value consistent with its entropy and volume. An atmosphere of such a phase could not furnish a source of mechanical power to any machine or chemical engine working within it, no other phases of the same matter might do. Nor can such phases be affected by any catalytic agent. A perfect catalytic agent would reduce any other phase of the gas-mixture to a phase of dissipated energy. The condition which the energy a minimum is that the potentials for the proximate components shall satisfy an equation similar to that which expresses the relation between the units of weight of those components. For example, if the components were hydrogen, oxygen and water, since one gram of hydrogen with eight grams of oxygen are chemically equivalent to nine grams of water, the potentials for those substances in a phase of dissipated energy must satisfy the relation

\[
\mu_1 + 8\mu_2 = 9\mu_3
\]

Gas-mixture with convertible components. The theory of the phases of dissipated energy of an ideal gas-mixture derives an especial interest from its possible application to the case of those gas-mixtures in which the chemical composition and condition of the components can take place in the gas-mixture itself, and actually does take place, so that the quantities of the proximate components are entirely determined by the quantities of a smaller number of ultimate components, with the temperature and pressure. These may be called gas-mixtures with convertible components. If the general laws of ideal gas-mixtures apply in any such case, it may easily be shown that the phases of dissipated energy are the only phases which can exist. We can form a fundamental equation which shall relate solely to these phases. For this end, we first form the equation in \( p, V, n, M, \) etc. for the gas-mixture, regarding its proximate components as not convertible. This equation will contain a potential for every proximate component of the gas-mixture. We then eliminate one (or more) of these potentials by means of the relations which exist between them in virtue of the convertibility of the components in which they relate, leaving the potentials which relate to those substances which naturally express the ultimate composition of the gas-mixture.

The validity of the results thus obtained depends upon the applicability of the laws of ideal gas-mixtures to cases in which chemical action takes place. Some of these laws are generally regarded as capable of such application, others are not so regarded. But it may be shown that in the very important case in which the components of a gas are convertible at certain temperatures, and not at others, the theory proposed may be established without other assumptions than such as are generally admitted.

It is, however, only by experiments upon gas-mixtures with convertible components, that the validity of any theory concerning them can be satisfactorily established.

The vapor of the pellucid of nitrogen appears to be a mixture of two different vapors, of one of which the molecular formula is double that of the other. If we suppose that the vapor conforms to the laws of an ideal gas-mixture in a state of dissipated energy, we may obtain an equation between the temperature, pressure, and density of the vapor, which exhibits a somewhat striking agreement with the results of experiment.

**Equilibrian of second order.**—The second paper commences with a discussion of the conditions of internal and external equilibrium for solids in contact with fluids with regard to all possible states of strain of the solids. These conditions are deduced by analytical processes from the general condition of
equilibrium (2). The condition of equilibrium which relates to the dissolving of the solid at a surface where it meets a fluid may be expressed by the equation

$$\mu = \frac{s + p\varepsilon}{\varepsilon}$$

(27)

where $s$, $p$, and $\varepsilon$ denote respectively the energy, entropy, volume, and mass of the solid, if it is homogeneous in nature and state of strain; otherwise, of any small portion which may be treated as such homogeneous, $p$, the potential in the fluid for the substance of which the solid consists, $\varepsilon$ the pressure in the fluid and therefore one of the principal pressures in the solid, and $s$ the temperature. It will be observed that when the pressure in the solid is isotropic, the second member of this equation represents the potential in the solid for the substance of which it consists (see (9)), and the condition reduces to the equality of the potential in the two masses, just as if it were a case of two fluids. But if the stresses in the solid are not isotropic, the value of the second member of the equation is not entirely determined by the nature and state of the solid, but has in general three different values (for the same solid at the same temperature, and in the same state of strain) corresponding to the three principal pressures in the solid. If a solid in the form of a right parallelepiped is subject to different pressures on its three pairs of opposite sides by fluids in which it is soluble, it is in general necessary for equilibrium that the composition of the fluids shall be different.

The fundamental equations which have been described above are limited in their application to solids, to the case in which the stresses in the solid are isotropic. An example of a more general form of fundamental equation for a solid is afforded by an equation between the energy and entropy of a given quantity of the solid, and the quantities which express its state of strain, or by an equation between $\mu$ (see (27)) as determined for a given quantity of the solid, the temperature, and the quantities which express the state of strain.

Equilibrium.—The solution of the problem which precedes may be regarded as a first approximation, in which the peculiar state of thermodynamic equilibrium about the surfaces of discontinuity is neglected. To take account of the condition of things at these surfaces, thefollowing method is used. Let us suppose that two homogeneous fluid masses are separated by a surface of discontinuity, i.e., by a very thin non-homogeneous film. Now we may imagine a state of things in which each of the homogeneous masses extends without variation of the densities of its several components, or of the densities of energy and entropy, quite up to a geometrical surface to be called the dividing surface (at which the masses meet). We may suppose this surface to be sensibly coincident with the physical surface of discontinuity. Now if we compare the actual state of things with the supposed state, there will be in the former the excess of the surface a certain (positive or negative) excess of energy, of entropy, and of each of the component substances. These quantities are denoted by $\sigma, \eta, n, \eta_0, n_0, \eta_1, n_1, \eta_2, n_2$, etc., and are treated as belonging to the surface. The $\sigma$ is used simply as a distinguishing mark, and must not be taken for an algebraic exponent.

It is shown that the conditions of equilibrium already obtained relating to the temperature and the potentials of the homogeneous masses are not affected by the surfaces of discontinuity, and that the complete value of $\sigma$ is given by the equation

$$\sigma = \mu + p\varepsilon \pm s + \eta_0 \varepsilon \pm n_0 \varepsilon \pm \eta_1 \varepsilon \pm n_1 \varepsilon, \pm \eta_2 \varepsilon \pm n_2 \varepsilon$$

(28)

in which $s$ denotes the area of the surface considered, $\varepsilon$ the temperature, $\mu, \eta, n, \eta_0, n_0, \eta_1, n_1, \eta_2, n_2$ etc., the potentials for the various components in the adjacent masses. It may be, however, that some of the components are found only at the surface of discontinuity, in which case the letter $p$ with the suffix relating to such a substance denotes, as the equation shows, the rate of increase of energy at the surface per unit of the substance added, when the entropy, the area of the surface, and the quantities of the other components are unchanged. The quantity $s$ we may regard as defined by the equation itself, or by the following, which is obtained by integration:

$$\sigma = \mu + p\varepsilon + \eta_0 \varepsilon + n_0 \varepsilon + \eta_1 \varepsilon + n_1 \varepsilon + \eta_2 \varepsilon + n_2 \varepsilon$$

(29)

There are terms relating to variations of the curvatures of the surface which might be added, but it is shown that we can give the dividing surface such a position as to make these terms vanish, and it is found convenient to regard its position as thus determined. It is always sensibly coincident with the physical surface of discontinuity. (Yet in treating of plane surfaces, this supposition in regard to the position of the dividing surface is unnecessary, and it is sometimes convenient to suppose that its position is determined by other considerations.)

With the aid of (28), the remaining condition of equilibrium for contiguous homogeneous masses is found, viz.: 

$$\sigma = \eta_0 \varepsilon + \eta_1 \varepsilon + \eta_2 \varepsilon$$

(30)

where $\mu, p, \eta$ denote the pressures in the two masses, and $\eta_0, \eta_1, \eta_2$ the principal curvatures of the surface. Since this equation has the same form as if we assumed equal $\sigma$ residing at the surface, the quantity $\sigma$ is called (as is usual) the superficial tension, and the dividing surface in the particular position above mentioned is called the surface of tension.
By differentiation of (24) and comparison with (23), we obtain
\[ \sigma = 1, \quad \rho, \quad \rho_{0}, \quad \rho_{1}, \quad \rho'_{0}, \quad \rho'_{1}, \quad \text{etc.}, \]
where \( \rho_{0}, \rho_{1}, \rho'_{0}, \rho'_{1}, \) etc. are written for \( \rho_{x}, \rho_{y}, \rho_{z}, \rho'_{x}, \rho'_{y}, \rho'_{z}, \) etc., and denote the superficial densities of entropy and of the various substances. We may regard \( \sigma \) as a function of \( x, \rho_{0}, \rho_{1}, \rho'_{0}, \rho'_{1}, \) etc., from which \( \sigma_{0}, \sigma_{1}, \sigma'_{0}, \sigma'_{1}, \) etc., may be determined in terms of the same variables. An equation between \( \sigma_{0}, \sigma_{1}, \rho_{0}, \rho_{1}, \) etc. may therefore be called a fundamental equation for the surface of discontinuity. The same may be said of an equation between \( x, \rho_{0}, \rho_{1}, \rho'_{0}, \rho'_{1}, \) etc.,

It is necessary for the stability of a surface of discontinuity that its tension shall be as small as that of any other surface which can exist between the same homogeneous masses with the same temperature and potentials. Under this condition, which relates to the nature of the surface of discontinuity, there are other conditions of stability, which relate to the possible motion of such surfaces. One of these is that the tension shall be positive. The others are of a less simple nature, depending upon the extent and form of the surface of discontinuity, and in general upon the whole system of which it is a part. The most simple case of a system with a surface of discontinuity is that of two coexisting phases separated by a spherical surface, the outer mass being of indefinite extent. When the interior mass and the surface of discontinuity are formed entirely of substances which are components of the surrounding mass, the equilibrium is always unstable, in other cases, the equilibrium may be stable. Thus, the equilibrium of a drop of water in an atmosphere of vapor is unstable, but may be made stable by the addition of a little salt. The analytical conditions which determine the stability or instability of the system are easily found, when the temperature and potentials of the system are regarded as known, as well as the fundamental equations for the interior mass and the surface of discontinuity.

The study of surfaces of discontinuity throws considerable light upon the subject of the stability of such phases of fluids as have a less pressure than other phases of the same components with the same temperature and potentials. Let the pressure of the phase of which the stability is to be questioned be denoted by \( p' \), and that of the other phase of the same temperature and potential by \( p'' \). A spherical mass of the second phase and of a radius determined by the equation
\[ \frac{2}{3} \pi r^3 = \frac{1}{2} (p'' - p'), \]
would be in equilibrium with a surrounding mass of the first phase. This equilibrium, as we have just seen, is unstable, when the surrounding mass is indefinitely extended. A spherical mass a little larger would tend to increase indefinitely. The work required to form such a spherical mass, by a reversible process, in the interior of an infinite mass of the other phase, is given by the equation
\[ W = \frac{1}{2} (p'' - p') r^2. \]

The term \( W \) represents the work spent in forming the surface, and the term \( (p'' - p') r^2 \) the work gained in forming the interior mass. The second of these quantities is always equal to two-thirds of the first. The value of \( W \) is therefore positive, and the phase is in a state of unstable, the quantity \( W \) furnishing a kind of measure of its stability. We may easily express the value of \( W \) in a form which does not involve any geometrical magnitudes, viz:
\[ W = \frac{16}{3} \pi r^4 \left( \frac{p'' - p'}{2} \right)^{1/3} \]
where \( p'', p' \) and \( \sigma \) may be regarded as functions of the temperature and potentials. It will be seen that the stability, thus measured, is infinite for an infinitesimal difference of pressure, but decreases very rapidly as the difference of pressures increases. These conclusions are all, however, practically limited to the case in which the value of \( r \), as determined by equation (27), is of sensible magnitude.

With respect to the somewhat similar problem of the stability of the surface of contact of two phases with respect to the formation of a new phase, the following results are obtained. Let the phases (supposed to have the same temperature and potentials) be denoted by \( A, B, \) and \( C \); their pressures by \( p_{A}, p_{B}, \) and \( p_{C} \), and the tensions of the three possible surfaces \( \sigma_{AB}, \sigma_{AC}, \sigma_{BC} \). If \( p_{B} \) is less than
\[ \sigma_{AB} + \sigma_{AC} + \sigma_{BC}, \]
there will be no tendency toward the formation of the new phase at the surface between \( A \) and \( B \). If the temperature or potentials are now varied until \( p_{B} \) is equal to the above expression, there are two cases to be distinguished. The tension \( \sigma_{AB} \) will be either equal to \( \sigma_{AC} + \sigma_{BC} \), or less. (A greater value could only relate to an unstable and therefore unusual surface.) If \( \sigma_{AB} = \sigma_{AC} + \sigma_{BC} \), a further variation of the temperature or potentials, making \( p_{B} \) greater than the above expression, would cause the phase \( C \) to be formed at the surface between \( A \) and \( B \). But if \( \sigma_{AB} < \sigma_{AC} + \sigma_{BC} \), the surface between \( A \) and \( B \) would remain stable, but with rapidly diminishing stability, after \( p_{B} \) has passed the limit mentioned.

The conditions of stability for a line, when several surfaces of discontinuity meet, with respect to the possible formation of
a new surface, are capable of a very simple expression. If the
surfaces A, B, C, D, meet along a line, it is necessary for equilibrium that their
tension and direction at any point of the line should be such
that a quadrilateral A, B, C, D may be formed with sides repre-
senting in direction and length the normals and tensions of
the respective surfaces. For the stability of the system with
reference to the possible formation of surfaces between A and
C, or between B and D, it is further necessary that the tensions
at A and C should be greater than the diagonals of and pD
respectively. The conditions of stability are entirely anal-
ogous in the case of a greater number of surfaces. For the
growth of a film at a line at which these surfaces of discontinuity meet,
the reader is referred to the original paper.

Laplace's Law. When a fluid exists in the form of a very
thin film between other fluids, the great inequality of its ex-
tension in different directions will give rise to certain peculiar
properties, even when its thickness is sufficient for its interior
properties, even when the fluid is of matter in mass. The most important
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The thickness of the film is reduced until the limit is reached at which the interior ceases to have
the properties of matter in mass. The elasticity of the film, which determines its stability with respect to extension and
contraction, does not vanish at this limit. But a certain kind
of instability will generally arise, in virtue of which inequal-
ties in the thickness of the film will tend to increase through
progression in the interior of the film. This probably leads to the
destruction of the film, in the case of most liquids. In a film
of soap-water, the kind of instability described seems to be
manifested in the breaking out of the black spots. But the
sudden diminution in thickness which takes place in parts of
the film is arrested by some unknown cause, possibly by vis-
cosity or gelatinous properties, so that the rupture of the film
does not necessarily follow.

Electromotive force. The conditions of equilibrium may be
modified by electromotive force. Of such cases a galvanic
or electrolytic cell may be regarded as the type. With respect to
the potentials for the ions and the electrical potential the fol-
lowing relation may be noticed:

\[
\delta \nu = (V - V')\sigma \alpha + \delta n d W + d W_{\text{m}}
\]
in which $ds$ denotes the increment of the intrinsic energy in the apparatus, $d\gamma$ the increment of entropy, $de$ the quantity of electricity which passes through it, $V'$ and $V''$ the electrical potentials in pieces of the same kind of metal connected with the anode and cathode respectively, $dW_o$ the work done by gravity, and $dW_p$ the work done by the pressures which act on the external surface of the apparatus. The term $dW_o$ may generally be neglected. The same is true of $dW_p$, when gases are not concerned. If no heat is supplied or withdrawn the term $t\lambda\gamma$ will vanish. But in the calculation of electromotive forces, which is the most important application of the equation, it is convenient and customary to suppose that the temperature is maintained constant. Now this term $t\lambda\gamma$, which represents the heat absorbed by the cell, is frequently neglected in the consideration of cells of which the temperature is supposed to remain constant. In other words, it is frequently assumed that neither heat or cold is produced by the passage of an electrical current through a perfect electro-chemical apparatus (except that heat which may be indefinitely diminished by increasing the time in which a given quantity of electricity passes), unless it be by processes of a secondary nature, which are not immediately or necessarily connected with the process of electrolysis.

That this assumption is incorrect is shown by the electromotive force of a gas battery charged with hydrogen and nitrogen, by the currents caused by differences in the concentration of the electrolyte, by electrodes of zinc and mercury in a solution of sulphate of zinc, by a priori considerations based on the phenomena exhibited in the direct combination of the elements of water or of hydrochloric acid, by the absorption of heat which M. Fayre has in many cases observed in a galvanic or electrolytic cell, and by the fact that the solid or liquid state of an electrode (at its temperature of fusion) does not affect the electromotive force.