PART - II

1877

[From the Transactions of the Connecticut Academy of Arts and Sciences,
Vol. III, Part 2.]

ON THE EQUILIBRIUM

OF

HETEROGENEOUS SUBSTANCES.

Second Part.

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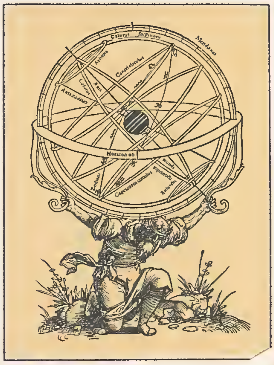

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On the Equilibrium of Heterogeneous Substances.

By J. Willard Gibbs.

(*Continued from page* 248).

THE CONDITIONS OF INTERNAL AND EXTERNAL EQUILIBRIUM FOR SOLIDS IN CONTACT WITH FLUIDS WITH REGARD TO ALL POSSIBLE STATES OF STRAIN OF THE SOLIDS.

In treating of the physical properties of a solid, it is necessary to consider its *state of strain.* A body is said to be *strained* when the relative position of its parts is altered, and by its *state of strain* is meant its state in respect to the relative position of its parts. We have hitherto considered the equilibrium of solids only in the case in which their state of strain is determined by pressures having the same values in all directions about any point. Let us now consider the subject without this limitation.

If x', y', z' are the rectangular co-ordinates of a point of a solid body in any completely determined state of strain, which we shall call the *state of reference*, and x, y, z, the rectangular co-ordinates of the same point of the body in the state in which its properties are the subject of discussion, we may regard x, y, z as functions of x', y', z', the form of the functions determining the second state of strain. For brevity, we may sometimes distinguish the variable state, to which x, y, z relate, and the constant state (state of reference), to which x', y', z' relate, as the *strained* and the *unstrained* states; but it must be remembered that these terms have reference merely to the change of form or *strain* determined by the functions which express the relations of x, y, z and x', y', z', and do not imply any particular physical properties in either of the two states, nor prevent their possible coincidence. The axes to which the co-ordinates x, y, z, and x', y', z' relate will be distinguished as the axes of X, Y, Z, and X', Y', Z'. It is not necessary, nor always convenient, to regard these systems of axes as identical, but they should be similar, i. e., capable of superposition.

The state of strain of any element of the body is determined by the values of the differential coefficients of x, y, and z with respect to x', y', and z'; for changes in the values of x, y, z, when the differential coefficients remain the same, only cause motions of translation of the body. When the differential coefficients of the first order do not vary sensibly except for distances greater than the radius of sensible molecular action, we may regard them as completely determining the state of strain of any element. There are nine of these differential coefficients, viz.,

$$\left.\begin{matrix} \frac{dx}{dx'}, & \frac{dx}{dy'}, & \frac{dx}{dz'}, \\ \frac{dy}{dx'}, & \frac{dy}{dy'}, & \frac{dy}{dz'}, \\ \frac{dz}{dx'}, & \frac{dz}{dy'}, & \frac{dz}{dz'}. \end{matrix}\right\} \qquad (354)$$

It will be observed that these quantities determine the orientation of the element as well as its strain, and both these particulars must be given in order to determine the nine differential coefficients. Therefore, since the orientation is capable of three independent variations, which do not affect the strain, the strain of the element, considered without regard to directions in space, must be capable of six independent variations.

The physical state of any given element of a solid in any unvarying state of strain is capable of one variation, which is produced by addition or subtraction of heat. If we write $\varepsilon_{V'}$ and $\eta_{V'}$ for the energy and entropy of the element divided by its volume in the state of reference, we shall have for any constant state of strain

$$\delta\varepsilon_{V'} = t\,\delta\eta_{V'}.$$

But if the strain varies, we may consider $\varepsilon_{V'}$ as a function of $\eta_{V'}$ and the nine quantities in (354), and may write

$$\begin{aligned} \delta\varepsilon_{V'} = t\,\delta\eta_{V'} &+ X_{X'}\,\delta\frac{dx}{dx'} + X_{Y'}\,\delta\frac{dx}{dy'} + X_{Z'}\,\delta\frac{dx}{dz'} \\ &+ Y_{X'}\,\delta\frac{dy}{dx'} + Y_{Y'}\,\delta\frac{dy}{dy'} + Y_{Z'}\,\delta\frac{dy}{dz'} \\ &+ Z_{X'}\,\delta\frac{dz}{dx'} + Z_{Y'}\,\delta\frac{dz}{dy'} + Z_{Z'}\,\delta\frac{dz}{dz'}, \end{aligned} \qquad (355)$$

where $X_{X'}, \ldots Z_{Z'}$ denote the differential coefficients of $\varepsilon_{V'}$ taken with respect to $\frac{dx}{dx'}, \ldots \frac{dz}{dz'}$. The physical signification of these quantities will be apparent, if we apply the formula to an element which in the state of reference is a right parallelopiped having the edges dx', dy', dz', and suppose that in the strained state the face in which x' has the smaller constant value remains fixed, while the opposite face is moved parallel to the axis of X. If we also suppose no heat to be imparted to the element, we shall have, on multiplying by $dx'\,dy'\,dz'$,

$$\delta\varepsilon_{V'}\,dx'\,dy'\,dz' = X_{X'}\,\delta\frac{dx}{dx'}\,dx'\,dy'\,dz'.$$

Now the first member of this equation evidently represents the work done upon the element by the surrounding elements; the second member must therefore have the same value. Since we must regard the forces acting on opposite faces of the elementary parallelopiped as equal and opposite, the whole work done will be zero except for the face which moves parallel to X. And since $\delta\frac{dx}{dx'}\,dx'$ represents the distance moved by this face, $X_{X'}\,dy'\,dz'$ must be equal to the component parallel to X of the force acting upon this face. In general, therefore, if by the positive side of a surface for which x' is constant we understand the side on which x' has the greater value, we may say that $X_{X'}$ denotes the component parallel to X of the force exerted by the matter on the positive side of a surface for which x' is constant upon the matter on the negative side of that surface per unit of the surface measured in the state of reference. The same may be said, *mutatis mutandis*, of the other symbols of the same type.

It will be convenient to use Σ and Σ' to denote summation with respect to quantities relating to the axes X, Y, Z, and to the axes X', Y', Z', respectively. With this understanding we may write

$$\delta\varepsilon_{V'} = t\,\delta\eta_{V'} + \Sigma\,\Sigma'\left(X_{X'}\,\delta\frac{dx}{dx'}\right). \tag{356}$$

This is the complete value of the variation of $\varepsilon_{V'}$ for a given element of the solid. If we multiply by $dx'\,dy'\,dz'$, and take the integral for the whole body, we shall obtain the value of the variation of the total energy of the body, when this is supposed invariable in substance. But if we suppose the body to be increased or diminished in substance at its surface (the increment being continuous in nature and state with the part of the body to which it is joined), to obtain the complete value of the variation of the energy of the body, we must add the integral

$$\int \varepsilon_{V'}\,\delta N'\,Ds'$$

in which Ds' denotes an element of the surface measured in the state of reference, and $\delta N'$ the change in position of this surface (due to the substance added or taken away) measured normally and outward in the state of reference. The complete value of the variation of the intrinsic energy of the solid is therefore

$$\int\int\int t\delta\eta_{V'}dx'dy'dz' + \int\int\int \Sigma\Sigma'\left(X_{X'}\delta\frac{dx}{dx'}\right)dx'dy'dz' + \int \varepsilon_{V'}\delta N'Ds'. \quad (357)$$

This is entirely independent of any supposition in regard to the homogeneity of the solid.

To obtain the conditions of equilibrium for solid and fluid masses in contact, we should make the variation of the energy of the whole equal to or greater than zero. But since we have already examined the conditions of equilibrium for fluids, we need here only seek the conditions of equilibrium for the interior of a solid mass and for the surfaces where it comes in contact with fluids. For this it will be necessary to consider the variations of the energy of the fluids only so far as they are immediately connected with the changes in the solid. We may suppose the solid with so much of the fluid as is in close proximity to it to be enclosed in a fixed envelop, which is impermeable to matter and to heat, and to which the solid is firmly attached wherever they meet. We may also suppose that in the narrow space or spaces between the solid and the envelop, which are filled with fluid, there is no motion of matter or transmission of heat across any surfaces which can be generated by moving normals to the surface of the solid, since the terms in the condition of equilibrium relating to such processes may be cancelled on account of the internal equilibrium of the fluids. It will be observed that this method is perfectly applicable to the case in which a fluid mass is entirely enclosed in a solid. A detached portion of the envelop will then be necessary to separate the great mass of the fluid from the small portion adjacent to the solid, which alone we have to consider. Now the variation of the energy of the fluid mass will be, by equation (13),

$$\int^{F} t\,\delta D\eta - \int^{F} p\,\delta Dv + \Sigma_1 \int^{F} \mu_1\,\delta Dm_1, \quad (358)$$

where $\int^{F}$ denotes an integration extending over all the elements of the fluid (within the envelop), and Σ_1 denotes a summation with regard to those independently variable components of the fluid of which the solid is composed. Where the solid does not consist of substances which are components, actual or possible (see page 117), of the fluid, this term is of course to be cancelled.

If we wish to take account of gravity, we may suppose that it acts in the negative direction of the axis of Z. It is evident that the variation of the energy due to gravity for the whole mass considered is simply

$$\int\int\int g\,\Gamma'\,\delta z\,dx'\,dy'\,dz', \quad (359)$$

where g denotes the force of gravity, and Γ' the density of the element in the state of reference, and the triple integration, as before, extends throughout the solid.

We have, then, for the general condition of equilibrium,

$$\int\int\int t\,\delta\eta_{V'}\,dx'\,dy'\,dz' + \int\int\int \Sigma\,\Sigma' \left(X_{X'}\,\delta\frac{dx}{dx'}\right) dx'\,dy'\,dz'$$
$$+ \int\int\int g\,\Gamma'\,\delta z\,dx'\,dy'\,dz' + \int \varepsilon_{V'}\,\delta N'\,Ds'$$
$$+ \int^{F} t\,\delta D\eta - \int^{F} p\,\delta Dv + \Sigma_1 \int^{F} \mu_1\,\delta Dm_1 \geqq 0. \qquad (360)$$

The equations of condition to which these variations are subject are: (1) that which expresses the constancy of the total entropy,

$$\int\int\int \delta\eta_{V'}\,dx'\,dy'\,dz' + \int \eta_{V'}\,\delta N'\,Ds' + \int^{F} \delta D\eta = 0; \qquad (361)$$

(2) that which expresses how the value of δDv for any element of the fluid is determined by changes in the solid,

$$\delta Dv = -(\alpha\,\delta x + \beta\,\delta y + \gamma\,\delta z)\,Ds - v_{V'}\,\delta N'\,Ds', \qquad (362)$$

where α, β, γ denote the direction cosines of the normal to the surface of the body in the state to which x, y, z relate, Ds the element of the surface in this state corresponding to Ds' in the state of reference, and $v_{V'}$ the volume of an element of the solid divided by its volume in the state of reference;

(3) those which express how the values of δDm_1, δDm_2, etc. for any element of the fluid are determined by the changes in the solid,

$$\left.\begin{aligned} \delta Dm_1 &= -\Gamma_1'\,\delta N'\,Ds', \\ \delta Dm_2 &= -\Gamma_2'\,\delta N'\,Ds', \\ \text{etc.,} & \end{aligned}\right\} \qquad (363)$$

where Γ_1', Γ_2', etc. denote the separate densities of the several components in the solid in the state of reference.

Now, since the variations of entropy are independent of all the other variations, the condition of equilibrium (360), considered with regard to the equation of condition (361), evidently requires that throughout the whole system

$$t = \text{const.} \qquad (364)$$

We may therefore use (361) to eliminate the first and fifth integrals from (360). If we multiply (362) by p, and take the integrals for the whole surface of the solid and for the fluid in contact with it, we obtain the equation

$$\int^{F} p\,\delta Dv = -\int p\,(\alpha\,\delta x + \beta\,\delta y + \gamma\,\delta z)\,Ds - \int p\,v_{V'}\,\delta N'\,Ds', \qquad (365)$$

by means of which we may eliminate the sixth integral from (360). If we add equations (363) multiplied respectively by μ_1, μ_2, etc., and take the integrals, we obtain the equation

$$\Sigma_1 \int^{\mathrm{F}} \mu_1 \delta D m_1 = -\int \Sigma_1 (\mu_1 \Gamma_1') \, \delta N' \, Ds', \tag{366}$$

by means of which we may eliminate the last integral from (360).

The condition of equilibrium is thus reduced to the form

$$\int\int\int \Sigma \, \Sigma' \left(X_{\mathrm{X'}} \, \delta \frac{dx}{dx'} \right) dx' \, dy' \, dz' + \int\int\int g \, \Gamma' \, \delta z \, dx' \, dy' \, dz'$$
$$+ \int \varepsilon_{\mathrm{V'}} \, \delta N' \, Ds' - \int t \, \eta_{\mathrm{V'}} \, \delta N' \, Ds' + \int p \, (\alpha \, \delta x + \beta \, \delta y + \gamma \, \delta z) \, Ds$$
$$+ \int p \, v_{\mathrm{V'}} \, \delta N' \, Ds' - \int \Sigma_1 \, (\mu_1 \Gamma_1') \, \delta N' \, Ds' \geqq 0, \tag{367}$$

in which the variations are independent of the equations of condition, and in which the only quantities relating to the fluids are p and μ_1, μ_2, etc.

Now by the ordinary method of the calculus of variations, if we write α', β', γ' for the direction-cosines of the normal to the surface of the solid in the state of reference, we have

$$\int\int\int X_{\mathrm{X'}} \, \delta \frac{dx}{dx'} \, dx' \, dy' \, dz'$$
$$= \int \alpha' \, X_{\mathrm{X'}} \, \delta x \, Ds' - \int\int\int \frac{dX_{\mathrm{X'}}}{dx'} \, \delta x \, dx' \, dy' \, dz', \tag{368}$$

with similar expressions for the other parts into which the first integral in (367) may be divided. The condition of equilibrium is thus reduced to the form

$$-\int\int\int \Sigma \, \Sigma' \left(\frac{dX_{\mathrm{X'}}}{dx'} \, \delta x \right) dx' \, dy' \, dz' + \int\int\int g \, \Gamma' \, \delta z \, dx' \, dy' \, dz'$$
$$+ \int \Sigma \, \Sigma' \, (\alpha' \, X_{\mathrm{X'}} \, \delta x) \, Ds' + \int p \, \Sigma \, (\alpha \, \delta x) \, Ds$$
$$+ \int [\varepsilon_{\mathrm{V'}} - t \, \eta_{\mathrm{V'}} + p \, v_{\mathrm{V'}} - \Sigma_1 \, (\mu_1 \Gamma_1')] \, \delta N' \, Ds' \geqq 0. \tag{369}$$

It must be observed that if the solid mass is not continuous throughout in nature and state, the surface-integral in (368), and therefore the first surface-integral in (369), must be taken to apply not only to the external surface of the solid, but also to every surface of discontinuity within it, and that with reference to each of the two masses separated by the surface. To satisfy the condition of equilibrium, as thus understood, it is necessary and sufficient that throughout the solid mass

$$\Sigma \, \Sigma' \left(\frac{dX_{\mathrm{X'}}}{dx'} \, \delta x \right) - g \, \Gamma' \, \delta z = 0; \tag{370}$$

that throughout the surfaces where the solid meets the fluid

$$Ds' \, \Sigma \, \Sigma' \, (\alpha' \, X_{\mathrm{X'}} \, \delta x) + Ds \, p \, \Sigma \, (\alpha \, \delta x) = 0, \tag{371}$$

and

$$[\varepsilon_{\mathrm{V'}} - t \, \eta_{\mathrm{V'}} + p \, v_{\mathrm{V'}} - \Sigma_1 (\mu_1 \Gamma_1')] \, \delta N' \geqq 0; \tag{372}$$

and that throughout the internal surfaces of discontinuity

$$\Sigma\,\Sigma'\,(\alpha' X_{X'}\,\delta x)_1 + \Sigma\,\Sigma'\,(\alpha' X_{X'}\,\delta x)_2 = 0, \tag{373}$$

where the suffixed numerals distinguish the expressions relating to the masses on opposite sides of a surface of discontinuity.

Equation (370) expresses the mechanical conditions of internal equilibrium for a continuous solid under the influence of gravity. If we expand the first term, and set the coefficients of δx, δy, and δz separately equal to zero, we obtain

$$\left.\begin{aligned} \frac{dX_{X'}}{dx'} + \frac{dX_{Y'}}{dy'} + \frac{dX_{Z'}}{dz'} &= 0, \\ \frac{dY_{X'}}{dx'} + \frac{dY_{Y'}}{dy'} + \frac{dY_{Z'}}{dz'} &= 0, \\ \frac{dZ_{X'}}{dx'} + \frac{dZ_{Y'}}{dy'} + \frac{dZ_{Z'}}{dz'} &= g\,\Gamma'. \end{aligned}\right\} \tag{374}$$

The first member of any one of these equations multiplied by $dx'\,dy'\,dz'$ evidently represents the sum of the components parallel to one of the axes X, Y, Z of the forces exerted on the six faces of the element $dx'\,dy'\,dz'$ by the neighboring elements.

As the state which we have called the state of reference is arbitrary, it may be convenient for some purposes to make it coincide with the state to which x, y, z relate, and the axes X', Y', Z' with the axes X, Y, Z. The values of $X_{X'}$, . . . $Z_{Z'}$ on this particular supposition may be represented by the symbols X_X, . . . Z_Z. Since

$$X_{Y'} = \frac{d\varepsilon_{V'}}{d\dfrac{dx}{dy'}}, \quad \text{and} \quad Y_{X'} = \frac{d\varepsilon_{V'}}{d\dfrac{dy}{dx'}},$$

and since, when the states x, y, z and x', y', z' coincide, and the axes X, Y, Z, and X', Y', Z', $d\dfrac{dx}{dy'}$ and $d\dfrac{dy}{dx'}$ represent displacements which differ only by a rotation, we must have

$$X_Y = Y_X, \tag{375}$$

and for similar reasons,

$$Y_Z = Z_Y, \qquad Z_X = X_Z. \tag{376}$$

The six quantities X_X, Y_Y, Z_Z, X_Y or Y_X, Y_Z or Z_Y, and Z_X or X_Z are called the *rectangular components of stress*, the three first being the *longitudinal stresses* and the three last the *shearing stresses.* The mechanical conditions of internal equilibrium for a solid under the influence of gravity may therefore be expressed by the equations

$$\left.\begin{aligned}\frac{dX_{\mathrm{X}}}{dx}+\frac{dX_{\mathrm{Y}}}{dy}+\frac{dX_{\mathrm{Z}}}{dz}&=0,\\ \frac{dY_{\mathrm{X}}}{dx}+\frac{dY_{\mathrm{Y}}}{dy}+\frac{dY_{\mathrm{Z}}}{dz}&=0,\\ \frac{dZ_{\mathrm{X}}}{dx}+\frac{dZ_{\mathrm{Y}}}{dy}+\frac{dZ_{\mathrm{Z}}}{dz}&=g\,\Gamma,\end{aligned}\right\}\qquad(377)$$

where Γ denotes the density of the element to which the other symbols relate. Equations (375), (376) are rather to be regarded as expressing necessary relations (when $X_{\mathrm{X}}, \ldots Z_{\mathrm{Z}}$ are regarded as internal forces determined by the state of strain of the solid) than as expressing conditions of equilibrium. They will hold true of a solid which is not in equilibrium,—of one, for example, through which vibrations are propagated,—which is not the case with equations (377).

Equation (373) expresses the mechanical conditions of equilibrium for a surface of discontinuity within the solid. If we set the coefficients of δx, δy, δz, separately equal to zero we obtain

$$\left.\begin{aligned}(\alpha' X_{\mathrm{X}'}+\beta' X_{\mathrm{Y}'}+\gamma' X_{\mathrm{Z}'})_1+(\alpha' X_{\mathrm{X}'}+\beta' X_{\mathrm{Y}'}+\gamma' X_{\mathrm{Z}'})_2&=0,\\ (\alpha' Y_{\mathrm{X}'}+\beta' Y_{\mathrm{Y}'}+\gamma' Y_{\mathrm{Z}'})_1+(\alpha' Y_{\mathrm{X}'}+\beta' Y_{\mathrm{Y}'}+\gamma' Y_{\mathrm{Z}'})_2&=0,\\ (\alpha' Z_{\mathrm{X}'}+\beta' Z_{\mathrm{Y}'}+\gamma' Z_{\mathrm{Z}'})_1+(\alpha' Z_{\mathrm{X}'}+\beta' Z_{\mathrm{Y}'}+\gamma' Z_{\mathrm{Z}'})_2&=0.\end{aligned}\right\}\qquad(378)$$

Now when the α', β', γ' represent the direction-cosines of the normal in the state of reference on the positive side of any surface within the solid, an expression of the form

$$\alpha' X_{\mathrm{X}'}+\beta' X_{\mathrm{Y}'}+\gamma' X_{\mathrm{Z}'} \qquad (379)$$

represents the component parallel to X of the force exerted upon the surface in the strained state by the matter on the positive side per unit of area measured in the state of reference. This is evident from the consideration that in estimating the force upon any surface we may substitute for the given surface a broken one consisting of elements for each of which either x' or y' or z' is constant. Applied to a surface bounding a solid, or any portion of a solid which may not be continuous with the rest, when the normal is drawn outward as usual, the same expression taken negatively represents the component parallel to X of the force exerted upon the surface (per unit of surface measured in the state of reference) by the interior of the solid, or of the portion considered. Equations (378) therefore express the condition that the force exerted upon the surface of discontinuity by the matter on one side and determined by its state of strain shall be equal and opposite to that exerted by the matter on the other side. Since

$$(\alpha')_1 = -(\alpha')_2, \qquad (\beta')_1 = -(\beta')_2, \qquad (\gamma')_1 = -(\gamma')_2,$$

we may also write

$$\left.\begin{array}{l}\alpha'(X_{X'})_1 + \beta'(X_{Y'})_1 + \gamma'(X_{Z'})_1 = \alpha'(X_{X'})_2 + \beta'(X_{Y'})_2 + \gamma'(X_{Z'})_2, \\ \text{etc.,}\end{array}\right\} \quad (380)$$

where the signs of α', β', γ' may be determined by the normal on either side of the surface of discontinuity.

Equation (371) expresses the mechanical condition of equilibrium for a surface where the solid meets a fluid. It involves the separate equations

$$\left.\begin{aligned} \alpha' X_{X'} + \beta' X_{Y'} + \gamma' X_{Z'} &= -\alpha p \frac{Ds}{Ds'}, \\ \alpha' Y_{X'} + \beta' Y_{Y'} + \gamma' Y_{Z'} &= -\beta p \frac{Ds}{Ds'}, \\ \alpha' Z_{X'} + \beta' Z_{Y'} + \gamma' Z_{Z'} &= -\gamma p \frac{Ds}{Ds'}, \end{aligned}\right\} \qquad (381)$$

the fraction $\frac{Ds}{Ds'}$ denoting the ratio of the areas of the same element of the surface in the strained and unstrained states of the solid. These equations evidently express that the force exerted by the interior of the solid upon an element of its surface, and determined by the strain of the solid, must be normal to the surface and equal (but acting in the opposite direction) to the pressure exerted by the fluid upon the same element of surface.

If we wish to replace α and Ds by α', β', γ', and the quantities which express the strain of the element, we may make use of the following considerations. The product $\alpha\, Ds$ is the projection of the element Ds on the Y-Z plane. Now since the ratio $\frac{Ds}{Ds'}$ is independent of the form of the element, we may suppose that it has any convenient form. Let it be bounded by the three surfaces $x' =$ const., $y' =$ const., $z' =$ const., and let the parts of each of these surfaces included by the two others with the surface of the body be denoted by L, M, and N, or by L', M' and N', according as we have reference to the strained or unstrained state of the body. The areas of L', M', and N' are evidently $\alpha' Ds'$, $\beta' Ds'$, and $\gamma' Ds'$; and the sum of the projections of L, M and N upon any plane is equal to the projection of Ds upon that plane, since L, M, and N with Ds include a solid figure. (In propositions of this kind the *sides* of surfaces must be distinguished. If the normal to Ds falls outward from the small solid figure, the normals to L, M, and N must fall inward, and *vice* *versa*). Now L' is a right-angled triangle of which the perpendicular sides may be called dy' and dz'. The projection of L on the Y-Z plane will be a triangle, the angular points of which are determined by the co-ordinates

$$y, \quad z; \quad y+\frac{dy}{dy'}dy', \quad z+\frac{dz}{dy'}dy'; \quad y+\frac{dy}{dz'}dz', \quad z+\frac{dz}{dz'}dz';$$

the area of such a triangle is

$$\tfrac{1}{2}\left(\frac{dy}{dy'}\frac{dz}{dz'}-\frac{dz}{dy'}\frac{dy}{dz'}\right)dy'\,dz',$$

or, since $\frac{1}{2}\,dy'\,dz'$ represents the area of L',

$$\left(\frac{dy}{dy'}\frac{dz}{dz'}-\frac{dz}{dy'}\frac{dy}{dz'}\right)\alpha'\,Ds'.$$

(That this expression has the proper sign will appear if we suppose for the moment that the strain vanishes.) The areas of the projections of M and N upon the same plane will be obtained by changing y', z' and α' in this expression into z', x', and β', and into x', y', and γ'. The sum of the three expressions may be substituted for $\alpha\,Ds$ in (381).

We shall hereafter use Σ' to denote the sum of the three terms obtained by rotary substitutions of quantities relating to the axes X', Y', Z', (i. e., by changing x', y', z' into y', z', x', and into z', x', y', with similar changes in regard to α', β', γ', and other quantities relating to these axes,) and Σ to denote the sum of the three terms obtained by similar rotary changes of quantities relating to the axes X, Y, Z. This is only an extension of our previous use of these symbols.

With this understanding, equations (381) may be reduced to the form

$$\left.\begin{array}{l}\Sigma'(\alpha' X_{X'}) + p\,\Sigma'\left\{\alpha'\left(\dfrac{dy}{dy'}\dfrac{dz}{dz'}-\dfrac{dz}{dy'}\dfrac{dy}{dz'}\right)\right\} = 0,\\ \text{etc.}\end{array}\right\} \qquad (382)$$

The formula (372) expresses the additional condition of equilibrium which relates to the dissolving of the solid, or its growth without discontinuity. If the solid consists entirely of substances which are actual components of the fluid, and there are no passive resistances which impede the formation or dissolving of the solid, $\delta N'$ may have either positive or negative values, and we must have

$$\varepsilon_{V'} - t\,\eta_{V'} + p\,v_{V'} = \Sigma_1(\mu_1\Gamma_1'). \qquad (383)$$

But if some of the components of the solid are only possible components (see page 117) of the fluid, $\delta N'$ is incapable of positive values, as the quantity of the solid cannot be increased, and it is sufficient for equilibrium that

$$\varepsilon_{V\prime} - t\,\eta_{V\prime} + p_{V\prime} \leqq \Sigma_1 (\mu_1 \Gamma_1'). \tag{384}$$

To express condition (383) in a form independent of the state of reference, we may use ε_V, η_V, Γ_1, etc., to denote the densities of energy, of entropy, and of the several component substances in the *variable* state of the solid. We shall obtain, on dividing the equation by $v_{V\prime}$,

$$\varepsilon_V - t\,\eta_V + p = \Sigma_1 (\mu_1 \Gamma_1). \tag{385}$$

It will be remembered that the summation relates to the several components of the solid. If the solid is of uniform composition throughout, or if we only care to consider the contact of the solid and the fluid at a single point, we may treat the solid as composed of a single substance. If we use μ_1 to denote the potential for this substance in the fluid, and Γ to denote the density of the solid in the variable state, (Γ', as before denoting its density in the state of reference,) we shall have

$$\varepsilon_{V\prime} - t\,\eta_{V\prime} + p\,v_{V\prime} = \mu_1 \Gamma', \tag{386}$$

and

$$\varepsilon_V - t\,\eta_V + p = \mu_1 \Gamma. \tag{387}$$

To fix our ideas in discussing this condition, let us apply it to the case of a solid body which is homogeneous in nature and in state of strain. If we denote by ε, η, v, and m, its energy, entropy, volume, and mass, we have

$$\varepsilon - t\,\eta + p\,v = \mu_1\, m. \tag{388}$$

Now the mechanical conditions of equilibrium for the surface where a solid meets a fluid require that the traction upon the surface determined by the state of strain of the solid shall be normal to the surface. This condition is always satisfied with respect to three surfaces at right angles to one another. In proving this well known proposition, we shall lose nothing in generality, if we make the state of reference, which is arbitrary, coincident with the state under discussion, the axes to which these states are referred being also coincident. We shall then have, for the normal component of the traction per unit of surface across any surface for which the direction-cosines of the normal are α, β, γ, [compare (379), and for the notation X_X, etc., page 349,]

$$S = \alpha(\alpha X_X + \beta X_Y + \gamma X_Z)$$
$$+ \beta(\alpha Y_X + \beta Y_Y + \gamma Y_Z)$$
$$+ \gamma(\alpha Z_X + \beta Z_Y + \gamma Z_Z),$$

or, by (375), (376),

$$S = \alpha^2 X_X + \beta^2 Y_Y + \gamma^2 Z_Z$$
$$+ 2\,\alpha\,\beta\,X_Y + 2\,\beta\,\gamma\,Y_Z + 2\,\gamma\,\alpha\,Z_X. \tag{389}$$

We may also choose any convenient directions for the co-ordinate axes. Let us suppose that the direction of the axis of X is so chosen that the value of S for the surface perpendicular to this axis is as great as for any other surface, and that the direction of the axis of Y (supposed at right angles to X) is such that the value of S for the surface perpendicular to it is as great as for any other surface passing through the axis of X. Then, if we write $\frac{dS}{d\alpha}, \frac{dS}{d\beta}, \frac{dS}{d\gamma}$ for the differential coefficients derived from the last equation by treating α, β, and γ as *independent* variables,

$$\frac{dS}{d\alpha}d\alpha + \frac{dS}{d\beta}d\beta + \frac{dS}{d\gamma}d\gamma = 0,$$

when

$$\alpha\,d\alpha + \beta\,d\beta + \gamma\,d\gamma = 0,$$

and

$$\alpha = 1, \qquad \beta = 0, \qquad \gamma = 0.$$

That is,

$$\frac{dS}{d\beta} = 0, \quad \text{and} \quad \frac{dS}{d\gamma} = 0,$$

when

$$\alpha = 1, \qquad \beta = 0, \qquad \gamma = 0.$$

Hence,

$$X_Y = 0, \quad \text{and} \quad Z_X = 0. \tag{390}$$

Moreover,

$$\frac{dS}{d\beta}d\beta + \frac{dS}{d\gamma}d\gamma = 0,$$

when

$$\alpha = 0, \qquad d\alpha = 0,$$
$$\beta\,d\beta + \gamma\,d\gamma = 0,$$

and

$$\beta = 1, \qquad \gamma = 0.$$

Hence

$$Y_Z = 0. \tag{391}$$

Therefore, when the co-ordinate axes have the supposed directions, which are called the *principal axes of stress*, the rectangular components of the traction across any surface (α, β, γ) are by (379)

$$\alpha\,X_X, \qquad \beta\,Y_Y, \qquad \gamma\,Z_Z. \tag{392}$$

Hence, the traction across any surface will be normal to that surface,—

(1), when the surface is perpendicular to a principal axis of stress;

(2), if two of the *principal tractions* X_X, Y_Y, Z_Z are equal, when the surface is perpendicular to the plane containing the two corresponding axes, (in this case the traction across any such surface is equal to the common value of the two principal tractions);

(3), if the principal tractions are all equal, the traction is normal and constant for all surfaces.

It will be observed that in the second and third cases the position of the principal axes of stress are partially or wholly indeterminate, (so that these cases may be regarded as included in the first,) but the values of the principal tractions are always determinate, although not always different.

If, therefore, a solid which is homogeneous in nature and in state of strain is bounded by six surfaces perpendicular to the principal axes of strain, the mechanical conditions of equilibrium for these surfaces may be satisfied by the contact of fluids having the proper pressures, [see (381),] which will in general be different for the different pairs of opposite sides, and may be denoted by p', p'', p'''. (These pressures are equal to the principal tractions of the solid taken negatively.) It will then be necessary for equilibrium with respect to the tendency of the solid to dissolve that the potential for the substance of the solid in the fluids shall have values μ_1', μ_1'', μ_1''' determined by the equations stress

$$\varepsilon - t\eta + p'v = \mu_1' m, \tag{393}$$

$$\varepsilon - t\eta + p''v = \mu_1'' m, \tag{394}$$

$$\varepsilon - t\eta + p'''v = \mu_1''' m. \tag{395}$$

These values, it will be observed, are entirely determined by the nature and state of the solid, and their differences are equal to the differences of the corresponding pressures divided by the density of the solid.

It may be interesting to compare one of these potentials, as μ_1', with the potential (for the same substance) in a fluid of the same temperature t and pressure p' which would be in equilibrium with the same solid subjected on all sides to the uniform pressure p'. If we write $[\varepsilon]_{p'}$, $[\eta]_{p'}$, $[v]_{p'}$, and $[\mu_1]_{p'}$ for the values which ε, η, v, and μ_1 would receive on this supposition, we shall have

$$[\varepsilon]_{p'} - t[\eta]_{p'} + p'[v]_{p'} = [\mu_1]_{p'} m. \tag{396}$$

Subtracting this from (393), we obtain

$$\varepsilon - [\varepsilon]_{p'} - t\eta + t[\eta]_{p'} + p'v - p'[v]_{p'} = \mu_1 m - [\mu_1]_{p'} m. \tag{397}$$

Now it follows immediately from the definitions of energy and entropy that the first four terms of this equation represent the work spent upon the solid in bringing it from the state of hydrostatic stress to the other state without change of temperature, and $p' v - p' [v]_{p'}$, evidently denotes the work done in displacing a fluid of pressure p' surrounding the solid during the operation. Therefore, the first number of the equation represents the total work done in bringing the solid *when surrounded by a fluid of pressure* p' from the state of hydrostatic stress p' to the state of stress p', p'', p'''. This quantity is necessarily positive, except of course in the limiting case when $p' = p'' = p'''$. If the quantity of matter of the solid body be unity, the increase of the potential in the fluid on the side of the solid on which the pressure remains constant, which will be necessary to maintain equilibrium, is equal to the work done as above described. Hence, $\mu_1{}'$ is greater than $[\mu_1]_{p'}$, and for similar reasons, $\mu_1{}''$ is greater than the value of the potential which would be necessary for equilibrium if the solid were subjected to the uniform pressure p'', and $\mu_1{}'''$ greater than that which would be necessary for equilibrium if the solid were subjected to the uniform pressure p'''. That is, (if we adapt our language to what we may regard as the most general case, viz., that in which the fluids contain the substance of the solid but are not wholly composed of that substance,) the fluids in equilibrium with the solid are all supersaturated with respect to the substance of the solid, except when the solid is in a state of hydrostatic stress; so that if there were present in any one of these fluids any small fragment of the same kind of solid subject to the hydrostatic pressure of the fluid, such a fragment would tend to increase. Even when no such fragment is present, although there must be perfect equilibrium so far as concerns the tendency of the solid to dissolve or to increase by the accretion of similarly strained matter, yet the presence of the solid which is subject to the distorting stresses, will doubtless facilitate the commencement of the formation of a solid of hydrostatic stress upon its surface, to the same extent, perhaps, in the case of an amorphous body, as if it were itself subject only to hydrostatic stress. This may sometimes, or perhaps generally, make it a necessary condition of equilibrium in cases of contact between a fluid and an amorphous solid which can be formed out of it that the solid at the surface where it meets the fluid shall be sensibly in a state of hydrostatic stress.

of Conti[illegible] crystalline structure

But in the case of a crystalline solid, subjected to distorting stresses and in contact with solutions satisfying the conditions deduced above, although crystals of hydrostatic stress would doubtless commence to form upon its surface (if the distorting stresses and consequent supersaturation of the fluid should be carried too far), before they would commence to be formed within the fluid or on the surface of most other bodies, yet within certain limits the relations expressed by equations (393)–(395) must admit of realization, especially when the solutions are such as can be easily supersaturated.*

It may be interesting to compare the variations of p, the pressure in the fluid which determines in part the stresses and the state of strain of the solid, with other variations of the stresses or strains in the solid, with respect to the relation expressed by equation (388). To examine this point with complete generality, we may proceed in the following manner.

Let us consider so much of the solid as has in the state of reference the form of a cube, the edges of which are equal to unity, and parallel to the co-ordinate axes. We may suppose this body to be homogeneous in nature and in state of strain both in its state of reference and in its variable state. (This involves no loss of generality, since we may make the unit of length as small as we choose.) Let the fluid meet the solid on one or both of the surfaces for which Z' is constant. We may suppose these surfaces to remain perpendicular to the axis of Z in the variable state of the solid, and the edges in which y' and z' are both constant to remain parallel to the axis of X. It will be observed that these suppositions only fix the position of the strained body relatively to the co-ordinate axes, and do not in any way limit its state of strain.

It follows from the suppositions which we have made that

$$\frac{dz}{dx'} = \text{const.} = 0, \quad \frac{dz}{dy'} = \text{const.} = 0, \quad \frac{dy}{dx'} = \text{const.} = 0; \quad (398)$$

and

$$X_{Z'} = 0, \quad Y_{Z'} = 0, \quad Z_{Z'} = -p\,\frac{dx}{dx'}\,\frac{dy}{dy'}. \quad (399)$$

Hence, by (355),

$$d\varepsilon_{V'} = t\,d\eta_{V'} + X_{X'}\,d\frac{dx}{dx'} + X_{Y'}\,d\frac{dx}{dy'} + Y_{Y'}\,d\frac{dy}{dy'} - p\,\frac{dx}{dx'}\,\frac{dy}{dy'}\,d\,\frac{dz}{dz'}. \quad (400)$$

Again, by (388),

* The effect of distorting stresses in a solid on the phenomena of crystallization and liquefaction, as well as the effect of change of hydrostatic pressure common to the solid and liquid, was first described by Professor James Thomson. See *Trans. R. S. Edin.*, vol. xvi, p. 575; and *Proc. Roy. Soc.*, vol. xi, p. 473, or *Phil. Mag.*, S. 4, vol. xxiv, p. 395.

$$d\varepsilon = t\,d\eta + \eta\,dt - p\,dv - v\,dp + m\,d\mu_1. \tag{401}$$

Now the suppositions which have been made require that

$$v = \frac{dx}{dx'}\,\frac{dy}{dy'}\,\frac{dz}{dz'}, \tag{402}$$

and

$$dv = \frac{dy}{dy'}\,\frac{dz}{dz'}\,d\frac{dx}{dx'} + \frac{dz}{dz'}\,\frac{dx}{dx'}\,d\frac{dy}{dy'} + \frac{dx}{dx'}\,\frac{dy}{dy'}\,d\frac{dz}{dz'}. \tag{403}$$

Combining equations (400), (401), and (403), and observing that $\varepsilon_{V'}$ and $\eta_{V'}$ are equivalent to ε and η, we obtain

$$\eta\,dt - v\,dp + m\,d\mu_1$$
$$= \left(X_{X'} + p\frac{dy}{dy'}\,\frac{dz}{dz'}\right)d\frac{dx}{dx'} + X_{Y'}d\frac{dx}{dy'} + \left(Y_{Y'} + p\,\frac{dz}{dz'}\,\frac{dx}{dx'}\right)d\frac{dy}{dy'}. \tag{404}$$

The reader will observe that when the solid is subjected on all sides to the uniform normal pressure p, the coefficients of the differentials in the second member of this equation will vanish. For the expression $\frac{dy}{dy'}\,\frac{dz}{dz'}$ represents the projection on the Y-Z plane of a side of the parallelopiped for which x' is constant, and multiplied by p it will be equal to the component parallel to the axis of X of the total pressure across this side, i. e., it will be equal to $X_{X'}$ taken negatively. The case is similar with respect to the coefficient of $d\frac{dy}{dy'}$; and $X_{Y'}$ evidently denotes a force tangential to the surface on which it acts. It will also be observed, that if we regard the forces acting upon the sides of the solid parallelopiped as composed of the hydrostatic pressure p together with addition forces, the work done in any infinitesimal variation of the state of strain of the solid by these additional forces will be represented by the second member of the equation.

We will first consider the case in which the fluid is identical in substance with the solid. We have then, by equation (97), for a mass of the fluid equal to that of the solid,

$$\eta_F\,dt - v_F\,dp + m\,d\mu_1 = 0, \tag{405}$$

η_F and v_F denoting the entropy and volume of the fluid. By subtraction we obtain

$$-(\eta_F - \eta)\,dt + (v_F - v)\,dp$$
$$= \left(X_{X'} + p\,\frac{dy}{dy'}\,\frac{dz}{dz'}\right)d\frac{dx}{dx'} + X_{Y'}\,d\frac{dx}{dy'} + \left(Y_{Y'} + p\,\frac{dz}{dz'}\,\frac{dx}{dx'}\right)d\frac{dy}{dy'}. \tag{406}$$

Now if the quantities $\frac{dx}{dx'}$, $\frac{dx}{dy'}$, $\frac{dy}{dy'}$ remain constant, we shall have for the relation between the variations of temperature and pressure which is necessary for the preservation of equilibrium

$$\frac{dt}{dp} = \frac{v_{\text{F}} - v}{\eta_{\text{F}} - \eta} = t\frac{v_{\text{F}} - v}{Q}, \tag{407}$$

where Q denotes the heat which would be absorbed if the solid body should pass into the fluid state without change of temperature or pressure. This equation is similar to (131), which applies to bodies subject to hydrostatic pressure. But the value of $\frac{dt}{dp}$ will not generally be the same as if the solid were subject on all sides to the uniform normal pressure p; for the quantities v and η (and therefore Q) will in general have different values. But when the pressures on all sides are normal and equal, the value of $\frac{dt}{dp}$ will be the same, whether we consider the pressure when varied as still normal and equal on all sides, or consider the quantities $\frac{dx}{dx'}$, $\frac{dx}{dy'}$, $\frac{dy}{dy'}$ as constant.

But if we wish to know how the temperature is affected if the pressure between the solid and fluid remains constant, but the strain of the solid is varied in any way consistent with this supposition, the differential coefficients of t with respect to the quantities which express the strain are indicated by equation (406). These differential coefficients all vanish, when the pressures on all sides are normal and equal, but the differential coefficient $\frac{dt}{dp}$, when $\frac{dx}{dx'}$, $\frac{dx}{dy'}$, $\frac{dy}{dy'}$ are constant, or when the pressures on all sides are normal and equal, vanishes only when the density of the fluid is equal to that of the solid.

The case is nearly the same when the fluid is not identical in substance with the solid, if we suppose the composition of the fluid to remain unchanged. We have necessarily with respect to the fluid

$$d\mu_1 = \left(\frac{d\mu_1}{dt}\right)^{(\text{F})}_{p,\,m} dt + \left(\frac{d\mu_1}{dp}\right)^{(\text{F})}_{t,\,m} dp,^* \tag{408}$$

where the index (F) is used to indicate that the expression to which it is affixed relates to the fluid. But by equation (92)

$$\left(\frac{d\mu_1}{dt}\right)^{(\text{F})}_{p,\,m} = -\left(\frac{d\eta}{dm_1}\right)^{(\text{F})}_{t,\,p,\,m}, \quad \text{and} \quad \left(\frac{d\mu_1}{dp}\right)^{(\text{F})}_{t,\,m} = \left(\frac{dv}{dm_1}\right)^{(\text{F})}_{t,\,p,\,m}. \tag{409}$$

Substituting these values in the preceding equation, transposing terms, and multiplying by m, we obtain

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* A suffixed m stands here, as elsewhere in this paper, for all the symbols m_1, m_2, etc., except such as may occur in the differential coefficient.

$$m\left(\frac{d\eta}{dm_1}\right)^{(F)}_{t,\,p,\,m} dt - m\left(\frac{dv}{dm_1}\right)^{(F)}_{t,\,p,\,m} dp + m\,d\mu_1 = 0. \qquad (410)$$

By subtracting this equation from (404) we may obtain an equation similar to (406), except that in place of η_F and v_F we shall have the expressions

$$m\left(\frac{d\eta}{dm_1}\right)^{(F)}_{t,\,p,\,m} \quad \text{and} \quad m\left(\frac{dv}{dm_1}\right)^{(F)}_{t,\,p,\,m}.$$

The discussion of equation (406) will therefore apply *mutatis mutandis* to this case.

We may also wish to find the variations in the composition of the fluid which will be necessary for equilibrium when the pressure p or the quantities $\frac{dx}{dx'}, \frac{dx}{dy'}, \frac{dy}{dy'}$ are varied, the temperature remaining constant. If we know the value for the fluid of the quantity represented by ζ on page 142 in terms of t, p, and the quantities of the several components m_1, m_2, m_3, etc., the first of which relates to the substance of which the solid is formed, we can easily find the value of μ_1 in terms of the same variables. Now in considering variations in the composition of the ~~solid~~, fluid it will be sufficient if we make all but one of the components variable. We may therefore give to m_1 a constant value, and making t also constant, we shall have

$$d\mu_1 = \left(\frac{d\mu_1}{dp}\right)^{(F)}_{t,\,m} dp + \left(\frac{d\mu_1}{dm_2}\right)^{(F)}_{t,\,p,\,m} dm_2 + \left(\frac{d\mu_1}{dm_3}\right)^{(F)}_{t,\,p,\,m} dm_3 + \text{etc.}$$

Substituting this value in equation (404), and cancelling the term containing dt, we obtain

$$\left\{ m\left(\frac{d\mu_1}{dp}\right)^{(F)}_{t,\,m} - v \right\} dp + m\left(\frac{d\mu_1}{dm_2}\right)^{(F)}_{t,\,p,\,m} dm_2$$
$$+ m\left(\frac{d\mu_1}{dm_3}\right)^{(F)}_{t,\,p,\,m} dm_3 + \text{etc.} = \left(X_{X'} + p\frac{dy}{dy'}\frac{dz}{dz'}\right) d\frac{dx}{dx'}$$
$$+ X_{Y'}\,d\frac{dx}{dy'} + \left(Y_{Y'} + p\frac{dz}{dz'}\frac{dx}{dx'}\right) d\frac{dy}{dy'}. \qquad (411)$$

This equation shows the variation in the quantity of any one of the components of the fluid (other than the substance which forms the solid) which will balance a variation of p, or of $\frac{dx}{dx'}, \frac{dx}{dy'}, \frac{dy}{dy'}$, with respect to the tendency of the solid to dissolve.

Fundamental Equations for Solids.

The principles developed in the preceding pages show that the solution of problems relating to the equilibrium of a solid, or at least their reduction to purely analytical processes, may be made to depend upon our knowledge of the composition and density of the solid at every point in some particular state, which we have called the state of reference, and of the relation existing between the quantities which have been represented by $\varepsilon_{V'}$, $\eta_{V'}$, $\frac{dx}{dx'}$, $\frac{dx}{dy'}$, . . . $\frac{dz}{dz'}$, x', y', and z'. When the solid is in contact with fluids, a certain knowledge of the properties of the fluids is also requisite, but only such as is necessary for the solution of problems relating to the equilibrium of fluids among themselves.

If in any state of which a solid is capable, it is homogeneous in its nature and in its state of strain, we may choose this state as the state of reference, and the relation between $\varepsilon_{V'}$, $\eta_{V'}$, $\frac{dx}{dx'}$, . . $\frac{dz}{dz'}$, will be independent of x', y', z'. But it is not always possible, even in the case of bodies which are homogeneous in nature, to bring all the elements simultaneously into the same state of strain. It would not be possible, for example, in the case of a Prince Rupert's drop.

If, however, we know the relation between $\varepsilon_{V'}$, $\eta_{V'}$, $\frac{dx}{dx'}$, . . . $\frac{dz}{dz'}$, for any kind of homogeneous solid, with respect to any given state of reference, we may derive from it a similar relation with respect to any other state as a state of reference. For if x', y', z' denote the co-ordinates of points of the solid in the first state of reference, and x'', y'', z'' the co-ordinates of the same points in the second state of reference, we shall have necessarily

$$\frac{dx}{dx'} = \frac{dx}{dx''}\frac{dx''}{dx'} + \frac{dx}{dy''}\frac{dy''}{dx'} + \frac{dx}{dz''}\frac{dz''}{dx'}, \text{ etc. (nine equations)}, \qquad (412)$$

and if we write R for the volume of an element in the state (x'', y'', z'') divided by its volume in the state (x', y', z'), we shall have

$$R = \begin{vmatrix} \frac{dx''}{dx'} & \frac{dx''}{dy'} & \frac{dx''}{dz'} \\ \frac{dy''}{dx'} & \frac{dy''}{dy'} & \frac{dy''}{dz'} \\ \frac{dz''}{dx'} & \frac{dz''}{dy'} & \frac{dz''}{dz'} \end{vmatrix}, \qquad (413)$$

$$\varepsilon_{V'} = R\,\varepsilon_{V''}, \qquad \eta_{V'} = R\,\eta_{V''}. \tag{414}$$

If, then, we have ascertained by experiment the value of $\varepsilon_{V'}$ in terms of $\eta_{V'}$, $\frac{dx}{dx'}, \ldots \frac{dz}{dz'}$, and the quantities which express the composition of the body, by the substitution of the values given in (412)–(414), we shall obtain $\varepsilon_{V''}$ in terms of $\eta_{V''}$, $\frac{dx}{dx''}, \ldots \frac{dz}{dz''}, \frac{dx''}{dx'}, \ldots \frac{dz''}{dz'}$, and the quantities which express the composition of the body.

We may apply this to the elements of a body which may be variable from point to point in composition and state of strain in a given state of reference (x'', y'', z''), and if the body is fully described in that state of reference, both in respect to its composition and to the displacement which it would be necessary to give to a homogeneous solid of the same composition, for which $\varepsilon_{V'}$ is known in terms of $\eta_{V'}$, $\frac{dx}{dx'}, \ldots \frac{dz}{dz'}$, and the quantities which express its composition, to bring it from the state of reference (x', y', z') into a similar and similarly situated state of strain with that of the element of the non-homogeneous body, we may evidently regard $\frac{dx''}{dx'}, \ldots \frac{dz''}{dz'}$ as known for each element of the body, that is, as known in terms of x'', y'', z''. We shall then have $\varepsilon_{V''}$ in terms of $\eta_{V''}$, $\frac{dx}{dx''}, \ldots \frac{dz}{dz''}$, x'', y'', z''; and since the composition of the body is known in terms of x'', y'', z'', and the density, if not given directly, can be determined from the density of the homogeneous body in its state of reference (x', y', z'), this is sufficient for determining the equilibrium of any given state of the non-homogeneous solid.

An equation, therefore, which expresses for any kind of solid, and with reference to any determined state of reference, the relation between the quantities denoted by $\varepsilon_{V'}$, $\eta_{V'}$, $\frac{dx}{dx'}, \ldots \frac{dz}{dz'}$, involving also the quantities which express the composition of the body, when that is capable of continuous variation, or any other equation from which the same relations may be deduced, may be called a *fundamental equation* for that kind of solid. It will be observed that the sense in which this term is here used, is entirely analogous to that in which we have already applied the term to fluids and solids which are subject only to hydrostatic pressure.

When the fundamental equation between $\varepsilon_{V'}$, $\eta_{V'}$, $\frac{dx}{dx'}, \ldots \frac{dz}{dz'}$ is known, we may obtain by differentiation the values of t, $X_{X'}$, . . . $Z_{Z'}$ in terms of the former quantities, which will give eleven independent relations between the twenty-one quantities

$$\varepsilon_{V'},\ \eta_{V'},\ \frac{dx}{dx'},\ \ldots\ \frac{dz}{dz'},\ t,\ X_{X'},\ \ldots\ Z_{Z'}, \tag{415}$$

which are all that exist, since ten of these quantities are independent. All these equations may also involve variables which express the composition of the body, when that is capable of continuous variation.

If we use the symbol $\psi_{V'}$ to denote the value of ψ (as defined on pages 144, 145) for any element of a solid divided by the volume of the element in the state of reference, we shall have

$$\psi_{V'} = \varepsilon_{V'} - t\,\eta_{V'}. \tag{416}$$

The equation (356) may be reduced to the form

$$\delta\psi_{V'} = -\,\eta_{V'}\,\delta t + \Sigma\,\Sigma'\left(X_{X'}\,\delta\frac{dx}{dx'}\right). \tag{417}$$

Therefore, if we know the value of $\psi_{V'}$ in terms of the variables t, $\frac{dx}{dx'}$, . . . $\frac{dz}{dz'}$, together with those which express the composition of the body, we may obtain by differentiation the values of $\eta_{V'}$, $X_{X'}$, . . . $Z_{Z'}$ in terms of the same variables. This will make eleven independent relations between the same quantities as before, except that we shall have $\psi_{V'}$ instead of $\varepsilon_{V'}$. Or if we eliminate $\psi_{V'}$ by means of equation (416), we shall obtain eleven independent equations between the quantities in (415) and those which express the composition of the body. An equation, therefore, which determines the value of $\psi_{V'}$, as a function of the quantities t, $\frac{dx}{dx'}$, . . . $\frac{dz}{dz'}$, and the quantities which express the composition of the body when it is capable of continuous variation, is a fundamental equation for the kind of solid to which it relates.

In the discussion of the conditions of equilibrium of a solid, we might have started with the principle that it is necessary and sufficient for equilibrium that the temperature shall be uniform throughout the whole mass in question, and that the variation of the force-function $(-\psi)$ of the same mass shall be null or negative for any variation in the state of the mass not affecting its temperature. We might have assumed that the value of ψ for any same element of the solid is a function of the temperature and the state of strain, so that for constant temperature we might write

$$\delta\psi_{V'} = \Sigma\,\Sigma'\left(X_{X'}\,\delta\frac{dx}{dx'}\right),$$

the quantities $X_{X'}, \ldots Z_{Z'}$ being defined by this equation. This would be only a formal change in the definition of $X_{X'}, \ldots Z_{Z'}$ and would not affect their values, for this equation holds true of $X_{X'}, \ldots Z_{Z'}$ as defined by equation (355). With such data, by transformations similar to those which we have employed, we might obtain similar results.* It is evident that the only difference in the equations would be that $\psi_{V'}$ would take the place of $\varepsilon_{V'}$, and that the terms relating to entropy would be wanting. Such a method is evidently preferable with respect to the directness with which the results are obtained. The method of this paper shows more distinctly the *rôle* of *energy* and *entropy* in the theory of equilibrium, and can be extended more naturally to those dynamical problems in which motions take place under the condition of constancy of entropy of the elements of a solid (as when vibrations are propagated through a solid), just as the other method can be more naturally extended to dynamical problems in which the temperature is constant. (See note on page 145.)

We have already had occasion to remark that the state of strain of any element considered without reference to directions in space is capable of only six independent variations. Hence, it must be possible to express the state of strain of an element by six functions of $\frac{dx}{dx'}, \ldots \frac{dz}{dz'}$, which are independent of the position of the element. For these quantities we may choose the squares of the ratios of elongation of lines parallel to the three co-ordinate axes in the state of reference, and the products of the ratios of elongation for each pair of these lines multiplied by the cosine of the angle which they include in the variable state of the solid. If we denote these quantities by A, B, C, a, b, c, we shall have

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* For an example of this method, see Thomson and Tait's *Natural Philosophy*, vol. i, p. 705. With regard to the general theory of elastic solids, compare also Thomson's Memoir "On the Thermo-elastic and Thermo-magnetic Properties of Matter" in the *Quarterly Journal of Mathematics*, vol. i, p. 57 (1855), and Green's memoirs on the propagation, reflection, and refraction of light in the *Transactions of the Cambridge Philosophical Society*, vol. vii.

$$A = \Sigma\left(\frac{dx}{dx'}\right)^2, \quad B = \Sigma\left(\frac{dx}{dy'}\right)^2, \quad C = \Sigma\left(\frac{dx}{dz'}\right)^2, \tag{418}$$

$$a = \Sigma\left(\frac{dx}{dy'}\frac{dx}{dz'}\right), \quad b = \Sigma\left(\frac{dx}{dz'}\frac{dx}{dx'}\right), \quad c = \Sigma\left(\frac{dx}{dx'}\frac{dx}{dy'}\right). \tag{419}$$

The determination of the fundamental equation for a solid is thus reduced to the determination of the relation between $\varepsilon_{V'}$, $\eta_{V'}$, A, B, C, a, b, c, or of the relation between $\psi_{V'}$, t, A, B, C, a, b, c.

In the case of isotropic solids, the state of strain of an element, so far as it can affect the relation of $\varepsilon_{V'}$ and $\eta_{V'}$, or of $\psi_{V'}$ and t, is capable of only three independent variations. This appears most distinctly as a consequence of the proposition that for any given strain of an element there are three lines in the element which are at right angles to one another both in its unstrained and in its strained state. If the unstrained element is isotropic, the ratios of elongation for these three lines must with $\eta_{V'}$ determine the value $\varepsilon_{V'}$, or with t determine the value of $\psi_{V'}$.

To demonstrate the existence of such lines, which are called the *principal axes of strain*, and to find the relations of the elongations of such lines to the quantities $\frac{dx}{dx'}, \ldots \frac{dz}{dz'}$, we may proceed as follows. The ratio of elongation r of any line of which α', β', γ' are the direction-cosines in the state of reference is evidently given by the equation

$$\begin{aligned} r^2 = &\left(\frac{dx}{dx'}\alpha' + \frac{dx}{dy'}\beta' + \frac{dx}{dz'}\gamma'\right)^2 \\ &+ \left(\frac{dy}{dx'}\alpha' + \frac{dy}{dy'}\beta' + \frac{dy}{dz'}\gamma'\right)^2 \\ &+ \left(\frac{dz}{dx'}\alpha' + \frac{dz}{dy'}\beta' + \frac{dz}{dz'}\gamma'\right)^2. \end{aligned} \tag{420}$$

Now the proposition to be established is evidently equivalent to this —that it is always possible to give such directions to the two systems of rectangular axes X', Y', Z', and X, Y, Z, that

$$\left.\begin{aligned} \frac{dx}{dy'} = 0, \quad \frac{dx}{dz'} = 0, \quad \frac{dy}{dz'} = 0, \\ \frac{dy}{dx'} = 0, \quad \frac{dz}{dx'} = 0, \quad \frac{dz}{dy'} = 0. \end{aligned}\right\} \tag{421}$$

We may choose a line in the element for which the value of r is at least as great as for any other, and make the axes of X and X' parallel to this line in the strained and unstrained states respectively.

Then $$\frac{dy}{dx'} = 0, \quad \frac{dz}{dx'} = 0. \tag{422}$$

Moreover, if we write $\frac{d(r^2)}{d\alpha'}, \frac{d(r^2)}{d\beta'}, \frac{d(r^2)}{d\gamma'}$ for the differential coefficients obtained from (420) by treating α', β', γ' as *independent* variables,

$$\frac{d(r^2)}{d\alpha'} d\alpha' + \frac{d(r^2)}{d\beta'} d\beta' + \frac{d(r^2)}{d\gamma'} d\gamma' = 0,$$

when $$\alpha' \, d\alpha' + \beta' \, d\beta' + \gamma' \, d\gamma' = 0,$$

and $$\alpha' = 1, \quad \beta' = 0, \quad \gamma' = 0.$$

That is, $$\frac{d(r^2)}{d\beta'} = 0, \quad \text{and} \quad \frac{d(r^2)}{d\gamma'} = 0,$$

when $$\alpha' = 1, \quad \beta' = 0, \quad \gamma' = 0.$$

Hence, $$\frac{dx}{dy'} = 0, \quad \frac{dx}{dz'} = 0. \tag{423}$$

Therefore a line of the element which in the unstrained state is perpendicular to X' is perpendicular to X in the strained state. Of all such lines we may choose one for which the value of r is at least as great as for any other, and make the axes of Y' and Y parallel to this line in the unstrained and in the strained state respectively. Then

$$\frac{dz}{dy'} = 0; \tag{424}$$

and it may easily be shown by reasoning similar to that which has just been employed that

$$\frac{dy}{dz'} = 0. \tag{425}$$

Lines parallel to the axes of X', Y', and Z' in the unstrained body will therefore be parallel to X, Y, and Z in the strained body, and the ratios of elongation for such lines will be

$$\frac{dx}{dx'}, \quad \frac{dy}{dy'}, \quad \frac{dz}{dz'}.$$

These lines have the common property of a stationary value of the ratio of elongation for varying directions of the line. This appears from the form to which the general value of r^2 is reduced by the positions of the co-ordinate axes, viz.,

$$r^2 = \left(\frac{dx}{dx'}\right)^2 \alpha'^2 + \left(\frac{dy}{dy'}\right)^2 \beta'^2 + \left(\frac{dz}{dz'}\right)^2 \gamma'^2.$$

Having thus proved the existence of lines, with reference to any particular strain, which have the properties mentioned, let us proceed to find the relations between the ratios of elongation for these lines (the *principal axes of strain*) and the quantities $\frac{dx}{dx'}, \ldots \frac{dz}{dz'}$ under the most general supposition with respect to the position of the co-ordinate axes.

For any principal axis of strain we have

$$\frac{d(r^2)}{d\alpha'}\,d\alpha' + \frac{d(r^2)}{d\beta'}\,d\beta' + \frac{d(r^2)}{d\gamma'}\,d\gamma' = 0,$$

when $$\alpha'\,d\alpha' + \beta'\,d\beta' + \gamma'\,d\gamma' = 0,$$

the differential coefficients in the first of these equations being determined from (420) as before. Therefore,

$$\frac{1}{\alpha'}\frac{d(r^2)}{d\alpha'} = \frac{1}{\beta'}\frac{d(r^2)}{d\beta'} = \frac{1}{\gamma'}\frac{d(r^2)}{d\gamma'}. \tag{426}$$

From (420) we obtain directly

$$\frac{\alpha'}{2}\frac{d(r^2)}{d\alpha'} + \frac{\beta'}{2}\frac{d(r^2)}{d\beta'} + \frac{\gamma'}{2}\frac{d(r^2)}{d\gamma'} = r^2. \tag{427}$$

From the two last equations, in virtue of the necessary relation $\alpha'^2 + \beta'^2 + \gamma'^2 = 1$, we obtain

$$\tfrac{1}{2}\frac{d(r^2)}{d\alpha'} = \alpha'\,r^2, \quad \tfrac{1}{2}\frac{d(r^2)}{d\beta'} = \beta'\,r^2, \quad \tfrac{1}{2}\frac{d(r^2)}{d\gamma'} = \gamma'\,r^2, \tag{428}$$

or, if we substitute the values of the differential coefficients taken from (420),

$$\left.\begin{aligned}
\alpha'\,\Sigma\left(\frac{dx}{dx'}\right)^2 + \beta'\,\Sigma\left(\frac{dx}{dx'}\frac{dx}{dy'}\right) + \gamma'\,\Sigma\left(\frac{dx}{dx'}\frac{dx}{dz'}\right) &= \alpha'\,r^2,\\
\alpha'\,\Sigma\left(\frac{dx}{dy'}\frac{dx}{dx'}\right) + \beta'\,\Sigma\left(\frac{dx}{dy'}\right)^2 + \gamma'\,\Sigma\left(\frac{dx}{dy'}\frac{dx}{dz'}\right) &= \beta'\,r^2,\\
\alpha'\,\Sigma\left(\frac{dx}{dz'}\frac{dx}{dx'}\right) + \beta'\,\Sigma\left(\frac{dx}{dz'}\frac{dx}{dy'}\right) + \gamma'\,\Sigma\left(\frac{dx}{dz'}\right)^2 &= \gamma'\,r^2.
\end{aligned}\right\} \tag{429}$$

If we eliminate α', β', γ' from these equations, we may write the result in the form,

$$\begin{vmatrix}
\Sigma\left(\frac{dx}{dx'}\right)^2 - r^2 & \Sigma\left(\frac{dx}{dx'}\frac{dx}{dy'}\right) & \Sigma\left(\frac{dx}{dx'}\frac{dx}{dz'}\right)\\
\Sigma\left(\frac{dx}{dy'}\frac{dx}{dx'}\right) & \Sigma\left(\frac{dx}{dy'}\right)^2 - r^2 & \Sigma\left(\frac{dx}{dy'}\frac{dx}{dz'}\right)\\
\Sigma\left(\frac{dx}{dz'}\frac{dx}{dx'}\right) & \Sigma\left(\frac{dx}{dz'}\frac{dx}{dy'}\right) & \Sigma\left(\frac{dx}{dz'}\right)^2 - r^2
\end{vmatrix} = 0. \tag{430}$$

We may write

$$-r^6 + Er^4 - Fr^2 + G = 0. \tag{431}$$

Then

$$E = \Sigma' \, \Sigma \left(\frac{dx}{dx'}\right)^2. \tag{432}$$

Also*

$$F = \Sigma' \left\{ \Sigma \left(\frac{dx}{dx'}\right)^2 \Sigma \left(\frac{dx}{dy'}\right)^2 - \Sigma \left(\frac{dx}{dx'}\frac{dx}{dy'}\right) \Sigma \left(\frac{dx}{dx'}\frac{dx}{dy'}\right) \right\}$$

$$= \Sigma' \, \Sigma \left\{ \left(\frac{dx}{dx'}\right)^2 \Sigma \left(\frac{dx}{dy'}\right)^2 - \frac{dx}{dx'}\frac{dx}{dy'} \Sigma \left(\frac{dx}{dx'}\frac{dx}{dy'}\right) \right\} =$$

$$\Sigma' \, \Sigma \left\{ \left(\frac{dx}{dx'}\right)^2 \left(\frac{dy}{dy'}\right)^2 + \left(\frac{dx}{dx'}\right)^2 \left(\frac{dz}{dy'}\right)^2 - \frac{dx}{dx'}\frac{dx}{dy'}\frac{dy}{dx'}\frac{dy}{dy'} - \frac{dx}{dx'}\frac{dx}{dy'}\frac{dz}{dx'}\frac{dz}{dy'} \right\}$$

$$= \Sigma' \, \Sigma \left\{ \left(\frac{dx}{dx'}\right)^2 \left(\frac{dy}{dy'}\right)^2 + \left(\frac{dy}{dx'}\right)^2 \left(\frac{dx}{dy'}\right)^2 - 2\frac{dx}{dx'}\frac{dx}{dy'}\frac{dy}{dx'}\frac{dy}{dy'} \right\}$$

$$= \Sigma' \, \Sigma \left(\frac{dx}{dx'}\frac{dy}{dy'} - \frac{dy}{dx'}\frac{dx}{dy'}\right)^2. \tag{433}$$

This may also be written

$$F = \Sigma' \, \Sigma \begin{vmatrix} \frac{dx}{dx'} & \frac{dx}{dy'} \\ \frac{dy}{dx'} & \frac{dy}{dy'} \end{vmatrix}^2. \tag{434}$$

In the reduction of the value of G, it will be convenient to use the symbol $\underset{3+3}{\Sigma}$ to denote the sum of the *six* terms formed by changing x, y, z, into y, z, x; z, x, y; x, z, y; y, x, z; and z, y, x; and the symbol $\underset{3-3}{\Sigma}$ in the same sense except that the last three terms are to be taken negatively; also to use $\underset{3-3}{\Sigma'}$ in a similar sense with respect to x', y', z'; and to use x', y', z' as equivalent to x', y', z', except that they are not to be affected by the sign of summation. With this understanding we may write

$$G = \underset{3-3}{\Sigma'} \left\{ \Sigma \left(\frac{dx}{d\mathrm{x}'}\frac{dx}{dx'}\right) \Sigma \left(\frac{dx}{d\mathrm{y}'}\frac{dx}{dy'}\right) \Sigma \left(\frac{dx}{d\mathrm{z}'}\frac{dx}{dz'}\right) \right\}. \tag{435}$$

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* The values of F and G given in equations (434) and (438), which are here deduced at length, may be derived from inspection of equation (430) by means of the usual theorems relating to the multiplication of determinants. See Salmon's *Lessons Introductory to the Modern Higher Algebra*, 2d Ed., Lesson III; or Baltzer's *Theorie und Anwendung der Determinanten*, § 5.

In expanding the product of the three sums, we may cancel on account of the sign $\underset{3-3}{\Sigma'}$ the terms which do not contain all the three expressions dx, dy, and dz. Hence we may write

$$G = \underset{3-3}{\Sigma'} \underset{3+3}{\Sigma} \left(\frac{dx}{dx'}\frac{dx}{dx'}\frac{dy}{dy'}\frac{dy}{dy'}\frac{dz}{dz'}\frac{dz}{dz'}\right)$$

$$= \underset{3+3}{\Sigma} \left\{ \frac{dx}{dx'}\frac{dy}{dy'}\frac{dz}{dz'} \underset{3-3}{\Sigma'}\left(\frac{dx}{dx'}\frac{dy}{dy'}\frac{dz}{dz'}\right)\right\}$$

$$= \underset{3-3}{\Sigma}\left(\frac{dx}{dx'}\frac{dy}{dy'}\frac{dz}{dz'}\right) \underset{3-3}{\Sigma'}\left(\frac{dx}{dx'}\frac{dy}{dy'}\frac{dz}{dz'}\right). \tag{436}$$

Or, if we set

$$H = \begin{vmatrix} \frac{dx}{dx'} & \frac{dx}{dy'} & \frac{dx}{dz'} \\ \frac{dy}{dx'} & \frac{dy}{dy'} & \frac{dy}{dz'} \\ \frac{dz}{dx'} & \frac{dz}{dy'} & \frac{dz}{dz'} \end{vmatrix}, \tag{437}$$

we shall have

$$G = H^2. \tag{438}$$

It will be observed that F represents the sum of the squares of the nine minors which can be formed from the determinant in (437), and that E represents the sum of the squares of the nine constituents of the same determinant.

Now we know by the theory of equations that equation (431) will be satisfied in general by three different values of r^2, which we may denote by r_1^2, r_2^2, r_3^2, and which must represent the squares of the ratios of elongation for the three principal axes of strain; also that E, F, G, are symmetrical functions of r_1^2, r_2^2, r_3^2, viz.,

$$\left.\begin{array}{c} E = r_1^2 + r_2^2 + r_3^2, \quad F = r_1^2 r_2^2 + r_2^2 r_3^2 + r_3^2 r_1^2, \\ G = r_1^2 r_2^2 r_3^2. \end{array}\right\} \tag{439}$$

Hence, although it is possible to solve equation (431) by the use of trigonometrical functions, it will be more simple to regard $\varepsilon_{V'}$ as a function of $\eta_{V'}$ and the quantities E, F, G (or H), which we have expressed in terms of $\frac{dx}{dx'}, \ldots \frac{dz}{dz'}$. Since $\varepsilon_{V'}$ is a single-valued function of $\eta_{V'}$ and r_1^2, r_2^2, r_3^2 (with respect to all the changes of which the body is capable), and a symmetrical function with respect to r_1^2, r_2^2, r_3^2, and since r_1^2, r_2^2, r_3^2 are *collectively* determined without ambiguity by the values of E, F, and H, the quantity $\varepsilon_{V'}$ must be a single-valued function of $\eta_{V'}$, E, F, and H. The determination of the fundamental equation for isotropic bodies is therefore reduced to the determination of this function, or (as appears from similar considerations) the determination of $\psi_{V'}$ as a function of t, E, F, and H.

It appears from equations (439) that E represents the sum of the squares of the ratios of elongation for the principal axes of strain, that F represents the sum of the squares of the ratios of enlargement for the three surfaces determined by these axes, and that G represents the square of the ratio of enlargement of volume. Again, equation (432) shows that E represents the sum of the squares of the ratios of elongation for lines parallel to X', Y', and Z'; equation (434) shows that F represents the sum of the squares of the ratios of enlargement for surfaces parallel to the planes X'-Y', Y'-Z', Z'-X'; and equation (438), like (439), shows that G represents the square of the ratio of enlargement of volume. Since the position of the co-ordinate axes is arbitrary, it follows that the sum of the squares of the ratios of elongation or enlargement of three lines or surfaces which in the unstrained state are at right angles to one another, is otherwise independent of the direction of the lines or surfaces. Hence, $\frac{1}{3}E$ and $\frac{1}{3}F$ are the mean squares of the ratios of linear elongation and of superficial enlargement, for all possible directions in the unstrained solid.

There is not only a practical advantage in regarding the strain as determined by E, F, and H, instead of E, F, and G, because H is more simply expressed in terms of $\frac{dx}{dx'}$, . . . $\frac{dz}{dz'}$, but there is also a certain theoretical advantage on the side of E, F, H. If the systems of co-ordinate axes X, Y, Z, and X', Y', Z', are either identical or such as are capable of superposition, which it will always be convenient to suppose, the determinant H will always have a positive value for any strain of which a body can be capable. But it is possible to give to x, y, z such values as functions of x', y', z' that H shall have a negative value. For example, we may make

$$x = x', \quad y = y', \quad z = -z'. \tag{440}$$

This will give $H = -1$, while

$$x = x', \quad y = y', \quad z = z' \tag{441}$$

will give $H = 1$. Both (440) and (441) give $G = 1$. Now although such a change in the position of the particles of a body as is represented by (440) cannot take place while the body remains solid, yet a method of representing strains may be considered incomplete, which confuses the cases represented by (440) and (441).

We may avoid all such confusion by using E, F, and H to represent a strain. Let us consider an element of the body strained which in the state (x', y', z') is a cube with its edges parallel to the axes of X', Y', Z', and call the edges dx', dy', dz according to the axes to which they are parallel, and consider the ends of the edges as positive for which the values of x', y', or z' are the greater. Whatever may be the nature of the parallelopiped in the state (x, y, z) which corresponds to the cube dx', dy', dz' and is determined by the quantities $\frac{dx}{dx'}, \ldots \frac{dz}{dz'}$, it may always be brought by continuous changes to the form of a cube and to a position in which the edges dx', dy' shall be parallel to the axes of X and Y, the positive ends of the edges toward the positive directions of the axes, and this may be done without giving the volume of the parallelopiped the value zero, and therefore without changing the sign of H. Now two cases are possible;—the positive end of the edge dz' may be turned toward the positive or toward the negative direction of the axis of Z. In the first case, H is evidently positive; in the second, negative. The determinant H will therefore be positive or negative,—we may say, if we choose, that the volume will be positive or negative,—according as the element can or cannot be brought from the state (x, y, z) to the state (x', y', z') by continuous changes without giving its volume the value zero.

If we now recur to the consideration of the principal axes of strain and the principal ratios of elongation r_1, r_2, r_3, and denote by U_1, U_2, U_3 and U_1', U_2', U_3' the principal axes of strain in the strained and unstrained element respectively, it is evident that the sign of r_1, for example, depends upon the direction in U_1 which we regard as corresponding to a given direction in U_1'. If we choose to associate directions in these axes so that r_1, r_2, r_3 shall all be positive, the positive or negative value of H will determine whether the system of axes U_1, U_2, U_3 is or is not capable of superposition upon the system U_1', U_2', U_3' so that corresponding directions in the axes shall coincide. Or, if we prefer to associate directions in the two systems of axes, so that they shall be capable of superposition, corresponding directions coinciding, the positive or negative value of H will determine whether an even or an odd number of the quantities r_1, r_2, r_3 are negative. In this case we may write

$$r_1\,r_2\,r_3=H=\begin{vmatrix}\frac{dx}{dx'} & \frac{dx}{dy'} & \frac{dx}{dz'}\\ \frac{dy}{dx'} & \frac{dy}{dy'} & \frac{dy}{dz'}\\ \frac{dz}{dx'} & \frac{dz}{dy'} & \frac{dz}{dz'}\end{vmatrix}. \tag{442}$$

It will be observed that to change the signs of two of the quantities r_1, r_2, r_3 is simply to give a certain rotation to the body without changing its state of strain.

Whichever supposition we make with respect to the axes U_1, U_2, U_3, it is evident that the state of strain is completely determined by the values E, F, and H, not only when we limit ourselves to the consideration of such strains as are consistent with the idea of solidity, but also when we regard any values of $\frac{dx}{dx'}, \ldots \frac{dz}{dz'}$ as possible.

Approximative Formulæ.—For many purposes the value of $\varepsilon_{V'}$ for an isotropic solid may be represented with sufficient accuracy by the formula

$$\varepsilon_{V'}=i'+e'\,E+f'\,F+h'\,H, \tag{443}$$

where i', e', f', and h' denote functions of $\eta_{V'}$; or the value of $\psi_{V'}$ by the formula

$$\psi_{V'}=i+e\,E+f\,F+h\,H, \tag{444}$$

where i, e, f, and h denote functions of t. Let us first consider the second of these formulæ. Since E, F, and H are symmetrical functions of r_1, r_2, r_3, if $\psi_{V'}$ is any function of t, E, F, H, we must have

$$\left.\begin{aligned}\frac{d\psi_{V'}}{dr_1}&=\frac{d\psi_{V'}}{dr_2}=\frac{d\psi_{V'}}{dr_3},\\ \frac{d^2\psi_{V'}}{dr_1^{\,2}}&=\frac{d^2\psi_{V'}}{dr_2^{\,2}}=\frac{d^2\psi_{V'}}{dr_3^{\,2}},\\ \frac{d^2\psi_{V'}}{dr_1\,dr_2}&=\frac{d^2\psi_{V'}}{dr_2\,dr_3}=\frac{d^2\psi_{V'}}{dr_3\,dr_1},\end{aligned}\right\} \tag{445}$$

whenever $r_1=r_2=r_3$. Now i, e, f, and h may be determined (as functions of t) so as to give to

$$\psi_{V'},\quad \frac{d\psi_{V'}}{dr_1},\quad \frac{d^2\psi_{V'}}{dr_1^{\,2}},\quad \frac{d^2\psi_{V'}}{dr_1\,dr_2}$$

their proper values at every temperature for some isotropic state of strain, which may be determined by any desired condition. We shall suppose that they are determined so as to give the proper values to $\psi_{V'}$, etc., when the stresses in the solid vanish. If we denote by r_0 the common value of r_1, r_2, r_3 which will make the stresses vanish at any given temperature, and imagine the true value of $\psi_{V'}$, and also the value given by equation (444) to be expressed in terms of the ascending powers of

$$r_1 - r_0, \quad r_2 - r_0, \quad r_3 - r_0, \tag{446}$$

it is evident that the expressions will coincide as far as the terms of the second degree *inclusive.* That is, the errors of the values of $\psi_{V'}$ given by equation (444) are of the same order of magnitude as the cubes of the above differences. The errors of the values of

$$\frac{d\psi_{V'}}{dr_1}, \quad \frac{d\psi_{V'}}{dr_2}, \quad \frac{d\psi_{V'}}{dr_3}$$

will be of the same order of magnitude as the squares of the same differences. Therefore, since

$$\frac{d\psi_{V'}}{d\frac{dx}{dx'}} = \frac{d\psi_{V'}}{dr_1}\frac{dr_1}{d\frac{dx}{dx'}} + \frac{d\psi_{V'}}{dr_2}\frac{dr_2}{d\frac{dx}{dx'}} + \frac{d\psi_{V'}}{dr_3}\frac{dr_3}{d\frac{dx}{dx'}} \tag{447}$$

whether we regard the true value of $\psi_{V'}$ or the value given by equation (444), and since the error in (444) does not affect the values of

$$\frac{dr_1}{d\frac{dx}{dx'}}, \quad \frac{dr_2}{d\frac{dx}{dx'}}, \quad \frac{dr_3}{d\frac{dx}{dx'}},$$

which we may regard as determined by equations (431), (432), (434), (437) and (438), the errors in the values of $X_{X'}$ derived from (444) will be of the same order of magnitude as the squares of the differences in (446). The same will be true with respect to $X_{Y'}$, $X_{Z'}$, $Y_{X'}$, etc., etc.

It will be interesting to see how the quantities e, f, and h are related to those which most simply represent the elastic properties of isotropic solids. If we denote by V and R the *elasticity of volume* and the *rigidity** (both determined under the condition of constant temperature and for states of vanishing stress), we shall have as definitions:

$$V = -v\left(\frac{dp}{dv}\right)_t, \quad \text{when} \quad v = r_0{}^3\, v', \tag{448}$$

* See Thomson and Tait's *Natural Philosophy*, vol. i, p. 711.

where p denotes a uniform pressure to which the solid is subjected, v its volume, and v' its volume in the state of reference; and

$$\left.\begin{aligned} &R = \frac{dX_{Y'}}{d\frac{dx}{dy'}} = \frac{d^2\psi_{V'}}{\left(d\frac{dx}{dy'}\right)^2}, \\ \text{when} \qquad &\frac{dx}{dx'} = \frac{dy}{dy'} = \frac{dz}{dz'} = r_0, \\ \text{and} \qquad &\frac{dx}{dy'} = \frac{dx}{dz'} = \frac{dy}{dz'} = \frac{dy}{dx'} = \frac{dz}{dx'} = \frac{dz}{dy'} = 0. \end{aligned}\right\} \tag{449}$$

Now when the solid is subject to uniform pressure on all sides, if we consider so much of it as has the volume unity in the state of reference, we shall have

$$r_1 = r_2 = r_3 = v^{\frac{1}{3}}, \tag{450}$$

and by (444) and (439),

$$\psi_{V'} = i + 3\,e\,v^{\frac{2}{3}} + 3\,f\,v^{\frac{4}{3}} + h\,v. \tag{451}$$

Hence, by equation (88), since $\psi_{V'}$ is equivalent to ψ,

$$-p = \left(\frac{d\psi}{dv}\right)_t = 2\,e\,v^{-\frac{1}{3}} + 4\,f\,v^{\frac{1}{3}} + h, \tag{452}$$

$$-v\left(\frac{dp}{dv}\right)_t = -\tfrac{2}{3}\,e\,v^{-\frac{1}{3}} + \tfrac{4}{3}\,f\,v^{\frac{1}{3}}; \tag{453}$$

and by (448),

$R = \frac{2e}{r_0} + 2 f r_0$

$$V = -\tfrac{2}{3}\frac{e}{r_0} + \tfrac{4}{3} f r_0. \tag{454}$$

To obtain the value of R in accordance with the definition (449), we may suppose the values of E, F, and H given by equations (432), (434), and (437) to be substituted in equation (444). This will give for the value of R

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$$r_0 \quad R = 2\,e + 4\,f\,r_0^{\,2}. \tag{455}$$

Moreover, since p must vanish in (452) when $v = r_0^{\,3}$, we have

$$2\,e + 4\,f\,r_0^{\,2} + h\,r_0 = 0. \tag{456}$$

From the three last equations may be obtained the values of e, f, h, in terms of r_0, V, and R; viz.,

$$e = \frac{R - 3\,r_0\,V}{4}, \quad f = \frac{R + 3\,r_0\,V}{8\,r_0^{\,2}}, \quad h = -\frac{R}{r_0}. \tag{457}$$

The quantity r_0, like R and V, is a function of the temperature, the differential coefficient $\frac{d \log r_0}{dt}$ representing the rate of linear expansion of the solid when without stress.

$e = \frac{1}{3} r_0 R - \frac{1}{2} r_0 V \qquad f = \frac{R + 3V}{6 r_0} \qquad h = \frac{4}{3} R - V \qquad (457)$

It will not be necessary to discuss equation (443) at length, as the case is entirely analogous to that which has just been treated. [It must be remembered that $\eta_{V'}$, in the discussion of (443) will take the place everywhere of the temperature in the discussion of (444).] If we denote by V' and R' the *elasticity of volume* and the *rigidity*, both determined under the condition of *constant entropy*, (i. e., of *no transmission of heat*,) and for states of vanishing stress, we shall have the equations:

$$V' = -\frac{2e'}{3r_0} + \tfrac{4}{3} f' r_0, \tag{458}$$

$$R' = 2\,e' + 4\,f'\,{r_0}^2, \tag{459}$$

$$2\,e' + 4\,f'\,{r_0}^2 + h'\,r_0 = 0. \tag{460}$$

Whence

$$e' = \frac{R' - 3\,r_0\,V'}{4}, \quad f' = \frac{R' + 3\,r_0\,V'}{8\,{r_0}^2}, \quad h' = -\frac{R'}{r_0}. \tag{461}$$

In these equations r_0, R', and V' are to be regarded as functions of the quantity $\eta_{V'}$.

If we wish to change from one state of reference to another (also isotropic), the changes required in the fundamental equation are easily made. If a denotes the length of any line of the solid in the second state of reference divided by its length in the first, it is evident that when we change from the first state of reference to the second the values of the symbols $\varepsilon_{V'}$, $\eta_{V'}$, $\psi_{V'}$, H are divided by a^3, that of E by a^2, and that of F by a^4. In making the change of the state of reference, we must therefore substitute in the fundamental equation of the form (444) $a^3\psi_{V'}$, a^2E, a^4F, a^3H for $\psi_{V'}$, E, F, and H, respectively. In the fundamental equation of the form (443), we must make the analogous substitutions, and also substitute $a^3\eta_{V'}$ for $\eta_{V'}$. [It will be remembered that i', e', f', and h' represent functions of $\eta_{V'}$, and that it is only when their values in terms of $\eta_{V'}$ are substituted, that equation (443) becomes a fundamental equation.]

Concerning Solids which absorb Fluids.

There are certain bodies which are solid with respect to some of their components, while they have other components which are fluid. In the following discussion, we shall suppose both the solidity and the fluidity to be perfect, so far as any properties are concerned which can affect the conditions of equilibrium,—i. e., we shall suppose that the solid matter of the body is entirely free from plasticity, and that there are no passive resistances to the motion of the fluid

$e' = \frac{1}{3} r_0 R' - \frac{1}{2} r_0 V'$, $f' = \frac{R' + 3V'}{6 r_0}$, $h' = -\frac{4}{3} R' - V'$ (461)

components except such as vanish with the velocity of the motion,—leaving it to be determined by experiment how far and in what cases these suppositions are realized.

It is evident that equation (356) must hold true with regard to such a body, when the quantities of the fluid components contained in a given element of the solid remain constant. Let Γ_a', Γ_b', etc., denote the quantities of the several fluid components contained in an element of the body divided by the volume of the element in the state of reference, or, in other words, let these symbols denote the densities which the several fluid components would have, if the body should be brought to the state of reference while the matter contained in each element remained unchanged. We may then say that equation (356) will hold true, when Γ_a', Γ_b', etc., are constant. The complete value of the differential of $\varepsilon_{V'}$ will therefore be given by an equation of the form

$$d\varepsilon_{V'} = t\, d\eta_{V'} + \Sigma\, \Sigma' \left(X_{X'}\, d\frac{dx}{dx'} \right) + L_a\, d\Gamma_a' + L_b\, d\Gamma_b' + \text{etc.} \tag{462}$$

Now when the body is in a state of hydrostatic stress, the term in this equation containing the signs of summation will reduce to $-p\, dv_{V'}$ ($v_{V'}$ denoting, as elsewhere, the volume of the element divided by its volume in the state of reference). For in this case

$$X_{X'} = -p \left(\frac{dy}{dy'} \frac{dz}{dz'} - \frac{dz}{dy'} \frac{dy}{dz'} \right), \tag{463}$$

$$\begin{aligned} \Sigma\, \Sigma' \left(X_{X'}\, d\frac{dx}{dx'} \right) &= -p\, \Sigma\, \Sigma' \left\{ \left(\frac{dy}{dy'} \frac{dz}{dz'} - \frac{dz}{dy'} \frac{dy}{dz'} \right) d\frac{dx}{dx'} \right\} \\ &= -p\, d \begin{vmatrix} \frac{dx}{dx'} & \frac{dx}{dy'} & \frac{dx}{dz'} \\ \frac{dy}{dx'} & \frac{dy}{dy'} & \frac{dy}{dz'} \\ \frac{dz}{dx'} & \frac{dz}{dy'} & \frac{dz}{dz'} \end{vmatrix} \\ &= -p\, dv_{V'}. \end{aligned} \tag{464}$$

We have, therefore, for a state of hydrostatic stress,

$$d\varepsilon_{V'} = t\, d\eta_{V'} - p\, dv_{V'} + L_a\, d\Gamma_a' + L_b\, d\Gamma_b' + \text{etc.}, \tag{465}$$

and multiplying by the volume of the element in the state of reference, which we may regard as constant,

$$d\varepsilon = t\, d\eta - p\, dv + L_a\, dm_a + L_b\, dm_b + \text{etc.}, \tag{466}$$

where ε, η, v, m_a, m_b, etc., denote the energy, entropy, and volume of the element, and the quantities of its several fluid components. It is evident that the equation will also hold true, if these symbols are understood as relating to a homogeneous body of finite size. The only limitation with respect to the variations is that the element or body to which the symbols relate shall always contain the same solid matter. The varied state may be one of hydrostatic stress or otherwise.

But when the body is in a state of hydrostatic stress, and the solid matter is considered invariable, we have by equation (12)

$$d\varepsilon = t\, d\eta - p\, dv + \mu_a\, dm_a + \mu_b\, dm_b + \text{etc.} \tag{467}$$

It should be remembered that the equation cited occurs in a discussion which relates only to bodies of hydrostatic stress, so that the varied state as well as the initial is there regarded as one of hydrostatic stress. But a comparison of the two last equations shows that the last will hold true without any such limitation, and moreover, that the quantities L_a, L_b, etc., when determined for a state of hydrostatic stress, are equal to the potentials μ_a, μ_b, etc.

Since we have hitherto used the term *potential* solely with reference to bodies of hydrostatic stress, we may apply this term as we choose with regard to other bodies. We may therefore call the quantities L_a, L_b, etc., the *potentials* for the several fluid components in the body considered, whether the state of the body is one of hydrostatic stress or not, since this use of the term involves only an extension of its former definition. It will also be convenient to use our ordinary symbol for a potential to represent these quantities. Equation (462) may then be written

$$d\varepsilon_{\mathrm{V}'} = t\, d\eta_{\mathrm{V}'} + \Sigma\, \Sigma' \left(X_{\mathrm{X}'}\, d\frac{dx}{dx'} \right) + \mu_a\, d\Gamma_a' + \mu_b\, d\Gamma_b' + \text{etc.} \tag{468}$$

This equation holds true of solids having fluid components without any limitation with respect to the initial state or to the variations, except that the solid matter to which the symbols relate shall remain the same.

In regard to the conditions of equilibrium for a body of this kind, it is evident in the first place that if we make Γ_a', Γ_b', etc., constant, we shall obtain from the general criterion of equilibrium all the conditions which we have obtained for ordinary solids, and which are expressed by the formulæ (364), (374), (380), (382)–(384). The quantities Γ_1', Γ_2', etc., in the last two formulæ include of course those which have just been represented by Γ_a', Γ_b', etc., and which relate to the fluid components of the body, as well as the corresponding quantities relating to its solid components. Again, if we suppose the solid matter of the body to remain without variation in quantity or position, it will easily appear that the potentials for the substances which form the fluid components of the solid body must satisfy the same conditions in the solid body and in the fluids in contact with it, as in the case of entirely fluid masses. See eqs. (22).

The above conditions must however be slightly modified in order to make them sufficient for equilibrium. It is evident that if the solid is dissolved at its surface, the fluid components which are set free may be absorbed by the solid as well as by the fluid mass, and in like manner if the quantity of the solid is increased, the fluid components of the new portion may be taken from the previously existing solid mass. Hence, whenever the *solid* components of the solid body are actual components of the fluid mass, (whether the case is the same with the *fluid* components of the solid body or not,) an equation of the form (383) must be satisfied, in which the potentials μ_a, μ_b, etc., contained implicitly in the second member of the equation are determined from the solid body. Also if the *solid* components of the solid body are all possible but not all actual components of the fluid mass, a condition of the form (384) must be satisfied, the values of the potentials in the second member being determined as in the preceding case.

The quantities

$$t, \quad X_{X'}, \ldots Z_{Z'}, \quad \mu_a, \quad \mu_b, \quad \text{etc.,} \tag{469}$$

being differential coefficients of $\varepsilon_{V'}$ with respect to the variables

$$\eta_{V'}, \quad \frac{dx}{dx'}, \ldots \frac{dz}{dz'}, \quad \Gamma_a', \quad \Gamma_b', \quad \text{etc.,} \tag{470}$$

will of course satisfy the necessary relations

$$\frac{dt}{d\frac{dx}{dx'}} = \frac{dX_{X'}}{d\eta_{V'}}, \quad \text{etc.} \tag{471}$$

This result may be generalized as follows. Not only is the second member of equation (468) a complete differential in its present form, but it will remain such if we transfer the sign of differentiation (d) from one factor to the other of any term (the sum indicated by the symbol $\Sigma\,\Sigma'$ is here supposed to be expanded into nine terms), and at the same time change the sign of the term from $+$ to $-$. For to substitute $-\eta_{V'} dt$ for $t\, d\eta_{V'}$, for example, is equivalent to subtracting the complete differential $d(t\,\eta_{V'})$. Therefore, if we consider the quantities in (469) and (470) which occur in any same term in equation (468) as forming a pair, we may choose as independent variables either quantity of each pair, and the differential coefficient of the remaining quantity of any pair with respect to the independent variable of another pair will be equal to the differential coefficient of the remaining quantity of the second pair with respect to the independent variable of the first, taken positively, if the independent variables of these pairs are both affected by the sign d in equation (468), or are neither thus affected, but otherwise taken negatively. Thus

$$\left(\frac{dX_{X'}}{d\Gamma_a'}\right)_{\frac{dx}{dx'}} = \left(\frac{d\mu_a}{d\frac{dx}{dx'}}\right)_{\Gamma_a'}, \quad \left(\frac{dX_{X'}}{d\mu_a}\right)_{\frac{dx}{dx'}} = -\left(\frac{d\Gamma_a'}{d\frac{dx}{dx'}}\right)_{\mu_a}, \tag{472}$$

$$\left(\frac{d\frac{dx}{dx'}}{d\mu_a}\right)_{X_{X'}} = \left(\frac{d\Gamma_a'}{dX_{X'}}\right)_{\mu_a}, \quad \left(\frac{d\frac{dx}{dx'}}{d\Gamma_a'}\right)_{X_{X'}} = -\left(\frac{d\mu_a}{dX_{X'}}\right)_{\Gamma_a'}, \tag{473}$$

where in addition to the quantities indicated by the suffixes, the following are to be considered as constant: either t or $\eta_{V'}$, either $X_{Y'}$ or $\frac{dx}{dy'}$, . . . either $Z_{Z'}$ or $\frac{dz}{dz'}$, either μ_b or Γ_b', etc.

It will be observed that when the temperature is constant the conditions $\mu_a = \text{const.}$, $\mu_b = \text{const.}$ represent the physical condition of a body in contact with a fluid of which the phase does not vary, and which contains the components to which the potentials relate. Also that when Γ_a', Γ_b', etc., are constant, the heat absorbed by the body in any infinitesimal change of condition per unit of volume measured in the state of reference is represented by $t\, d\eta_{V'}$. If we denote this quantity by $d\,Q_{V'}$, and use the suffix $_Q$ to denote the condition of no transmission of heat, we may write

$$\left(\frac{d\log t}{d\frac{dx}{dx'}}\right)_Q = \left(\frac{dX_{X'}}{dQ_{V'}}\right)_{\frac{dx}{dx'}}, \quad \left(\frac{d\log t}{dX_{X'}}\right)_Q = -\left(\frac{d\frac{dx}{dx'}}{dQ_{V'}}\right)_{X_{X'}}, \tag{474}$$

$$\left(\frac{dQ_{V'}}{dX_{X'}}\right)_t = \left(\frac{d\frac{dx}{dx'}}{d\log t}\right)_{X_{X'}}, \quad \left(\frac{dQ_{V'}}{d\frac{dx}{dx'}}\right)_t = -\left(\frac{dX_{X'}}{d\log t}\right)_{\frac{dx}{dx'}}, \tag{475}$$

where Γ_a', Γ_b', etc., must be regarded as constant in all the equations, and either $X_{Y'}$ or $\frac{dx}{dy'}$, . . . either $Z_{Z'}$ or $\frac{dz}{dz'}$, in each equation.

Influence of surfaces of discontinuity upon the equilibrium of heterogeneous masses.—Theory of capillarity.

We have hitherto supposed, in treating of heterogeneous masses in contact, that they might be considered as separated by mathematical surfaces, each mass being unaffected by the vicinity of the others, so that it might be homogeneous quite up to the separating surfaces both with respect to the density of each of its various components and also with respect to the densities of energy and entropy. That such is not rigorously the case is evident from the consideration that if it were so with respect to the densities of the components it could not be so in general with respect to the density of energy, as the sphere of molecular action is not infinitely small. But we know from observation that it is only within very small distances of such a surface that any mass is sensibly affected by its vicinity,—a natural consequence of the exceedingly small sphere of sensible molecular action,—and this fact renders possible a simple method of taking account of the variations in the densities of the component substances and of energy and entropy, which occur in the vicinity of surfaces of discontinuity. We may use this term, for the sake of brevity, without implying that the discontinuity is absolute, or that the term distinguishes any surface with mathematical precision. It may be taken to denote the non-homogeneous film which separates homogeneous or nearly homogeneous masses.

Let us consider such a surface of discontinuity in a fluid mass which is in equilibrium and uninfluenced by gravity. For the precise measurement of the quantities with which we have to do, it will be convenient to be able to refer to a geometrical surface, which shall be sensibly coincident with the physical surface of discontinuity, but shall have a precisely determined position. For this end, let us take some point in or very near to the physical surface of discontinuity, and imagine a geometrical surface to pass through this point and all other points which are similarly situated with respect to the condition of the adjacent matter. Let this geometrical surface be called the *dividing surface*, and designated by the symbol S. It will be observed that the position of this surface is as yet to a certain extent arbitrary, but that the directions of its normals are already everywhere determined, since all the surfaces which can be formed in the manner described are evidently parallel to one another. Let us also imagine a closed surface cutting the surface S and including a part of the homogeneous mass on each side. We will so far limit the form of this closed surface as to suppose that on each side of S, as far as there is any want of perfect homogeneity in the fluid masses, the closed surface is such as may be generated by a moving normal to S. Let the portion of S which is included by the closed surface be denoted by **s**, and the area of this portion by s. Moreover, let the mass contained within the closed surface be divided into three parts by two surfaces, one on each side of S, and very near to that surface, although at such distance as to lie entirely beyond the influence of the discontinuity in its vicinity. Let us call the part which contains the surface **s** (with the physical surface of discontinuity) M, and the homogeneous parts M′ and M″, and distinguish by ε, ε', ε'', η, η', η'', m_1, m_1', m_1'', m_2, m_2', m_2'', etc., the energies and entropies of these masses, and the quantities which they contain of their various components.

It is necessary, however, to define more precisely what is to be understood in cases like the present by the energy of masses which are only separated from other masses by imaginary surfaces. A part of the total energy which belongs to the matter in the vicinity of the separating surface, relates to pairs of particles which are on different sides of the surface, and such energy is not in the nature of things referable to either mass by itself. Yet, to avoid the necessity of taking separate account of such energy, it will often be convenient to include it in the energies which we refer to the separate masses. When there is no break in the homogeneity at the surface, it is natural to treat the energy as distributed with a uniform density. This is essentially the case with the initial state of the system which we are considering, for it has been divided by surfaces passing in general through homogeneous masses. The only exception—that of the surface which cuts at right angles the non-homogeneous film—(apart from the consideration that without any important loss of generality we may regard the part of this surface within the film as very small compared with the other surfaces) is rather apparent than real, as there is no change in the state of the matter *in the direction perpendicular to this surface.* But in the variations to be considered in the state of the system, it will not be convenient to limit ourselves to such as do not create any discontinuity at the surfaces bounding the masses M, M′, M″: we must therefore determine how we will estimate the energies of the masses in case of such infinitesimal discontinuities as may be supposed to arise. Now the energy of each mass will be most easily estimated by neglecting the discontinuity, i. e., if we estimate the energy on the supposition that beyond the bounding surface the phase is identical with that within the surface. This will evidently be allowable, if it does not affect the total amount of energy. To show that it does not affect this quantity, we have only to observe that, if the energy of the mass on one side of a surface where there is an infinitesimal discontinuity of phase is greater as determined by this rule than if determined by any other (suitable) rule, the energy of the mass on the other side must be less by the same amount when determined by the first rule than when determined by the second, since the discontinuity relative to the second mass is equal but opposite in character to the discontinuity relative to the first.

If the entropy of the mass which occupies any one of the spaces considered is not in the nature of things determined without reference to the surrounding masses, we may suppose a similar method to be applied to the estimation of entropy.

With this understanding, let us return to the consideration of the equilibrium of the three masses M, M′, and M″. We shall suppose that there are no limitations to the possible variations of the system due to any want of perfect mobility of the components by means of which we express the composition of the masses, and that these components are independent, i. e., that no one of them can be formed out of the others.

With regard to the mass M, which includes the surface of discontinuity, it is necessary for its internal equilibrium that when its boundaries are considered constant, and when we consider only *reversible* variations (i. e., those of which the opposite are also possible), the variation of its energy should vanish with the variations of its entropy and of the quantities of its various components. For changes within this mass will not affect the energy or the entropy of the surrounding masses (when these quantities are estimated on the principle which we have adopted), and it may therefore be treated as an isolated system. For fixed boundaries of the mass M, and for reversible variations, we may therefore write

$$\delta\varepsilon = A_0\,\delta\eta + A_1\,\delta m_1 + A_2\,\delta m_2 + \text{etc.,} \qquad (476)$$

where A_0, A_1, A_2, etc., are quantities determined by the initial (unvaried) condition of the system. It is evident that A_0 is the temperature of the lamelliform mass to which the equation relates, or the *temperature at the surface of discontinuity.* By comparison of this equation with (12) it will be seen that the definition of A_1, A_2, etc., is entirely analogous to that of the potentials in homogeneous masses, although the mass to which the former quantities relate is not homogeneous, while in our previous definition of potentials, only homogeneous masses were considered. By a natural extension of the term *potential*, we may call the quantities A_1, A_2, etc., the *potentials at the surface of discontinuity*. This designation will be farther justified by the fact, which will appear hereafter, that the value of these quantities is independent of the thickness of the lamina (M) to which they relate. If we employ our ordinary symbols for temperature and potentials, we may write

$$\delta\varepsilon = t\,\delta\eta + \mu_1\,\delta m_1 + \mu_2\,\delta m_2 + \text{etc.} \qquad (477)$$

If we substitue $\geqq$ for $=$ in this equation, the formula will hold true of all variations whether reversible or not;* for if the variation of energy could have a value less than that of the second member of the equation, there must be variation in the condition of M in which its energy is diminished without change of its entropy or of the quantities of its various components.

It is important, however, to observe that for any given values of $\delta\eta$, δm_1, δm_2, etc., while there *may* be possible variations of the nature and state of M for which the value of $\delta\varepsilon$ is greater than that of the second member of (477), there *must* always be possible variations for which the value of $\delta\varepsilon$ is equal to that of the second member.

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* To illustrate the difference between variations which are reversible, and those which are not, we may conceive of two entirely different substances meeting in equilibrium at a mathematical surface without being at all mixed. We may also conceive of them as mixed in a thin film about the surface where they meet, and then the amount of mixture is capable of variation both by increase and by diminution. But when they are absolutely unmixed, the amount of mixture can be increased, but is incapable of diminution, and it is then consistent with equilibrium that the value of $\delta\varepsilon$ (for a variation of the system in which the substances commence to mix) should be greater than the second member of (477). It is not necessary to determine whether precisely such cases actually occur; but it would not be legitimate to overlook the possible occurrence of cases in which variations may be possible while the opposite variations are not.

It will be observed that the sense in which the term *reversible* is here used is entirely different from that in which it is frequently used in treatises on thermodynamics, where a process by which a system is brought from a state A to a state B is called reversible, to signify that the system may also be brought from the state B to the state A through the same series of intermediate states taken in the reverse order by means of external agencies of the opposite character. The variation of a system from a state A to a state B (supposed to differ infinitely little from the first) is here called reversible when the system is capable of another state B′ which bears the same relation to the state A that A bears to B.

It will be convenient to have a notation which will enable us to express this by an equation. Let $\mathfrak{d}\varepsilon$ denote the smallest value (i. e., the value nearest to $-\infty$) of $\delta\varepsilon$ consistent with given values of the other variations, then

$$\mathfrak{d}\varepsilon = t\,\delta\eta + \mu_1\,\delta m_1 + \mu_2\,\delta m_2 + \text{etc.} \tag{478}$$

For the internal equilibrium of the whole mass which consists of the parts M, M′, M″, it is necessary that

$$\delta\varepsilon + \delta\varepsilon' + \delta\varepsilon'' \geqq 0 \tag{479}$$

for all variations which do not affect the enclosing surface or the total entropy or the total quantity of any of the various components. If we also regard the surfaces separating M, M′, and M″ as invariable, we may derive from this condition, by equations (478) and (12), the following as a *necessary* condition of equilibrium:

$$\begin{aligned} &t\,\delta\eta + \mu_1\,\delta m_1 + \mu_2\,\delta m_2 + \text{etc.} \\ &+ t'\,\delta\eta' + \mu_1'\,\delta m_1' + \mu_2'\,\delta m_2' + \text{etc.} \\ &+ t''\,\delta\eta'' + \mu_1''\,\delta m_1'' + \mu_2''\,\delta m_2'' + \text{etc.} \geqq 0, \end{aligned} \tag{480}$$

the variations being subject to the equations of conditions

$$\left.\begin{aligned} &\delta\eta + \delta\eta' + \delta\eta'' = 0, \\ &\delta m_1 + \delta m_1' + \delta m_1'' = 0, \\ &\delta m_2 + \delta m_2' + \delta m_2'' = 0, \\ &\text{etc.} \end{aligned}\right\} \tag{481}$$

It may also be the case that some of the quantities $\delta m_1'$, $\delta m_1''$, $\delta m_2'$, $\delta m_2''$, etc., are incapable of negative values or can only have the value zero. This will be the case when the substances to which these quantities relate are not actual or possible components of M′ or M″. (See page 117.) To satisfy the above condition it is necessary and sufficient that

$$t = t' = t'', \tag{482}$$

$$\mu_1'\,\delta m_1' \geqq \mu_1\,\delta m_1', \quad \mu_2'\,\delta m_2' \geqq \mu_2\,\delta m_2', \quad \text{etc.,} \tag{483}$$

$$\mu_1''\,\delta m_1'' \geqq \mu_1\,\delta m_1'', \quad \mu_2''\,\delta m_2'' \geqq \mu_2\,\delta m_2'', \quad \text{etc.} \tag{484}$$

It will be observed that, if the substance to which μ_1, for instance, relates is an actual component of each of the homogeneous masses, we shall have $\mu_1 = \mu_1' = \mu_1''$. If it is an actual component of the first only of these masses, we shall have $\mu_1 = \mu_1'$. If it is also a possible component of the second homogeneous mass, we shall also have $\mu_1 \geqq \mu_1''$. If this substance occurs only at the surface of discontinuity, the value of the potential μ_1 will not be determined by any equation, but cannot be greater than the potential for the same substance in either of the homogeneous masses in which it may be a possible component.

It appears, therefore, that the particular conditions of equilibrium *relating to temperature and the potentials* which we have before obtained by neglecting the influence of the surfaces of discontinuity (pp. 119, 120, 128) are not invalidated by the influence of such discontinuity in their application to homogeneous parts of the system bounded like M′ and M″ by imaginary surfaces lying within the limits of homogeneity,—a condition which may be fulfilled by surfaces very near to the surfaces of discontinuity. It appears also that similar conditions will apply to the non-homogeneous films like M′, which separate such homogeneous masses. The properties of such films, which are of course different from those of homogeneous masses, require our farther attention.

The volume occupied by the mass M is divided by the surface **s** into two parts, which we will call v''' and v'''', v''' lying next to M′, and v'''' to M″. Let us imagine these volumes filled by masses having throughout the same temperature, pressure and potentials, and the same densities of energy and entropy, and of the various components, as the masses M′ and M″ respectively. We shall then have, by equation (12), if we regard the volumes as constant,

$$\delta\varepsilon''' = t'\,\delta\eta''' + \mu_1'\,\delta m_1''' + \mu_2'\,\delta m_2''' + \text{etc.}, \tag{485}$$

$$\delta\varepsilon'''' = t''\,\delta\eta'''' + \mu_1''\,\delta m_1'''' + \mu_2''\,\delta m_2'''' + \text{etc.}; \tag{486}$$

whence, by (482)–(484), we have for reversible variations

$$\delta\varepsilon''' = t\,\delta\eta''' + \mu_1\,\delta m_1''' + \mu_2\,\delta m_2''' + \text{etc.}, \tag{487}$$

$$\delta\varepsilon'''' = t\,\delta\eta'''' + \mu_1\,\delta m_1'''' + \mu_2\,\delta m_2'''' + \text{etc.} \tag{488}$$

From these equations and (477), we have for reversible variations

$$\delta(\varepsilon - \varepsilon''' - \varepsilon'''') = t\,\delta(\eta - \eta''' - \eta'''')$$
$$+ \mu_1\,\delta(m_1 - m_1''' - m_1'''') + \mu_2\,\delta(m_2 - m_2''' - m_2'''') + \text{etc.} \tag{489}$$

Or, if we set*

$$\varepsilon^{\mathrm{S}} = \varepsilon - \varepsilon''' - \varepsilon'''', \quad \eta^{\mathrm{S}} = \eta - \eta''' - \eta'''', \tag{490}$$

$$m_1^{\mathrm{S}} = m_1 - m_1''' - m_1'''', \quad m_2^{\mathrm{S}} = m_2 - m_2''' - m_2'''', \quad \text{etc.}, \tag{491}$$

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* It will be understood that the $^{\mathrm{S}}$ here used is not an algebraic exponent, but is only intended as a distinguishing mark. The Roman letter S has not been used to denote any *quantity*.

we may write

$$\delta\varepsilon^S = t\,\delta\eta^S + \mu_1\,\delta m_1^S + \mu_2\,\delta m_2^S + \text{etc.} \qquad (492)$$

This is true of reversible variations in which the surfaces which have been considered are fixed. It will be observed that ε^S denotes the excess of the energy of the actual mass which occupies the total volume which we have considered over that energy which it would have, if on each side of the surface S the density of energy had the same uniform value quite up to that surface which it has at a sensible distance from it; and that η^S, m_S^1, m_2^S, etc., have analogous significations. It will be convenient, and need not be a source of any misconception, to call ε^S and η^S the energy and entropy *of the surface* (or the *superficial* energy and entropy), $\frac{\varepsilon^S}{s}$ and $\frac{\eta^S}{s}$ the *superficial densities* of energy and entropy, $\frac{m_1^S}{s}$, $\frac{m_2^S}{s}$, etc., the *superficial densities* of the several components.

Now these quantities (ε^S, η^S, m_1^S, etc.) are determined partly by the state of the physical system which we are considering, and partly by the various imaginary surfaces by means of which these quantities have been defined. The position of these surfaces, it will be remembered, has been regarded as fixed in the variation of the system. It is evident, however, that the form of that portion of these surfaces, which lies in the region of homogeneity on either side of the surface of discontinuity cannot affect the values of these quantities. To obtain the complete value of $\delta\varepsilon^S$ for reversible variations, we have therefore only to regard variations in the position and form of the limited surface **s**, as this determines all of the surfaces in question lying within the region of non-homogeneity. Let us first suppose the form of **s** to remain unvaried and only its position in space to vary, either by translation or rotation. No change in (492) will be necessary to make it valid in this case. For the equation is valid if **s** remains fixed and the material system is varied in position; also, if the material system and **s** are both varied in position, while their relative position remains unchanged. Therefore, it will be valid if the surface alone varies its position.

But if the form of **s** be varied, we must add to the second member (492) terms which shall represent the value of

$$\delta\varepsilon^S - t\,\delta\eta^S - \mu_1\,\delta m_1^S - \mu_2\,\delta m_2^S - \text{etc.}$$

due to such variation in the form of **s**. If we suppose **s** to be sufficiently small to be considered uniform throughout in its curvatures and in respect to the state of the surrounding matter, the value of the above expression will be determined by the variation of its area δs and the variations of its principal curvatures δc_1 and δc_2, and we may write

$$\delta \varepsilon^S = t\, \delta \eta^S + \mu_1\, \delta m_1^S + \mu_2\, \delta m_2^S + \text{etc.} \\ + \sigma\, \delta s + C_1\, \delta c_1 + C_2\, \delta c_2, \tag{493}$$

or

$$\delta \varepsilon^S = t\, \delta \eta^S + \mu_1\, \delta m_1^S + \mu_2\, \delta m_2^S + \text{etc.} \\ + \sigma\, \delta s + \tfrac{1}{2}(C_1 + C_2)\, \delta(c_1 + c_2) + \tfrac{1}{2}(C_1 - C_2)\, \delta(c_1 - c_2), \tag{494}$$

σ, C_1, and C_2 denoting quantities which are determined by the initial state of the system and position and form of **s**. The above is the complete value of the variation of ε^S for reversible variations of the system. But it is always possible to give such a position to the surface **s** that $C_1 + C_2$ shall vanish.

To show this, it will be convenient to write the equation in the longer form [see (490), (491)]

$$\delta \varepsilon - t\, \delta \eta - \mu_1\, \delta m_1 - \mu_2\, \delta m_2 - \text{etc.} \\ - \delta \varepsilon''' + t\, \delta \eta''' + \mu_1\, \delta m_1''' + \mu_2\, \delta m_1''' + \text{etc.} \\ - \delta \varepsilon'''' + t\, \delta \eta'''' + \mu_1\, \delta m_1'''' + \mu_2\, \delta m_2'''' + \text{etc.} \\ = \sigma\, \delta s + \tfrac{1}{2}(C_1 + C_2)\, \delta(c_1 + c_2) + \tfrac{1}{2}(C_1 - C_2)\, \delta(c_1 - c_2), \tag{495}$$

i. e., by (482)–(484) and (12),

$$\delta \varepsilon - t\, \delta \eta - \mu_1\, \delta m_1 - \mu_2\, \delta m_2 - \text{etc.} + p'\, \delta v''' + p''\, \delta v'''' \\ = \sigma\, \delta s + \tfrac{1}{2}(C_1 + C_2)\, \delta(c_1 + c_2) + \tfrac{1}{2}(C_3 - C_2)\, \delta(c_1 - c_2). \tag{496}$$

From this equation it appears in the first place that the pressure is the same in the two homogeneous masses separated by a plane surface of discontinuity. For let us imagine the material system to remain unchanged, while the plane surface **s** without change of area or of form moves in the direction of its normal. As this does not affect the boundaries of the mass M,

$$\delta \varepsilon - t\, \delta \eta - \mu_1\, \delta m_1 - \mu_2\, \delta m_2 - \text{etc.} = 0.$$

Also $\delta s = 0$, $\delta(c_1 + c_2) = 0$, $\delta(c_1 - c_2) = 0$, and $\delta v''' = - \delta v''''$. Hence $p' = p''$, when the surface of discontinuity is plane.

Let us now examine the effect of different positions of the surface **s** in the same material system upon the value of $C_1 + C_2$, supposing at first that in the initial state of the system the surface of discontinuity is plane. Let us give the surface **s** some particular position. In the initial state of the system this surface will of course be plane like the physical surface of discontinuity, to which it is parallel. In the varied state of the system, let it become a portion of a spherical surface having positive curvature; and at sensible distances from this surface let the matter be homogeneous and with the same phases as in the initial state of the system; also at and about the surface let the state of the matter so far as possible be the same as at and about the plane surface in the initial state of the system. (Such a variation in the system may evidently take place negatively as well as positively, as the surface may be curved toward either side. But whether such a variation is consistent with the maintenance of equilibrium is of no consequence, since in the preceding equations only the initial state is supposed to be one of equilibrium.) Let the surface **s**, placed as supposed, whether in the initial or the varied state of the surface, be distinguished by the symbol **s**′. Without changing either the initial or the varied state of the material system, let us make another supposition with respect to the imaginary surface **s**. In the unvaried system let it be parallel to its former position but removed from it a distance λ on the side on which lie the centers of positive curvature. In the varied state of the system, let it be spherical and concentric with **s**′, and separated from it by the same distance λ. It will of course lie on the same side of **s**′ as in the unvaried system. Let the surface **s**, placed in accordance with this second supposition, be distinguished by the symbol **s**″. Both in the initial and the varied state, let the perimeters of **s**′ and **s**″ be traced by a common normal. Now the value of

$$\delta\varepsilon - t\,\delta\eta - \mu_1\,\delta m_1 - \mu_2\,\delta m_2 - \text{etc.}$$

in equation (496) is not affected by the position of **s**, being determined simply by the body M: the same is true $p'\,\delta v''' + p''\,\delta v''''$ or $p'\delta(v''' + v'''')$, $v''' + v''''$ being the volume of M. Therefore the second member of (496) will have the same value whether the expressions relate to **s**′ or **s**″. Moreover, $\delta(c_1 - c_2) = 0$ both for **s**′ and **s**″. If we distinguish the quantities determined for **s**′ and for **s**″ by the marks ′ and ″, we may therefore write

$$\sigma'\,\delta s' + \tfrac{1}{2}(C_1' + C_2')\,\delta(c_1' + c_2') = \sigma''\,\delta s'' + \tfrac{1}{2}(C_1'' + C_2'')\,\delta(c_1'' + c_2'').$$

Now if we make $$\delta s'' = 0,$$

we shall have by geometrical necessity

$$\delta s' = s\,\lambda\,\delta(c_1'' + c_2'').$$

Hence

$$\sigma' s\lambda\delta(c_1''+c_2'')+\tfrac{1}{2}(C_1'+C_2')\,\delta(c_1'+c_2')=\tfrac{1}{2}(C_2''+C_2'')\,\delta(c_1''+c_2'').$$

But $$\delta(c_1'+c_2')=\delta(c_1''+c_2'').$$

Therefore, $$C_1'+C_2'+2\,\sigma'\,s\,\lambda=C_1''+C_2''.$$

This equation shows that we may give a positive or negative value to $C_1''+C_2''$ by placing $\mathbf{s}''$ a sufficient distance on one or on the other side of $\mathbf{s}'$. Since this is true when the (unvaried) surface is plane, it must also be true when the surface is nearly plane. And for this purpose a surface may be regarded as nearly plane, when the radii of curvature are very large in proportion to the thickness of the non-homogeneous film. This is the case when the radii of curvature have any sensible size. In general, therefore, whether the surface of discontinuity is plane or curved it is possible to place the surface $\mathbf{s}$ so that C_1+C_2 in equation (494) shall vanish.

Now we may easily convince ourselves by equation (493) that if $\mathbf{s}$ is placed within the non-homogeneous film, and $s=1$, the quantity σ is of the same order of magnitude as the values of ε^{S}, η^{S}, m_1^{S}, m_2^{S}, etc., while the values of C_1 and C_2 are of the same order of magnitude as the changes in the values of the former quantities caused by increasing the curvature of $\mathbf{s}$ by unity. Hence, on account of the thinness of the non-homogeneous film, since it can be very little affected by such a change of curvature in $\mathbf{s}$, the values of C_1 and C_2 must in general be very small relatively to σ. And hence, if $\mathbf{s}'$ be placed within the non-homogeneous film, the value of λ which will make $C_1''+C_2''$ vanish must be very small (of the same order of magnitude as the thickness of the non-homogeneous film). The position of $\mathbf{s}$, therefore, which will make C_1+C_2 in (494) vanish, will in general be sensibly coincident with the physical surface of discontinuity.

We shall hereafter suppose, when the contrary is not distinctly indicated that the surface $\mathbf{s}$, in the unvaried state of the system, has such a position as to make $C_1+C_2=0$. It will be remembered that the surface $\mathbf{s}$ is a part of a larger surface S, which we have called the *dividing surface*, and which is coextensive with the physical surface of discontinuity. We may suppose that the position of the dividing surface is everywhere determined by similar considerations. This is evidently consistent with the suppositions made on page 380 with regard to this surface.

We may therefore cancel the term

$$\tfrac{1}{2}(C_1 + C_2)\,\delta\,(c_1 + c_2)$$

in (494). In regard to the following term, it will be observed that C_1 must necessarily be equal to C_2, when $c_1 = c_2$, which is the case when the surface of discontinuity is plane. Now on account of the thinness of the non-homogeneous film, we may always regard it as composed of parts which are approximately plane. Therefore, without danger of sensible error, we may also cancel the term

$$\tfrac{1}{2}(C_1 - C_2)\,\delta\,(c_1 - c_2).$$

Equation (494) is thus reduced to the form

$$\delta\varepsilon^{S} = t\,\delta\eta^{S} + \sigma\,\delta s + \mu_1\,\delta m_1^{S} + \mu_2\,\delta m_2^{S} + \text{etc.} \tag{497}$$

We may regard this as the complete value of $\delta\varepsilon^{S}$, for all reversible variations in the state of the system supposed initially in equilibrium, when the dividing surface has its initial position determined in the manner described.

The above equation is of fundamental importance in the theory of capillarity. It expresses a relation with regard to surfaces of discontinuity analogous to that expressed by equation (12) with regard to homogeneous masses. From the two equations may be directly deduced the conditions of equilibrium of heterogeneous masses in contact, subject or not to the action of gravity, without disregard of the influence of the surfaces of discontinuity. The general problem, including the action of gravity, we shall take up hereafter: at present we shall only consider, as hitherto, a small part of a surface of discontinuity with a part of the homogeneous mass on either side, in order to deduce the additional condition which may be found when we take account of the motion of the dividing surface.

We suppose as before that the mass especially considered is bounded by a surface of which all that lies in the region of non-homogeneity is such as may be traced by a moving normal to the dividing surface. But instead of dividing the mass as before into four parts, it will be sufficient to regard it as divided into two parts by the dividing surface. The energy, entropy, etc., of these parts, estimated on the supposition that its nature (including density of energy, etc.) is uniform quite up to the dividing surface, will be denoted by ε', η', etc., ε'', η'', etc. Then the total energy will be $\varepsilon^{S} + \varepsilon' + \varepsilon''$, and the general condition of internal equilibrium will be that

$$\delta\varepsilon^{S} + \delta\varepsilon' + \delta\varepsilon'' \geqq 0, \tag{498}$$

when the bounding surface is fixed, and the total entropy and total quantities of the various components are constant. We may suppose η^S, η', η'', m_1^S, m_1', m_1'', m_2^S, m_2', m_2'', etc., to be all constant. Then by (497) and (12) the condition reduces to

$$\sigma\,\delta s - p'\,\delta v' - p''\,\delta v'' = 0. \qquad (499)$$

(We may set $=$ for $\geqq$, since changes in the position of the dividing surface can evidently take place in either of two opposite directions.) This equation has evidently the same form as if a membrane without rigidity and having a tension σ, uniform in all directions, existed at the dividing surface. Hence, the particular position which we have chosen for this surface may be called the surface of tension, and σ the superficial tension. If all parts of the dividing surface move a uniform normal distance δN, we shall have

$$\delta s = (c_1 + c_2)\, s\,\delta N, \qquad \delta v' = s\,\delta N, \qquad \delta v'' = -s\,\delta N;$$

whence

$$\sigma\,(c_1 + c_2) = p' - p'', \qquad (500)$$

the curvatures being positive when their centers lie on the side to which p' relates. This is the condition which takes the place of that of equality of pressure (see pp. 119, 128) for heterogeneous fluid masses in contact, when we take account of the influence of the surfaces of discontinuity. We have already seen that the conditions relating to temperature and the potentials are not affected by these surfaces.

Fundamental Equations for Surfaces of Discontinuity. Between Fluid Masses

In equation (497) the initial state of the system is supposed to be one of equilibrium. The only limitation with respect to the varied state is that the variation shall be reversible, i. e., that an opposite variation shall be possible. Let us now confine our attention to variations in which the system remains in equilibrium. To distinguish this case, we may use the character d instead δ, and write

$$d\epsilon^S = t\,d\eta^S + \sigma\,ds + \mu_1\,dm_1^S + \mu_2\,dm_2^S + \text{etc.} \qquad (501)$$

Both the states considered being states of equilibrium, the limitation with respect to the reversibility of the variations may be neglected, since the variations will always be reversible in at least one of the states considered.

If we integrate this equation, supposing the area s to increase from zero to any finite value s, while the material system to a part of which the equation relates remains without change, we obtain

$$\epsilon^S = t\,\eta^S + \sigma\,s + \mu_1\,m_1^S + \mu_2\,m_2^S + \text{etc.}, \qquad (502)$$

which may be applied to any portion of any surface of discontinuity (in equilibrium) which is of the same nature throughout, or throughout which the values of t, σ, μ_1, μ_2, etc. are constant.

If we differentiate this equation, regarding all the quantities as variable, and compare the result with (501), we obtain

$$\eta^S\, dt + s\, d\sigma + m_1^S\, d\mu_1 + m_2^S\, d\mu_2 + \text{etc.} = 0. \tag{503}$$

If we denote the *superficial densities* of energy, of entropy, and of the several component substances (see page 386) by ε_S, η_S, Γ_1, Γ_2, etc., we have

$$\varepsilon_S = \frac{\varepsilon^S}{s}, \qquad \eta_S = \frac{\eta^S}{s}, \tag{504}$$

$$\Gamma_1 = \frac{m_1^S}{s}, \qquad \Gamma_2 = \frac{m_2^S}{s}, \qquad \text{etc.}, \tag{505}$$

and the preceding equations may be reduced to the form:—

$$d\varepsilon_S = t\, d\eta_S + \mu_1\, d\Gamma_1 + \mu_2\, d\Gamma_2 + \text{etc.}, \tag{506}$$

$$\varepsilon_S = t\, \eta_S + \sigma + \mu_1\, \Gamma_1 + \mu_2\, \Gamma_2 + \text{etc.}, \tag{507}$$

$$d\sigma = -\eta_S\, dt - \Gamma_1\, d\mu_1 - \Gamma_2\, d\mu_2 - \text{etc.} \tag{508}$$

Now the contact of the two homogeneous masses does not impose any restriction upon the variations of phase of either, except that the temperature and the potentials for actual components shall have the same value in both. [See (482)–(484) and (500).] For however the values of the pressures in the homogeneous masses may vary (on account of arbitrary variations of the temperature and potentials), and however the superficial tension may vary, equation (500) may always be satisfied by giving the proper curvature to the surface of tension, so long, at least, as the difference of pressures is not great. Moreover, if any of the potentials μ_1, μ_2, etc. relate to substances which are found only at the surface of discontinuity, their values may be varied by varying the superficial densities of those substances. The values of t, μ_1, μ_2, etc. are therefore independently variable, and it appears from equation (508) that σ is a function of these quantities. If the form of this function is known, we may derive from it by differentiation $n+1$ equations (n denoting the total number of component substances) giving the values of η_S, Γ_1, Γ_2, etc. in terms of the variables just mentioned. This will give us, with (507), $n+3$ independent equations between the $2n+4$ quantities which occur in that equation. These are all that exist, since $n+1$

of these quantities are independently variable. Or, we may consider that we have $n+3$ independent equations between the $2n+5$ quantities occurring in equation (502), of which $n+2$ are independently variable.

An equation, therefore, between

$$\sigma, \quad t, \quad \mu_1, \quad \mu_2, \quad \text{etc.,} \tag{509}$$

may be called a fundamental equation for the surface of discontinuity. An equation between

$$\varepsilon^S, \quad \eta^S, \quad s, \quad m_1^S \quad m_2^S, \quad \text{etc.,} \tag{510}$$

or between

$$\varepsilon_S, \quad \eta_S, \quad \Gamma_1, \quad \Gamma_2, \quad \text{etc.,} \tag{511}$$

may also be called a fundamental equation in the same sense. For it is evident from (501) that an equation may be regarded as subsisting between the variables (510), and if this equation be known, since $n+2$ of the variables may be regarded as independent (viz., $n+1$ for the $n+1$ variations in the nature of the surface of discontinuity, and one for the area of the surface considered), we may obtain by differentiation and comparison with (501), $n+2$ additional equations between the $2n+5$ quantities occurring in (502). Equation (506) shows that equivalent relations can be deduced from an equation between the variables (511). It is moreover quite evident that an equation between the variables (510) must be reducible to the form of an equation between the ratios of these variables, and therefore to an equation between the variables (511).

The same designation may be applied to any equation from which, by differentiation and the aid only of general principles and relations, $n+3$ independent relations between the same $2n+5$ quantities may be obtained.

If we set

$$\psi^S = \varepsilon^S - t\,\eta^S, \tag{512}$$

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we obtain by differentiation and comparison with (501)

$$d\psi^S = -\eta^S\,dt + \sigma\,ds + \mu_1\,dm_1^S + \mu_2\,dm_2^S + \text{etc.} \tag{513}$$

An equation, therefore, between ψ^S, t, s, m_1^S, m_2^S, etc., is a fundamental equation, and is to be regarded as entirely equivalent to either of the other fundamental equations which have been mentioned.

The reader will not fail to notice the analogy between these fundamental equations, which relate to surfaces of discontinuity, and those relating to homogeneous masses, which have been described on pages 140–144.

On the Experimental Determination of Fundamental Equations for Surfaces of Discontinuity.

When all the substances which are found at a surface of discontinuity are components of one or the other of the homogeneous masses, the potentials μ_1, μ_2, etc., as well as the temperature, may be determined from these homogeneous masses.* The tension σ may be determined by means of the relation (500). But our measurements are practically confined to cases in which the difference of the pressures in the homogeneous masses is small; for with increasing differences of pressure the radii of curvature soon become too small for measurement. Therefore, although the equation $p' = p''$ (which is equivalent to an equation between t, μ_1, μ_2, etc., since p' and p'' are both functions of these variables) may not be exactly satisfied in cases in which it is convenient to measure the tension, yet this equation is so nearly satisfied in all the measurements of tension which we can make, that we must regard such measurements as simply establishing the values of σ for values of t, μ_1, μ_2, etc., which satisfy the equation $p' = p''$, but not as sufficient to establish the rate of change in the value of σ for variations of t, μ_1, μ_2, etc., which are inconsistent with the equation $p' = p''$.

To show this more distinctly, let t, μ_2, m_3, etc. remain constant, then by (508) and (98)

$$d\sigma = -\Gamma_1\, d\mu_1,$$
$$dp' = \gamma_1'\, d\mu_1,$$
$$dp'' = \gamma_1''\, d\mu_1,$$

γ_1' and γ_1'' denoting the densities $\frac{m_1'}{v'}$ and $\frac{m_1''}{v''}$. Hence,

$$dp' - dp'' = (\gamma_1' - \gamma_1'')\, d\mu_1,$$

and $$\Gamma_1\, d(p' - p'') = (\gamma_1'' - \gamma_1')\, d\sigma.$$

But by (500)

$$(c_1 + c_2)\, d\sigma + \sigma\, d(c_1 + c_2) = d(p' - p'').$$

Therefore,

$$\Gamma_1 (c_1 + c_2)\, d\sigma + \Gamma_1\, \sigma\, d(c_1 + c_2) = (\gamma_1'' - \gamma_1')\, d\sigma,$$

or $$\{\gamma_1'' - \gamma_1' - \Gamma_1 (c_1 + c_2)\}\, d\sigma = \Gamma_1\, \sigma\, d(c_1 + c_2).$$

* It is here supposed that the thermodynamic properties of the homogeneous masses have already been investigated, and that the fundamental equations of these masses may be regarded as known.

Now $\Gamma_1 (c_1 + c_2)$ will generally be very small compared with $\gamma_1'' - \gamma_1'$. Neglecting the former term, we have

$$\frac{d\sigma}{\sigma} = \frac{\Gamma_1}{\gamma_1'' - \gamma_1'} d(c_1 + c_2).$$

To integrate this equation, we may regard Γ_1, γ_1', γ_1'' as constant. This will give, as an approximate value,

$$\log \frac{\sigma}{\sigma'} = \frac{\Gamma_1}{\gamma_1'' - \gamma_1'} (c_1 + c_2),$$

σ' denoting the value of σ when the surface is plane. From this it appears that when the radii of curvature have any sensible magnitude, the value of σ will be sensibly the same as when the surface is plane and the temperature and all the potentials except one have the same values, unless the component for which the potential has not the same value has very nearly the same density in the two homogeneous masses, in which case, the condition under which the variations take place is nearly equivalent to the condition that the pressures shall remain equal.

Accordingly, we cannot in general expect to determine the superficial density Γ_1 from its value $-\left(\frac{d\sigma}{d\mu_1}\right)_{t,\mu}$ * by measurements of superficial tensions. The case will be the same with Γ_2, Γ_3, etc., and also with η_S, the superficial density of entropy.

The quantities ε_S, η_S, Γ_1, Γ_2, etc. are evidently too small in general to admit of direct measurement. When one of the components, however, is found only at the surface of discontinuity, it may be more easy to measure its superficial density than its potential. But except in this case, which is of secondary interest, it will generally be easy to determine σ in terms of t, μ_1, μ_2, etc., with considerable accuracy for plane surfaces, and extremely difficult or impossible to determine the fundamental equation more completely.

Fundamental Equations for Plane Surfaces of Discontinuity. between Fluid Masses

An equation giving σ in terms of t, μ_1, μ_2, etc., which will hold true only so long as the surface of discontinuity is plane, may be called a fundamental equation for a plane surface of discontinuity. It will be interesting to see precisely what results can be obtained from such an equation, especially with respect to the energy and entropy

* The suffixed μ is used to denote that all the potentials except that occurring in the denominator of the differential coefficient are to be regarded as constant.

and the quantities of the component substances in the vicinity of the surface of discontinuity.

These results can be exhibited in a more simple form, if we deviate to a certain extent from the method which we have been following. The particular position adopted for the dividing surface (which determines the superficial densities) was chosen in order to make the term $\frac{1}{2}(C_1+C_2)\,\delta\,(c_1+c_2)$ in (494) vanish. But when the curvature of the surface is not supposed to vary, such a position of the dividing surface is not necessary for the simplification of the formula. It is evident that equation (501) will hold true for plane surfaces (supposed to remain such) without reference to the position of the dividing surfaces, except that it shall be parallel to the surface of discontinuity. We are therefore at liberty to choose such a position for the dividing surface as may for any purpose be convenient.

None of the equations (502)–(513), which are either derived from (501), or serve to define new symbols, will be affected by such a change in the position of the dividing surface. But the expressions ε^{S}, η^{S}, m_1^{S}, m_2^{S}, etc., as also ε_{S}, η_{S}, Γ_1, Γ_2, etc. and ψ^{S}, will of course have different values when the position of that surface is changed. The quantity σ, however, which we may regard as defined by equations (501), or, if we choose, by (502) or (507), will not be affected in value by such a change. For if the dividing surface be moved a distance λ measured normally and toward the side to which v'' relates, the quantities

$$\varepsilon_{\mathrm{S}},\quad \eta_{\mathrm{S}},\quad \Gamma_1,\quad \Gamma_2,\quad \text{etc.},$$

will evidently receive the respective increments

$$\lambda\,(\varepsilon_{\mathrm{V}}''-\varepsilon_{\mathrm{V}}'),\quad \lambda\,(\eta_{\mathrm{V}}''-\eta_{\mathrm{V}}'),\quad \lambda\,(\gamma_1''-\gamma_1'),\quad \lambda\,(\gamma_2''-\gamma_2'),\quad \text{etc.},$$

$\varepsilon_{\mathrm{V}}'$, $\varepsilon_{\mathrm{V}}''$, η_{V}', η_{V}'' denoting the densities of energy and entropy in the two homogeneous masses. Hence, by equation (507), σ will receive the increment

$$\lambda(\varepsilon_{\mathrm{V}}''-\varepsilon_{\mathrm{V}}')-t\,\lambda(\eta_{\mathrm{V}}''-\eta_{\mathrm{V}}')-\mu_1\lambda(\gamma_1''-\gamma_1')-\mu_2\lambda(\gamma_2''-\gamma_2')-\text{etc.}$$

But by (93)

$$-p''=\varepsilon_{\mathrm{V}}''-t\,\eta_{\mathrm{V}}''-\mu_1\,\gamma_1''-\mu_2\,\gamma_2''-\text{etc.},$$
$$-p'=\varepsilon_{\mathrm{V}}'-t\,\eta_{\mathrm{V}}'-\mu_1\,\gamma_1'-\mu_2\,\gamma_2'-\text{etc.}$$

Therefore, since $p'=p''$, the increment in the value of σ is zero. The value of σ is therefore independent of the position of the dividing surface, when this surface is plane. But when we call this quantity the superficial tension, we must remember that it will not have its characteristic properties as a tension with reference to any arbitrary surface. Considered as a tension, its position is in the surface which we have called the surface of tension, and, strictly speaking, nowhere else. The positions of the dividing surface, however, which we shall consider, will not vary from the surface of tension sufficiently to make this distinction of any practical importance.

It is generally possible to place the dividing surface so that the total quantity of any desired component in the vicinity of the surface of discontinuity shall be the same as if the density of that component were uniform on each side quite up to the dividing surface. In other words, we may place the dividing surface so as to make any one of the quantities Γ_1, Γ_2, etc., vanish. The only exception is with regard to a component which has the same density in the two homogeneous masses. With regard to a component which has very nearly the same density in the two masses such a location of the dividing surface might be objectionable, as the dividing surface might fail to coincide sensibly with the physical surface of discontinuity. Let us suppose that $\gamma_1{}'$ is not equal (nor very nearly equal) to $\gamma_1{}''$, and that the dividing surface is so placed as to make $\Gamma_1 = 0$. Then equation (508) reduces to

$$d\sigma = -\eta_{S(1)}\,dt - \Gamma_{2(1)}\,d\mu_2 - \Gamma_{3(1)}\,d\mu_3 - \text{etc.}, \qquad (514)$$

where the symbols $\eta_{S(1)}$, $\Gamma_{2(1)}$, etc., are used for greater distinctness to denote the values of η_S, Γ_2, etc., as determined by a dividing surface placed so that $\Gamma_1 = 0$. Now we may consider all the differentials in the second member of this equation as independent, without violating the condition that the surface shall remain plane, i. e., that $dp' = dp''$. This appears at once from the values of dp' and dp'' given by equation (98). Moreover, as has already been observed, when the fundamental equations of the two homogeneous masses are known, the equation $p' = p''$ affords a relation between the quantities t, μ_1, μ_2, etc. Hence, when the value of σ is also known for plane surfaces in terms of t, μ_1, μ_2, etc., we can eliminate μ_1 from this expression by means of the relation derived from the equality of pressures, and obtain the value of σ for plane surfaces in terms of t, μ_2, μ_3, etc. From this, by differentiation, we may obtain directly the values of $\eta_{S(1)}$, $\Gamma_{2(1)}$, $\Gamma_{3(1)}$, etc., in terms of t, μ_2, μ_3, etc. This would be a convenient form of the fundamental equation. But, if the elimination of p', p'', and μ_1 from the finite equations presents algebraic difficulties, we can in all cases easily eliminate dp', dp'', $d\mu_1$ from the corresponding differential equations and thus obtain a differential equation from which the values of $\eta_{S(1)}$, $\Gamma_{2(1)}$, $\Gamma_{3(1)}$, etc. in terms of t, μ_1, μ_2, etc., may be at once obtained by comparison with (514).*

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* If liquid mercury meets the mixed vapors of water and mercury in a plane surface, and we use μ_1 and μ_2 to denote the potentials of mercury and water respectively, and place the dividing surface so that $\Gamma_1=0$, i. e., so that the total quantity of mercury is the same as if the liquid mercury reached this surface on one side and the mercury vapor on the other without change of density on either side, then $\Gamma_{2(1)}$ will represent the amount of water in the vicinity of this surface, per unit of surface, above that which there would be, if the water-vapor just reached the surface without change of density, and this quantity (which we may call the quantity of water condensed upon the surface of the mercury) will be determined by the equation

$$\Gamma_{2(1)} = -\frac{d\sigma}{d\mu_2}.$$

(In this differential coefficient as well as the following, the temperature is supposed to remain constant and the surface of discontinuity plane. Practically, the latter condition may be regarded as fulfilled in the case of any ordinary curvatures.)

If the pressure in the mixed vapors conforms to the law of Dalton (see pp. 215, 218), we shall have for constant temperature

$$dp_2 = \gamma_2\, d\mu_2,$$

where p_2 denotes the part of the pressure in the vapor due to the water-vapor, and γ_2 the density of the water-vapor. Hence we obtain

$$\Gamma_{2(1)} = -\gamma_2 \frac{d\sigma}{dp_2}.$$

For temperatures below 100° centigrade, this will certainly be accurate, since the pressure due to the vapor of mercury may be neglected.

The value of σ for $p_2=0$ and the temperature of 20° centigrade must be nearly the same as the superficial tension of mercury in contact with air, or 55.03 grammes per linear metre according to Quincke (Pogg. Ann., Bd. 139, p. 27). The value of σ at the same temperature, when the condensed water begins to have the properties of water in mass, will be equal to the sum of the superficial tensions of mercury in contact with water and of water in contact with its own vapor. This will be, according to the same authority, 42.58 + 8.25, or 50.83 grammes per metre, if we neglect the difference of the tensions of water with its vapor and water with air. As p_2, therefore, increases from zero to 236400 grammes per square metre (when water begins to be condensed *in mass*), σ diminishes from about 55.03 to about 50.83 grammes per linear metre. If the general course of the values of σ for intermediate values of p_2 were determined by experiment, we could easily form an approximate estimate of the values of the superficial density $\Gamma_{2(1)}$ for different pressures less than that of saturated vapor. It will be observed that the determination of the superficial density does not by any means depend upon inappreciable differences of superficial tension. The greatest difficulty in the determination would doubtless be that of distinguishing between the diminution of superficial tension due to the water and that due to other substances which might accidentally be present. Such determinations are of considerable practical importance on account of the use of mercury in measurements of the specific gravity of vapors.

The same physical relations may of course be deduced without giving up the use of the surface of tension as a dividing surface, but the formulæ which express them will be less simple. If we make t, μ_3, μ_4, etc. constant, we have by (98) and (508)

$$dp' = \gamma_1' \, d\mu_1 + \gamma_2' \, d\mu_2,$$
$$dp'' = \gamma_1'' \, d\mu_1 + \gamma_2'' \, d\mu_2,$$
$$d\sigma = -\Gamma_1 \, d\mu_1 - \Gamma_2 \, d\mu_2,$$

where we may suppose Γ_1 and Γ_2 to be determined with reference to the surface of tension. Then, if $dp' = dp''$,

$$(\gamma_1' - \gamma_1'') \, d\mu_1 + (\gamma_2' - \gamma_2'') \, d\mu_2 = 0,$$

and

$$d\sigma = \Gamma_1 \frac{\gamma_2' - \gamma_2''}{\gamma_1' - \gamma_1''} d\mu_2 - \Gamma_2 \, d\mu_2.$$

That is,

$$\left(\frac{d\sigma}{d\mu_2}\right)_{p'-p'',\, t,\, \mu_3,\, \mu_4,\, \text{etc.}} = -\Gamma_2 + \Gamma_1 \frac{\gamma_2' - \gamma_2''}{\gamma_1' - \gamma_1''}. \qquad (515)$$

The reader will observe that $\dfrac{\Gamma_1}{\gamma_1' - \gamma_1''}$ represents the distance between the surface of tension and that dividing surface which would make $\Gamma_1 = 0$; the second number of the last equation is therefore equivalent to $-\Gamma_{2(1)}$.

If any component substance has the same density in the two homogeneous masses separated by a plane surface of discontinuity, the value of the superficial density for that component is independent of the position of the dividing surface. In this case alone we may derive the value of the superficial density of a component with reference to the surface of tension from the fundamental equation for plane surfaces alone. Thus in the last equation, when $\gamma_2' = \gamma_2''$, the second member will reduce to $-\Gamma_2$. It will be observed that to make $p' - p''$, t, μ_3, μ_4, etc. constant is in this case equivalent to making t, μ_1, μ_3, μ_4, etc. constant.

Substantially the same is true of the superficial density of entropy or of energy, when either of these has the same density in the two homogeneous masses.*

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* With respect to questions which concern only the *form* of surfaces of discontinuity, such precision as we have employed in regard to the position of the dividing surface is evidently quite unnecessary. This precision has not been used for the sake of the mechanical part of the problem, which does not require the surface to be defined with greater nicety than we can employ in our observations, but in order to give

Fluid Masses

Concerning the Stability of Surfaces of Discontinuity. between

We shall first consider the stability of a film separating homogeneous masses with respect to changes in its nature, while its position and the nature of the homogeneous masses are not altered. For this purpose, it will be convenient to suppose that the homogeneous masses are very large, and thoroughly stable with respect to the possible formation of any different homogeneous masses out of their components, and that the surface of discontinuity is plane and uniform.

Let us distinguish the quantities which relate to the actual components of one or both of the homogeneous masses by the suffixes $_a$, $_b$, etc., and those which relate to components which are found only at the surface of discontinuity by the suffixes $_g$, $_h$, etc., and consider the variation of the energy of the whole system in consequence of a given change in the nature of a small part of the surface of discontinuity, while the entropy of the whole system and the total quantities of the several components remain constant, as well as the volume of each of the homogeneous masses, as determined by the surface of tension. This small part of the surface of discontinuity in its changed state is supposed to be still uniform in nature, and such as may subsist in equilibrium between the given homogeneous masses, which will evidently not be sensibly altered in nature or thermodynamic state. The remainder of the surface of discontinuity is also supposed to remain uniform, and on account of its infinitely greater size to be infinitely less altered in its nature than the first part. Let $\varDelta\varepsilon^S$ denote the increment of the superficial energy of this first part, $\varDelta\eta^S$, $\varDelta m_a^S$, $\varDelta m_b^S$, etc., $\varDelta m_g^S$, $\varDelta m_h^S$, etc., the increments of its superficial

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determinate values to the superficial densities of energy, entropy, and the component substances, which quantities, as has been seen, play an important part in the relations between the tension of a surface of discontinuity, and the composition of the masses which it separates.

The product σs of the superficial tension and the area of the surface, may be regarded as the *available energy* due to the surface in a system in which the temperature and the potentials μ_1, μ_2, etc.—or the differences of these potentials and the gravitational potential (see page 208) when the system is subject to gravity—are maintained sensibly constant. The value of σ, as well as that of s, is sensibly independent of the precise position which we may assign to the dividing surface (so long as this is sensibly coincident with the surface of discontinuity), but ε_S, the *superficial density of energy*, as the term is used in this paper, like the superficial densities of entropy and of the component substances, requires a more precise localization of the dividing surface.

entropy and of the quantities of the components which we regard as belonging to the surface. The increments of entropy and of the various components which the rest of the system receive will be expressed by

$$-\Delta\eta^S, \quad -\Delta m_a^S, \quad -\Delta m_b^S, \quad \text{etc.,} \quad -\Delta m_g^S, \quad -\Delta m_h^S, \quad \text{etc.,}$$

and the consequent increment of energy will be by (12) and (501)

$$-t\,\Delta\eta^S - \mu_a\,\Delta m_a^S - \mu_b\,\Delta m_b^S - \text{etc.} - \mu_g\,\Delta m_g^S - \mu_h\,\Delta m_h^S - \text{etc.}$$

Hence the total increment of energy in the whole system will be

$$\left.\begin{aligned}\Delta\varepsilon^S - t\,\Delta\eta^S - \mu_a\,\Delta m_a^S - \mu_b\,\Delta m_b^S - \text{etc.}\\ - \mu_g\,\Delta m_g^S - \mu_h\Delta m_h^S - \text{etc.}\end{aligned}\right\} \qquad (516)$$

If the value of this expression is necessarily positive, for finite changes as well as infinitesimal in the nature of the part of the film to which $\Delta\varepsilon^S$, etc. relate,* the increment of energy of the whole system will be positive for any possible changes in the nature of the film, and the film will be stable, at least with respect to changes in its nature, as distinguished from its position. For, if we write

$$D\varepsilon^S, \quad D\eta^S, \quad Dm_a^S, \quad Dm_b^S, \quad \text{etc.,} \quad Dm_g^S, \quad Dm_h^S, \quad \text{etc.}$$

for the energy, etc. of any element of the surface of discontinuity, we have from the supposition just made

$$\begin{aligned}\Delta D\varepsilon^S - t\,\Delta D\eta^S - \mu_a\,\Delta Dm_a^S - \mu_b\,\Delta Dm_b^S - \text{etc.}\\ - \mu_g\,\Delta Dm_g^S - \mu_h\,\Delta Dm_h^S - \text{etc.} > 0;\end{aligned} \qquad (517)$$

and integrating for the whole surface, since

$$\Delta\int Dm_g^S = 0, \quad \Delta\int Dm_h^S = 0, \quad \text{etc.,}$$

we have

$$\Delta\int D\varepsilon^S - t\,\Delta\int D\eta^S - \mu_a\,\Delta\int Dm_a^S - \mu_b\,\Delta\int Dm_b^S - \text{etc.} > 0. \qquad (518)$$

Now $\Delta\int D\eta^S$ is the increment of the entropy of the whole surface, and $-\Delta\int D\eta^S$ is therefore the increment of the entropy of the two homogeneous masses. In like manner, $-\Delta\int Dm_a^S$, $-\Delta\int Dm_b^S$, etc. are the increments of the quantities of the components in these masses. The expression

$$-t\,\Delta\int D\eta^S - \mu_a\,\Delta\int Dm_a^S - \mu_b\,\Delta\int Dm_b^S - \text{etc.}$$

* In the case of infinitesimal changes in the nature of the film, the sign Δ must be interpreted, as elsewhere in this paper, without neglect of infinitesimals of the higher orders. Otherwise, by equation (501), the above expression would have the value zero.

denotes therefore, according to equation (12), the increment of energy of the two homogeneous masses, and since $\Delta \int D\varepsilon^{S}$ denotes the increment of energy of the surface, the above condition expresses that the increment of the total energy of the system is positive. That we have only considered the possible formation of such films as are capable of existing in equilibrium between the given homogeneous masses can not invalidate the conclusion in regard to the stability of the film, for in considering whether any state of the system will have less energy than the given state, we need only consider the state of least energy, which is necessarily one of equilibrium.

If the expression (516) is capable of a negative value for an infinitesimal change in the nature of the part of the film to which the symbols relate, the film is obviously unstable.

If the expression is capable of a negative value, but only for finite and not for infinitesimal changes in the nature of this part of the film, the film is *practically unstable*,* i. e., if such a change were made in a small part of the film, the disturbance would tend to increase. But it might be necessary that the initial disturbance should also have a finite magnitude in respect to the extent of surface in which it occurs; for we cannot suppose that the thermodynamic relations of an infinitesimal part of a surface of discontinuity are independent of the adjacent parts. On the other hand, the changes which we have been considering are such that every part of the film remains in equilibrium with the homogeneous masses on each side; and if the energy of the system can be diminished by a finite change satisfying this condition, it may perhaps be capable of diminution by an infinitesimal change which does not satisfy the same condition. We must therefore leave it undetermined whether the film, which in this case is practically unstable, is or is not unstable in the strict mathematical sense of the term.

Let us consider more particularly the condition of practical stability, in which we need not distinguish between finite and infinitesimal changes. To determine whether the expression (516) is capable of a negative value, we need only consider the least value of which it is capable. Let us write it in the fuller form

$$\left.\begin{aligned}\varepsilon^{S''} - \varepsilon^{S'} - t\,(\eta^{S''} - \eta^{S'}) - \mu_a\,(m_a^{S''} - m_a^{S'}) - \mu_b\,(m_b^{S''} - m_b^{S'}) - \text{etc.}\\ - \mu'_g\,(m_g^{S''} - m_g^{S'}) - \mu'_h\,(m_h^{S''} - m_h^{S'}) - \text{etc.},\end{aligned}\right\}\quad(519)$$

where the single and double accents distinguish the quantities which

* With respect to the sense in which this term is used, compare page 133.

relate to the first and second states of the film, the letters without accents denoting those quantities which have the same value in both states. The differential of this expression when the quantities distin guished by double accents are alone considered variable, and the area of the surface is constant, will reduce by (501) to the form

$$(\mu_g'' - \mu_g')\, dm_g^{S''} + (\mu_h'' - \mu_h')\, dm_h^{S''} + \text{etc.}$$

To make this incapable of a negative value, we must have

$$\mu_g'' = \mu_g', \quad \text{unless} \quad m_g^{S''} = 0,$$

$$\mu_h'' = \mu_h', \quad \text{unless} \quad m_h^{S''} = 0.$$

In virtue of these relations and by equation (502), the expression (519), i. e., (516), will reduce to

$$\sigma'' s - \sigma' s,$$

which will be positive or negative according as

$$\sigma'' - \sigma' \tag{520}$$

is positive or negative.

That is, if the tension of the film is less than that of any other film of the same components which can exist between the same homogeneous masses (which has therefore the same values of t, μ_a, μ_b, etc.), and which moreover has the same values of the potentials μ_g, μ_h, etc., so far as it contains the substances to which these relate, then the first film will be stable. But the film will be practically unstable, if any other such film has a less tension. [Compare the expression (141), by which the practical stability of homogeneous masses is tested.]

It is, however, evidently necessary for the stability of the surface of discontinuity with respect to *deformation*, that the value of the superficial tension should be positive. Moreover, since we have by (502) for the surface of discontinuity

$$\varepsilon^S - t\,\eta^S - \mu_a m_a^S - \mu_b m_b^S - \text{etc.} - \mu_g m_g^S - \mu_h m_h^S - \text{etc.} = \sigma s,$$

and by (93) for the two homogeneous masses

$$\varepsilon' - t\,\eta' + p\,v' - \mu_a m_a' - \mu_b m_b' - \text{etc.} = 0,$$

$$\varepsilon'' - t\,\eta'' + p\,v'' - \mu_a m_a'' - \mu_b m_b'' - \text{etc.} = 0,$$

if we denote by

$$\varepsilon, \quad \eta, \quad v, \quad m_a, \quad m_b, \quad \text{etc.}, \quad m_g, \quad m_h, \quad \text{etc.},$$

the total energy, etc. of a composite mass consisting of two such homogeneous masses divided by such a surface of discontinuity, we shall have by addition of these equations

$$\varepsilon - t\eta + pv - \mu_a m_a - \mu_b m_b - \text{etc.} - \mu_g m_g - \mu_h m_h - \text{etc.} = \sigma s.$$

Now if the value of σ is negative, the value of the first member of this equation will decrease as s increases, and may therefore be decreased by making the mass to consist of thin alternate strata of the two kinds of homogeneous masses which we are considering. There will be no limit to the decrease which is thus possible with a given value of v, so long as the equation is applicable, i. e., so long as the strata have the properties of similar bodies in mass. But it may easily be shown (as in a similar case on pages 131, 132) that when the values of

$$t, \quad p, \quad \mu_a, \quad \mu_b, \quad \text{etc.}, \quad \mu_g, \quad \mu_h, \quad \text{etc.}$$

are regarded as fixed, being determined by the surface of discontinuity in question, and the values of

$$\varepsilon, \quad \eta, \quad m_a, \quad m_b, \quad \text{etc.}, \quad m_g, \quad m_h, \quad \text{etc.}$$

are variable and may be determined by any body having the given volume v, the first member of this equation cannot have an infinite negative value, and must therefore have a least possible value, which will be negative, if any value is negative, that is, if σ is negative.

The body determining ε, η, etc. which will give this least value to this expression will evidently be sensibly homogeneous. With respect to the formation of such a body, the system consisting of the two homogeneous masses and the surface of discontinuity with the negative tension is by (53) (see also page 133) at least practically unstable, if the surface of discontinuity is very large, so that it can afford the requisite material without sensible alteration of the values of the potentials. (This limitation disappears, if all the component substances are found in the homogeneous masses.) Therefore, in a system satisfying the conditions of practical stability with respect to the possible formation of all kinds of homogeneous masses, negative tensions of the surfaces of discontinuity are necessarily excluded.

Let us now consider the condition which we obtain by applying (516) to infinitesimal changes. The expression may be expanded as before to the form (519), and then reduced by equation (502) to the form

$$s(\sigma'' - \sigma') + m_g^{S''}(\mu_g'' - \mu_g') + m_h^{S''}(\mu_h'' - \mu_h') + \text{etc.}$$

That the value of this expression shall be positive when the quantities are determined by two films which differ infinitely little is a necessary condition of the stability of the film to which the single accents relate. But if one film is stable, the other will in general be so too, and the distinction between the films with respect to stability is of importance only at the limits of stability. If all films for all values of μ_g, μ_h, etc. are stable, or all within certain limits, it is evident that the value of the expression must be positive when the quantities are determined by any two infinitesimally different films within the same limits. For such collective determinations of stability the condition may be written

$$-s\,\Delta\sigma - m_g^S\,\Delta\mu_g - m_h^S\,\Delta\mu_h - \text{etc.} > 0,$$

or

$$\Delta\sigma < -\Gamma_g\,\Delta\mu_g - \Gamma_h\,\Delta\mu_h - \text{etc.} \qquad (521)$$

On comparison of this formula with (508), it appears that within the limits of stability the second and higher differential coefficients of the tension considered as a function of the potentials for the substances which are found only at the surface of discontinuity (the potentials for the substances found in the homogeneous masses and the temperature being regarded as constant) satisfy the conditions which would make the tension a maximum if the necessary conditions relative to the first differential coefficients were fulfilled.

In the foregoing discussion of stability, the surface of discontinuity is supposed plane. In this case, as the tension is supposed positive, there can be no tendency to a change of form of the surface. We now pass to the consideration of changes consisting in or connected with motion and change of form of the surface of tension, which we shall at first suppose to be and to remain spherical and uniform throughout.

In order that the equilibrium of a spherical mass entirely surrounded by an indefinitely large mass of different nature shall be neutral with respect to changes in the value of r, the radius of the sphere, it is evidently necessary that equation (500), which in this case
may be written

$$2\,\sigma = r\,(p' - p''), \qquad (522)$$

as well as the other conditions of equilibrium, shall continue to hold true for varying values of r. Hence, for a state of equilibrium which is on the limit between stability and instability, it is necessary that the equation

$$2\,d\sigma = (p' - p'')\,dr + r\,dp'$$

shall be satisfied, when the relations between $d\sigma$, dp', and dr are determined from the fundamental equations on the supposition that the conditions of equilibrium relating to temperature and the potentials remain satisfied. (The differential coefficients in the equations which follow are to be determined on this supposition.) Moreover, if

$$r\frac{dp'}{dr} < 2\frac{d\sigma}{dr} - p' + p'', \tag{523}$$

i. e., if the pressure of the interior mass increases less rapidly (or decreases more rapidly) with increasing radius than is necessary to preserve neutral equilibrium, the equilibrium is stable. But if

$$r\frac{dp'}{dr} > 2\frac{d\sigma}{dr} - p' + p'', \tag{524}$$

the equilibrium is unstable. In the remaining case, when

$$r\frac{dp'}{dr} = 2\frac{d\sigma}{dr} - p' + p'', \tag{525}$$

farther conditions are of course necessary to determine absolutely whether the equilibrium is stable or unstable, but in general the equilibrium will be stable in respect to change in one direction and unstable in respect to change in the opposite direction, and is therefore to be considered unstable. In general, therefore, we may call (523) the condition of stability.

When the interior mass and the surface of discontinuity are formed entirely of substances which are components of the external mass, p' and σ cannot vary and condition (524) being satisfied the equilibrium is unstable.

But if either the interior homogeneous mass or the surface of discontinuity contains substances which are not components of the enveloping mass, the equilibrium may be stable. If there is but one such substance, and we denote its densities and potential by γ'_1, Γ_1, and μ_1, the condition of stability (523) will reduce to the form

$$\left(r\frac{dp'}{d\mu_1} - 2\frac{d\sigma}{d\mu_1}\right)\frac{d\mu_1}{dr} < p'' - p',$$

or, by (98) and (508),

$$(r\gamma_1' + 2\Gamma_1)\frac{d\mu_1}{dr} < p'' - p'. \tag{526}$$

In these equations and in all which follow in the discussion of this case, the temperature and the potentials μ_2, μ_3, etc. are to be regarded as constant. But

$$\gamma_1' v' + \Gamma_1 s,$$

which represents the total quantity of the component specified by the suffix, must be constant. It is evidently equal to

$$\tfrac{4}{3}\pi r^3 \gamma_1' + 4\pi r^2 \Gamma_1.$$

Dividing by 4π and differentiating, we obtain

$$(r^2 \gamma_1' + 2 r \Gamma_1)\, dr + \tfrac{1}{3} r^3\, d\gamma_1' + r^2\, d\Gamma_1 = 0,$$

or, since γ_1' and Γ_1 are functions of μ_1,

$$(r \gamma_1' + 2\Gamma_1)\, dr + \left(\frac{r^2}{3}\frac{d\gamma_1'}{d\mu_1} + r\frac{d\Gamma_1}{d\mu_1}\right) d\mu_1 = 0. \tag{527}$$

By means of this equation, the condition of stability is brought to the form

$$\frac{(r\gamma_1' + 2\Gamma_1)^2}{\dfrac{r^2}{3}\dfrac{d\gamma_1'}{d\mu_1} + r\dfrac{d\Gamma_1}{d\mu_1}} > p' - p''. \tag{528}$$

If we eliminate r by equation (522), we have

$$\frac{\left(\dfrac{\gamma_1'}{p'-p''} + \dfrac{\Gamma_1}{\sigma}\right)^2}{\dfrac{1}{3(p'-p'')}\dfrac{d\gamma_1'}{d\mu_1} + \dfrac{1}{2\sigma}\dfrac{d\Gamma_1}{d\mu_1}} > 1. \tag{529}$$

If p' and σ are known in terms of t, μ_1, μ_2, etc., we may express the first member of this condition in terms of the same variables and p''. This will enable us to determine, for any given state of the external mass, the values of μ_1 which will make the equilibrium stable or unstable.

If the component to which γ_1' and Γ_1 relate is found only at the surface of discontinuity, the condition of stability reduces to

$$\frac{\Gamma_1^2}{\sigma}\frac{d\mu_1}{d\Gamma_1} > \frac{1}{2}. \tag{530}$$

Since
$$\Gamma_1 = -\frac{d\sigma}{d\mu_1},$$
we may also write

$$\frac{\Gamma_1}{\sigma}\frac{d\sigma}{d\Gamma_1} < -\frac{1}{2}, \quad \text{or} \quad \frac{d\log\sigma}{d\log\Gamma_1} < -\frac{1}{2}. \tag{531}$$

Again, if $\Gamma_1 = 0$ and $\dfrac{d\Gamma_1}{d\mu_1} = 0$, the condition of stability reduces to

$$\frac{3\gamma_1'^2}{p'-p''}\frac{d\mu_1}{d\gamma_1'} > 1. \tag{532}$$

Since
$$\gamma_1' = \frac{dp'}{d\mu_1},$$
we may also write

$$\frac{\gamma_1'}{p'-p''}\frac{dp'}{d\gamma_1'} > \frac{1}{3}, \quad \text{or} \quad \frac{d\log(p'-p'')}{d\log\gamma_1'} > \frac{1}{3}. \tag{533}$$

When r is large, this will be a close approximation for any values of Γ_1, unless γ_1' is very small. The two special conditions (531) and (533) might be derived from very elementary considerations.

Similar conditions of stability may be found when there are more substances than one in the inner mass or the surface of discontinuity, which are not components of the enveloping mass. In this case, we have instead of (526) a condition of the form

$$(r\,\gamma_1' + 2\,\Gamma_1)\,\frac{d\mu_1}{dr} + (r\,\gamma_2' + 2\,\Gamma_2)\,\frac{d\mu_2}{dr} + \text{etc.} < p'' - p', \quad (534)$$

from which $\frac{d\mu_1}{dr}$, $\frac{d\mu_2}{dr}$, etc. may be eliminated by means of equations derived from the conditions that

$$\gamma_1'\,v' + \Gamma_1\,s, \quad \gamma_2'\,v' + \Gamma_2\,s, \quad \text{etc.}$$

must be constant.

Nearly the same method may be applied to the following problem. Two different homogeneous fluids are separated by a diaphragm having a circular orifice, their volumes being invariable except by the motion of the surface of discontinuity, which adheres to the edge of the orifice:—to determine the stability or instability of this surface when in equilibrium.

The condition of stability derived from (522) may in this case be written

$$r\,\frac{d(p'-p'')}{dv'} < 2\,\frac{d\sigma}{dv'} - (p' - p'')\,\frac{dr}{dv'}, \quad (535)$$

where the quantities relating to the concave side of the surface of tension are distinguished by a single accent.

If both the masses are infinitely large, or if one which contains all the components of the system is infinitely large, $p'-p''$ and σ will be constant, and the condition reduces to

$$\frac{dr}{dv'} < 0.$$

The equilibrium will therefore be stable or unstable according as the surface of tension is less or greater than a hemisphere.

To return to the general problem:—if we denote by x the part of the axis of the circular orifice intercepted between the center of the orifice and the surface of tension, by R the radius of the orifice, and by V' the value of v' when the surface of tension is plane, we shall have the geometrical relations

$$R^2 = 2\,r\,x - x^2,$$

and

$$\begin{aligned} v' &= V' + \tfrac{2}{3}\,\pi\,r^2\,x - \tfrac{1}{3}\,\pi\,R^2\,(r - x) \\ &= V' + \pi\,r\,x^2 - \tfrac{1}{3}\,\pi\,x^3. \end{aligned}$$

By differentiation we obtain

$$(r - x)\, dx + x\, dr = 0,$$

and $$dv' = \pi x^2\, dr + (2\, \pi\, r\, x - \pi\, x^2)\, dx;$$

whence $$(r - x)\, dv' = - \pi\, r\, x^2\, dr. \tag{536}$$

By means of this relation, the condition of stability may be reduced to the form

$$\frac{dp'}{dv'} - \frac{dp''}{dv'} - \frac{2}{r}\frac{d\sigma}{dv'} < (p' - p'')\, \frac{r - x}{\pi\, r^2\, x^2}. \tag{537}$$

Let us now suppose that the temperature and all the potentials except one, μ_1, are to be regarded as constant. This will be the case when one of the homogeneous masses is very large and contains all the components of the system except one, or when both these masses are very large and there is a single substance at the surface of discontinuity which is not a component of either; also when the whole system contains but a single component, and is exposed to a constant temperature at its surface. Condition (537) will reduce by (98) and (508) to the form

$$\left(\gamma_1' - \gamma_1'' + \frac{2\, \Gamma_1}{r}\right) \frac{d\mu_1}{dv'} < (p' - p'')\, \frac{r - x}{\pi\, r^2\, x^2}. \tag{538}$$

But $$\gamma_1' v' + \gamma_1'' v'' + \Gamma_1\, s$$

(the total quantity of the component specified by the suffix) must be constant; therefore, since

$$dv'' = - dv', \quad \text{and} \quad ds = \frac{2}{r}\, dv',$$

$$\left(v' \frac{d\gamma_1'}{d\mu_1} + v'' \frac{d\gamma_1''}{d\mu_1} + s\, \frac{d\Gamma_1}{d\mu_1}\right) d\mu_1 + \left(\gamma_1' - \gamma_1'' + \frac{2\, \Gamma_1}{r}\right) dv' = 0. \tag{539}$$

By this equation, the condition of stability is brought to the form

$$\frac{\left(\gamma_1' - \gamma_1'' + \frac{2\, \Gamma_1}{r}\right)^2}{v' \frac{d\gamma_1'}{d\mu_1} + v'' \frac{d\gamma_1''}{d\mu_1} + s\, \frac{d\Gamma_1}{d\mu_1}} > (p' - p'')\, \frac{x - r}{\pi\, x^2\, r^2}. \tag{540}$$

When the substance specified by the suffix is a component of either of the homogeneous masses, the terms $\frac{2\, \Gamma_1}{r}$ and $s\, \frac{d\Gamma_1}{d\mu_1}$ may generally be neglected. When it is not a component of either, the terms γ_1', γ_1'', $v' \frac{d\gamma_1'}{d\mu_1}$, $v'' \frac{d\gamma_1''}{d\mu_1}$ may of course be cancelled, but we must not apply the formula to cases in which the substance spreads over the diaphragm separating the homogeneous masses.

In the cases just discussed, the problem of the stability of certain surfaces of tension has been solved by considering the case of neutral equilibrium,—a condition of neutral equilibrium affording the equation of the limit of stability. This method probably leads as directly as any to the result, when that consists in the determination of the value of a certain quantity at the limit of stability, or of the relation which exists at that limit between certain quantities specifying the state of the system. But problems of a more general character may require a more general treatment.

Let it be required to ascertain the stability or instability of a fluid system in a given state of equilibrium with respect to motion of the surfaces of tension and accompanying changes. It is supposed that the conditions of internal stability for the separate homogeneous masses are satisfied, as well as those conditions of stability for the surfaces of discontinuity which relate to small portions of these surfaces with the adjacent masses. (The conditions of stability which are here supposed to be satisfied have been already discussed in part and will be farther discussed hereafter.) The fundamental equations for all the masses and surfaces occurring in the system are supposed to be known. In applying the general criteria of stability which are given on page 110, we encounter the following difficulty.

The question of the stability of the system is to be determined by the consideration of states of the system which are slightly varied from that of which the stability is in question. These varied states of the system are not in general states of equilibrium, and the relations expressed by the fundamental equations may not hold true of them. More than this,—if we attempt to describe a varied state of the system by varied values of the quantities which describe the initial state, if these varied values are such as are inconsistent with equilibrium, they may fail to determine with precision any state of the system. Thus, when the phases of two contiguous homogeneous masses are specified, if these phases are such as satisfy all the conditions of equilibrium, the nature of the surface of discontinuity (if without additional components) is entirely determined; but if the phases do not satisfy all the conditions of equilibrium, the nature of the surface of discontinuity is not only undetermined, but incapable of determination by specified values of such quantities as we have employed to express the nature of surfaces of discontinuity in equilibrium. For example, if the temperatures in contiguous homogeneous masses are different, we cannot specify the thermal state of the surface of discontinuity by assigning to it any particular temperature. It would be necessary to give the law by which the temperature passes over from one value to the other. And if this were given, we could make no use of it in the determination of other quantities, unless the rate of change of the temperature were so gradual, that at every point we could regard the thermodynamic state as unaffected by the change of temperature in its vicinity. It is true that we are also ignorant in respect to surfaces of discontinuity *in equilibrium* of the law of change of those quantities which are different in the two phases in contact, such as the densities of the components, but this, although unknown to us, is entirely determined by the nature of the phases in contact, so that no vagueness is occasioned in the definition of any of the quantities which we have occasion to use with reference to such surfaces of discontinuity.

It may be observed that we have established certain differential equations, especially (497), in which only the initial state is necessarily one of equilibrium. Such equations may be regarded as establishing certain properties of states bordering upon those of equilibrium. But these are properties which hold true only when we disregard quantities proportional to the square of those which express the degree of variation of the system from equilibrium. Such equations are therefore sufficient for the determination of the conditions of equilibrium, but not sufficient for the determination of the conditions of stability

We may, however, use the following method to decide the question of stability in such a case as has been described.

Beside the real system of which the stability is in question, it will be convenient to conceive of another system, to which we shall attribute in its initial state the same homogeneous masses and surfaces of discontinuity which belong to the real system. We shall also suppose that the homogeneous masses and surfaces of discontinuity of this system, which we may call the imaginary system, have the same fundamental equations as those of the real system. But the imaginary system is to differ from the real in that the variations of its state are limited to such as do not violate the conditions of equilibrium relating to temperature and the potentials, and that the fundamental equations of the surfaces of discontinuity hold true for these varied states, although the condition of equilibrium expressed by equation (500) may not be satisfied.

Before proceeding farther, we must decide whether we are to examine the question of stability under the condition of a constant external temperature, or under the condition of no transmission of heat to or from external bodies, and in general, to what external influences we are to regard the system as subject. It will be convenient to suppose that the exterior of the system is fixed, and that neither matter nor heat can be transmitted through it. Other cases may easily be reduced to this, or treated in a manner entirely analogous.

Now if the real system in the given state is unstable, there must be some slightly varied state in which the energy is less, but the entropy and the quantities of the components the same as in the given state, and the exterior of the system unvaried. But it may easily be shown that the given state of the system may be made stable by constraining the surfaces of discontinuity to pass through certain fixed lines situated in the unvaried surfaces. Hence, if the surfaces of discontinuity are constrained to pass through corresponding fixed lines in the surfaces of discontinuity belonging to the varied state just mentioned, there must be a state of stable equilibrium for the system thus constrained which will differ infinitely little from the given state of the system, the stability of which is in question, and will have the same entropy, quantities of components and exterior, but less energy. The imaginary system will have a similar state, since the real and imaginary systems do not differ in respect to those states which satisfy all the conditions of equilibrium for each surface of discontinuity. That is, the imaginary system has a state, differing infinitely little from the given state, and with the same entropy, quantities of components, and exterior, but with less energy.

Conversely, if the imaginary system has such a state as that just described, the real system will also have such a state. This may be shown by fixing certain lines in the surfaces of discontinnity of the imaginary system in its state of less energy and then making the energy a minimum under the conditions. The state thus determined will satisfy all the conditions of equilibrium for each surface of discontinuity, and the real system will therefore have a corresponding state, in which the entropy, quantities of components, and exterior will be the same as in the given state, but the energy less.

We may therefore determine whether the given system is or is not unstable, by applying the general criterion of instability (7) to the imaginary system.

If the system is not unstable, the equilibrium is either neutral or stable. Of course we can determine which of these is the case by reference to the imaginary system, since this determination depends upon states of equilibrium, in regard to which the real and imaginary systems do not differ. We may therefore determine whether the equilibrium of the given system is stable, neutral, or unstable, by applying the criteria (3)–(7) to the imaginary system.

The result which we have obtained may be expressed as follows:—In applying to a fluid system which is in equilibrium, and of which all the small parts taken separately are stable, the criteria of stable, neutral, and unstable equilibrium, we may regard the system as under constraint to satisfy the conditions of equilibrium relating to temperature and the potentials, and as satisfying the relations expressed by the fundamental equations for masses and surfaces, even when the condition of equilibrium relating to pressure [equation (500)] is not satisfied.

It follows immediately from this principle, in connection with equations (501) and (86), that in a stable system each surface of tension must be a surface of minimum area for constant values of the volumes which it divides, when the other surfaces bounding these volumes and the perimeter of the surface of tension are regarded as fixed; that in a system in neutral equilibrium each surface of tension will have as small an area as it can receive by any slight variations under the same limitations; and that in seeking the remaining conditions of stable or neutral equilibrium, when these are satisfied, it is only necessary to consider such varied surfaces of tension as have similar properties with reference to the varied volumes and perimeters.

We may illustrate the method which has been described by applying it to a problem but slightly different from one already (pp. 408, 409) discussed by a different method. It is required to determine the conditions of stability for a system in equilibrium, consisting of two different homogeneous masses meeting at a surface of discontinuity, the perimeter of which is invariable, as well as the exterior of the whole system, which is also impermeable to heat.

To determine what is necessary for stability in addition to the condition of minimum area for the surface of tension, we need only consider those varied surfaces of tension which satisfy the same condition. We may therefore regard the surface of tension as determined by v', the volume of one of the homogeneous masses. But the state of the system would evidently be completely determined by the position of the surface of tension and the temperature and potentials, if the entropy and the quantities of the components were variable; and therefore, since the entropy and the quantities of the components are constant, the state of the system must be completely determined by the position of the surface of tension. We may therefore regard all the quantities relating to the system as functions of v', and the condition of stability may be written

$$\frac{d\varepsilon}{dv'}\,dv' + \frac{1}{2}\frac{d^2\varepsilon}{dv'^2}\,dv'^2 + \text{etc.} > 0,$$

where ε denotes the total energy of the system. Now the conditions of equilibrium require that

$$\frac{d\varepsilon}{dv'} = 0,$$

Hence, the general condition of stability is that

$$\frac{d^2\varepsilon}{dv'^2} > 0. \tag{541}$$

Now if we write ε', ε'', ε^{S} for the energies of the two masses and of the surface, we have by (86) and (501), since the total entropy and the total quantities of the several components are constant,

$$d\varepsilon = d\varepsilon' + d\varepsilon'' + d\varepsilon^{\mathrm{S}} = -p'\,dv' - p''\,dv'' + \sigma\,ds,$$

or, since $dv'' = -\,dv'$,

$$\frac{d\varepsilon}{dv'} = -p' + p'' + \sigma\frac{ds}{dv'}. \tag{542}$$

Hence,

$$\frac{d^2\varepsilon}{dv'^2} = -\frac{dp'}{dv'} + \frac{dp''}{dv'} + \frac{d\sigma}{dv'}\frac{ds}{dv'} + \sigma\frac{d^2 s}{dv'^2}, \tag{543}$$

and the condition of stability may be written

$$\sigma\frac{d^2 s}{dv'^2} > \frac{dp'}{dv'} - \frac{dp''}{dv'} - \frac{d\sigma}{dv'}\frac{ds}{dv'}. \tag{544}$$

If we now simplify the problem by supposing, as in the similar case on page 409, that we may disregard the variations of the temperature and of all the potentials except one, the condition will reduce to

$$\sigma\frac{d^2 s}{dv'^2} > \left(\gamma_1' - \gamma_1'' + \Gamma_1\frac{ds}{dv'}\right)\frac{d\mu_1}{dv'}. \tag{545}$$

The total quantity of the substance indicated by the suffix $_1$ is

$$\gamma_1' v' + \gamma_1'' v'' + \Gamma_1 s.$$

Making this constant, we have

$$\left(\gamma_1' - \gamma_1'' + \Gamma_1\frac{ds}{dv'}\right)dv' + \left(v'\frac{d\gamma_1'}{d\mu_1} + v''\frac{d\gamma_1''}{d\mu_1} + s\frac{d\Gamma_1}{d\mu_1}\right)d\mu_1 = 0. \tag{546}$$

The condition of equilibrium is thus reduced to the form

$$\sigma\frac{d^2 s}{dv'^2} > -\frac{\left(\gamma_1' - \gamma_1'' + \Gamma_1\frac{ds}{dv'}\right)^2}{v'\frac{d\gamma_1'}{d\mu_1} + v''\frac{d\gamma_1''}{d\mu_1} + s\frac{d\Gamma_1}{d\mu_1}}, \tag{547}$$

where $\frac{ds}{dv'}$ and $\frac{d^2 s}{dv'}$ are to be determined from the form of the surface of tension by purely geometrical considerations, and the other differential coefficients are to be determined from the fundamental equations of the homogeneous masses and the surface of discontinuity. Condition (540) may be easily deduced from this as a particular case.

The condition of stability with reference to motion of surfaces of discontinuity admits of a very simple expression when we can treat the temperature and potentials as constant. This will be the case when one or more of the homogeneous masses, containing together all the component substances, may be considered as indefinitely large, the surfaces of discontinuity being finite. For if we write $\Sigma\varDelta\varepsilon$ for the sum of the variations of the energies of the several homogeneous masses, and $\Sigma\varDelta\varepsilon^{\mathrm{S}}$ for the sum of the variations of the energies of the several surfaces of discontinuity, the condition of stability may be written

$$\Sigma\varDelta\varepsilon + \Sigma\varDelta\varepsilon^{\mathrm{S}} > 0, \tag{548}$$

the total entropy and the total quantities of the several components being constant. The variations to be considered are infinitesimal, but the character $\varDelta$ signifies, as elsewhere in this paper, that the expression is to be interpreted without neglect of infinitesimals of the higher orders. Since the temperature and potentials are sensibly constant, the same will be true of the pressures and surface-tensions, and by integration of (86) and (501) we may obtain for any homogeneous mass

$$\varDelta\varepsilon = t\,\varDelta\eta - p\,\varDelta v + \mu_1\,\varDelta m_1 + \mu_2\,\varDelta m_2 + \text{etc.},$$

and for any surface of discontinuity

$$\varDelta\varepsilon^{\mathrm{S}} = t\,\varDelta\eta^{\mathrm{S}} + \sigma\,\varDelta s + \mu_1\,\varDelta m_1^{\mathrm{S}} + \mu_2^{\mathrm{S}}\,\varDelta m_2 + \text{etc.}$$

These equations will hold true of finite differences, when $t, p, \sigma, \mu_1, \mu_2$, etc. are constant, and will therefore hold true of infinitesimal differences, under the same limitations, without neglect of the infinitesimals of the higher orders. By substitution of these values, the condition of stability will reduce to the form

$$-\Sigma(p\varDelta v) + \Sigma(\sigma\varDelta s) > 0,$$

or

$$\Sigma(p\varDelta v) - \Sigma(\sigma\varDelta s) < 0. \tag{549}$$

That is, the sum of the products of the volumes of the masses by their pressures diminished by the sum of the products of the areas of the surfaces of discontinuity by their tensions must be a maximum. This is a purely geometrical condition, since the pressures and tensions are constant. This condition is of interest, because it is always *sufficient* for stability with reference to motion of surfaces of discontinuity. For any system may be reduced to the kind described by putting certain parts of the system in communication (by means of fine tubes if necessary) with large masses of the proper temperatures and potentials. This may be done without introducing any new movable surfaces of discontinuity. The condition (549) when applied to the altered system is therefore the same as when applied to the original system. But it is sufficient for the stability of the altered system, and therefore sufficient for its stability if we diminish its freedom by breaking the connection between the original system and the additional parts, and therefore sufficient for the stability of the original system.

On the Possibility of the Formation of a Fluid of different Phase within any Homogeneous Fluid.

The study of surfaces of discontinuity throws considerable light upon the subject of the stability of such homogeneous fluid masses as have a less pressure than others formed of the same components (or some of them) and having the same temperature and the same potentials for their actual components.*

In considering this subject, we must first of all inquire how far our method of treating surfaces of discontinuity is applicable to cases in which the radii of curvature of the surfaces are of insensible magnitude. That it should not be applied to such cases without limitation is evident from the consideration that we have neglected the term $\frac{1}{2}(C_1 - C_2)\delta(c_1 - c_2)$ in equation (494) on account of the magnitude of the radii of curvature compared with the thickness of the non-homogeneous film. (See page 390). When, however, only spherical masses are considered, this term will always disappear, since C_1 and C_2 will necessarily be equal.

Again, the surfaces of discontinuity have been regarded as separating homogeneous masses. But we may easily conceive that a globular mass (surrounded by a large homogeneous mass of different nature) may be so small that no part of it will be homogeneous, and that even at its center the matter cannot be regarded as having any phase of matter *in mass.* This, however, will cause no difficulty, if we regard the phase of the interior mass as determined by the same

* See page 161, where the term stable is used (as indicated on page 159) in a less strict sense than in the discussion which here follows.

relations to the exterior mass as in other cases. Beside the phase of the exterior mass, there will always be another phase having the same temperature and potentials, but of the general nature of the small globule which is surrounded by that mass and in equilibrium with it. This phase is completely determined by the system considered, and in general entirely stable and perfectly capable of realization in mass, although not such that the exterior mass could exist in contact with it at a plane surface. This is the phase which we are to attribute to the mass which we conceive as existing within the dividing surface.*

With this understanding with regard to the phase of the fictitious interior mass, there will be no ambiguity in the meaning of any of the symbols which we have employed, when applied to cases in which the surface of discontinuity is spherical, however small the radius may be. Nor will the demonstration of the general theorems require any material modification. The dividing surface, which determines the value of ε^S, η^S, m_1^S, m_2^S, etc., is as in other cases to be placed so as to make the term $\frac{1}{2}(C_1 + C_1)\delta(c_1 + c_2)$ in equation (494) vanish, i. e., so as to make equation (497) valid. It has been shown on pages 387–389 that when thus placed it will sensibly coincide with the physical surface of discontinuity, when this consists of a non-homogeneous film separating homogeneous masses, and having radii of curvature which are large compared with its thickness. But in regard to globular masses too small for this theorem to have any application, it will be worth while to examine how far we may be certain that the radius of the dividing surface will have a real and positive value, since it is only then that our method will have any natural application.

The value of the radius of the dividing surface, supposed spherical, of any globule in equilibrium with a surrounding homogeneous fluid may be most easily obtained by eliminating σ from equations (500) and (502), which have been derived from (497), and contain the radius implicitly. If we write r for this radius, equation (500) may be written

$$2\,\sigma = (p' - p'')\,r, \tag{550}$$

the single and double accents referring respectively to the interior and exterior masses. If we write $[\varepsilon]$, $[\eta]$, $[m_1]$, $[m_2]$, etc. for the

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* For example, in applying our formulæ to a microscopic globule of water in steam, by the density or pressure of the interior mass we should understand, not the actual density or pressure at the center of the globule, but the density of liquid water (in large quantities) which has the temperature and potential of the steam.

excess of the total energy, entropy, etc. in and about the globular mass above what would be in the same space if it were uniformly filled with matter of the phase of the exterior mass, we shall have necessarily with reference to the whole dividing surface

$$\varepsilon^S = [\varepsilon] - v'(\varepsilon_V' - \varepsilon_V''), \quad \eta^S = [\eta] - v'(\eta_V' - \eta_V''),$$

$$m_1^S = [m_1] - v'(\gamma_1' - \gamma_1''), \quad m_2^S = [m_2] - v'(\gamma_2' - \gamma_2''), \text{ etc.},$$

where ε_V', ε_V'', η_V', η_V'', γ_1', γ_1'', etc. denote, in accordance with our usage elsewhere, the volume-densities of energy, of entropy, and of the various components, in the two homogeneous masses. We may thus obtain from equation (502)

$$\sigma s = [\varepsilon] - v'(\varepsilon_V' - \varepsilon_V'') - t[\eta] + t v'(\eta_V' - \eta_V'')$$
$$- \mu_1[m_1] + \mu_1 v'(\gamma_1' - \gamma_1'') - \mu_2[m_2] + \mu_2 v'(\gamma_2' - \gamma_2'') - \text{etc.} \qquad (551)$$

But by (93),

$$p' = -\varepsilon_V' + t\eta_V' + \mu_1\gamma_1' + \mu_2\gamma_2' + \text{etc.},$$
$$p'' = -\varepsilon_V'' + t\eta_V'' + \mu_1\gamma_1'' + \mu_2\gamma_2'' + \text{etc.}$$

Let us also write for brevity

$$W = [\varepsilon] - t[\eta] - \mu_1[m_1] - \mu_2[m_2] - \text{etc.} \qquad (552)$$

(It will be observed that the value of W is entirely determined by the nature of the physical system considered, and that the notion of the dividing surface does not in any way enter into its definition.) We shall then have

$$\sigma s = W + v'(p' - p''), \qquad (553)$$

or, substituting for s and v' their values in terms of r,

$$4\pi r^2 \sigma = W + \tfrac{4}{3}\pi r^3 (p' - p''), \qquad (554)$$

and eliminating σ by (550),

$$\tfrac{2}{3}\pi r^3 (p' - p'') = W, \qquad (555)$$

$$r = \left(\frac{3W}{2\pi(p' - p'')}\right)^{\frac{1}{3}}. \qquad (556)$$

If we eliminate r instead σ, we have

$$\frac{16\pi\sigma^3}{3(p' - p'')^2} = W, \qquad (557)$$

$$\sigma = \left(\frac{3W(p' - p'')^2}{16\pi}\right)^{\frac{1}{3}}. \qquad (558)$$

Now, if we first suppose the difference of the pressures in the homogeneous masses to be very small, so that the surface of discontinuity is nearly plane, since without any important loss of generality we may regard σ as positive (for if σ is not positive when $p'=p''$, the surface when plane would not be stable in regard to position, as it certainly is, in every actual case, when the proper conditions are fulfilled with respect to its perimeter), we see by (550) that the pressure in the interior mass must be the greater; i. e., we may regard σ, $p'-p''$, and r as all positive. By (555), the value of W will also be positive. But it is evident from equation (552), which defines W, that the value of this quantity is necessarily real, in any possible case of equilibrium, and can only become infinite when r becomes infinite and $p'=p''$. Hence, by (556) and (558), as $p'-p''$ increases from very small values, W, r, and σ have single, real, and positive values until they simultaneously reach the value zero. Within this limit, our method is evidently applicable; beyond this limit, if such exist, it will hardly be profitable to seek to interpret the equations. But it must be remembered that the vanishing of the radius of the somewhat arbitrarily determined *dividing surface* may not necessarily involve the vanishing of the physical heterogeneity. It is evident, however, (see pp. 387–389,) that the globule must become insensible in magnitude before r can vanish.

It may easily be shown that the quantity denoted by W is the work which would be required to form (by a reversible process) the heterogeneous globule in the interior of a very large mass having initially the uniform phase of the exterior mass. For this work is equal to the increment of energy of the system when the globule is formed without change of the entropy or volume of the whole system or of the quantities of the several components. Now $[\eta]$, $[m_1]$, $[m_2]$, etc. denote the increments of entropy and of the components in the space where the globule is formed. Hence these quantities with the negative sign will be equal to the increments of entropy and of the components in the rest of the system. And hence, by equation (86),

$$-t\,[\eta] - \mu_1\,[m_1] - \mu_2\,[m_2] - \text{etc.}$$

will denote the increment of energy in all the system except where the globule is formed. But $[\varepsilon]$ denotes the increment of energy in that part of the system. Therefore, by (552), W denotes the total increment of energy in the circumstances supposed, or the work required for the formation of the globule.

The conclusions which may be drawn from these considerations with respect to the stability of the homogeneous mass of the pressure p'' (supposed less than p', the pressure belonging to a different phase of the same temperature and potentials) are very obvious.

Within those limits within which the method used has been justified, the mass in question must be regarded as in strictness stable with respect to the growth of a globule of the kind considered, since W, the work required for the formation of such a globule of a certain size (viz., that which would be in equilibrium with the surrounding mass), will always be positive. Nor can smaller globules be formed, for they can neither be in equilibrium with the surrounding mass, being too small, nor grow to the size of that to which W relates. If, however, by any external agency such a globular mass (of the size necessary for equilibrium) were formed, the equilibrium has already (page 406) been shown to be unstable, and with the least excess in size, the interior mass would tend to increase without limit except that depending on the magnitude of the exterior mass. We may therefore regard the quantity W as affording a kind of measure of the *stability* of the phase to which p'' relates. In equation (557) the value of W is given in terms of σ and $p'-p''$. If the three fundamental equations which give σ, p', and p'' in terms of the temperature and the potentials were known, we might regard the stability (W) as known in terms of the same variables. It will be observed that when $p'=p''$ the value of W is infinite. If $p'-p''$ increases without greater changes of the phases than are necessary for such increase, W will vary at first very nearly inversely as the square of $p'-p''$. If $p'-p''$ continues to increase, it may perhaps occur that W reaches the value zero; but until this occurs the phase is certainly stable with respect to the kind of change considered. Another kind of change is conceivable, which initially is small in degree but may be great in its extent in space. Stability in this respect or *stability in respect to continuous changes of phase* has already been discussed (see page 162), and its limits determined. These limits depend entirely upon the fundamental equation of the homogeneous mass of which the stability is in question. But with respect to the kind of changes here considered, which are initially small in extent but great in degree, it does not appear how we can fix the limits of stability with the same precision. But it is safe to say that if there is such a limit it must be at or beyond the limit at which σ vanishes. This latter limit is determined entirely by the fundamental equation of the surface of discontinuity between the phase of which the stability is in question and that of which the possible formation is in question. We have already seen that when σ vanishes, the radius of the dividing surface and the work W vanish with it. If the fault in the homogeneity of the mass vanishes at the same time, (it evidently cannot vanish sooner,) the phase becomes unstable at this limit. But if the fault in the homogeneity of the physical mass does not vanish with r, σ and W,—and no sufficient reason appears why this should not be considered as the general case,—although the amount of work necessary to upset the equilibrium of the phase is infinitesimal, this is not enough to make the phase unstable. It appears therefore that W is a somewhat one-sided measure of stability.

It must be remembered in this connection that the fundamental equation of a surface of discontinuity can hardly be regarded as capable of experimental determination, except for plane surfaces, (see pp. 394, 395,) although the relation for spherical surfaces is in the nature of things entirely determined, at least so far as the phases are separately capable of existence. Yet the foregoing discussion yields the following practical results. It has been shown that the real stability of a phase extends in general beyond that limit (discussed on pages 160, 161), which may be called the limit of practical stability, at which the phase can exist in contact with another at a plane surface, and a formula has been deduced to express the degree of stability in such cases as measured by the amount of work necessary to upset the equilibrium of the phase when supposed to extend indefinitely in space. It has also been shown to be entirely consistent with the principles established that this stability should have limits, and the manner in which the general equations would accommodate themselves to this case has been pointed out.

By equation (553), which may be written

$$W = \sigma s - (p' - p'') v', \tag{559}$$

we see that the work W consists of two parts, of which one is always positive, and is expressed by the product of the superficial tension and the area of the surface of tension, and the other is always negative, and is numerically equal to the product of the difference of pressure by the volume of the interior mass. We may regard the first part as expressing the work spent in forming the surface of tension, and the second part the work gained in forming the interior mass.*

* To make the physical significance of the above more clear, we may suppose the two processes to be performed separately in the following manner. We may suppose a large mass of the same phase as that which has the volume v' to exist initially in the interior of the other. Of course, it must be surrounded by a resisting envelop, on account of the difference of the pressures. We may, however, suppose this envelop permeable to all the component substances, although not of such properties that a mass can form on the exterior like that within. We may allow the

Moreover, the second of these quantities, if we neglect its sign, is always equal to two-thirds of the first, as appears from equation (550) and the geometrical relation $v' = \frac{1}{3} rs$. We may therefore write

$$W = \tfrac{1}{3}\,\sigma\, s = \tfrac{1}{2}\,(p' - p'')\, v'. \tag{560}$$

On the Possible Formation at the Surface where two different Homogeneous Fluids meet of a Fluid of different Phase from either.

Let A, B, and C be three different fluid phases of matter, which satisfy all the conditions necessary for equilibrium when they meet at plane surfaces. The components of A and B may be the same or different, but C must have no components except such as belong to A or B. Let us suppose masses of the phases A and B to be separated by a very thin sheet of the phase C. This sheet will not necessarily be plane, but the sum of its principal curvatures must be zero. We may treat such a system as consisting simply of masses of the phases A and B with a certain surface of discontinuity, for in our previous discussion there has been nothing to limit the thickness or the nature of the film separating homogeneous masses, except that its thickness has generally been supposed to be small in comparison with its radii of curvature. The value of the superficial tension for such a film will be $\sigma_{AC} + \sigma_{BC}$, if we denote by these symbols the tensions of the surfaces of contact of the phases A and C, and B and C, respectively. This not only appears from evident mechanical considerations, but may also be easily verified by equations (502) and (93), the first of which may be regarded as defining the quantity σ. This value will not be affected by diminishing the thickness of the film, until the

envelop to yield to the internal pressure until its contents are increased by v' without materially affecting its superficial area. If this be done sufficiently slowly, the phase of the mass within will remain constant. (See page 139.) A homogeneous mass of the volume v' and of the desired phase has thus been produced, and the work gained is evidently $(p' - p'')v'$.

Let us suppose that a small aperture is now opened and closed in the envelop so as to let out exactly the volume v' of the mass within, the envelop being pressed inwards in another place so as to diminish its contents by this amount. During the extrusion of the drop and until the orifice is entirely closed, the surface of the drop must adhere to the edge of the orifice, but not elsewhere to the outside surface of the envelop. The work done in forming the surface of the drop will evidently be σs or $\frac{3}{2}(p' - p'')v'$. Of this work, the amount $(p' - p'')v'$ will be expended in pressing the envelop inward, and the rest in opening and closing the orifice. Both the opening and the closing will be resisted by the capillary tension. If the orifice is circular, it must have, when widest open, the radius determined by equation (550).

limit is reached at which the interior of the film ceases to have the properties of matter in mass. Now if $\sigma_{AC}+\sigma_{BC}$ is greater than σ_{AB}, the tension of the ordinary surface between A and B, such a film will be at least practically unstable. (See page 403.) We cannot suppose that $\sigma_{AB}>\sigma_{AC}+\sigma_{BC}$, for this would make the ordinary surface between A and B unstable and difficult to realize. If $\sigma_{AB}=\sigma_{AC}+\sigma_{BC}$, we may assume, in general, that this relation is not accidental, and that the ordinary surface of contact for A and B is of the kind which we have described.

Let us now suppose the phases A and B to vary, so as still to satisfy the conditions of equilibrium at plane contact, but so that the pressure of the phase C determined by the temperature and potentials of A and B shall become less than the pressure of A and B. A system consisting of the phases A and B will be entirely stable with respect to the formation of any phase like C. (The case is not quite identical with that considered on page 161, since the system in question contains two different phases, but the principles involved are entirely the same.)

With respect to variations of the phases A and B in the opposite direction we must consider two cases separately. It will be convenient to denote the pressures of the three phases by p_A, p_B, p_C, and to regard these quantities as functions of the temperature and potentials.

If $\sigma_{AB}=\sigma_{AC}+\sigma_{BC}$ for values of the temperature and potentials which make $p_A=p_B=p_C$, it will not be possible to alter the temperature and potentials at the surface of contact of the phases A and B so that $p_A=p_B$, and $p_C>p_A$, for the relation of the temperature and potentials necessary for the equality of the three pressures will be preserved by the increase of the mass of the phase C. Such variations of the phases A and B might be brought about in separate masses, but if these were brought into contact, there would be an immediate formation of a mass of the phase C, with reduction of the phases of the adjacent masses to such as satisfy the conditions of equilibrium with that phase.

But if $\sigma_{AB}<\sigma_{AC}+\sigma_{BC}$, we can vary the temperature and potentials so that $p_A=p_B$, and $p_C>p_A$, and it will not be possible for a sheet of the phase of C to form *immediately*, i. e., while the pressure of C is sensibly equal to that of A and B; for mechanical work equal to $\sigma_{AC}+\sigma_{BC}-\sigma_{AB}$ per unit of surface might be obtained by bringing the system into its original condition, and therefore produced without any external expenditure, unless it be that of heat at the temperature of the system, which is evidently incapable of producing the work.

The stability of the system in respect to such a change must therefore extend beyond the point where the pressure of C commences to be greater— ~~less~~ than that of A and B. We arrive at the same result if we use the expression (520) as a test of stability. Since this expression has a finite positive value when the pressures of the phases are all equal, the ordinary surface of discontinuity must be stable, and it must require a finite change in the circumstances of the case to make it become unstable.*

In the preceding paragraph it is shown that the surface of contact of phases A and B is stable under certain circumstances, with respect to the formation of a thin sheet of the phase C. To complete the demonstration of the stability of the surface with respect to the formation of the phase C, it is necessary to show that this phase cannot be formed at the surface in lentiform masses. This is the more necessary, since it is in this manner, if at all, that the phase is likely to be formed, for an incipient sheet of phase C would evidently be unstable when $\sigma_{AB} < \sigma_{AC} + \sigma_{BC}$, and would immediately break up into lentiform masses.

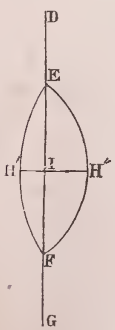

FIG. 10.

It will be convenient to consider first a lentiform mass of phase C in equilibrium between masses of phases A and B which meet in a plane surface. Let figure 10 represent a section of such a system through the centers of the spherical surfaces, the mass of phase A lying on the left of D E H′ F G, and that of phase B on the right of D E H″ F G. Let the line joining the centers cut the spherical surfaces in H′ and H″, and the plane of the surface of contact of A and B in I. Let the radii of E H′ F and E H″ F be denoted by r', r'', and the segments I H′, I H″ by x', x''. Also let I E, the radius of the circle in which the spherical surfaces intersect, be denoted by R. By a suitable application of the general condition of equilibrium we may easily obtain the equation

$$\sigma_{AC}\frac{r'-x'}{r'} + \sigma_{BC}\frac{r''-x''}{r''} = \sigma_{AB}, \tag{561}$$

* It is true that such a case as we are now considering is formally excluded in the discussion referred to, which relates to a plane surface, and in which the system is supposed thoroughly stable with respect to the possible formation of any different homogeneous masses. Yet the reader will easily convince himself that the criterion (520) is perfectly valid in this case with respect to the possible formation of a thin sheet of the phase C, which, as we have seen, may be treated simply as a different kind of surface of discontinuity.

which signifies that the components parallel to EF of the tension σ_{AC} and σ_{BC} are together equal to σ_{AB}. If we denote by W the amount of work which must be expended in order to form such a lentiform mass as we are considering between masses of indefinite extent having the phases A and B, we may write

$$W = M - N, \tag{562}$$

where M denotes the work expended in replacing the surface between A and B by the surfaces between A and C and B and C, and N denotes the work gained in replacing the masses of phases A and B by the mass of phase C. Then

$$M = \sigma_{AC}\, s_{AC} + \sigma_{BC}\, s_{BC} - \sigma_{AB}\, s_{AB}, \tag{563}$$

where s_{AC}, s_{BC}, s_{AB} denote the areas of the three surfaces concerned; and

$$N = V'\,(p_C - p_A) + V''\,(p_C - p_B), \tag{564}$$

where V' and V'' denote the volumes of the masses of the phases A and B which are replaced. Now by (500),

$$p_C - p_A = \frac{2\sigma_{AC}}{r'}, \quad \text{and} \quad p_C - p_B = \frac{2\sigma_{BC}}{r''}. \tag{565}$$

We have also the geometrical relations

$$\left.\begin{aligned} V' &= \tfrac{2}{3}\,\pi\, r'^2\, x' - \tfrac{1}{3}\,\pi\, R^2\,(r' - x'), \\ V'' &= \tfrac{2}{3}\,\pi\, r''^2\, x'' - \tfrac{1}{3}\,\pi\, R^2\,(r'' - x''). \end{aligned}\right\} \tag{566}$$

By substitution we obtain

$$\begin{aligned} N = {} & \tfrac{4}{3}\,\pi\,\sigma_{AC}\, r'\, x' - \tfrac{2}{3}\,\pi\, R^2\,\sigma_{AC}\frac{r' - x'}{r'} \\ & + \tfrac{4}{3}\,\pi\,\sigma_{BC}\, r''\, x'' - \tfrac{2}{3}\,\pi\, R^2\,\sigma_{BC}\frac{r'' - x''}{r''}, \end{aligned} \tag{567}$$

and by (561),

$$N = \tfrac{4}{3}\,\pi\,\sigma_{AC}\, r'\, x' + \tfrac{4}{3}\,\pi\,\sigma_{BC}\, r''\, x'' - \tfrac{2}{3}\,\pi\, R^2\,\sigma_{AB}. \tag{568}$$

Since

$$2\,\pi\, r'\, x' = s_{AC}, \quad 2\,\pi\, r''\, x'' = s_{BC}, \quad \pi\, R^2 = s_{AB},$$

we may write

$$N = \tfrac{2}{3}\,(\sigma_{AC}\, s_{AC} + \sigma_{BC}\, s_{BC} - \sigma_{AB}\, s_{AB}). \tag{569}$$

(The reader will observe that the ratio of M and N is the same as that of the corresponding quantities in the case of the spherical mass treated on pages 416–422.) We have therefore

$$W = \tfrac{1}{3}\,(\sigma_{AC}\, s_{AC} + \sigma_{BC}\, s_{BC} - \sigma_{AB}\, s_{AB}). \tag{570}$$

This value is positive so long as

$$\sigma_{AC} + \sigma_{BC} > \sigma_{AB},$$

since $$s_{AC} > s_{AB}, \quad \text{and} \quad s_{BC} > s_{AB}.$$

But at the limit, when

$$\sigma_{AC} + \sigma_{BC} = \sigma_{AB},$$

we see by (561) that

$$s_{AC} = s_{AB}, \quad \text{and} \quad s_{BC} = s_{AB},$$

and therefore $$W = 0.$$

It should however be observed that in the immediate vicinity of the circle in which the three surfaces of discontinuity intersect, the physical state of each of these surfaces must be affected by the vicinity of the others. We cannot, therefore, rely upon the formula (570) except when the dimensions of the lentiform mass are of sensible magnitude.

We may conclude that after we pass the limit at which p_C becomes greater than p_A and p_B (supposed equal) lentiform masses of phase C will not be formed until either $\sigma_{AB} = \sigma_{AC} + \sigma_{BC}$, or $p_C - p_A$ becomes so great that the lentiform mass which would be in equilibrium is one of insensible magnitude. [The diminution of the radii with increasing values of $p_C - p_A$ is indicated by equation (565).] Hence, no mass of phase C will be formed until one of these limits is reached. Although the demonstration relates to a *plane* surface between A and B, the result must be applicable whenever the radii of curvature have a sensible magnitude, since the effect of such curvature may be disregarded when the lentiform mass is of sufficiently small.

The equilibrium of the lentiform mass of phase C is easily proved to be unstable, so that the quantity W affords a kind of measure of the stability of plane surfaces of contact of the phases A and B.*

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* If we represent phases by the position of points in such a manner that coexistent phases (in the sense in which the term is used on page 152) are represented by the same point, and allow ourselves, for brevity, to speak of the phases as having the positions of the points by which they are represented, we may say that three coexistent phases are situated where three series of pairs of coexistent phases meet or intersect. If the three phases are all fluid, or when the effects of solidity may be disregarded, two cases are to be distinguished. Either the three series of coexistent phases all intersect,—this is when each of the three surface-tensions is less than the sum of the two others,—or one of the series terminates where the two others intersect,—this is where one surface tension is equal to the sum of the others. The series of coexistent phases will be represented by lines or surfaces, according as the phases have one or two independently variable components. Similar relations exist when the number of components is greater, except that they are not capable of geometrical representation without some limitation, as that of constant temperature or pressure or certain constant potentials.

Essentially the same principles apply to the more general problem in which the phases A and B have moderately different pressures, so that their surfaces of contact must be curved, but the radii of curvature have a sensible magnitude.

In order that a thin film of the phase C may be in equilibrium between masses of the phases A and B, the following equations must be satisfied—

$$\sigma_{AC}(c_1 + c_2) = p_A - p_C,$$

$$\sigma_{BC}(c_1 + c_2) = p_C - p_B,$$

where c_1 and c_2 denote the principal curvatures of the film, the centers of positive curvature lying in the mass having the phase A. Eliminating $c_1 + c_2$, we have

$$\sigma_{BC}(p_A - p_C) = \sigma_{AC}(p_C - p_B),$$

or

$$p_C = \frac{\sigma_{BC}\, p_A + \sigma_{AC}\, p_B}{\sigma_{BC} + \sigma_{AC}}. \tag{571}$$

It is evident that if p_C has a value greater than that determined by this equation, such a film will develop into a larger mass; if p_C has a less value, such a film will tend to diminish. Hence, when

$$p_C < \frac{\sigma_{BC}\, p_A + \sigma_{AC}\, p_B}{\sigma_{BC} + \sigma_{AC}}, \tag{572}$$

the phases A and B have a stable surface of contact.

Again, if more than one kind of surface of discontinuity is possible between A and B, for any given values of the temperature and potentials, it will be impossible for that having the greater tension to displace the other, at the temperature and with the potentials considered. Hence, when p_C has the value determined by equation (571), and consequently $\sigma_{AC} + \sigma_{BC}$ is one value of the tension for the surface between A and B, it is impossible that the ordinary tension of the surface σ_{AB} should be greater than this. If $\sigma_{AB} = \sigma_{AC} + \sigma_{BC}$, when equation (571) is satisfied, we may presume that a thin film of the phase C actually exists at the surface between A and B, and that a variation of the phases such as would make p_C greater than the second number of (571) cannot be brought about at that surface, as it would be prevented by the formation of a larger mass of the phase C. But if $\sigma_{AB} < \sigma_{AC} + \sigma_{BC}$ when equation (571) is satisfied, this equation does not mark the limit of the stability of the surface between A and B, for the temperature or potentials must receive a finite change before the film of phase C, or (as we shall see in the following paragraph) a lentiform mass of that phase, can be formed.

The work which must be expended in order to form on the surface between indefinitely large masses of phases A and B a lentiform mass of phase C in equilibrium, may evidently be represented by the formula

$$W = \sigma_{AC} S_{AC} + \sigma_{BC} S_{BC} - \sigma_{AB} S_{AB} \\ - p_C V_C + p_A V_A + p_B V_B, \tag{573}$$

where S_{AC}, S_{BC} denote the areas of the surfaces formed between A and C, and B and C, S_{AB} the diminution of the area of the surface between A and B, V_C the volume formed of the phase C, and V_A, V_B the diminution of the volumes of the phases A and B. Let us now suppose σ_{AC}, σ_{BC}, σ_{AB}, p_A, p_B to remain constant and the external boundary of the surface between A and B to remain fixed, while p_C increases and the surfaces of tension receive such alterations as are necessary for equilibrium. It is not necessary that this should be physically possible in the actual system; we may suppose the changes to take place, for the sake of argument, although involving changes in the fundamental equations of the masses and surfaces considered. Then, regarding W simply as an abbreviation for the second member of the preceding equation, we have

$$dW = \sigma_{AC}\, dS_{AC} + \sigma_{BC}\, dS_{BC} - \sigma_{AB}\, dS_{AB} \\ - p_C\, dV_C + p_A\, dV_A + p_B\, dV_B - V_C\, dp_C. \tag{574}$$

But the conditions of equilibrium require that

$$\sigma_{AC}\, dS_{AC} + \sigma_{BC}\, dS_{BC} - \sigma_{AB}\, dS_{AB} \\ - p_C\, dV_C + p_A\, dV_A + p_B\, dV_B = 0. \tag{575}$$

Hence,

$$dW = - V_C\, dp_C. \tag{576}$$

Now it is evident that V_C will diminish as p_C increases. Let us integrate the last equation supposing p_C to increase from its original value until V_C vanishes. This will give

$$W'' - W' = \text{a negative quantity}, \tag{577}$$

where W' and W'' denote the initial and final values of W. But $W''=0$. Hence W' is positive. But this is the value of W in the original system containing the lentiform mass, and expresses the work necessary to form the mass between the phases A and B. It is therefore impossible that such a mass should form on a surface between these phases. We must however observe the same limitation as in the less general case already discussed,—that $p_C - p_A$, $p_C - p_B$ must not be so great that the dimensions of the lentiform mass are of insensible magnitude. It may also be observed that the value of these differences may be so small that there will not be room on the surface between the masses of phases A and B for a mass of phase C sufficiently large for equilibrium. In this case we may consider a mass of phase C which is in equilibrium upon the surface between A and B in virtue of a *constraint* applied to the line in which the three surfaces of discontinuity intersect, which will not allow this line to become longer, although not preventing it from becoming shorter. We may prove that the value of W is positive by such an integration as we have used before.

Substitution of Pressures for Potentials in Fundamental Equations for Surfaces.

The fundamental equation of a surface which gives the value of the tension in terms of the temperature and potentials seems best adapted to the purposes of theoretical discussion, especially when the number of components is large or undetermined. But the experimental determination of the fundamental equations, or the application of any result indicated by theory to actual cases, will be facilitated by the use of other quantities in place of the potentials, which shall be capable of more direct measurement, and of which the numerical expression (when the necessary measurements have been made) shall depend upon less complex considerations. The numerical value of a potential depends not only upon the system of units employed, but also upon the arbitrary constants involved in the definition of the energy and entropy of the substance to which the potential relates, or, it may be, of the elementary substances of which that substance is formed. (See page 152.) This fact and the want of means of direct measurement may give a certain vagueness to the idea of the potentials, and render the equations which involve them less fitted to give a clear idea of physical relations.

Now the fundamental equation of each of the homogeneous masses which are separated by any surface of discontinuity affords a relation between the pressure in that mass and the temperature and potentials. We are therefore able to eliminate one or two potentials from the fundamental equation of a surface by introducing the pressures in the adjacent masses. Again, when one of these masses is a gas-mixture which satisfies Dalton's law as given on page 215, the potential for each simple gas may be expressed in terms of the temperature and the partial pressure belonging to that gas. By the introduction of these partial pressures we may eliminate as many potentials from the fundamental equation of the surface as there are simple gases in the gas-mixture.

An equation obtained by such substitutions may be regarded as a fundamental equation for the surface of discontinuity to which it relates, for when the fundamental equations of the adjacent masses are known, the equation in question is evidently equivalent to an equation between the tension, temperature, and potentials, and we must regard the knowledge of the properties of the adjacent masses as an indispensable preliminary, or an essential part, of a complete knowledge of any surface of discontinuity. It is evident, however, that from these fundamental equations involving pressures instead of potentials we cannot obtain by differentiation (without the use of the fundamental equations of the homogeneous masses) precisely the same relations as by the differentiation of the equations between the tensions, temperatures, and potentials. It will be interesting to inquire, at least in the more important cases, what relations may be obtained by differentiation from the fundamental equations just described alone.

If there is but one component, the fundamental equations of the two homogeneous masses afford one relation more than is necessary for the elimination of the potential. It may be convenient to regard the tension as a function of the temperature and the difference of the pressures. Now we have by (508) and (98)

$$d\sigma = -\eta_S\, dt - \Gamma\, d\mu_1,$$

$$d(p'-p'') = (\eta_V{}'-\eta_V{}'')\, dt + (\gamma'-\gamma'')\, d\mu_1.$$

Hence we derive the equation

$$d\sigma = -\left(\eta_S - \frac{\Gamma}{\gamma'-\gamma''}(\eta_V{}'-\eta_V{}'')\right) dt - \frac{\Gamma}{\gamma'-\gamma''}\, d(p'-p''), \quad (578)$$

which indicates the differential coefficients of σ with respect to t and $p'-p''$. For surfaces which may be regarded as nearly plane, it is evident that $\frac{\Gamma}{\gamma'-\gamma''}$ represents the distance from the surface of tension to a dividing surface located so as to make the superficial density of the single component vanish, (being positive, when the latter surface is on the side specified by the double accents,) and that the coefficient of dt (without the negative sign) represents the superficial density of entropy as determined by the latter dividing surface, i. e., the quantity denoted by $\eta_{S(1)}$ on page 397.

When there are two components, neither of which is confined to the surface of discontinuity, we may regard the tension as a function of the temperature and the pressures in the two homogeneous masses. The values of the differential coefficients of the tension with respect to these variables may be represented in a simple form if we choose such substances for the components that in the particular state considered each mass shall consist of a single component. This will always be possible when the composition of the two masses is not identical, and will evidently not affect the values of the differential coefficients. We then have

$$d\sigma = -\eta_S\, dt - \Gamma_{,}\, d\mu_{,} - \Gamma_{,,}\, d\mu_{,,},$$
$$dp' = \eta_V{}'\, dt + \gamma'\, d\mu_{,},$$
$$dp'' = \eta_V{}''\, dt + \gamma''\, d\mu_{,,},$$

where the marks $_{,}$ and $_{,,}$ are used instead of the usual $_1$ and $_2$ to indicate the identity of the component specified with the substance of the homogeneous masses specified by $'$ and $''$. Eliminating $d\mu_{,}$ and $d\mu_{,,}$ we obtain

$$d\sigma = -\left(\eta_S - \frac{\Gamma_{,}}{\gamma'}\eta_V{}' - \frac{\Gamma_{,,}}{\gamma''}\eta_V{}''\right) dt - \frac{\Gamma_{,}}{\gamma'}dp' - \frac{\Gamma_{,,}}{\gamma''}dp''. \qquad (579)$$

We may generally neglect the difference of p' and p'', and write

$$d\sigma = -\left(\eta_S - \frac{\Gamma_{,}}{\gamma'}\eta_V{}' - \frac{\Gamma_{,,}}{\gamma''}\eta_V{}''\right) dt - \left(\frac{\Gamma_{,}}{\gamma'} + \frac{\Gamma_{,,}}{\gamma''}\right) dp. \qquad (580)$$

The equation thus modified is strictly to be regarded as the equation for a plane surface. It is evident that $\frac{\Gamma_{,}}{\gamma'}$ and $\frac{\Gamma_{,}}{\gamma'}$ represent the distances from the surface of tension of the two surfaces of which one would make $\Gamma_{,}$ vanish, and the other $\Gamma_{,,}$, that $\frac{\Gamma_{,}}{\gamma'} + \frac{\Gamma_{,,}}{\gamma''}$ represents the distance between these two surfaces, or the *diminution of volume* due to a unit of the surface of discontinuity, and that the coefficient of dt (without the negative sign) represents the excess of entropy in a system consisting of a unit of the surface of discontinuity with a part of each of the adjacent masses above that which the same matter would have if it existed in two homogeneous masses of the same phases but without any surface of discontinuity.

(A mass thus existing without any surface of discontinuity must of course be entirely surrounded by matter of the same phase.)*

The form in which the values of $\left(\dfrac{d\sigma}{dt}\right)_p$ and $\left(\dfrac{d\sigma}{dp}\right)_t$ are given in equation (580) is adapted to give a clear idea of the relations of these quantities to the particular state of the system for which they are to be determined, but not to show how they vary with the state of the system. For this purpose it will be convenient to have the values of these differential coefficients expressed with reference to ordinary components. Let these be specified as usual by $_1$ and $_2$. If we eliminate $d\mu_1$ and $d\mu_2$ from the equations

$$-\,d\sigma = \eta_{\mathrm{S}}\, dt + \Gamma_1\, d\mu_1 + \Gamma_2\, d\mu_2,$$
$$dp = \eta_{\mathrm{V}}'\, dt + \gamma_1{}'\, d\mu_1 + \gamma_2{}'\, d\mu_2,$$
$$dp = \eta_{\mathrm{V}}''\, dt + \gamma_1{}''\, d\mu_1 + \gamma_2{}'',\, d\mu_2,$$

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* If we set

$$V = -\frac{\Gamma_{\prime}}{\gamma'} - \frac{\Gamma_{\prime\prime}}{\gamma''}, \tag{a}$$

$$\mathrm{H_s} = \eta_{\mathrm{s}} - \frac{\Gamma_{\prime}}{\gamma'}\eta_{\mathrm{V}}' - \frac{\Gamma_{\prime\prime}}{\gamma''}\eta_{\mathrm{V}}'', \tag{b}$$

and in like manner

$$\mathrm{E_s} = \varepsilon_{\mathrm{s}} - \frac{\Gamma_{\prime}}{\gamma'}\varepsilon_{\mathrm{V}}' - \frac{\Gamma_{\prime\prime}}{\gamma''}\varepsilon_{\mathrm{V}}'', \tag{c}$$

we may easily obtain, by means of equations (93) and (507),

$$\mathrm{E_s} = t\,\mathrm{H_s} + \sigma - pV. \tag{d}$$

Now equation (580) may be written

$$d\sigma = -\,\mathrm{H_s}\, dt + V\, dp. \tag{e}$$

Differentiating (*d*), and comparing the result with (*e*), we obtain

$$d\mathrm{E_s} = t\, d\mathrm{H_s} - p\, dV. \tag{f}$$

The quantities $\mathrm{E_s}$ and $\mathrm{H_s}$ might be called the superficial densities of energy and entropy quite as properly as those which we denote by ε_s and η_s. In fact, when the composition of both of the homogeneous masses is invariable, the quantities $\mathrm{E_s}$ and H arc much more simple in their definition than ε_s and η_s, and would probably be Hs more naturally suggested by the terms *superficial density of energy* and *of entropy*. It would also be natural in this case to regard the quantities of the homogeneous masses as determined by the total quantities of matter, and not by the surface of tension or any other dividing surface. But such a nomenclature and method could not readily be extended so as to treat cases of more than two components with entire generality.

In the treatment of surfaces of discontinuity in this paper, the definitions and nomenclature which have been adopted will be strictly adhered to. The object of this note is to suggest to the reader how a different method might be used in some cases with advantage, and to show the precise relations between the quantities which are used in this paper and others which might be confounded with them, and which may be made more prominent when the subject is treated differently.

we obtain

$$d\sigma = \frac{B}{A}\,dt + \frac{C}{A}\,dp, \tag{581}$$

where

$$A = \gamma_1{}'' \gamma_2{}' - \gamma_1{}' \gamma_2{}'', \tag{582}$$

$$B = \begin{vmatrix} \eta_S & \Gamma_1 & \Gamma_2 \\ \eta_V{}' & \gamma_1{}' & \gamma_2{}' \\ \eta_V{}'' & \gamma_1{}'' & \gamma_2{}'' \end{vmatrix}, \tag{583}$$

$$C = \Gamma_1\,(\gamma_2{}'' - \gamma_2{}') + \Gamma_2\,(\gamma_1{}' - \gamma_1{}''). \tag{584}$$

It will be observed that A vanishes when the composition of the two homogeneous masses is identical, while B and C do not, in general, and that the value of A is negative or positive according as the mass specified by $'$ contains the component specified by $_1$ in a greater or less proportion than the other mass. Hence, the values both of $\left(\frac{d\sigma}{dt}\right)_p$ and of $\left(\frac{d\sigma}{dp}\right)_t$ become infinite when the difference in the composition of the masses vanishes, and change sign when the greater proportion of a component passes from one mass to the other. This might be inferred from the statements on page 155 respecting coexistent phases which are identical in composition, from which it appears that when two coexistent phases have nearly the same composition, a small variation of the temperature or pressure of the coexistent phases will cause a relatively very great variation in the composition of the phases. The same relations are indicated by the graphical method represented in figure 6 on page 184.

With regard to gas-mixtures which conform to Dalton's law, we shall only consider the fundamental equation for plane surfaces, and shall suppose that there is not more than one component in the liquid which does not appear in the gas-mixture. We have already seen that in limiting the fundamental equation to plane surfaces we can get rid of one potential by choosing such a dividing surface that the superficial density of one of the components vanishes. Let this be done with respect to the component peculiar to the liquid, if such there is; if there is no such component, let it be done with respect to one of the gaseous components. Let the remaining potentials be eliminated by means of the fundamental equations of the simple gases. We may thus obtain an equation between the superficial tension, the temperature, and the several pressures of the simple gases in the gas-mixture or all but one of these pressures. Now, if we eliminate $d\mu_2$, $d\mu_3$, etc. from the equations

$$d\sigma = -\eta_{S(1)}\,dt - \Gamma_{2(1)}\,d\mu_2 + \Gamma_{3(1)}\,d\mu_3 + \text{etc.},$$
$$dp_2 = \eta_{V2}\,dt + \gamma_2\,d\mu_2,$$
$$dp_3 = \eta_{V3}\,dt + \gamma_3\,d\mu_3,$$
$$\text{etc.},$$

where the suffix $_1$ relates to the component of which the surface-density has been made to vanish, and γ_2, γ_3, etc. denote the densities of the gases specified in the gas mixture, and p_2, p_3, etc., η_{V2}, η_{V3}, etc. the pressures and the densities of entropy due to these several gases, we obtain

$$d\sigma = -\left(\eta_{S(1)} - \frac{\Gamma_{2(1)}}{\gamma_2}\eta_{V2} - \frac{\Gamma_{3(1)}}{\gamma_3}\eta_{V3} - \text{etc.}\right)dt$$
$$- \frac{\Gamma_{2(1)}}{\gamma_2}\,dp_2 - \frac{\Gamma_{3(1)}}{\gamma_3}\,dp_3 - \text{etc.} \qquad (585)$$

This equation affords values of the differential coefficients of σ with respect to t, p_2, p_3, etc., which may be set equal to those obtained by differentiating the equation between these variables.

Thermal and Mechanical Relations pertaining to the Extension of a Surface of Discontinuity.

The fundamental equation of a surface of discontinuity with one or two component substances, beside its statical applications, is of use to determine the heat absorbed when the surface is extended under certain conditions.

Let us first consider the case in which there is only a single component substance. We may treat the surface as plane, and place the dividing surface so that the surface density of the single component vanishes. (See page 397.) If we suppose the area of the surface to be increased by unity without change of temperature or of the quantities of liquid and vapor, the entropy of the whole will be increased by $\eta_{S(1)}$. Therefore, if we denote by Q the quantity of heat which must be added to satisfy the conditions, we shall have

$$Q = t\,\eta_{S(1)}, \qquad (586)$$

and by (514),

$$Q = -t\frac{d\sigma}{dt} = -\frac{d\sigma}{d\log t}, \qquad (587)$$

It will be observed that the condition of constant quantities of liquid and vapor as determined by the dividing surface which we have adopted is equivalent to the condition that the total volume shall remain constant.

Again, if the surface is extended without application of heat, while the pressure in the liquid and vapor remains constant, the temperature will evidently be maintained constant by condensation of the vapor. If we denote by M the mass of vapor condensed per unit of surface formed, and by η_{M}' and η_{M}'' the entropies of the liquid and vapor per unit of mass, the condition of no addition of heat will require that

$$M\,(\eta_{\text{M}}'' - \eta_{\text{M}}') = \eta_{\text{S}(1)}. \tag{588}$$

The increase of the volume of liquid will be

$$\frac{\eta_{\text{S}(1)}}{\gamma'\,(\eta_{\text{M}}'' - \eta_{\text{M}}')}, \tag{589}$$

and the diminution of the volume of vapor

$$\frac{\eta_{\text{S}(1)}}{\gamma''\,(\eta_{\text{M}}'' - \eta_{\text{M}}')}. \tag{590}$$

Hence, for the work done (per unit of surface formed) by the external bodies which maintain the pressure, we shall have

$$W = \frac{p\,\eta_{\text{S}(1)}}{\eta_{\text{M}}'' - \eta_{\text{M}}'}\left(\frac{1}{\gamma''} - \frac{1}{\gamma'}\right). \tag{591}$$

and, by (514) and (131),

$$W = -p\frac{d\sigma}{dt}\frac{dt}{dp} = -p\frac{d\sigma}{dp} = -\frac{d\sigma}{d\log p}. \tag{592}$$

The work expended directly in extending the film will of course be equal to σ.

Let us now consider the case in which there are two component substances, neither of which is confined to the surface. Since we cannot make the superficial density of both these substances vanish by any dividing surface, it will be best to regard the surface of tension as the dividing surface. We may, however, simplify the formula by choosing such substances for components that each homogeneous mass shall consist of a single component. Quantities relating to these components will be distinguished as on page 431. If the surface is extended until its area is increased by unity, while heat is added at the surface so as to keep the temperature constant, and the pressure of the homogeneous masses is also kept constant, the phase of these masses will necessarily remain unchanged, but the quantity of one will be diminished by $\Gamma_{,}$, and that of the other by $\Gamma_{,,}$. Their entropies will therefore be diminished by $\frac{\Gamma_{,}}{\gamma'}\eta_{\text{V}}'$ and $\frac{\Gamma_{,,}}{\gamma''}\eta_{\text{V}}''$, respectively. Hence, since the surface receives the increment of entropy η_S, the total quantity of entropy will be increased by

$$\eta_S - \frac{\Gamma_{\prime}}{\gamma'} \eta_V{}' - \frac{\Gamma_{\prime\prime}}{\gamma''} \eta_V{}'',$$

which by equation (580) is equal to

$$-\left(\frac{d\sigma}{dt}\right)_p.$$

Therefore, for the quantity of heat Q imparted to the surface, we shall have

$$Q = -t\left(\frac{d\sigma}{dt}\right)_p = -\left(\frac{d\sigma}{d \log t}\right)_p. \tag{593}$$

We must notice the difference between this formula and (587). In (593) the quantity of heat Q is determined by the condition that the temperature and pressures shall remain constant. In (587) these conditions are equivalent and insufficient to determine the quantity of heat. The additional condition by which Q is determined may be most simply expressed by saying that the total volume must remain constant. Again, the differential coefficient in (593) is defined by considering p as constant; in the differential coefficient in (587) p cannot be considered as constant, and no condition is necessary to give the expression a definite value. Yet, notwithstanding the difference of the two cases, it is quite possible to give a single demonstration which shall be applicable to both. This may be done by considering a cycle of operations after the method employed by Sir William Thomson, who first pointed out these relations.*

The diminution of volume (per unit of surface formed) will be

$$V = \frac{\Gamma_{\prime}}{\gamma'} + \frac{\Gamma_{\prime\prime}}{\gamma''} = -\left(\frac{d\sigma}{dp}\right)_t; \tag{594}$$

and the work done (per unit of surface formed) by the external bodies which maintain the pressure constant will be

$$W = -p\left(\frac{d\sigma}{dp}\right)_t = -\left(\frac{d\sigma}{d \log p}\right)_t. \tag{595}$$

Compare equation (592).

The values of Q and W may also be expressed in terms of quantities relating to the ordinary components. By substitution in (593) and (595) of the values of the differential coefficients which are given by (581), we obtain

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* See *Proc. Roy. Soc.*, vol. ix, p. 255, (June, 1858); or *Phil. Mag.*, Ser. 4, vol. xvii, p. 61.

$$Q = -t\frac{B}{A}, \qquad W = -p\frac{C}{A}. \tag{596}$$

where A, B, and C represent the expressions indicated by (582)–(584). It will be observed that the values of Q and W are in general infinite for the surface of discontinuity between coexistent phases which differ infinitesimally in composition, and change sign with the quantity A. When the phases are absolutely identical in composition, it is not in general possible to counteract the effect of extension of the surface of discontinuity by any supply of heat. For the matter at the surface will not in general have the same composition as the homogeneous masses, and the matter required for the increased surface cannot be obtained from these masses without altering their phase. The infinite values of Q and W are explained by the fact that when the phases are nearly identical in composition, the extension of the surface of discontinuity is accompanied by the vaporization or condensation of a very large mass, according as the liquid or the vapor is the richer in that component which is necessary for the formation of the surface of discontinuity.

If, instead of considering the amount of heat necessary to keep the phases from altering while the surface of discontinuity is extended, we consider the variation of temperature caused by the extension of the surface while the pressures remain constant, it appears that this variation of temperature changes sign with $\gamma_1''\gamma_2' - \gamma_1'\gamma_2''$, but vanishes with this quantity, i. e., vanishes when the composition of the phases becomes the same. This may be inferred from the statements on page 155, or from a consideration of the figure on page 184. When the composition of the homogeneous masses is initially absolutely identical, the effect on the temperature of a finite extension or contraction of the surface of discontinuity will be the same,—either of the two will lower or raise the temperature according as the temperature is a maximum or minimum for constant pressure.

The effect of the extension of a surface of discontinuity which is most easily verified by experiment is the effect upon the tension before complete equilibrium has been reëstablished throughout the adjacent masses. A fresh surface between coexistent phases may be regarded in this connection as an extreme case of a recently extended surface. When sufficient time has elapsed after the extension of a surface originally in equilibrium between coexistent phases, the superficial tension will evidently have sensibly its original value, unless there are substances at the surface which are either not found at all in the adjacent masses, or are found only in quantities comparable to those in which they exist at the surface. But a surface newly formed or extended may have a very different tension.

This will not be the case, however, when there is only a single component substance, since all the processes necessary for equilibrium are confined to a film of insensible thickness, and will require no appreciable time for their completion.

When there are two components, neither of which is confined to the surface of discontinuity, the reëstablishment of equilibrium after the extension of the surface does not necessitate any processes reaching into the interior of the masses except the transmission of heat between the surface of discontinuity and the interior of the masses. It appears from equation (593) that if the tension of the surface diminishes with a rise of temperature, heat must be supplied to the surface to maintain the temperature uniform when the surface is extended, i. e., the effect of extending the surface is to cool it; but if the tension of any surface increases with the temperature, the effect of extending the surface will be to raise its temperature. In either case, it will be observed, the immediate effect of extending the surface is to increase its tension. A contraction of the surface will of course have the opposite effect. But the time necessary for the reëstablishment of sensible thermal equilibrium after extension or contraction of the surface must in most cases be very short.

In regard to the formation or extension of a surface between two coexistent phases of more than two components, there are two extreme cases which it is desirable to notice. When the superficial density of each of the components is exceeding small compared with its density in either of the homogeneous masses, the matter (as well as the heat) necessary for the formation or extension of the normal surface can be taken from the immediate vicinity of the surface without sensibly changing the properties of the masses from which it is taken. But if any one of these superficial densities has a considerable value, while the density of the same component is very small in each of the homogeneous masses, both absolutely and relatively to the densities of the other components, the matter necessary for the formation or extension of the normal surface must come from a considerable distance. Especially if we consider that a small difference of density of such a component in one of the homogeneous masses will probably make a considerable difference in the value of the corresponding potential [see eq. (217)], and that a small difference in the value of the potential will make a considerable difference in the tension [see eq. (508)], it will be evident that in this case a considerable time will be necessary after the formation of a fresh surface or the extension of an old one for the reëstablishment of the normal value of the superficial tension. In intermediate cases, the reëstablishment of the normal tension will take place with different degrees of rapidity.

But whatever the number of component substances, provided that it is greater than one, and whether the reëstablishment of equilibrium is slow or rapid, extension of the surface will generally produce increase and contraction decrease of the tension. It would evidently be inconsistent with stability that the opposite effects should be produced. In general, therefore, a fresh surface between coexistent phases has a greater tension than an old one.* By the use of fresh surfaces, in experiments in capillarity, we may sometimes avoid the effect of minute quantities of foreign substances, which may be present without our knowledge or desire, in the fluids which meet at the surface investigated.

When the establishment of equilibrium is rapid, the variation of the tension from its normal value will be manifested especially during the extension or contraction of the surface, the phenomenon resembling that of viscosity, except that the variations of tension arising from variations in the densities at and about the surface will be the same in all directions, while the variations of tension due to any property of the surface really analogous to viscosity would be greatest in the direction of the most rapid extension.

We may here notice the different action of traces in the homogeneous masses of those substances which increase the tension and of those which diminish it. When the volume-densities of a component are very small, its surface-density may have a considerable positive value, but can only have a very minute negative one.† For the value when negative cannot exceed (numerically) the product of the greater volume-density by the thickness of the non-homogeneous

* When, however, homogeneous masses which have not coexistent phases are brought into contact, the superficial tension may increase with the course of time. The superficial tension of a drop of alcohol and water placed in a large room will increase as the potential for alcohol is equalized throughout the room, and is diminished in the vicinity of the surface of discontinuity.

† It is here supposed that we have chosen for components such substances as are incapable of resolution into other components which are independently variable in the homogeneous masses. In a mixture of alcohol and water, for example, the components must be pure alcohol and pure water.

film. Each of these quantities is exceedingly small. The surface-density when positive is of the same order of magnitude as the thickness of the non-homogeneous film, but is not necessarily small compared with other surface-densities because the volume-densities of the same substance in the adjacent masses are small. Now the potential of a substance which forms a very small part of a homogeneous mass certainly increases, and probably very rapidly, as the proportion of that component is increased. [See (171) and (217).] The pressure, temperature, and the other potentials, will not be sensibly affected. [See (98).] But the effect on the tension of this increase of the potential will be proportional to the surface-density, and will be to diminish the tension when the surface-density is positive. [See (508).] It is therefore quite possible that a very small trace of a substance in the homogeneous masses should greatly diminish the tension, but not possible that such a trace should greatly increase it.*

Impermeable Films.

We have so far supposed, in treating of surfaces of discontinuity, that they afford no obstacle to the passage of any of the component substances from either of the homogeneous masses to the other. The case, however, must be considered, in which there is a film of matter at the surface of discontinuity which is impermeable to some or all of

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* From the experiments of M. E. Duclaux, (*Annales de Chimie et de Physique*, Ser. 4, vol. xxi, p. 383,) it appears that one per cent. of alcohol in water will diminish the superficial tension to .933, the value for pure water being unity. The experiments do not extend to pure alcohol, but the difference of the tensions for mixtures of alcohol and water containing 10 and 20 per cent. water is comparatively small, the tensions being .322 and .336 respectively.

According to the same authority (page 427 of the volume cited), one 3200th part of Castile soap will reduce the superficial tension of water by one-fourth; one 800th part of soap by one-half. These determinations, as well as those relating to alcohol and water, are made by the method of drops, the weight of the drops of different liquids (from the same pipette) being regarded as proportional to their superficial tensions.

M. Athanase Dupré has determined the superficial tensions of solutions of soap by different methods. A statical method gives for one part of common soap in 5000 of water a superficial tension about one-half as great as for pure water, but if the tension be measured on a jet close to the orifice, the value (for the same solution) is sensibly identical with that of pure water. He explains these different values of the superficial tension of the same solution as well as the great effect on the superficial tension which a very small quantity of soap or other trifling impurity may produce, by the tendency of the soap or other substance to form a film on the surface of the liquid. (See *Annales de Chimie et de Physique*, Ser. 4, vol. vii, p. 409, and vol. ix, p. 379.)

the components of the contiguous masses. Such may be the case, for example, when a film of oil is spread on a surface of water, even when the film is too thin to exhibit the properties of the oil in mass. In such cases, if there is communication between the contiguous masses through other parts of the system to which they belong, such that the components in question can pass freely from one mass to the other, the impossibility of a direct passage through the film may be regarded as an immaterial circumstance, so far as states of equilibrium are concerned, and our formulæ will require no change. But when there is no such indirect communication, the potential for any component for which the film is impermeable may have entirely different values on opposite sides of the film, and the case evidently requires a modification of our usual method.

A single consideration will suggest the proper treatment of such cases. If a certain component which is found on both sides of a film cannot pass from either side to the other, the fact that the part of the component which is on one side is the same kind of matter with the part on the other side may be disregarded. All the general relations must hold true, which would hold if they were really different substances. We may therefore write μ_1 for the potential of the component on one side of the film, and μ_2 for the potential of the same substance (to be treated as if it were a different substance) on the other side; m_1^S for the excess of the quantity of the substance on the first side of the film above the quantity which would be on that side of the dividing surface (whether this is determined by the surface of tension or otherwise) if the density of the substance were the same near the dividing surface as at a distance, and m_2^S for a similar quantity relating to the other side of the film and dividing surface. On the same principle, we may use Γ_1 and Γ_2 to denote the values of m_1^S and m_2^S per unit of surface, and m_1', m_2'', γ_1', γ_2'' to denote the quantities of the substance and its densities in the two homogeneous masses.

With such a notation, which may be extended to cases in which the film is impermeable to any number of components, the equations relating to the surface and the contiguous masses will evidently have the same form as if the substances specified by the different suffixes were all really different. The superficial tension will be a function of μ_1 and μ_2, with the temperature and the potentials for the other components, and $-\Gamma_1$, $-\Gamma_2$ will be equal to its differential coefficients with respect to μ_1 and μ_2. In a word, all the general relations which have been demonstrated may be applied to this case, if we remember always to treat the component as a different substance according as it is found on one side or the other of the impermeable film.

When there is free passage for the component specified by the suffixes $_1$ and $_2$ through other parts of the system, (or through any flaws in the film,) we shall have in case of equilibrium $\mu_1 = \mu_2$. If we wish to obtain the fundamental equation for the surface when satisfying this condition, without reference to other possible states of the surface, we may set a single symbol for μ_1 and μ_2 in the more general form of the fundamental equation. Cases may occur of an impermeability which is not absolute, but which renders the transmission of some of the components exceedingly slow. In such cases, it may be necessary to distinguish at least two different fundamental equations, one relating to a state of approximate equilibrium which may be quickly established, and another relating to the ultimate state of complete equilibrium. The former may be derived from the latter by such substitutions as that just indicated.

The Conditions of Internal Equilibrium for a System of Heterogeneous Fluid Masses without neglect of the Influence of the Surfaces of Discontinuity or of Gravity.

Let us now seek the complete value of the variation of the energy of a system of heterogeneous fluid masses, in which the influence of gravity and of the surfaces of discontinuity shall be included, and deduce from it the conditions of internal equilibrium for such a system. In accordance with the method which has been developed, the intrinsic energy, (*i. e.*, the part of the energy which is independent of of gravity,) the entropy, and the quantities of the several components must each be divided into two parts, one of which we regard as belonging to the surfaces which divide approximately homogeneous masses, and the other as belonging to these masses. The elements of intrinsic energy, entropy, etc., relating to an element of surface Ds will be denoted by $D\varepsilon^S$, $D\eta^S$, Dm_1^S, Dm_2^S, etc., and those relating to an element of volume Dv, by $D\varepsilon^V$, $D\eta^V$, Dm_1^V, Dm_2^V, etc. We shall also use Dm^S or $\Gamma\, Ds$ and Dm^V or $\gamma\, Dv$ to denote the total quantities of matter relating to the elements Ds and Dv respectively. That is,

$$Dm^S = \Gamma\, Ds = Dm_1^S + Dm_2^S + \text{etc.}, \qquad (597)$$

$$Dm^V = \gamma\, Dv = Dm_1^V + Dm_2^V + \text{etc.} \qquad (598)$$

The part of the energy which is due to gravity must also be divided into two parts, one of which relates to the elements Dm^{S}, and the other to the elements Dm^{V}. The complete value of the variation of the energy of the system will be represented by the expression

$$\delta \int D\varepsilon^{\text{V}} + \delta \int D\varepsilon^{\text{S}} + \delta \int g\, z\, Dm^{\text{V}} + \delta \int g\, z\, Dm^{\text{S}}, \tag{599}$$

in which g denotes the force of gravity, and z the height of the element above a fixed horizontal plane.

It will be convenient to limit ourselves at first to the consideration of reversible variations. This will exclude the formation of new masses or surfaces. We may therefore regard any infinitesimal variation in the state of the system as consisting of infinitesimal variations of the quantities relating to its several elements, and bring the sign of variation in the preceding formula after the sign of integration. If we then substitute for $\delta D\varepsilon^{\text{V}}$, $\delta D\varepsilon^{\text{S}}$, δDm^{V}, δDm^{S}, the values given by equations (13), (497), (597), (598), we shall have for the condition of equilibrium with respect to reversible variations of the internal state of the system

$$\begin{aligned}
&\int t\, \delta D\eta^{\text{V}} - \int p\, \delta Dv + \int \mu_1\, \delta Dm_1^{\text{V}} + \int \mu_2\, \delta Dm_2^{\text{V}} + \text{etc.} \\
&+ \int t\, \delta D\eta^{\text{S}} + \int \sigma\, \delta Ds + \int \mu_1\, \delta Dm_1^{\text{S}} + \int \mu_2\, \delta Dm_2^{\text{S}} + \text{etc.} \\
&\qquad + \int g\, \delta z\, Dm^{\text{V}} + \int g\, z\, \delta Dm_1^{\text{V}} + \int g\, z\, \delta Dm_2^{\text{V}} + \text{etc.} \\
&\qquad + \int g\, \delta z\, Dm^{\text{S}} + \int g\, z\, \delta Dm_1^{\text{S}} + \int g\, z\, \delta Dm_2^{\text{S}} + \text{etc.} = 0,
\end{aligned} \tag{600}$$

Since equation (497) relates to surfaces of discontinuity which are initially in equilibrium, it might seem that this condition, although always necessary for equilibrium, may not always be sufficient. It is evident, however, from the form of the condition, that it includes the particular conditions of equilibrium relating to every possible deformation of the system, or reversible variation in the distribution of entropy or of the several components. It therefore includes all the relations between the different parts of the system which are necessary for equilibrium, so far as reversible variations are concerned. (The necessary relations between the various quantities relating to each element of the masses and surfaces are expressed by the fundamental equation of the mass or surface concerned, or may be immediately derived from it. See pp. 140–144 and 391–393.)

The variations in (600) are subject to the conditions which arise from the nature of the system and from the supposition that the changes in the system are not such as to affect external bodies. This supposition is necessary, unless we are to consider the variations in the state of the external bodies, and is evidently allowable in seeking the conditions of equilibrium which relate to the interior of the system.* But before we consider the equations of condition in detail, we may divide the condition of equilibrium (600) into the three conditions

$$\int t\, \delta D\eta^{\text{V}} + \int t\, \delta D\eta^{\text{S}} = 0, \tag{601}$$

$$-\int p\, \delta Dv + \int \sigma\, \delta Ds + \int g\, \delta z\, Dm^{\text{V}} + \int g\, \delta z\, Dm^{\text{S}} = 0, \tag{602}$$

$$\begin{aligned} &\int \mu_1\, \delta Dm_1^{\text{V}} + \int \mu_1\, \delta Dm_1^{\text{S}} + \int g z\, \delta Dm_1^{\text{V}} + \int g z\, \delta Dm_1^{\text{S}} \\ &+ \int \mu_2\, \delta Dm_2^{\text{V}} + \int \mu_2\, \delta Dm_2^{\text{S}} + \int g z\, \delta Dm_2^{\text{V}} + \int g z\, \delta Dm_2^{\text{S}} \\ &+ \text{etc.} = 0. \end{aligned} \tag{603}$$

For the variations which occur in any one of the three are evidently independent of those which occur in the other two, and the equations of condition will relate to one or another of these conditions separately.

The variations in condition (601) are subject to the condition that the entropy of the whole system shall remain constant. This may be expressed by the equation

$$\int \delta D\eta^{\text{V}} + \int \delta D\eta^{\text{S}} = 0. \tag{604}$$

To satisfy the condition thus limited it is necessary and sufficient that

$$t = \text{const.} \tag{605}$$

throughout the whole system, which is the condition of thermal equilibrium.

The conditions of mechanical equilibrium, or those that relate to the possible deformation of the system, are contained in (602), which may also be written

$$-\int p\, \delta Dv + \int \sigma\, \delta Ds + \int g\, \gamma\, \delta z\, Dv + \int g\, \Gamma\, \delta z\, Ds = 0. \tag{606}$$

It will be observed that this condition has the same form as if the different fluids were separated by heavy and elastic membranes without rigidity and having at every point a tension uniform in all directions in the plane of the surface. The variations in this formula,

* We have sometimes given a physical expression to a supposition of this kind, in problems in which the peculiar condition of matter in the vicinity of surfaces of discontinuity was to be neglected, by regarding the system as surrounded by a rigid and impermeable envelop. But the more exact treatment which we are now to give the problem of equilibrium would require us to take account of the influence of the envelop on the immediately adjacent matter. Since this involves the consideration of surfaces of discontinuity between solids and fluids, and we wish to limit ourselves at present to the consideration of the equilibrium of fluid masses, we shall give up the conception of an impermeable envelop, and regard the system as bounded simply by a imaginary surface, which is not a surface of discontinuity. The variations of the system must be such as do not deform the surface, nor affect the matter external to it.

beside their necessary geometrical relations, are subject to the conditions that the external surface of the system, and the lines in which the surfaces of discontinuity meet it, are fixed. The formula may be reduced by any of the usual methods, so as to give the particular conditions of mechanical equilibrium. Perhaps the following method will lead as directly as any to the desired result.

It will be observed the quantities affected by δ in (606) relate exclusively to the position and size of the elements of volume and surface into which the system is divided, and that the variations δp and $\delta \sigma$ do not enter into the formula either explicitly or implicitly. The equations of condition which concern this formula also relate exclusively to the variations of the system of geometrical elements, and do not contain either δp or $\delta \sigma$. Hence, in determining whether the first member of the formula has the value zero for every possible variation of the system of geometrical elements, we may assign to δp and $\delta \sigma$ any values whatever, which may simplify the solution of the problem, without inquiring whether such values are physically possible.

Now when the system is in its initial state, the pressure p, in each of the parts into which the system is divided by the surfaces of tension, is a function of the co-ordinates which determine the position of the element Dv, to which the pressure relates. In the varied state of the system, the element Dv will in general have a different position. Let the variation δp be determined solely by the change in position of the element Dv. This may be expressed by the equation

$$\delta p = \frac{dp}{dx}\,\delta x + \frac{dp}{dy}\,\delta y + \frac{dp}{dz}\,\delta z, \tag{607}$$

in which $\frac{dp}{dx}$, $\frac{dp}{dy}$, $\frac{dp}{dz}$ are determined by the function mentioned, and δx, δy, δz by the variation of the position of the element Dv.

Again, in the initial state of the system the tension σ, in each of the different surfaces of discontinuity, is a function of two co-ordinates, ω_1, ω_2, which determine the position of the element Ds. In the varied state of the system, this element will in general have a different position. The change of position may be resolved into a component lying in the surface and another normal to it. Let the variation $\delta \sigma$ be determined solely by the first of these components of the motion of Ds. This may be expressed by the equation

$$\delta \sigma = \frac{d\sigma}{d\omega_1}\,\delta\omega_1 + \frac{d\sigma}{d\omega_2}\,\delta\omega_2, \tag{608}$$

in which $\frac{d\sigma}{d\omega_1}$, $\frac{d\sigma}{d\omega_2}$ are determined by the function mentioned, and $\delta\omega_1$, $\delta\omega_2$, by the component of the motion of Ds which lies in the plane of the surface.

With this understanding, which is also to apply to δp and $\delta\sigma$ when contained implicitly in any expression, we shall proceed to the reduction of the condition (606).

With respect to any one of the volumes into which the system is divided by the surfaces of discontinuity, we may write

$$\int p\,\delta Dv = \delta \int p\,Dv - \int \delta p\,Dv.$$

But it is evident that

$$\delta \int p\,Dv = \int p\,\delta N\,Ds,$$

where the second integral relates to the surfaces of discontinuity bounding the volume considered, and δN denotes the normal component of the motion of an element of the surface, measured outward. Hence,

$$\int p\,\delta Dv = \int p\,\delta N\,Ds - \int \delta p\,Dv.$$

Since this equation is true of each separate volume into which the system is divided, we may write for the whole system

$$\int p\,\delta Dv = \int (p'-p'')\,\delta N\,Ds - \int \delta p\,Dv, \tag{609}$$

where p' and p'' denote the pressures on opposite sides of the element Ds, and δN is measured toward the side specified by double accents.

Again, for each of the surfaces of discontinuity, taken separately,

$$\int \sigma\,\delta Ds = \delta \int \sigma Ds - \int \delta\sigma\,Ds,$$

and

$$\delta \int \sigma\,Ds = \int \sigma\,(c_1 + c_2)\,\delta N\,Ds + \int \sigma\,\delta T Dl,$$

where c_1 and c_2 denote the principal curvatures of the surface, (positive, when the centers are on the side opposite to that toward which δN is measured,) Dl an element of the perimeter of the surface, and δT the component of the motion of this element which lies in the plane of the surface and is perpendicular to the perimeter, (positive, when it extends the surface). Hence we have for the whole system

$$\int \sigma\,\delta Ds = \int \sigma\,(c_1 + c_2)\,\delta N\,Ds + \int \Sigma\,(\sigma\,\delta T)\,Dl - \int \delta\sigma\,Ds, \tag{610}$$

where the integration of the elements Dl extends to all the lines in which the surfaces of discontinuity meet, and the symbol Σ denotes a summation with respect to the several surfaces which meet in such a line.

By equations (609) and (610), the general condition of mechanical equilibrium is reduced to the form

$$-\int(p'-p'')\,\delta N\,Ds+\int\delta p\,Dv+\int\sigma\,(c_1+c_2)\,\delta N\,Ds$$
$$+\int\Sigma(\sigma\,\delta T)\,Dl-\int\delta\sigma\,Ds+\int g\,\gamma\,\delta z\,Dv+\int g\,\Gamma\,\delta z\,Ds=0.$$

Arranging and combining terms, we have

$$\int(g\,\gamma\,\delta z+\delta p)\,Dv$$
$$+\int[\,(p''-p')\,\delta N+\sigma\,(c_1+c_2)\,\delta N+g\,\Gamma\,\delta z-\delta\sigma\,]\,Ds$$
$$+\int\Sigma(\sigma\,\delta T)\,Dl=0. \qquad (611)$$

To satisfy this condition, it is evidently necessary that the coefficients of Dv, Ds, and Dl shall vanish throughout the system.

In order that the coefficient of Dv shall vanish, it is necessary and sufficient that, in each of the masses into which the system is divided by the surfaces of tension, p shall be a function of z alone, such that

$$\frac{dp}{dz}=-g\,\gamma. \qquad (612)$$

In order that the coefficient of Ds shall vanish in all cases, it is necessary and sufficient that it shall vanish for normal and for tangential movements of the surface. For normal movements we may write

$$\delta\sigma=0, \quad \text{and} \quad \delta z=\cos\vartheta\,\delta N,$$

where ϑ denotes the angle which the normal makes with a vertical line. The first condition therefore gives the equation

$$p'-p''=\sigma\,(c_1+c_2)+g\,\Gamma\cos\vartheta, \qquad (613)$$

which must hold true at every point in every surface of discontinuity. The condition with respect to tangential movements shows that in each surface of tension σ is a function of z alone, such that

$$\frac{d\sigma}{dz}=g\,\Gamma. \qquad (614)$$

In order that the coefficient of Dl in (611) shall vanish, we must have, for every point in every line in which surfaces of discontinuity meet, and for any infinitesimal displacement of the line,

$$\Sigma(\sigma\,\delta T)=0. \qquad (615)$$

This condition evidently expresses the same relations between the tensions of the surfaces meeting in the line and the directions of perpendiculars to the line drawn in the planes of the various surfaces, which hold for the magnitudes and directions of forces in equilibrium in a plane.

In condition (603), the variations which relate to any component are to be regarded as having the value zero in any part of the system in which that substance is not an actual component.* The same is true with respect to the equations of condition, which are of the form

$$\left.\begin{array}{l}\int \delta Dm_1^{\mathrm{V}} + \int \delta Dm_1^{\mathrm{S}} = 0, \\ \int \delta Dm_2^{\mathrm{V}} + \int \delta Dm_2^{\mathrm{S}} = 0, \\ \text{etc.}\end{array}\right\} \tag{616}$$

(It is here supposed that the various components are independent, *i. e.*, that none can be formed out of others, and that the parts of the system in which any component actually occurs are not entirely separated by parts in which it does not occur.) To satisfy the condition (603), subject to these equations of condition, it is necessary and sufficient that the conditions

$$\left.\begin{array}{l}\mu_1 + g z = M_1, \\ \mu_2 + g z = M_2, \\ \text{etc.,}\end{array}\right\} \tag{617}$$

(M_1, M_2, etc. denoting constants,) shall each hold true in those parts of the system in which the substance specified is an actual component. We may here add the condition of equilibrium relative to the possible absorption of any substance (to be specified by the suffix $_a$) by parts of the system of which it is not an actual component, viz., that the expression $\mu_a + gz$ must not have a less value in such parts of the system than in a contiguous part in which the substance is an actual component.

From equation (613) with (605) and (617) we may easily obtain the differential equation of a surface of tension (in the geometrical sense of the term), when p', p'', and σ are known in terms of the temperature and potentials. For $c_1 + c_2$ and ϑ may be expressed in terms of the first and second differential coefficients of z with respect to the horizontal co-ordinates, and p', p'', σ, and Γ in terms of the temperature and potentials. But the temperature is constant, and for each of the potentials we may substitute $-gz$ increased by a constant. We thus obtain an equation in which the only variables are z and its first and second differential coefficients with respect to the horizontal co-ordinates. But it will rarely be necessary to use so exact a method. Within moderate differences of level, we may regard γ', γ'', and σ as constant. We may then integrate the equation [derived from (612)]

$$d\,(p' - p'') = g\,(\gamma'' - \gamma')\,dz,$$

* The term *actual component* has been defined for homogeneous masses on page 117, and the definition may be extended to surfaces of discontinuity. It will be observed that if a substance is an actual component of either of the masses separated by a surface of discontinuity, it must be regarded as an actual component for that surface, as well as when it occurs at the surface but not in either of the contiguous masses.

which will give

$$p'-p''=g\,(\gamma''-\gamma')\,z, \tag{618}$$

where z is to be measured from the horizontal plane for which $p'=p''$. Substituting this value in (613), and neglecting the term containing Γ, we have

$$c_1+c_2=\frac{g\,(\gamma''-\gamma')}{\sigma}\,z, \tag{619}$$

where the coefficient of z is to be regarded as constant. Now the value of z cannot be very large, in any surface of sensible dimensions, unless $\gamma''-\gamma'$ is very small. We may therefore consider this equation as practically exact, unless the densities of the contiguous masses are very nearly equal. If we substitute for the sum of the curvatures its value in terms of the differential coefficients of z with respect to the horizontal rectangular co-ordinates, x and y, we have

$$\frac{\left(1+\frac{dz^2}{dy^2}\right)\frac{d^2z}{dx^2}-2\frac{dz}{dx}\frac{dz}{dy}\frac{d^2z}{dxdy}+\left(1+\frac{dz^2}{dx^2}\right)\frac{d^2z}{dy^2}}{\left(1+\frac{dz^2}{dx^2}+\frac{dz^2}{dy^2}\right)^{\frac{3}{2}}}=\frac{g(\gamma''-\gamma')}{\sigma}z. \tag{620}$$

With regard to the sign of the root in the denominator of the fraction, it is to be observed that, if we always take the positive value of the root, the value of the whole fraction will be positive or negative according as the greater concavity is turned upward or downward. But we wish the value of the fraction to be positive when the greater concavity is turned toward the mass specified by a single accent. We should therefore take the positive or negative value of the root according as this mass is above or below the surface.

The particular conditions of equilibrium which are given in the last paragraph but one may be regarded in general as the conditions of chemical equilibrium between the different parts of the system, since they relate to the separate components.* But such a designation is not entirely appropriate unless the number of components is greater than one. In no case are the conditions of mechanical equilibrium entirely independent of those which relate to temperature and the potentials. For the conditions (612) and (614) may be regarded as consequences of (605) and (617) in virtue of the necessary relations (98) and (508).†

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* Concerning another kind of conditions of chemical equilibrium, which relate to the molecular arrangement of the components, and not to their sensible distribution in space, see pages 197–203.

† Compare page 206, where a similar problem is treated without regard to the influence of the surfaces of discontinuity.

The mechanical conditions of equilibrium, however, have an especial importance, since we may always regard them as satisfied in any liquid (and not decidedly viscous) mass in which no sensible motions are observable. In such a mass, when isolated, the attainment of mechanical equilibrium will take place very soon; thermal and chemical equilibrium will follow more slowly. The thermal equilibrium will generally require less time for its approximate attainment than the chemical; but the processes by which the latter is produced will generally cause certain inequalities of temperature until a state of complete equilibrium is reached.

When a surface of discontinuity has more components than one which do not occur in the contiguous masses, the adjustment of the potentials for these components in accordance with equations (617) may take place very slowly, or not at all, for want of sufficient mobility in the components of the surface. But when this surface has only one component which does not occur in the contiguous masses, and the temperature and potentials in these masses satisfy the conditions of equilibrium, the potential for the component peculiar to the surface will very quickly conform to the law expressed in (617), since this is a necessary consequence of the condition of mechanical equilibrium (614) in connection with the conditions relating to temperature and the potentials which we have supposed to be satisfied. The necessary distribution of the substance peculiar to the surface will be brought about by expansions and contractions of the surface. If the surface meets a third mass containing this component and no other which is foreign to the masses divided by the surface, the potential for this component in the surface will of course be determined by that in the mass which it meets.

The particular conditions of mechanical equilibrium (612)–(615), which may be regarded as expressing the relations which must subsist between contiguous portions of a fluid system in a state of mechanical equilibrium, are serviceable in determining whether a given system is or is not in such a state. But the mechanical theorems which relate to finite parts of the system, although they may be deduced from these conditions by integration, may generally be more easily obtained by a suitable application of the general condition of mechanical equilibrium (606), or by the application of ordinary mechanical principles to the system regarded as subject to the forces indicated by this equation.

It will be observed that the conditions of equilibrium relating to temperature and the potentials are not affected by the surfaces of discontinuity. [Compare (228) and (234).]* Since a phase cannot vary continuously without variations of the temperature or the potentials, it follows from these conditions that the phase at any point in a fluid system which has the same independently variable components throughout, and is in equilibrium under the influence of gravity, must be one of a certain number of phases which are completely determined by the phase at any given point and the difference of level of the two points considered. If the phases throughout the fluid system satisfy the general condition of practical stability for phases existing in large masses (viz., that the pressure shall be the least consistent with the temperature and potentials), they will be entirely determined by the phase at any given point and the differences of level. (Compare page 210, where the subject is treated without regard to the influence of the surfaces of discontinuity.)

Conditions of equilibrium relating to irreversible changes.—The conditions of equilibrium relating to the absorption by any part of the system of substances which are not actual components of that part have been given on page 448. Those relating to the formation of new masses and surfaces are included in the conditions of stability relating to such changes, and are not always distinguishable from them. They are evidently independent of the action of gravity. We have already discussed the conditions of stability with respect to the formation of new fluid masses within a homogeneous fluid and at the surface when two such masses meet (see pages 416–429), as well as the condition relating to the possibility of a change in the nature of a surface of discontinuity. (See pages 400–403, where the surface considered is plane, but the result may easily be extended to curved surfaces.) We shall hereafter consider, in some of the more important cases, the conditions of stability with respect to the formation of new masses and surfaces which are peculiar to lines in which several surfaces of discontinuity meet, and points in which several such lines meet.

Conditions of stability relating to the whole system.—Beside the conditions of stability relating to very small parts of a system, which are substantially independent of the action of gravity, and are discussed elsewhere, there are other conditions, which relate to the

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* If the fluid system is divided into separate masses by solid diaphragms which are permeable to all the components of the fluids independently, the conditions of equilibrium of the fluids relating to temperature and the potentials will not be affected. (Compare page 139.) The propositions which follow in the above paragraph may be extended to this case.

whole system or to considerable parts of it. To determine the question of the stability of a given fluid system under the influence of gravity, when all the conditions of equilibrium are satisfied as well as those conditions of stability which relate to small parts of the system taken separately, we may use the method described on page 413, the demonstration of which (pages 411, 412) will not require any essential modification on account of gravity.

When the variations of temperature and of the quantities M_1, M_2, etc. [see (617)] involved in the changes considered are so small that they may be neglected, the condition of stability takes a very simple form, as we have already seen to be the case with respect to a system uninfluenced by gravity. (See page 415.)

We have to consider a varied state of the system in which the total entropy and the total quantities of the various components are unchanged, and all variations vanish at the exterior of the system,—in which, moreover, the conditions of equilibrium relating to temperature and the potentials are satisfied, and the relations expressed by the fundamental equations of the masses and surfaces are to be regarded as satisfied, although the state of the system is not one of complete equilibrium. Let us imagine the state of the system to vary continuously in the course of time in accordance with these conditions and use the symbol d to denote the simultaneous changes which take place at any instant. If we denote the total energy of the system by E, the value of dE may be expanded like that of δE in (599) and (600), and then reduced (since the values of t, μ_1+gz, μ_2+gz, etc. are uniform throughout the system, and the total entropy and total quantities of the several components are constant) to the form

$$\begin{aligned} dE &= -\int p\, dDv + \int g\, dz\, Dm^{\mathrm{V}} + \int \sigma\, dDs + \int g\, dz\, Dm^{\mathrm{S}} \\ &= -\int p\, dDv + \int g\gamma\, dz\, Dv + \int \sigma\, dDs + \int g\,\Gamma\, dz\, Ds, \end{aligned} \qquad (621)$$

where the integrations relate to the elements expressed by the symbol D. The value of p at any point in any of the various masses, and that of σ at any point in any of the various surfaces of discontinuity are entirely determined by the temperature and potentials at the point considered. If the variations of t and M_1, M_2, etc. are to be neglected, the variations of p and σ will be determined solely by the change in position of the point considered. Therefore, by (612) and (614),

$$dp = -g\gamma\, dz, \quad d\sigma = g\,\Gamma\, dz;$$

and

$$
\begin{aligned}
dE &= -\int p\, dDv - \int dp\, Dv + \int \sigma\, dDs + \int d\sigma\, Ds \\
&= -d\int p\, Dv + d\int \sigma\, Ds. \qquad (622)
\end{aligned}
$$

If we now integrate with respect to d, commencing at the given state of the system, we obtain

$$\Delta E = -\Delta \int p\, Dv + \Delta \int \sigma\, Ds, \qquad (623)$$

where Δ denotes the value of a quantity in a varied state of the system diminished by its value in the given state. This is true for finite variations, and is therefore true for infinitesimal variations without neglect of the infinitesimals of the higher orders. The condition of stability is therefore that

$$\Delta \int p\, Dv - \Delta \int \sigma\, Ds < 0, \qquad (624)$$

or that the quantity

$$\int p\, Dv - \int \sigma\, Ds \qquad (625)$$

has a maximum value, the values of p and σ, for each different mass or surface, being regarded as determined functions of z. (In ordinary cases σ may be regarded as constant in each surface of discontinuity, and p as a linear function of z in each different mass.) It may easily be shown (compare page 416) that this condition is always *sufficient* for stability with reference to motion of surfaces of discontinuity, even when the variations of t, M_1, M_2, etc. cannot be neglected in the determination of the *necessary* condition of stability with respect to such changes.

On the Possibility of the Formation of a New Surface of Discontinuity where several Surfaces of Discontinuity meet.

When more than three surfaces of discontinuity between homogeneous masses meet along a line, we may conceive of a new surface being formed between any two of the masses which do not meet in a surface in the original state of the system. The condition of stability with respect to the formation of such a surface may be easily obtained by the consideration of the limit between stability and instability, as exemplified by a system which is in equilibrium when a very small surface of the kind is formed.

To fix our ideas, let us suppose that there are four homogeneous masses A, B, C, and D, which meet one another in four surfaces, which we may call A-B, B-C, C-D, and D-A, these surfaces all meeting along a line L. This is indicated in figure 11 by a section of the surfaces cutting the line L at right angles at a point O. In an infinitesimal variation of the state of the system, we may conceive of a small surface being formed between A and C (to be called A-C), so that the section of the surfaces of discontinuity by the same plane takes the form indicated in figure 12. Let us suppose that

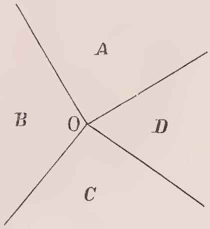

FIG. 11.

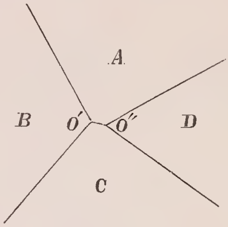

FIG. 12.

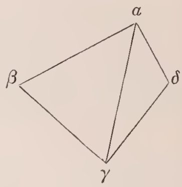

FIG. 13.

the condition of equilibrium (615) is satisfied both for the line L in which the surfaces of discontinuity meet in the original state of the system, and for the two such lines (which we may call L′ and L″) in the varied state of the system, at least at the points O′ and O″ where they are cut by the plane of section. We may therefore form a quadrilateral of which the sides $\alpha\beta$, $\beta\gamma$, $\gamma\delta$, $\delta\alpha$ are equal in numerical value to the tensions of the several surfaces A-B, B-C, C-D, D-A, and are parallel to the normals to these surfaces at the point O in the original state of the system. In like manner, for the varied state of the system we can construct two triangles having similar relations to the surfaces of discontinuity meeting at O′ and O″. But the directions of the normals to the surfaces A-B and B-C at O′ and to C-D and D-A at O″ in the varied state of the system differ infinitely little from the directions of the corresponding normals at O in the initial state. We may therefore regard $\alpha\beta$, $\beta\gamma$ as two sides of the triangle representing the surfaces meeting at O′, and $\gamma\delta$, $\delta\alpha$ as two sides of the triangle representing the surfaces meeting at O″. Therefore, if we join $\alpha\gamma$, this line will represent the direction of the normal to the surface A-C, and the value of its tension. If the tension of a surface between such masses as A and C had been greater than that represented by $\alpha\gamma$, it is evident that the initial state of the system of surfaces (represented in figure 11) would have been stable with respect to the possible formation of any such surface. If the tension had been less, the state of the system would have been at least practically unstable. To determine whether it is unstable in the strict sense of the term, or whether or not it is properly to be regarded as in equilibrium, would require a more refined analysis than we have used.*

The result which we have obtained may be generalized as follows. When more than three surfaces of discontinuity in a fluid system meet in equilibrium along a line, with respect to the surfaces and masses immediately adjacent to any point of this line we may form a polygon of which the angular points shall correspond in order to the different masses separated by the surfaces of discontinuity, and the sides to these surfaces, each side being perpendicular to the corresponding surface, and equal to its tension. With respect to the formation of new surfaces of discontinuity in the vicinity of the point especially considered, the system is stable, if every diagonal of the polygon is less, and practically unstable, if any diagonal is greater, than the tension which would belong to the surface of discontinuity between the corresponding masses. In the limiting case, when the diagonal is exactly equal to the tension of the corresponding surface, the system may often be determined to be unstable by the application of the principle enunciated to an adjacent point of the line in which the surfaces of discontinuity meet. But when, in the polygons constructed for all points of the line, no diagonal is in any case greater

---

* We may here remark that a nearer approximation in the theory of equilibrium and stability might be attained, by taking special account, in our general equations, of the lines in which surfaces of discontinuity meet. These lines might be treated in a manner entirely analogous to that in which we have treated surfaces of discontinuity. We might recognize linear densities of energy, of entropy, and of the several substances which occur about the line, also a certain linear tension. With respect to these quantities and the temperature and potentials, relations would hold analogous to those which have been demonstrated for surfaces of discontinuity. (See pp. 391–393.) If the sum of the tensions of the lines L′ and L″, mentioned above, is greater than the tension of the line L, this line will be in strictness stable (although practically unstable) with respect to the formation of a surface between A and C, when the tension of such a surface is a little less than that represented by the diagonal $\alpha\gamma$.

The different use of the term *practically unstable* in different parts of this paper need not create confusion, since the general meaning of the term is in all cases the same. A system is called practically unstable when a very small (not necessarily indefinitely small) disturbance or variation in its condition will produce a considerable change. In the former part of this paper, in which the influence of surfaces of discontinuity was neglected, a system was regarded as practically unstable when such a result would be produced by a disturbance of the same order of magnitude as the quantities relating to surfaces of discontinuity which were neglected. But where surfaces of discontinuity are considered, a system is not regarded as practically unstable, unless the disturbance which will produce such a result is very small compared with the quantities relating to surfaces of discontinuity of any appreciable magnitude.

than the tension of the corresponding surface, but a certain diagonal is equal to the tension in the polygons constructed for a finite portion of the line, farther investigations are necessary to determine the stability of the system. For this purpose, the method described on page 413 is evidently applicable.

A similar proposition may be enunciated in many cases with respect to a point about which the angular space is divided into solid angles by surfaces of discontinuity. If these surfaces are in equilibrium, we can always form a closed solid figure without re-entrant angles of which the angular points shall correspond to the several masses, the edges to the surfaces of discontinuity, and the sides to the lines in which these edges meet, the edges being perpendicular to the corresponding surfaces, and equal to their tensions, and the sides being perpendicular to the corresponding lines. Now if the solid angles in the physical system are such as may be subtended by the sides and bases of a triangular prism enclosing the vertical point, or can be derived from such by deformation, the figure representing the tensions will have the form of two triangular pyramids on opposite sides of the same base, and the system will be stable or practically unstable with respect to the formation of a surface between the masses which only meet in a point, according as the tension of a surface between such masses is greater or less than the diagonal joining the corresponding angular points of the solid representing the tensions. This will easily appear on consideration of the case in which a very small surface between the masses would be in equilibrium.

The Conditions of Stability for Fluids relating to the Formation of a New Phase at a Line in which Three Surfaces of Discontinuity meet.

With regard to the formation of new phases there are particular conditions of stability which relate to lines in which several surfaces of discontinuity meet. We may limit ourselves to the case in which there are three such surfaces, this being the only one of frequent occurrence, and may treat them as meeting in a straight line. It will be convenient to commence by considering the equilibrium of a system in which such a line is replaced by a filament of a different phase.

Let us suppose that three homogeneous fluid masses, A, B, and C, are separated by cylindrical (or plane) surfaces, A-B, B-C, C-A, which at first meet in a straight line, each of the surface-tensions σ_{AB}, σ_{BC}, σ_{CA} being less than the sum of the other two. Let us suppose that the system is then modified by the introduction of a fourth fluid mass D, which is placed between A, B, and C, and is separated from them by cylindrical surfaces D-A, D-B, D-C meeting A-B, B-C, and C-A in straight lines. The general form of the surfaces is shown by figure 14, in which the full lines represent a section perpendicular to all the surfaces. The system thus modified is to be in equilibrium, as well as the original system, the position of the surfaces A-B, B-C, C-A being unchanged. That the last condition is consistent with equilibrium will appear from the following mechanical considerations.

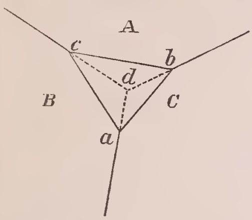

FIG. 14.

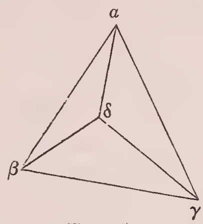

FIG. 15.

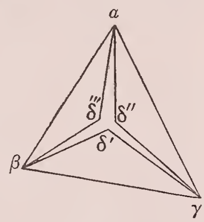

FIG. 16.

Let v_{D} denote the volume of the mass D per unit of length or the area of the curvilinear triangle $a\,b\,c$. Equilibrium is evidently possible for any values of the surface-tensions (if only σ_{AB}, σ_{BC}, σ_{CA} satisfy the condition mentioned above, and the tensions of the three surfaces meeting at each of the edges of D satisfy a similar condition) with any value (not too large) of v_{D}, if the edges of D are constrained to remain in the original surfaces A-B, B-C, and C-A, or these surfaces extended, if necessary, without change of curvature. (In certain cases one of the surfaces D-A, D-B, D-C may disappear and D will be bounded by only two cylindrical surfaces.) We may therefore regard the system as maintained in equilibrium by forces applied to the edges of D and acting at right angles to A-B, B-C, C-A. The same forces would keep the system in equilibrium if D were rigid. They must therefore have a zero resultant, since the nature of the mass D is immaterial when it is rigid, and no forces external to the system would be required to keep a corresponding part of the original system in equilibrium. But it is evident from the points of application and directions of these forces that they cannot have a zero resultant unless each force is zero. We may therefore introduce a fourth mass D without disturbing the parts which remain of the surfaces A-B, B-C, C-D.

It will be observed that all the angles at a, b, c, and d in figure 14 are entirely determined by the six surface-tensions σ_{AB}, σ_{BC}, σ_{CA}, σ_{DA}, σ_{DB}, σ_{DC}. [See (615).] The angles may be derived from the tensions by the following construction, which will also indicate some important properties. If we form a triangle $\alpha\,\beta\,\gamma$ (figure 15 or 16) having sides equal to σ_{AB}, σ_{BC}, σ_{CA}, the angles of the triangle will be supplements of the angles at d. To fix our ideas, we may suppose the sides of the triangle to be perpendicular to the surfaces at d. Upon $\beta\,\gamma$ we may then construct (as in figure 16) a triangle $\beta\,\gamma\,\delta'$ having sides equal to σ_{BC}, σ_{DC}, σ_{DB}, upon $\gamma\,\alpha$ a triangle $\gamma\,\alpha\,\delta''$ having sides equal to σ_{CA}, σ_{DA}, σ_{DC}, and upon $\alpha\,\beta$ a triangle $\alpha\beta\delta'''$ having sides equal to σ_{AB}, σ_{DB}, σ_{DA}. These triangles are to be on the same sides of the lines $\beta\,\gamma$, $\gamma\,\alpha$, $\alpha\,\beta$, respectively, as the triangle $\alpha\,\beta\,\gamma$. The angles of these triangles will be supplements of the angles of the surfaces of discontinuity at a, b, and c. Thus $\beta\,\gamma\,\delta' = d\,a\,b$, and $\alpha\,\gamma\,\delta'' = d\,b\,a$. Now if δ' and δ'' fall together in a single point δ within the triangle $\alpha\,\beta\,\gamma$, δ''' will fall in the same point, as in figure 15. In this case we shall have $\beta\,\gamma\,\delta + \alpha\,\gamma\,\delta = \alpha\,\gamma\,\beta$, and the three angles of the curvilinear triangle $a\,d\,b$ will be together equal to two right angles. The same will be true of the three angles of each of the triangles $b\,d\,c$, $c\,d\,a$, and hence of the three angles of the triangle $a\,b\,c$. But if δ', δ'', δ''' do not fall together in the same point within the triangle $\alpha\,\beta\,\gamma$, it is either possible to bring these points to coincide within the triangle by increasing some or all of the tensions σ_{DA}, σ_{DB}, σ_{DC}, or to effect the same result by diminishing some or all of these tensions. (This will easily appear when one of the points δ', δ'', δ''' falls within the triangle, if we let the two tensions which determine this point remain constant, and the third tension vary. When all the points δ', δ'', δ''' fall without the triangle $\alpha\,\beta\,\gamma$, we may suppose the greatest of the tensions σ_{DA}, σ_{DB}, σ_{DC}—the two greatest, when these are equal, and all three when they all are equal—to diminish until one of the points δ', δ'', δ''' is brought within the triangle $\alpha\,\beta\,\gamma$.) In the first case we may say that the tensions of the new surfaces are too small to be represented by the distances of an internal point from the vertices of the triangle representing the tensions of the original surfaces (or, for brevity, that they are too small to be represented as in figure 15); in the second case we may say that they are too great to be thus represented. In the first case, the sum of the angles in each of the triangles $a\,d\,b$, $b\,d\,c$, $c\,d\,a$ is less than two right angles (compare figures 14 and 16): in the second case, each pair of the triangles $\alpha\,\beta\,\delta'''$, $\beta\,\gamma\,\delta''$, $\gamma\,\alpha\,\delta''$ will overlap, at least when the tensions σ_{DA}, σ_{DB}, σ_{DC} are only a little too great to be represented as in figure 15, and the sum of the angles of each of the triangles $a\,d\,b$, $b\,d\,c$, $c\,d\,a$ will be greater than two right angles.

Let us denote by v_A, v_B, v_C the portions of v_D which were originally occupied by the masses A, B, C, respectively, by s_{DA}, s_{DB}, s_{DC}, the areas of the surfaces specified per unit of length of the mass D, and by s_{AB}, s_{BC}, s_{CA}, the areas of the surfaces specified which were replaced by the mass D per unit of its length. In numerical value, v_A, v_B, v_C will be equal to the areas of the curvilinear triangles $b\,c\,d$, $c\,a\,d$, $a\,b\,d$; and s_{DA}, s_{DB}, s_{DC}, s_{AB}, s_{BC}, s_{CA} to the lengths of the lines $b\,c$, $c\,a$, $a\,b$, $c\,d$, $a\,d$, $b\,d$. Also let

$$W_S = \sigma_{DA}\,s_{DA} + \sigma_{DB}\,s_{DB} + \sigma_{DC}\,s_{DC} - \sigma_{AB}\,s_{AB} - \sigma_{BC}\,s_{BC} - \sigma_{CA}\,s_{CA}, \quad (626)$$

and

$$W_V = p_D\,v_D - p_A\,v_A - p_B\,v_B - p_C\,v_C. \quad (627)$$

The general condition of mechanical equilibrium for a system of homogeneous masses not influenced by gravity, when the exterior of the whole system is fixed, may be written

$$\Sigma\,(\sigma\,\delta s) - \Sigma\,(p\,\delta v) = 0. \quad (628)$$

[See (606).] If we apply this both to the original system consisting of the masses A, B, and C, and to the system modified by the introduction of the mass D, and take the difference of the results, supposing the deformation of the system to be the same in each case, we shall have

$$\sigma_{DA}\,\delta s_{DA} + \sigma_{DB}\,\delta s_{DB} + \sigma_{DC}\,\delta s_{DC} - \sigma_{AB}\,\delta s_{AB} - \sigma_{BC}\,\delta s_{BC}$$
$$- \sigma_{CA}\,\delta s_{CA} - p_D\,\delta v_D + p_A\,\delta v_A + p_B\,\delta v_B + p_C\,\delta v_C = 0. \quad (629)$$

In view of this relation, if we differentiate (626) and (627) regarding all quantities except the pressures as variable, we obtain

$$d\,W_S - d\,W_V = s_{DA}\,d\sigma_{DA} + s_{DB}\,d\sigma_{DB} + s_{DC}\,d\sigma_{DC}$$
$$- s_{AB}\,d\sigma_{AB} - s_{BC}\,d\sigma_{BC} - s_{CA}\,d\sigma_{CA}. \quad (630)$$

Let us now suppose the system to vary in size, remaining always similar to itself in form, and that the tensions diminish in the same ratio as lines, while the pressures remain constant. Such changes will evidently not impair the equilibrium. Since all the quantities s_{DA}, σ_{DA}, s_{DB}, σ_{DB}, etc. vary in the same ratio,

$$s_{DA}\,d\sigma_{DA} = \tfrac{1}{2}\,d(\sigma_{DA}\,s_{DA}), \qquad s_{DB}\,d\sigma_{DB} = \tfrac{1}{2}\,d(\sigma_{DB}\,s_{DB}), \quad \text{etc.} \quad (631)$$

We have therefore by integration of (630)

$$W_S - W_V = \tfrac{1}{2}\,(\sigma_{DA}s_{DA} + \sigma_{DB}s_{DB} + \sigma_{DC}s_{DC} - \sigma_{AB}s_{AB} - \sigma_{BC}s_{BC} - \sigma_{CA}s_{CA}), \quad (632)$$

whence, by (626),

$$W_S = 2\,W_V, \quad (633)$$

The condition of stability for the system when the pressures and tensions are regarded as constant, and the position of the surfaces

A-B, B-C, C-A as fixed, is that $W_S - W_V$ shall be a minimum under the same conditions. [See (549).] Now for any constant values of the tensions and of p_A, p_B, p_C, we may make v_D so small that when it varies, the system remaining in equilibrium, (which will in general require a variation of p_D,) we may neglect the curvatures of the lines $d\,a$, $d\,b$, $d\,c$, and regard the figure $a\,b\,c\,d$ as remaining similar to itself. For the *total curvature* (*i. e.*, the curvature measured in degrees) of each of the lines $a\,b$, $b\,c$, $c\,a$ may be regarded as constant, being equal to the constant difference of the sum of the angles of one of the curvilinear triangles $a\,d\,b$, $b\,d\,c$, $c\,d\,a$ and two right angles. Therefore, when v_D is very small, and the system is so deformed that equilibrium would be preserved if p_D had the proper variation, but this pressure as well as the others and all the tensions remain constant, W_S will vary as the lines in the figure $a\,b\,c\,d$, and W_V as the square of these lines. Therefore, for such deformations,

$$W_V \propto W_S^2.$$

This shows that the system cannot be stable for constant pressures and tensions when v_D is small and W_V is positive, since $W_S - W_V$ will not be a minimum. It also shows that the system is stable when W_V is negative. For, to determine whether $W_S - W_V$ is a minimum for constant values of the pressures and tensions, it will evidently be sufficient to consider such varied forms of the system as give the least value to $W_S - W_V$ for any value of v_D in connection with the constant pressures and tensions. And it may easily be shown that such forms of the system are those which would preserve equilibrium if p_D had the proper value.

These results will enable us to determine the most important questions relating to the stability of a line along which three homogeneous fluids A, B, C meet, with respect to the formation of a different fluid D. The components of D must of course be such as are found in the surrounding bodies. We shall regard p_D and σ_{DA}, σ_{DB}, σ_{DC} as determined by that phase of D which satisfies the conditions of equilibrium with the other bodies relating to temperature and the potentials. These quantities are therefore determinable, by means of the fundamental equations of the mass D and of the surfaces D-A, D-B, D-C, from the temperature and potentials of the given system.

Let us first consider the case in which the tensions, thus determined, can be represented as in figure 15, and p_D has a value consistent with the equilibrium of a small mass such as we have been considering. It appears from the preceding discussion that when v_D is sufficiently small the figure $a\,b\,c\,d$ may be regarded as rectilinear, and that its angles are entirely determined by its tensions. Hence the ratios of v_A, v_B, v_C, v_D, for sufficiently small values of v_D, are determined by the tensions alone, and for convenience in calculating these ratios, we may suppose p_A, p_B, p_C to be equal, which will make the figure $a\,b\,c\,d$ absolutely rectilinear, and make p_D equal to the other pressures, since it is supposed that this quantity has the value necessary for equilibrium. We may obtain a simple expression for the ratios of v_A, v_B, v_C, v_D in terms of the tensions in the following manner. We shall write [D B C], [D C A], etc., to denote the areas of triangles having sides equal to the tensions of the surfaces between the masses specified.

$$
\begin{aligned}
v_A : v_B &:: \text{triangle } b\,d\,c : \text{triangle } a\,d\,c \\
&:: bc \sin bcd : ac \sin acd \\
&:: \sin bac \sin bcd : \sin abc \sin acd \\
&:: \sin \gamma\delta\beta \sin \delta\alpha\beta : \sin \gamma\delta\alpha \sin \delta\beta\alpha \\
&:: \sin \gamma\delta\beta \; \delta\beta : \sin \gamma\delta\alpha \; \delta\alpha \\
&:: \text{triangle } \gamma\,\delta\,\beta : \text{triangle } \gamma\,\delta\,\alpha \\
&:: [\mathrm{D\,B\,C}] : [\mathrm{D\,C\,A}].
\end{aligned}
$$

Hence,

$$
v_A : v_B : v_C : v_D :: [\mathrm{D\,B\,C}] : [\mathrm{D\,C\,A}] : [\mathrm{D\,A\,B}] : [\mathrm{A\,B\,C}], \tag{634}
$$

where

$$
\tfrac{1}{4}\surd[(\sigma_{AB}+\sigma_{BC}+\sigma_{CA})(\sigma_{AB}+\sigma_{BC}-\sigma_{CA})(\sigma_{BC}+\sigma_{CA}-\sigma_{AB})(\sigma_{CA}+\sigma_{AB}-\sigma_{BC})]
$$

may be written for [A B C], and analogous expressions for the other symbols, the sign $\surd$ denoting the positive root of the necessarily positive expression which follows. This proportion will hold true in any case of equilibrium, when the tensions satisfy the condition mentioned and v_D is sufficiently small. Now if $p_A = p_B = p_C$, p_D will have the same value, and we shall have by (627) $W_V = 0$, and by (633) $W_S = 0$. But when v_D is very small, the value of W_S is entirely determined by the tensions and v_D. Therefore, whenever the tensions satisfy the condition supposed, and v_D is very small (whether p_A, p_B, p_C are equal or unequal,)

$$
0 = W_S = W_V = p_D v_D - p_A v_A - p_B v_B - p_C v_C, \tag{635}
$$

which with (634) gives

$$
p_D = \frac{[\mathrm{D\,B\,C}]p_A + [\mathrm{D\,C\,A}]p_B + [\mathrm{D\,A\,B}]p_C}{[\mathrm{D\,B\,C}] + [\mathrm{D\,C\,A}] + [\mathrm{D\,A\,B}]}. \tag{636}
$$

Since this is the only value of p_D for which equilibrium is possible when the tensions satisfy the condition supposed and v_D is small, it follows that when p_D has a less value, the line where the fluids A, B, C meet is stable with respect to the formation of the fluid D. When p_D has a greater value, if such a line can exist at all, it must be at least practically unstable, *i. e.*, if only a very small mass of the fluid D should be formed it would tend to increase.

Let us next consider the case in which the tensions of the new surfaces are too small to be represented as in figure 15. If the pressures and tensions are consistent with equilibrium for any very small value of v_D, the angles of each of the curvilinear triangles $a\,d\,b$, $b\,d\,c$, $c\,d\,a$ will be together less than two right angles, and the lines $a\,b$, $b\,c$, $c\,a$, will be convex toward the mass D. For given values of the pressures and tensions, it will be easy to determine the magnitude of v_D. For the tensions will give the total curvatures (in degrees) of the lines $a\,b$, $b\,c$, $c\,a$; and the pressures will give the radii of curvature. These lines are thus completely determined. In order that v_D shall be very small it is evidently necessary that p_D shall be less than the other pressures. Yet if the tensions of the new surfaces are only a very little too small to be represented as in figure 15, v_D may be quite small when the value of p_D is only a little less than that given by equation (636). In any case, when the tensions of the new surfaces are too small to be represented as in figure 15, and v_D is small, W_V is negative, and the equilibrium of the mass D is stable. Moreover, $W_S - W_V$, which represents the work necessary to form the mass D with its surfaces in place of the other masses and surfaces, is negative.

With respect to the stability of a line in which the surfaces A-B, B-C, C-A meet, when the tensions of the new surfaces are too small to be represented as in figure 15, we first observe that when the pressures and tensions are such as to make v_D moderately small but not so small as to be neglected, [this will be when p_D is somewhat smaller than the second member of (636),—more or less smaller according as the tensions differ more or less from such as are represented in figure 15,] the equilibrium of such a line as that supposed (if it is capable of existing at all) is at least practically unstable. For greater values of p_D (with the same values of the other pressures and the tensions) the same will be true. For somewhat smaller values of p_D, the mass of the phase D which will be formed will be so small, that we may neglect this mass and regard the surfaces A-B, B-C, C-A as meeting in a line in stable equilibrium. For still smaller values of p_D, we may likewise regard the surfaces A-B, B-C, C-A as capable of meeting in stable equilibrium. It may be observed that when v_D, as determined by our equations, becomes quite insensible, the conception of a small mass D having the properties deducible from our equations ceases to be accurate, since the matter in the vicinity of a line where these surfaces of discontinuity meet must be in a peculiar state of equilibrium not recognized by our equations.* But this cannot affect the validity of our conclusion with respect to the stability of the line in question.

The case remains to be considered in which the tensions of the new surfaces are too great to be represented as in figure 15. Let us suppose that they are not very much too great to be thus represented. When the pressures are such as to make v_D moderately small (in case of equilibrium) but not so small that the mass D to which it relates ceases to have the properties of matter in mass, [this will be when p_D is somewhat greater than the second member of (636),—more or less greater according as the tensions differ more or less from such as are represented in figure 15,] the line where the surfaces A-B, B-C, C-A meet will be in stable equilibrium with respect to the formation of such a mass as we have considered, since $W_S - W_V$ will be positive. The same will be true for less values of p_D. For greater values of p_D, the value of $W_S - W_V$, which measures the stability with respect to the kind of change considered, diminishes. It does not vanish, according to our equations, for finite values of p_D. But these equations are not to be trusted beyond the limit at which the mass D ceases to be of sensible magnitude.

But when the tensions are such as we now suppose, we must also consider the possible formation of a mass D within a closed figure in which the surfaces D-A, D-B, D-C meet together (with the surfaces A-B, B-C, C-A) in two opposite points. If such a figure is to be in equilibrium, the six tensions must be such as can be represented by

---

* See note on page 455. We may here add that the linear tension there mentioned may have a negative value. This would be the case with respect to a line in which three surfaces of discontinuity are regarded as meeting, but where nevertheless there really exists in stable equilibrium a filament of different phase from the three surrounding masses. The value of the linear tension for the supposed line, would be nearly equal to the value of $W_S - W_V$ for the actually existing filament. (For the exact value of the linear tension it would be necessary to add the sum of the linear tensions of the three edges of the filament.) We may regard two soap-bubbles adhering together as an example of this case. The reader will easily convince himself that in an exact treatment of the equilibrium of such a double bubble we must recognize a certain negative tension in the line of intersection of the three surfaces of discontinuity.

the six distances of four points in space (see page 455),—a condition which evidently agrees with the supposition which we have made. If we denote by w_V the work gained in forming the mass D (of such size and form as to be in equilibrium) in place of the other masses, and by w_S the work expended in forming the new surfaces in place of the old, it may easily be shown by a method similar to that used on page 459 that $w_S = \frac{3}{2} w_V$. From this we obtain $w_S - w_V = \frac{1}{2} w_V$. This is evidently positive when p_D is greater than the other pressures. But it diminishes with increase of p_D, as easily appears from the equivalent expression $\frac{1}{3} w_S$. Hence the line of intersection of the surfaces of discontinuity A-B, B-C, C-A is stable for values of p_D greater than the other pressures (and therefore for all values of p_D) so long as our method is to be regarded as accurate, which will be so long as the mass D which would be in equilibrium has a sensible size.

In certain cases in which the tensions of the new surfaces are much too large to be represented as in figure 15, the reasoning of the two last paragraphs will cease to be applicable. These are cases in which the six tensions cannot be represented by the sides of a tetrahedron. It is not necessary to discuss these cases, which are distinguished by the different shape which the mass D would take if it should be formed, since it is evident that they can constitute no exception to the results which we have obtained. For an increase of the values of σ_{DA}, σ_{DB}, σ_{DC} cannot favor the formation of D, and hence cannot impair the stability of the line considered, as deduced from our equations. Nor can an increase of these tensions essentially affect the fact that the stability thus demonstrated may fail to be realized when p_D is considerably greater than the other pressures, since the *a priori* demonstration of the stability of any one of the surfaces A-B, B-C, C-A, taken singly, is subject to the limitation mentioned. (See page 426.)

The Condition of Stability for Fluids relating to the Formation of a New Phase at a Point where the Vertices of Four Different Masses meet.

Let four different fluid masses A, B, C, D meet about a point, so as to form the six surfaces of discontinuity A-B, B-C, C-A, D-A, D-B, D-C, which meet in the four lines A-B-C, B-C-D, C-D-A, D-A-B, these lines meeting in the vertical point. Let us suppose the system stable in other respects, and consider the conditions of stability for the vertical point with respect to the possible formation of a different fluid mass E.

If the system can be in equilibrium when the vertical point has been replaced by a mass E against which the four masses A, B, C, D abut, being truncated at their vertices, it is evident that E will have four vertices, at each of which six surfaces of discontinuity meet. (Thus at one vertex there will be the surfaces formed by A, B, C, and E.) The tensions of each set of six surfaces (like those of the six surfaces formed by A, B, C, and D) must therefore be such that they can be represented by the six edges of a tetrahedron. When the tensions do not satisfy these relations, there will be no particular condition of stability for the point about which A, B, C, and D meet, since if a mass E should be formed, it would distribute itself along some of the lines or surfaces which meet at the vertical point, and it is therefore sufficient to consider the stability of these lines and surfaces. We shall suppose that the relations mentioned are satisfied.

If we denote by W_V the work gained in forming the mass E (of such size and form as to be in equilibrium) in place of the portions of the other masses which are suppressed, and by W_S the work expended in forming the new surfaces in place of the old, it may easily be shown by a method similar to that used on page 459 that

$$W_S = \tfrac{3}{2} W_V, \tag{637}$$

whence

$$W_S - W_V = \tfrac{1}{2} W_V; \tag{638}$$

also, that when the volume E is small, the equilibrium of E will be stable or unstable according as W_S and W_V are negative or positive.

A critical relation for the tensions is that which makes equilibrium possible for the system of the five masses A, B, C, D, E, when all the surfaces are plane. The ten tensions may then be represented in magnitude and direction by the ten distances of five points in space α, β, γ, δ, ε, viz., the tension of A-B and the direction of its normal by the line $\alpha\beta$, etc. The point ε will lie within the tetrahedron formed by the other points. If we write v_E for the volume of E, and v_A, v_B, v_C, v_D for the volumes of the parts of the other masses which are suppressed to make room for E, we have evidently

$$W_V = p_E v_E - p_A v_A - p_B v_B - p_C v_C - p_D v_D. \tag{639}$$

Hence, when all the surfaces are plane, $W_V = 0$, and $W_S = 0$. Now equilibrium is always possible for a given small value of v_E with any given values of the tensions and of p_A, p_B, p_C, p_D. When the tensions satisfy the critical relation, $W_S = 0$, if $p_A = p_B = p_C = p_D$. But when v_E is small and constant, the value of W_S must be independent of p_A, p_B, p_C, p_D, since the angles of the surfaces are determined by the tensions and their curvatures may be neglected. Hence, $W_S = 0$, and

$W_V = 0$, when the critical relation is satisfied and v_E small. This gives

$$p_E = \frac{v_A p_A + v_B p_B + v_C p_C + v_D p_D}{v_E}. \tag{640}$$

In calculating the ratios of v_A, v_B, v_C, v_D, v_E, we may suppose all the surfaces to be plane. Then E will have the form of a tetrahedron, the vertices of which may be called a, b, c, d, (each vertex being named after the mass which is not found there,) and v_A, v_B, v_C, v_D will be the volumes of the tetrahedra into which it may be divided by planes passing through its edges and an interior point e. The volumes of these tetrahedra are proportional to those of the five tetrahedra of the figure $\alpha\,\beta\,\gamma\,\delta\,\varepsilon$, as will easily appear if we recollect that the line a b is common to the surfaces C-D, D-E, E-C, and therefore perpendicular to the surface common to the lines $\gamma\,\delta$, $\delta\,\varepsilon$, $\varepsilon\,\gamma$, *i. e.*, to the surface $\gamma\,\delta\,\varepsilon$, and so in other cases, (it will be observed that γ, δ, and ε are the letters which do not correspond to a or b); also that the surface a b c is the surface D-E and therefore perpendicular to $\delta\,\varepsilon$, etc. Let tetr abcd, trian abc, etc. denote the volume of the tetrahedron or the area of the triangle specified, sin (ab, bc), sin (abc, dbc), sin (abc, ad), etc. the sines of the angles made by the lines and surfaces specified, and [B C D E], [C D E A], etc., the volumes of tetrahedra having edges equal to the tensions of the surfaces between the masses specified. Then, since we may express the volume of a tetrahedron either by $\frac{1}{3}$ of the product of one side, an edge leading to the opposite vertex, and the sine of the angle which these make, or by $\frac{2}{3}$ of the product of two sides divided by the common edge and multiplied by the sine of the included angle,

$$\begin{aligned}
v_A : v_B &:: \text{tetr bcde} : \text{tetr acde} \\
&:: \text{bc} \sin(\text{bc, cde}) : \text{ac} \sin(\text{ac, cde}) \\
&:: \sin(\text{ba, ac}) \sin(\text{bc, cde}) : \sin(\text{ab, bc}) \sin(\text{ac, cde}) \\
&:: \sin(\gamma\delta\varepsilon, \beta\delta\varepsilon) \sin(\alpha\delta\varepsilon, \alpha\beta) : \sin(\gamma\delta\varepsilon, \alpha\delta\varepsilon) \sin(\beta\delta\varepsilon, \alpha\beta) \\
&:: \frac{\text{tetr}\,\gamma\beta\delta\varepsilon}{\text{trian}\,\beta\delta\varepsilon}\,\frac{\text{tetr}\,\beta\alpha\delta\varepsilon}{\text{trian}\,\alpha\delta\varepsilon} : \frac{\text{tetr}\,\gamma\alpha\delta\varepsilon}{\text{trian}\,\alpha\delta\varepsilon}\,\frac{\text{tetr}\,\alpha\beta\delta\varepsilon}{\text{trian}\,\beta\delta\varepsilon} \\
&:: \text{tetr}\,\gamma\beta\delta\varepsilon : \text{tetr}\,\gamma\alpha\delta\varepsilon \\
&:: [\text{B C D E}] : [\text{C D E A}].
\end{aligned}$$

Hence,

$$v_A : v_B : v_C : v_D :: [\text{B C D E}] : [\text{C D E A}] : [\text{D E A B}] : \text{E A B C}], \tag{641}$$

and (640) may be written

$$p_E = \frac{[\text{B C D E}]p_A + [\text{C D E A}]p_B + [\text{D E A B}]p_C + [\text{E A B C}]p_D}{[\text{B C D E}] + [\text{C D E A}] + [\text{D E A B}] + [\text{E A B C}]}. \tag{642}$$

If the value of p_E is less than this, when the tensions satisfy the critical relation, the point where vertices of the masses A, B, C, D meet is stable with respect to the formation of any mass of the nature of E. But if the value of p_E is greater, either the masses A, B, C, D cannot meet at a point in equilibrium, or the equilibrium will be at least practically unstable.

When the tensions of the new surfaces are too small to satisfy the critical relation with the other tensions, these surfaces will be convex toward E; when their tensions are too great for that relation, the surfaces will be concave toward E. In the first case, W_V is negative, and the equilibrium of the five masses A, B, C, D, E is stable, but the equilibrium of the four masses A, B, C, D meeting at a point is impossible or at least practically unstable. This is subject to the limitation that when p_E is sufficiently small the mass E which will form will be so small that it may be neglected. This will only be the case when p_E is smaller—in general considerably smaller—than the second number of (642). In the second case, the equilibrium of the five masses A, B, C, D, E will be unstable, but the equilibrium of the four masses A, B, C, D will be stable unless v_E (calculated for the case of the five masses) is of insensible magnitude. This will only be the case when p_E is greater—in general considerably greater—than the second member of (642).

Liquid Films.

When a fluid exists in the form of a thin film between other fluids, the great inequality of its extension in different directions will give rise to certain peculiar properties, even when its thickness is sufficient for its interior to have the properties of matter in mass. The frequent occurrence of such films, and the remarkable properties which they exhibit, entitle them to particular consideration. To fix our ideas, we shall suppose that the film is liquid and that the contiguous fluids are gaseous. The reader will observe our results are not dependent, so far as their general character is concerned, upon this supposition.

Let us imagine the film to be divided by surfaces perpendicular to its sides into small portions of which all the dimensions are of the same order of magnitude as the thickness of the film,—such portions to be called *elements of the film*,—it is evident that far less time will in general be required for the attainment of approximate equilibrium between the different parts of any such element and the other fluids which are immediately contiguous, than for the attainment of equilibrium between all the different elements of the film. There will accordingly be a time, commencing shortly after the formation of the film, in which its separate elements may be regarded as satisfying the conditions of internal equilibrium, and of equilibrium with the contiguous gases, while they may not satisfy all the conditions of equilibrium with each other. It is when the changes due to this want of complete equilibrium take place so slowly that the film appears to be at rest, except so far as it accommodates itself to any change in the external conditions to which it is subjected, that the characteristic properties of the film are most striking and most sharply defined.

Let us therefore consider the properties which will belong to a film sufficiently thick for its interior to have the properties of matter in mass, in virtue of the approximate equilibrium of all its elements taken separately, when the matter contained in each element is regarded as invariable, with the exception of certain substances which are components of the contiguous gas-masses and have their potentials thereby determined. The occurrence of a film which precisely satisfies these conditions may be exceptional, but the discussion of this somewhat ideal case will enable us to understand the principal laws which determine the behavior of liquid films in general.

Let us first consider the properties which will belong to each element of the film under the conditions mentioned. Let us suppose the element extended, while the temperature and the potentials which are determined by the contiguous gas-masses are unchanged. If the film has no components except those of which the potentials are maintained constant, there will be no variation of tension in its surfaces. The same will be true when the film has only one component of which the potential is not maintained constant, provided that this is a component of the interior of the film and not of its surface alone. If we regard the thickness of the film as determined by *dividing surfaces* which make the surface-density of this component vanish, the thickness will vary inversely as the area of the element of the film, but no change will be produced in the nature or the tension of its surfaces. If, however, the single component of which the potential is not maintained constant is confined to the surfaces of the film, an extension of the element will generally produce a decrease in the potential of this component, and an increase of tension. This will certainly be true in those cases in which the component shows a tendency to distribute itself with a uniform superficial density.

When the film has two or more components of which the potentials are not maintained constant by the contiguous gas masses, they will not in general exist in the same proportion in the interior of the film as on its surfaces, but those components which diminish the tensions will be found in greater proportion on the surfaces. When the film is extended, there will therefore not be enough of these substances to keep up the same volume- and surface-densities as before, and the deficiency will cause a certain increase of tension. The value of the *elasticity of the film*, (*i. e.*, the infinitesimal increase of the united tensions of its surfaces divided by the infinitesimal increase of area in a unit of surface), may be calculated from the quantities which specify the nature of the film, when the fundamental equations of the interior mass, of the contiguous gas-masses, and of the two surfaces of discontinuity are known. We may illustrate this by a simple example.

Let us suppose that the two surfaces of a plane film are entirely alike, that the contiguous gas-masses are identical in phase, and that they determine the potentials of all the components of the film except two. Let us call these components S_1 and S_2, the latter denoting that which occurs in greater proportion on the surface than in the interior of the film. Let us denote by γ_1 and γ_2 the densities of these components in the interior of the film, by λ the thickness of the film determined by such dividing surfaces as make the surface-density of S_1 vanish (see page 397), by $\Gamma_{2(1)}$ the surface-density of the other component as determined by the same surfaces, by σ and s the tension and area of one of these surfaces, and by E the elasticity of the film when extended under the supposition that the total quantities of S_1 and S_2 in the part of the film extended are invariable, as also the temperature and the potentials of the other components. From the definition of E we have

$$2\,d\sigma = E\frac{ds}{s}, \tag{643}$$

and from the conditions of the extension of the film

$$\frac{ds}{s} = -\frac{d(\lambda\,\gamma_1)}{\lambda\,\gamma_1} = -\frac{d(\lambda\,\gamma_2 + 2\,\Gamma_{2(1)})}{\lambda\,\gamma_2 + 2\,\Gamma_{2(1)}}. \tag{644}$$

Hence we obtain

$$\lambda\,\gamma_1\frac{ds}{s} = -\gamma_1\,d\lambda - \lambda\,d\gamma_1,$$

$$(\lambda\,\gamma_2 + 2\,\Gamma_{2(1)})\frac{ds}{s} = -\gamma_2\,d\lambda - \lambda\,d\gamma_2 - 2\,d\Gamma_{2(1)};$$

and eliminating $d\lambda$,

$$2\gamma_1 \Gamma_{2(1)} \frac{ds}{s} = -\lambda \gamma_1 d\gamma_2 + \lambda \gamma_2 d\gamma_1 - 2\gamma_1 d\Gamma_{2(1)}. \tag{645}$$

If we set

$$r = \frac{\gamma_2}{\gamma_1}, \tag{646}$$

we have

$$dr = \frac{\gamma_1 d\gamma_2 - \gamma_2 d\gamma_1}{\gamma_1^2}, \tag{647}$$

and

$$2\Gamma_{2(1)} \frac{ds}{s} = -\lambda \gamma_1 dr - 2 d\Gamma_{2(1)}. \tag{648}$$

With this equation we may eliminate ds from (643). We may also eliminate $d\sigma$ by the necessary relation [see (514)]

$$d\sigma = -\Gamma_{2(1)} d\mu_2.$$

This will give

$$4\Gamma_{2(1)}^2 d\mu_2 = E(\lambda \gamma_1 dr + 2 d\Gamma_{2(1)}), \tag{649}$$

or

$$\frac{4\Gamma_{2(1)}^2}{E} = \lambda \gamma_1 \frac{dr}{d\mu_2} + 2 \frac{d\Gamma_{2(1)}}{d\mu_2}, \tag{650}$$

where the differential coefficients are to be determined on the conditions that the temperature and all the potentials except μ_1 and μ_2 are constant, and that the pressure in the interior of the film shall remain equal to that in the contiguous gas-masses. The latter condition may be expressed by the equation

$$(\gamma_1 - \gamma_1') d\mu_1 + (\gamma_2 - \gamma_2') d\mu_2 = 0, \tag{651}$$

in which γ_1' and γ_2' denote the densities of S_1 and S_2 in the contiguous gas-masses. [See (98).] When the tension of the surfaces of the film and the pressures in its interior and in the contiguous gas-masses are known in terms of the temperature and potentials, equation (650) will give the value of E in terms of the same variables together with λ.

If we write G_1 and G_2 for the total quantities of S_1 and S_2 per unit of area of the film, we have

$$G_1 = \lambda \gamma_1, \tag{652}$$

$$G_2 = \lambda \gamma_2 + 2\Gamma_{2(1)}. \tag{653}$$

Therefore,

$$G_2 = G_1 r + 2\Gamma_{2(1)},$$

$$\left(\frac{dG_2}{d\mu_2}\right)_{G_1} = \lambda \gamma_1 \frac{dr}{d\mu_2} + 2 \frac{d\Gamma_{2(1)}}{d\mu_2}, \tag{654}$$

where the differential coefficients in the second member are to be determined as in (650), and that in the first member with the additional condition that G_1 is constant. Therefore,

$$\frac{4\,\Gamma_{2(1)}^{\,2}}{E} = \left(\frac{dG_2}{d\mu_2}\right)_{G_1},$$

and

$$E = 4\,\Gamma_{2(1)}^{\,2}\left(\frac{d\mu_2}{dG_2}\right)_{G_1}, \qquad (655)$$

the last differential coefficient being determined by the same conditions as that in the preceding equation. It will be observed that the value of E will be positive in any ordinary case.

These equations give the elasticity of any element of the film when the temperature and the potentials for the substances which are found in the contiguous gas-masses are regarded as constant, and the potentials for the other components, μ_1 and μ_2, have had time to equalize themselves throughout the element considered. The increase of tension immediately after a rapid extension will be greater than that given by these equations.

The existence of this elasticity, which has thus been established from *a priori* considerations, is clearly indicated by the phenomena which liquid films present. Yet it is not to be demonstrated simply by comparing the tensions of films of different thickness, even when they are made from the same liquid, for difference of thickness does not necessarily involve any difference of tension. When the phases within the films as well as without are the same, and the surfaces of the films are also the same, there will be no difference of tension. Nor will the tension of the same film be altered, if a part of the interior drains away in the course of time, without affecting the surfaces. In case the thickness of the film is reduced by evaporation, the tension may be either increased or diminished. (The evaporation of the substance S_1, in the case we have just considered, would diminish the tension.) Yet it may easily be shown that extension increases the tension of a film and contraction diminishes it. When a plane film is held vertically, the tension of the upper portions must evidently be greater than that of the lower. The tensions in every part of the film may be reduced to equality by turning it into a horizontal position. By restoring the original position we may restore the original tensions, or nearly so. It is evident that the same element of the film is capable of supporting very unequal tensions. Nor can this be always attributed to viscosity of the film. For in many cases, if we hold the film nearly horizontal, and elevate first one side and then another, the lighter portions of the film will dart from one side to the other, so as to show a very striking mobility in the film. The differences of tension which cause these rapid movements are only a very small fraction of the difference of tension in the upper and lower portions of the film when held vertically.

If we account for the power of an element of the film to support an increase of tension by viscosity, it will be necessary to suppose that the viscosity offers a resistance to a deformation of the film in which its surface is enlarged and its thickness diminished, which is enormously great in comparison with the resistance to a deformation in which the film is extended in the direction of one tangent and contracted in the direction of another, while its thickness and the areas of its surfaces remain constant. This is not to be readily admitted as a physical explanation, although to a certain extent the phenomena resemble those which would be caused by such a singular viscosity. (See page 439.) The only natural explanation of the phenomena is that the extension of an element of the film, which is the immediate result of an increase of external force applied to its perimeter, causes an increase of its tension, by which it is brought into true equilibrium with the external forces.

The phenomena to which we have referred are such as are apparent to a very cursory observation. In the following experiment, which is described by M. Plateau,* an increased tension is manifested in a film while contracting after a previous extension. The warmth of a finger brought near to a bubble of soap-water with glycerine, which is thin enough to show colors, causes a spot to appear indicating a diminution of thickness. When the finger is removed, the spot returns to its original color. This indicates a contraction, which would be resisted by any viscosity of the film, and can only be due to an excess of tension in the portion stretched on the return of its original temperature.

We have so far supposed that the film is thick enough for its interior to have the properties of matter in mass. Its properties are then entirely determined by those of the three phases and the two surfaces of discontinuity. From these we can also determine, in part at least, the properties of a film at the limit at which the interior ceases to have the properties of matter in mass. The elasticity of the film, which increases with its thinness, cannot of course vanish at that limit, so that the film cannot become unstable with respect to extension and contraction of its elements immediately after passing that limit.

Yet a certain kind of instability will probably arise, which we may

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* "Statique expérimentale et théorique des liquides soumis aux seules forces moléculaires," vol. i, p. 294.

here notice, although it relates to changes in which the condition of the invariability of the quantities of certain components in an element of the film is not satisfied. With respect to variations in the distribution of its components, a film will in general be stable, when its interior has the properties of matter in mass, with the single exception of variations affecting its thickness without any change of phase or of the nature of the surfaces. With respect to this kind of change, which may be brought about by a current in the interior of the film, the equilibrium is neutral. But when the interior ceases to have the properties of matter in mass, it is to be supposed that the equilibrium will generally become unstable in this respect. For it is not likely that the neutral equilibrium will be unaffected by such a change of circumstances, and since the film certainly becomes unstable when it is sufficiently reduced in thickness, it is most natural to suppose that the first effect of diminishing the thickness will be in the direction of instability rather than in that of stability. (We are here considering liquid films between gaseous masses. In certain other cases, the opposite supposition might be more natural, as in respect to a film of water between mercury and air, which would certainly become stable when sufficiently reduced in thickness.)

Let us now return to our former suppositions—that the film is thick enough for the interior to have the properties of matter in mass, and that the matter in each element is invariable, except with respect to those substances which have their potentials determined by the contiguous gas-masses—and consider what conditions are necessary for equilibrium in such a case.

In consequence of the supposed equilibrium of its several elements, such a film may be treated as a simple surface of discontinuity between the contiguous gas-masses (which may be similar or different), whenever its radius of curvature is very large in comparison with its thickness,—a condition which we shall always suppose to be fulfilled. With respect to the film considered in this light, the mechanical conditions of equilibrium will always be satisfied, or very nearly so, as soon as a state of approximate rest is attained, except in those cases in which the film exhibits a decided viscosity. That is, the relations (613), (614), (615) will hold true, when by σ we understand the tension of the film regarded as a simple surface of discontinuity (this is equivalent to the sum of the tensions of the two surfaces of the film), and by Γ its mass per unit of area diminished by the mass of gas which would occupy the same space if the film should be suppressed and the gases should meet at its surface of tension. This *surface of tension of the film* will evidently divide the distance between the surfaces of tension for the two surfaces of the film taken separately, in the inverse ratio of their tensions. For practical purposes, we may regard Γ simply as the mass of the film per unit of area. It will be observed that the terms containing Γ in (613) and (614) are not to be neglected in our present application of these equations.

But the mechanical conditions of equilibrium for the film regarded as an approximately homogeneous mass in the form of a thin sheet bounded by two surfaces of discontinuity are not necessarily satisfied when the film is in a state of apparent rest. In fact, these conditions cannot be satisfied (in any place where the force of gravity has an appreciable intensity) unless the film is horizontal. For the pressure in the interior of the film cannot satisfy simultaneously condition (612), which requires it to vary rapidly with the height z, and condition (613) applied separately to the different surfaces, which makes it a certain mean between the pressures in the adjacent gas-masses. Nor can these conditions be deduced from the general condition of mechanical equilibrium (606) or (611), without supposing that the interior of the film is free to move independently of the surfaces, which is contrary to what we have supposed.

Moreover, the potentials of the various components of the film will not in general satisfy conditions (617), and cannot (when the temperature is uniform) unless the film is horizontal. For if these conditions were satisfied, equation (612) would follow as a consequence. (See page 449.)

We may here remark that such a film as we are considering cannot form any exception to the principle indicated on page 450,—that when a surface of discontinuity which satisfies the conditions of mechanical equilibrium has only one component which is not found in the contiguous masses, and these masses satisfy all the conditions of equilibrium, the potential for the component mentioned must satisfy the law expressed in (617), as a consequence of the condition of mechanical equilibrium (614). Therefore, as we have just seen that it is impossible that all the potentials in a liquid film which is not horizontal should conform to (617) when the temperature is uniform, it follows that if a liquid film exhibits any persistence which is not due to viscosity, or to a horizontal position, or to differences of temperature, it must have more than one component of which the potential is not determined by the contiguous gas-masses in accordance with (617).

The difficulties of the quantitative experimental verification of the properties which have been described would be very great, even in cases in which the conditions we have imagined were entirely fulfilled. Yet the general effect of any divergence from these conditions will be easily perceived, and when allowance is made for such divergence, the general behavior of liquid films will be seen to agree with the requirements of theory.

The formation of a liquid film takes place most symmetrically when a bubble of air rises to the top of a mass of the liquid. The motion of the liquid, as it is displaced by the bubble, is evidently such as to stretch the two surfaces in which the liquid meets the air, where these surfaces approach one another. This will cause an increase of tension, which will tend to restrain the extension of the surfaces. The extent to which this effect is produced will vary with the nature of the liquid. Let us suppose that the case is one in which the liquid contains one or more components which, although constituting but a very small part of its mass, greatly reduce its tension. Such components will exist in excess on the surfaces of the liquid. In this case the restraint upon the extension of the surfaces will be considerable, and as the bubble of air rises above the general level of the liquid, the motion of the latter will consist largely of a running out from between the two surfaces. But this running out of the liquid will be greatly retarded by its viscosity as soon as it is reduced to the thickness of a film, and the effect of the extension of the surfaces in increasing their tension will become greater and more permanent as the quantity of liquid diminishes which is available for supplying the substances which go to form the increased surfaces.

We may form a rough estimate of the amount of motion which is possible for the interior of a liquid film, relatively to its exterior, by calculating the descent of water between parallel vertical planes at which the motion of the water is reduced to zero. If we use the coefficient of viscosity as determined by Helmholtz and Piotrowski,* we obtain

$$V = 581\, D^2, \tag{656}$$

where V denotes the mean velocity of the water (*i. e.*, that velocity

* Sitzungsberichte der Wiener Akademie, (mathemat.-naturwiss. Classe), B. xl, S. 607. The calculation of formula (656) and that of the factor ($\frac{8}{3}$) applied to the formula of Poiseuille, to adapt it to a current between plane surfaces, have been made by means of the general equations of the motion of a viscous liquid as given in the memoir referred to.

which, if it were uniform throughout the whole space between the fixed planes, would give the same discharge of water as the actual variable velocity) expressed in millimetres per second, and D denotes the distance in millimetres between the fixed planes, which is supposed to be very small in proportion to their other dimensions. This is for the temperature of 24.5° C. For the same temperature, the experiments of Poiseuille * give

$$V = 337\ D^2$$

for the descent of water in long capillary tubes, which is equivalent to

$$V = 899\ D^2 \tag{657}$$

for descent between parallel planes. The numerical coefficient in this equation differs considerably from that in (656), which is derived from experiments of an entirely different nature, but we may at least conclude that in a film of a liquid which has a viscosity and specific gravity not very different from those of water at the temperature mentioned the mean velocity of the interior relatively to the surfaces will not probably exceed 1000 D^2. This is a velocity of .1$^{\mathrm{mm}}$ per second for a thickness of .01$^{\mathrm{mm}}$, .06$^{\mathrm{mm}}$ per *minute* for a thickness of .001 (which corresponds to the red of the fifth order in a film of water), and .036$^{\mathrm{mm}}$ per *hour* for a thickness of .0001$^{\mathrm{mm}}$ (which corresponds to the white of the first order). Such an internal current is evidently consistent with great persistence of the film, especially in those cases in which the film can exist in a state of the greatest tenuity. On the other hand, the above equations give so large a value of V for thicknesses of 1$^{\mathrm{mm}}$ or .1$^{\mathrm{mm}}$, that the film can evidently be formed without carrying up any great weight of liquid, and any such thicknesses as these can have only a momentary existence.

A little consideration will show that the phenomenon is essentially of the same nature when films are formed in any other way, as by dipping a ring or the mouth of a cup in the liquid and then withdrawing it. When the film is formed in the mouth of a pipe, it may sometimes be extended so as to form a large bubble. Since the elasticity (*i. e.*, the increase of the tension with extension) is greater in the thinner parts, the thicker parts will be most extended, and the effect of this process (so far as it is not modified by gravity) will be to diminish the ratio of the greatest to the least thickness of the film. During this extension, as well as at other times, the increased elasticity due to imperfect communication of heat, etc., will serve to protect the bubble from fracture by shocks received from the air or the

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* Ibid., p. 653; or Mémoires des Savants Étrangers, vol. ix, p. 532.

pipe. If the bubble is now laid upon a suitable support, the condition (613) will be realized almost instantly. The bubble will then tend toward conformity with condition (614), the lighter portions rising to the top, more or less slowly, according to the viscosity of the film. The resulting difference of thickness between the upper and the lower parts of the bubble is due partly to the greater tension to which the upper parts are subject, and partly to a difference in the matter of which they are composed. When the film has only two components of which the potentials are not determined by the contiguous atmosphere, the laws which govern the arrangement of the elements of the film may be very simply expressed. If we call these components S_1 and S_2, the latter denoting (as on page 469) that which exists in excess at the surface, one element of the film will tend toward the same level with another, or a higher, or a lower level, according as the quantity of S_2 bears the same ratio to the quantity of S_1 in the first element as in the second, or a greater, or a less ratio.

When a film, however formed, satisfies both the conditions (613) and (614), its thickness being sufficient for its interior to have the properties of matter in mass, the interior will still be subject to the slow current which we have already described, if it is truly fluid, however great its viscosity may be. It seems probable, however, that this process is often totally arrested by a certain gelatinous consistency of the mass in question, in virtue of which, although practically fluid in its behavior with reference to ordinary stresses, it may have the properties of a solid with respect to such very small stresses as those which are caused by gravity in the interior of a very thin film which satisfies the conditions (613) and (614).

However this may be, there is another cause which is often more potent in producing changes in a film, when the conditions just mentioned are approximately satisfied, than the action of gravity on its interior. This will be seen if we turn our attention to the edge where the film is terminated. At such an edge we generally find a liquid mass, continuous in phase with the interior of the film, which is bounded by concave surfaces, and in which the pressure is therefore less than in the interior of the film. This liquid mass therefore exerts a strong suction upon the interior of the film, by which its thickness is rapidly reduced. This effect is best seen when a film which has been formed in a ring is held in a vertical position. Unless the film is very viscous, its diminished thickness near the edge causes a rapid upward current on each side, while the central portion slowly descends. Also at the bottom of the film, where the edge is nearly horizontal, portions which have become thinned escape from their position of unstable equilibrium beneath heavier portions, and pass upwards, traversing the central portion of the film until they find a position of stable equilibrium. By these processes, the whole film is rapidly reduced in thickness.

The energy of the suction which produces these effects may be inferred from the following considerations. The pressure in the slender liquid mass which encircles the film is of course variable, being greater in the lower portions than in the upper, but it is everywhere less than the pressure of the atmosphere. Let us take a point where the pressure is less than that of the atmosphere by an amount represented by a column of the liquid one centimetre in height. (It is probable that much greater differences of pressure occur.) At a point near by in the interior of the film the pressure is that of the atmosphere. Now if the difference of pressure of these two points were distributed uniformly through the space of one centimetre, the intensity of its action would be exactly equal to that of gravity. But since the change of pressure must take place very suddenly (in a small fraction of a millimetre), its effect in producing a current in a limited space must be enormously great compared with that of gravity.

Since the process just described is connected with the descent of the liquid in the mass encircling the film, we may regard it as another example of the downward tendency of the interior of the film. There is a third way in which this descent may take place, when the principal component of the interior is volatile, viz., through the air. Thus, in the case of a film of soap-water, if we suppose the atmosphere to be of such humidity that the potential for water at a level mid-way between the top and bottom of the film has the same value in the atmosphere as in the film, it may easily be shown that evaporation will take place in the upper portions and condensation in the lower. These processes, if the atmosphere were otherwise undisturbed, would occasion currents of diffusion and other currents, the general effect of which would be to carry the moisture downward. Such a precise adjustment would be hardly attainable, and the processes described would not be so rapid as to have a practical importance.

But when the potential for water in the atmosphere differs considerably from that in the film, as in the case of a film of soap-water in a dry atmosphere, or a film of soap-water with glycerine in a moist atmosphere, the effect of evaporation or condensation is not to be neglected. In the first case, the diminution of the thickness of the film will be accelerated, in the second, retarded. In the case of the film containing glycerine, it should be observed that the water condensed cannot in all respects replace the fluid carried down by the internal current but that the two processes together will tend to wash out the glycerine from the film.

But when a component which greatly diminishes the tension of the film, although forming but a small fraction of its mass, (therefore existing in excess at the surface,) is volatile, the effect of evaporation and condensation may be considerable, even when the mean value of the potential for that component is the same in the film as in the surrounding atmosphere. To illustrate this, let us take the simple case of two components S_1 and S_2, as before. (See page 469.) It appears from equation (508) that the potentials must vary in the film with the height z, since the tension does, and from (98) that these variations must (very nearly) satisfy the relation

$$\gamma_1 \frac{d\mu_1}{dz} + \gamma_2 \frac{d\mu_2}{dz} = 0, \tag{658}$$

γ_1 and γ_2 denoting the densities of S_1 and S_2 in the interior of the film. The variation of the potential of S_2 as we pass from one level to another is therefore as much more rapid than that of S_1, as its density in the interior of the film is less. If then the resistances restraining the evaporation, transmission through the atmosphere, and condensation of the two substances are the same, these processes will go on much more rapidly with respect to S_2. It will be observed that the values of $\frac{d\mu_1}{dz}$ and $\frac{d\mu_2}{dz}$ will have opposite signs, the tendency of S_1 being to pass down through the atmosphere, and that of S_2 to pass up. Moreover, it may easily be shown that the evaporation or condensation of S_2 will produce a very much greater effect than the evaporation or condensation of the same quantity of S_1. These effects are really of the same kind. For if condensation of S_2 takes place at the top of the film, it will cause a diminution of tension, and thus occasion an extension of this part of the film, by which its thickness will be reduced, as it would be by evaporation of S_1. We may infer that it is a general condition of the persistence of liquid films, that the substance which causes the diminution of tension in the ~~upper~~ parts of the film must not be volatile. lower

But apart from any action of the atmosphere, we have seen that a film which is truly fluid in its interior is in general subject to a continual diminution of thickness by the internal currents due to gravity and the suction at its edge. Sooner or later, the interior will somewhere cease to have the properties of matter in mass. The film will then probably become unstable with respect to a flux of the interior (see page 473), the thinnest parts tending to become still more thin (apart from any external cause) very much as if there were an attraction between the surfaces of the film, insensible at greater distances, but becoming sensible when the thickness of the film is sufficiently reduced. We should expect this to determine the rupture of the film, and such is doubtless the case with most liquids. In a film of soap-water, however, the rupture does not take place, and the processes which go on can be watched. It is apparent even to a very superficial observation that a film of which the tint is approaching the black exhibits a remarkable instability. The continuous change of tint is interrupted by the breaking out and rapid extension of black spots. That in the formation of these bright spots a separation of different substances takes place, and not simply an extension of a part of the film, is shown by the fact that the film is made thicker at the edge of these spots.

This is very distinctly seen in a plane vertical film, when a single black spot breaks out and spreads rapidly over a considerable area which was before of a nearly uniform tint approaching the black. The edge of the black spot as it spreads is marked as it were by a string of bright beads, which unite together on touching, and thus becoming larger, glide down across the bands of color below. Under favorable circumstances, there is often quite a shower of these bright spots. They are evidently small spots very much thicker—apparently many times thicker—than the part of the film out of which they are formed. Now if the formation of the black spots were due to a simple extension of the film, it is evident that no such appearance would be presented. The thickening of the edge of the film cannot be accounted for by *contraction*. For an extension of the upper portion of the film and contraction of the lower and thicker portion, with descent of the intervening portions, would be far less resisted by viscosity, and far more favored by gravity than such extensions and contractions as would produce the appearances described. But the rapid formation of a thin spot by an internal current would cause an accumulation at the edge of the spot of the material forming the interior of the film, and necessitate a thickening of the film in that place.

That which is most difficult to account for in the formation of the black spots is the arrest of the process by which the film grows thinner. It seems most natural to account for this, *if possible*, by passive resistance to motion due to a very viscous or gelatinous condition of the film. For it does not seem likely that the film, after becoming unstable by the flux of matter from its interior, would become stable (without the support of such resistance) by a continuance of the same process. On the other hand, gelatinous properties are very marked in soap-water which contains somewhat more soap than is best for the formation of films, and it is entirely natural that, even when such properties are wanting in the interior of a mass or thick film of a liquid, they may still exist in the immediate vicinity of the surface (where we know that the soap or some of its components exists in excess), or throughout a film which is so thin that the interior has ceased to have the properties of matter in mass.* But these considerations do not amount to any *a priori* probability of an arrest of the tendency toward an internal current between adjacent elements of a black spot which may differ slightly in thickness, in time to prevent rupture of the film. For, in a thick film, the increase of the tension with the extension, which is necessary for its stability with respect to extension, is connected with an excess of the soap (or of some of its components) at the surface as compared with the interior of the film. With respect to the black spots, although the interior has ceased to have the properties of matter in mass, and any quantitative determinations derived from the surfaces of a mass of the liquid will not be applicable, it is natural to account for the stability with reference to extension by supposing that the same general difference of composition still exists. If therefore we account for the arrest of internal currents by the increasing density of soap or some of its components in the interior of the film, we must still suppose that the characteristic difference of composition in the interior and surface of the film has not been obliterated.

The preceding discussion relates to liquid films between masses of gas. Similar considerations will apply to liquid films between other liquids or between a liquid and a gas, and to films of gas between

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* The experiments of M. Plateau (chapter VII of the work already cited) show that this is the case to a very remarkable degree with respect to a solution of saponine. With respect to soap-water, however, they do not indicate any greater superficial viscosity than belongs to pure water. But the resistance to an internal current, such as we are considering, is not necessarily measured by the resistance to such motions as those of the experiments referred to.

masses of liquid. The latter may be formed by gently depositing a liquid drop upon the surface of a mass of the same or a different liquid. This may be done (with suitable liquids) so that the continuity of the air separating the liquid drop and mass is not broken, but a film of air is formed, which, if the liquids are similar, is a counterpart of the liquid film which is formed by a bubble of air rising to the top of a mass of the liquid. (If the bubble has the same volume as the drop, the films will have precisely the same form, as well as the rest of the surfaces which bound the bubble and the drop.) Sometimes, when the weight and momentum of the drop carry it through the surface of the mass on which it falls, it appears surrounded by a complete spherical film of air, which is the counterpart on a small scale of a soap-bubble hovering in air.* Since, however, the substance to which the necessary differences of tension in the film are mainly due is a component of the liquid masses on each side of the air film, the necessary differences of the potential of this substance cannot be permanently maintained, and these films have little persistence compared with films of soap-water in air. In this respect, the case of these air-films is analogous to that of liquid films in an atmosphere containing substances by which their tension is greatly reduced. Compare page 479.

Surfaces of Discontinuity between Solids and Fluids.

We have hitherto treated of surfaces of discontinuity on the supposition that the contiguous masses are fluid. This is by far the most simple case for any rigorous treatment, since the masses are necessarily isotropic both in nature and in their state of strain. In this case, moreover, the mobility of the masses allows a satisfactory experimental verification of the mechanical conditions of equilibrium. On the other hand, the rigidity of solids is in general so great, that any tendency of the surfaces of discontinuity to variation in area or form may be neglected in comparison with the forces which are produced in the interior of the solids by any sensible strains, so that it is not generally necessary to take account of the surfaces of discontinuity in determining the state of strain of solid masses. But we must take account of the nature of the surfaces of discontinuity

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* These spherical air-films are easily formed in soap-water. They are distinguishable from ordinary air-bubbles by their general behavior and by their appearance. The two concentric spherical surfaces are distinctly seen, the diameter of one appearing to be about three-quarters as large as that of the other. This is of course an optical illusion, depending upon the index of refraction of the liquid.

between solids and fluids with reference to the tendency toward solidification or dissolution at such surfaces, and also with reference to the tendencies of different fluids to spread over the surfaces of solids.

Let us therefore consider a surface of discontinuity between a fluid and a solid, the latter being either isotropic or of a continuous crystalline structure, and subject to any kind of stress compatible with a state of mechanical equilibrium with the fluid. We shall not exclude the case in which substances foreign to the contiguous masses are present in small quantities at the surface of discontinuity, but we shall suppose that the nature of this surface (*i. e.*, of the non-homogeneous film between the approximately homogeneous masses), is entirely determined by the nature and state of the masses which it separates, and the quantities of the foreign substances which may be present. The notions of the *dividing surface*, and of the *superficial densities* of energy, entropy, and the several components, which we have used with respect to surfaces of discontinuity between fluids (see pages 380 and 386), will evidently apply without modification to the present case. We shall use the suffix $_1$ with reference to the substance of the solid, and shall suppose the dividing surface to be determined so as to make the superficial density of this substance vanish. The superficial densities of energy, of entropy, and of the other component substances may then be denoted by our usual symbols (see page 397),

$$\varepsilon_{S(1)}, \quad \eta_{S(1)}, \quad \Gamma_{2(1)}, \quad \Gamma_{3(1)}, \quad \text{etc.}$$

Let the quantity σ be defined by the equation

$$\sigma = \varepsilon_{S(1)} - t\,\eta_{S(1)} - \mu_2\,\Gamma_{2(1)} - \mu_3\,\Gamma_{3(1)} - \text{etc.}, \tag{659}$$

in which t denotes the temperature, and μ_2, μ_3, etc. the potentials for the substances specified at the surface of discontinuity.

As in the case of two fluid masses, (see page 421,) we may regard σ as expressing the work spent in forming a unit of the surface of discontinuity—under certain conditions, which we need not here specify—but it cannot properly be regarded as expressing the tension of the surface. The latter quantity depends upon the work spent in *stretching* the surface, while the quantity σ depends upon the work spent in *forming* the surface. With respect to perfectly fluid masses, these processes are not distinguishable, unless the surface of discontinuity has components which are not found in the contiguous masses, and even in this case, (since the surface must be supposed to be formed out of matter supplied at the same potentials which belong to the matter in the surface,) the work spent in increasing the surface infinitesimally by stretching is identical with that which must be spent in forming an equal infinitesimal amount of new surface. But when one of the masses is solid, and its states of strain are to be distinguished, there is no such equivalence between the stretching of the surface and the forming of new surface.*

With these preliminary notions, we now proceed to discuss the condition of equilibrium which relates to the dissolving of a solid at the surface where it meets a fluid, when the thermal and mechanical conditions of equilibrium are satisfied. It will be necessary for us to consider the case of isotropic and of crystallized bodies separately, since in the former the value of σ is independent of the direction of the surface, except so far as it may be influenced by the state of strain of the solid, while in the latter the value of σ varies greatly with the direction of the surface with respect to the axes of crystallization, and in such a manner as to have a large number of sharply defined minima.† This may be inferred from the phenomena which crystalline bodies present, as will appear more distinctly in the following discussion. Accordingly, while a variation in the direction of an

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* This will appear more distinctly if we consider a particular case. Let us consider a thin plane sheet of a crystal in a vacuum (which may be regarded as a limiting case of a very attenuated fluid), and let us suppose that the two surfaces of the sheet are alike. By applying the proper forces to the edges of the sheet, we can make all stress vanish in its interior. The *tensions* of the two surfaces, are in equilibrium with these forces, and are measured by them. But the tensions of the surfaces, thus determined, may evidently have different values in different directions, and are entirely different from the quantity which we denote by σ, which represents the work required to form a unit of the surface by any reversible process, and is not connected with any idea of direction.

In certain cases, however, it appears probable that the values of σ and of the superficial tension will not greatly differ. This is especially true of the numerous bodies which, although generally (and for many purposes properly) regarded as solids, are really very viscous fluids. Even when a body exhibits no fluid properties at its actual temperature, if its surface has been formed at a higher temperature, at which the body was fluid, and the change from the fluid to the solid state has been by insensible gradations, we may suppose that the value of σ coincided with the superficial tension until the body was decidedly solid, and that they will only differ so far as they may be differently affected by subsequent variations of temperature and of the stresses applied to the solid. Moreover, when an amorphous solid is in a state of equilibrium with a solvent, although it may have no fluid properties in its interior, it seems not improbable that the particles at its surface, which have a greater degree of mobility, may so arrange themselves that the value of σ will coincide with the superficial tension, as in the case of fluids.

† The differential coefficients of σ with respect to the direction-cosines of the surface appear to be discontinuous functions of the latter quantities.

element of the surface may be neglected (with respect to its effect on the value of σ) in the case of isotropic solids, it is quite otherwise with crystals. Also, while the surfaces of equilibrium between fluids and soluble isotropic solids are without discontinuities of direction, being in general curved, a crystal in a state of equilibrium with a fluid in which it can dissolve is bounded in general by a broken surface consisting of sensibly plane portions.

For isotropic solids, the conditions of equilibrium may be deduced as follows. If we suppose that the solid is unchanged, except that an infinitesimal portion is dissolved at the surface where it meets the fluid, and that the fluid is considerable in quantity and remains homogeneous, the increment of energy in the vicinity of the surface will be represented by the expression

$$\int [\varepsilon_V' - \varepsilon_V'' + (c_1 + c_2)\, \varepsilon_{S(1)}]\, \delta N\, Ds$$

where Ds denotes an element of the surface, δN the variation in its position (measured normally, and regarded as *negative* when the solid is dissolved), c_1 and c_2 its principal curvatures (positive when their centers lie on the same side as the solid), $\varepsilon_{S(1)}$ the surface-density of energy, ε_V' and ε_V'' the volume-densities of energy in the solid and fluid respectively, and the sign of integration relates to the elements Ds. In like manner, the increments of entropy and of the quantities of the several components in the vicinity of the surface will be

$$\int [\eta_V' - \eta_V'' + (c_1 + c_2)\, \eta_{S(1)}]\, \delta N\, Ds,$$

$$\int [\gamma_1' - \gamma_1'']\, \delta N\, Ds,$$

$$\int [-\gamma_2'' + (c_1 + c_2)\, \Gamma_{2(1)}]\, \delta N\, Ds,$$

etc.

The entropy and the matter of different kinds represented by these expressions we may suppose to be derived from the fluid mass. These expressions, therefore, with a change of sign, will represent the increments of entropy and of the quantities of the components in the whole space occupied by the fluid except that which is immediately contiguous to the solid. Since this space may be regarded as constant, the increment of energy in this space may be obtained [according to equation (12)] by multiplying the above expression relating to entropy by $-t$, and those relating to the components by $-\mu_1''$, $-\mu_2$, etc.,* and taking the sum. If to this

* The potential μ_1'' is marked by double accents in order to indicate that its value is to be determined in the fluid mass, and to distinguish it from the potential μ_1'

we add the above expression for the increment of energy near the surface, we obtain the increment of energy for the whole system. Now by (93) we have

$$p'' = -\varepsilon_V'' + t\,\eta_V'' + \mu_1''\,\gamma_1'' + \mu_2\,\gamma_2'' + \text{etc.}$$

By this equation and (659), our expression for the total increment of energy in the system may be reduced to the form

$$\int [\varepsilon_V' - t\,\eta_V' - \mu_1''\,\gamma_1' + p'' + (c_1 + c_2)\,\sigma]\,\delta N\,Ds. \qquad (660)$$

In order that this shall vanish for any values of δN, it is necessary that the coefficient of $\delta N\,Ds$ shall vanish. This gives for the condition of equilibrium

$$\mu_1'' = \frac{\varepsilon_V' - t\,\eta_V' + p'' + (c_1 + c_2)\,\sigma}{\gamma_1'}. \qquad (661)$$

This equation is identical with (387), with the exception of the term containing σ, which vanishes when the surface is plane.*

We may also observe that when the solid has no stresses except an isotropic pressure, if the quantity represented by σ is equal to the true tension of the surface, $p'' + (c_1 + c_2)\,\sigma$ will represent the pressure in the interior of the solid, and the second member of the equation will represent [see equation (93)] the value of the potential in the solid for the substance of which it consists. In this case, therefore, the equation reduces to

$$\mu_1'' = \mu_1',$$

that is, it expresses the equality of the potentials for the substance of the solid in the two masses—the same condition which would subsist if both masses were fluid.

Moreover, the compressibility of all solids is so small that, although σ may not represent the true tension of the surface, nor $p'' + (c_1 + c_2)\,\sigma$ the true pressure in the solid when its stresses are isotropic, the quantities ε_V' and η_V' if calculated for the pressure $p'' + (c_1 + c_2)\,\sigma$ with the actual temperature will have sensibly the same values as if calculated for the true pressure of the solid. Hence, the second member

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relating to the solid mass (when this is in a state of isotropic stress), which, as we shall see, may not always have the same value. The other potentials μ_2, etc., have the same values as in (659), and consist of two classes, one of which relates to substances which are components of the fluid mass, (these might be marked by the double accents,) and the other relates to substances found only at the surface of discontinuity. The expressions to be multiplied by the potentials of this latter class all have the value zero.

* In equation (387), the density of the solid is denoted by Γ, which is therefore equivalent to γ_1' in (661).

of equation (661), when the stresses of the solid are sensibly isotropic, is sensibly equal to the potential of the same body at the same temperature but with the pressure $p'' + (c_1 + c_2)\,\sigma$, and the condition of equilibrium with respect to dissolving for a solid of isotropic stresses may be expressed with sufficient accuracy by saying that the potential for the substance of the solid in the fluid must have this value. In like manner, when the solid is not in a state of isotropic stress, the difference of the two pressures in question will not sensibly affect the values of $\varepsilon_V{}'$ and $\eta_V{}'$, and the value of the second member of the equation may be calculated as if $p'' + (c_1 + c_2)\,\sigma$ represented the true pressure in the solid in the direction of the normal to the surface. Therefore, if we had taken for granted that the quantity σ represents the tension of a surface between a solid and a fluid, as it does when both masses are fluid, this assumption would not have led us into any practical error in determining the value of the potential $\mu_1{}''$ which is necessary for equilibrium. On the other hand, if in the case of any amorphous body the value of σ differs notably from the true surface-tension, the latter quantity substituted for σ in (661) will make the second member of the equation equal to the true value of $\mu_1{}'$, when the stresses are isotropic, but this will not be equal to the value of $\mu_1{}''$ in case of equilibrium, unless $c_1 + c_2 = 0$.

When the stresses in the solid are not isotropic, equation (661) may be regarded as expressing the condition of equilibrium with respect to the dissolving of the solid, and is to be distinguished from the condition of equilibrium with respect to an increase of solid matter, since the new matter would doubtless be deposited in a state of isotropic stress. (The case would of course be different with crystalline bodies, which are not considered here.) The value of $\mu_1{}''$ necessary for equilibrium with respect to the formation of new matter is a little less than that necessary for equilibrium with respect to the dissolving of the solid. In regard to the actual behavior of the solid and fluid, all that the theory enables us to predict with certainty is that the solid will not dissolve if the value of the potential $\mu_1{}''$ is greater than that given by the equation for the solid with its distorting stresses, and that new matter will not be formed if the value of $\mu_1{}''$ is less than the same equation would give for the case of the solid with isotropic stresses.* It seems probable, however, that

* The possibility that the new solid matter might differ in composition from the original solid is here left out of account. This point has been discussed on pages 134–137, but without reference to the state of strain of the solid or the influence of the curvature of the surface of discontinuity. The statement made above may be

if the fluid in contact with the solid is not renewed, the system will generally find a state of equilibrium in which the outermost portion of the solid will be in a state of isotropic stress. If at first the solid should dissolve, this would supersaturate the fluid, perhaps until a state is reached satisfying the condition of equilibrium with the stressed solid, and then, if not before, a deposition of solid matter in a state of isotropic stress would be likely to commence and go on until the fluid is reduced to a state of equilibrium with this new solid matter.

The action of gravity will not affect the nature of the condition of equilibrium for any single point at which the fluid meets the solid, but it will cause the values of p'' and μ_1'' in (661) to vary according to the laws expressed by (612) and (617). If we suppose that the outer part of the solid is in a state of isotropic stress, which is the most important case, since it is the only one in which the equilibrium is in every sense stable, we have seen that the condition (661) is at least sensibly equivalent to this:—that the potential for the substance of the solid which would belong to the solid mass at the temperature t and the pressure $p''+(c_1+c_2)\,\sigma$ must be equal to μ_1''. Or, if we denote by (p') the pressure belonging to solid with the temperature t and the potential equal to μ_1'', the condition may be expressed in the form

$$(p')=p''+(c_1+c_2)\,\sigma. \tag{662}$$

Now if we write γ'' for the total density of the fluid, we have by (612)

$$dp''=-g\,\gamma''dz.$$

By (98)
$$d(p')=\gamma_1'\,d\mu_1'',$$

and by (617)
$$d\mu_1''=-g\,dz;$$

whence
$$d(p')=-g\,\gamma_1'\,dz.$$

Accordingly we have

$$d(p')-dp''=g\,(\gamma''-\gamma_1')\,dz,$$

and

$$(p')-p''=g\,(\gamma''-\gamma_1')\,z,$$

z being measured from the horizontal plane for which $(p')=p''$. Substituting this value in (662), we obtain

$$c_1+c_2=\frac{g\,(\gamma''-\gamma_1')}{\sigma}\,z, \tag{663}$$

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generalized so as to hold true of the formation of new solid matter of any kind on the surface as follows:—that new solid matter of any kind will not be formed upon the surface (with more than insensible thickness), if the second member of (661) calculated for such new matter is greater than the potential in the fluid for such matter.

precisely as if both masses were fluid, and σ denoted the tension of their common surface, and (p') the true pressure in the mass specified. [Compare (619).]

The obstacles to an exact experimental realization of these relations are very great, principally from the want of absolute uniformity in the internal structure of amorphous solids, and on account of the passive resistances to the processes which are necessary to bring about a state satisfying the conditions of theoretical equilibrium, but it may be easy to verify the general tendency toward diminution of surface, which is implied in the foregoing equations.*

Let us apply the same method to the case in which the solid is a crystal. The surface between the solid and fluid will now consist of plane portions, the directions of which may be regarded as invari-

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* It seems probable that a tendency of this kind plays an important part in some of the phenomena which have been observed with respect to the freezing together of pieces of ice. (See especially Professor Faraday's "Note on Regelation" in the *Proceedings of the Royal Society*, vol. x, p. 440; or in the *Philosophical Magazine*, 4th ser., vol. xxi, p. 146.) Although this is a body of crystalline structure, and the action which takes place is doubtless influenced to a certain extent by the directions of the axes of crystallization, yet, since the phenomena have not been observed to depend upon the orientation of the pieces of ice, we may conclude that the effect, so far as its general character is concerned, is such as might take place with an isotropic body. In other words, for the purposes of a general explanation of the phenomena we may neglect the differences in the values of σ_{IW} (the suffixes are used to indicate that the symbol relates to the surface between ice and water) for different orientations of the axes of crystallization, and also neglect the influence of the surface of discontinuity with respect to crystalline structure, which must be formed by the freezing together of the two masses of ice when the axes of crystallization in the two masses are not similarly directed. In reality, this surface—or the necessity of the formation of such a surface if the pieces of ice freeze together—must exert an influence adverse to their union, measured by a quantity σ_{II}, which is determined for this surface by the same principles as when one of two contiguous masses is fluid, and varies with the orientations of the two systems of crystallographic axes relatively to each other and to the surface. But under the circumstances of the experiment, since we may neglect the possibility of the two systems of axes having precisely the same directions, this influence is probably of a tolerably constant character, and is evidently not sufficient to alter the general nature of the result. In order wholly to prevent the tendency of pieces of ice to freeze together, when meeting in water with curved surfaces and without pressure, it would be necessary that $\sigma_{\mathrm{II}} \geqq 2\sigma_{\mathrm{IW}}$, except so far as the case is modified by passive resistances to change, and by the inequality in the values of σ_{II} and σ_{IW} for different directions of the axes of crystallization.

It will be observed that this view of the phenomena is in harmony with the opinion of Professor Faraday. With respect to the union of pieces of ice as an indirect consequence of pressure, see page 198 of volume xi of the *Proceedings of the Royal Society*; or the *Philosophical Magazine*, 4th ser., vol. xxiii, p. 407.

able. If the crystal grows on one side a distance δN, without other change, the increment of energy in the vicinity of the surface will be

$$(\varepsilon_V' - \varepsilon_V'')\, s\, \delta N + \Sigma'(\varepsilon_{S(1)}'\, l' \operatorname{cosec} \omega' - \varepsilon_{S(1)}\, l' \cot \omega')\, \delta N,$$

where ε_V' and ε_V'' denote the volume-densities of energy in the crystal and fluid respectively, s the area of the side on which the crystal grows, $\varepsilon_{S(1)}$ the surface-density of energy on that side, $\varepsilon_{S(1)}'$ the surface-density of energy on an adjacent side, ω' the external angle of these two sides, l' their common edge, and the symbol Σ' a summation with respect to the different sides adjacent to the first. The increments of entropy and of the quantities of the several components will be represented by analogous formulæ, and if we deduce as on pages 485, 486 the expression for the increase of energy in the whole system due to the growth of the crystal without change of the total entropy or volume, and set this expression equal to zero, we shall obtain for the condition of equilibrium

$$\begin{aligned}(\varepsilon_V' - t\,\eta_V' - \mu_1''\,\gamma_1' + p'')\, s\, \delta N \\ + \Sigma'(\sigma'\, l' \operatorname{cosec} \omega' - \sigma\, l' \cot \omega')\, \delta N = 0,\end{aligned} \tag{664}$$

where σ and σ' relate respectively to the same sides as $\varepsilon_{S(1)}$ and $\varepsilon_{S(1)}'$ in the preceding formula. This gives

$$\mu_1'' = \frac{\varepsilon_V' - t\,\eta_V' + p''}{\gamma_1'} + \frac{\Sigma'(\sigma'\, l' \operatorname{cosec} \omega' - \sigma\, l' \cot \omega')}{s\,\gamma_1'}. \tag{665}$$

It will be observed that unless the side especially considered is small or narrow, we may neglect the second fraction in this equation, which will then give the same value of μ_1'' as equation (387), or as equation (661) applied to a plane surface.

Since a similar equation must hold true with respect to every other side of the crystal of which the equilibrium is not affected by meeting some other body, the condition of equilibrium for the crystalline form (when unaffected by gravity) is that the expression

$$\frac{\Sigma'(\sigma'\, l' \operatorname{cosec} \omega' - \sigma\, l' \cot \omega')}{s} \tag{666}$$

shall have the same value for each side of the crystal. (By the value of this expression for any side of the crystal is meant its value when σ and s are determined by that side and the other quantities by the surrounding sides in succession in connection with the first side.) This condition will not be affected by a change in the size of a crystal while its proportions remain the same. But the tendencies of similar crystals toward the form required by this condition, as measured by the inequalities in the composition or the temperature of the surrounding fluid which would counterbalance them, will be inversely as the linear dimensions of the crystals, as appears from the preceding equation.

If we write v for the volume of a crystal, and $\Sigma(\sigma\, s)$ for the sum of the areas of all its sides multiplied each by the corresponding value of σ, the numerator and denominator of the fraction (666), multiplied each by δN, may be represented by $\delta\Sigma(\sigma\, s)$ and δv respectively. The value of the fraction is therefore equal to that of the differential coefficient

$$\frac{d\Sigma(\sigma\, s)}{dv}$$

as determined by the displacement of a particular side while the other sides are fixed. The condition of equilibrium for the form of a crystal (when the influence of gravity may be neglected) is that the value of this differential coefficient must be independent of the particular side which is supposed to be displaced. For a constant volume of the crystal, $\Sigma(\sigma\, s)$ has therefore a minimum value when the condition of equilibrium is satisfied, as may easily be proved more directly.

When there are no foreign substances at the surfaces of the crystal, and the surrounding fluid is indefinitely extended, the quantity $\Sigma(\sigma\, s)$ represents the work required to form the surfaces of the crystal, and the coefficient of $s\,\delta N$ in (664) with its sign reversed represents the work gained in forming a mass of volume unity like the crystal but regarded as without surfaces. We may denote the work required to form the crystal by

$$W_{\text{S}} - W_{\text{V}},$$

W_{S} denoting the work required to form the surfaces [*i. e.*, $\Sigma(\sigma\, s)$], and W_{V} the work gained in forming the mass as distinguished from the surfaces. Equation (664) may then be written

$$-\delta\, W_{\text{V}} + \Sigma(\sigma\, \delta s) = 0. \qquad (667)$$

Now (664) would evidently continue to hold true if the crystal were diminished in size, remaining similar to itself in form and in nature, if the values of σ in all the sides were supposed to diminish in the same ratio as the linear dimensions of the crystal. The variation of W_{S} would then be determined by the relation

$$d\, W_{\text{S}} = d\Sigma(\sigma\, s) = \tfrac{3}{2}\, \Sigma(\sigma\, ds),$$

and that of W_{V} by (667). Hence,

$$d\, W_{\text{S}} = \tfrac{3}{2}\, d\, W_{\text{V}},$$

and, since W_S and W_V vanish together,

$$W_S = \tfrac{3}{2} W_V,$$

$$W_S - W_V = \tfrac{1}{3} W_S = \tfrac{1}{2} W_V, \tag{668}$$

—the same relation which we have before seen to subsist with respect to a spherical mass of fluid as well as in other cases. (See pages 421, 425, 465.)

The equilibrium of the crystal is unstable with respect to variations in size when the surrounding fluid is indefinitely extended, but it may be made stable by limiting the quantity of the fluid.

To take account of the influence of gravity, we must give to μ_1'' and p'' in (665) their average values in the side considered. These coincide (when the fluid is in a state of internal equilibrium) with their values at the center of gravity of the side. The values of γ_1', ε_V', η_V' may be regarded as constant, so far as the influence of gravity is concerned. Now since by (612) and (617)

$$dp'' = -g\,\gamma''\,dz,$$

and

$$d\mu_1'' = -g\,dz,$$

we have

$$d(\gamma_1'\mu_1'' - p'') = g\,(\gamma'' - \gamma_1')\,dz.$$

Comparing (664), we see that the upper or the lower faces of the crystal will have the greater tendency to grow, (other things being equal,) according as the crystal is lighter or heavier than the fluid. When the densities of the two masses are equal, the effect of gravity on the form of the crystal may be neglected.

In the preceding paragraph the fluid is regarded as in a state of internal equilibrium. If we suppose the composition and temperature of the fluid to be uniform, the condition which will make the effect of gravity vanish will be that

$$\frac{d(\gamma_1'\mu_1'' - p'')}{dz} = 0,$$

when the value of the differential coefficient is determined in accordance with this supposition. This condition reduces to

$$\left(\frac{d\mu_1}{dp}\right)''_{t,\,m} = \frac{1}{\gamma_1'},\text{*}$$

which, by equation (92), is equivalent to

$$\left(\frac{dv}{dm_1}\right)''_{t,\,p,\,m} = \frac{1}{\gamma_1'}. \tag{669}$$

* A suffixed m is used to represent all the symbols m_1, m_2, etc., except such as may occur in the differential coefficient.

The tendency of a crystal to grow will be greater in the upper or lower parts of the fluid, according as the growth of a crystal at constant temperature and pressure will produce expansion or contraction.

Again, we may suppose the composition of the fluid and its entropy per unit of mass to be uniform. The temperature will then vary with the pressure, that is, with z. We may also suppose the temperature of different crystals or different parts of the same crystal to be determined by the fluid in contact with them. These conditions express a state which may perhaps be realized when the fluid is gently stirred. Owing to the differences of temperature we cannot regard ε_V' and η_V' in (664) as constant, but we may regard their variations as subject to the relation $d\varepsilon_V' = t\, d\eta_V'$. Therefore, if we make $\eta_V' = 0$ for the mean temperature of the fluid, (which involves no real loss of generality,) we may treat $\varepsilon_V' - t\,\eta_V'$ as constant. We shall then have for the condition that the effect of gravity shall vanish—

$$\frac{d(\gamma_1'\,\mu_1'' - p'')}{dz} = 0,$$

which signifies in the present case that

$$\left(\frac{d\mu_1}{dp}\right)''_{\eta,\, m} = \frac{1}{\gamma_1'},$$

or, by (90),

$$\left(\frac{dv}{dm_1}\right)''_{\eta,\, p,\, m} = \frac{1}{\gamma_1'}. \tag{670}$$

Since the entropy of the crystal is zero, this equation expresses that the dissolving of a small crystal in a considerable quantity of the fluid will produce neither expansion nor contraction, when the pressure is maintained constant and no heat is supplied or taken away.

The manner in which crystals actually grow or dissolve is often principally determined by other differences of phase in the surrounding fluid than those which have been considered in the preceding paragraph. This is especially the case when the crystal is growing or dissolving rapidly. When the great mass of the fluid is considerably supersaturated, the action of the crystal keeps the part immediately contiguous to it nearer the state of exact saturation. The farthest projecting parts of the crystal will therefore be most exposed to the action of the supersaturated fluid, and will grow most rapidly. The same parts of a crystal will dissolve most rapidly in a fluid considerably below saturation.*

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* See O. Lehmann "Ueber das Wachsthum der Krystalle," *Zeitschrift für Krystallographie und Mineralogie*, Bd. i, S. 453; or the review of the paper in Wiedemann's *Beiblätter*, Bd. ii, S. 1.

But even when the fluid is supersaturated only so much as is necessary in order that the crystal shall grow at all, it is not to be expected that the form in which $\Sigma(\sigma s)$ has a minimum value (or such a modification of that form as may be due to gravity or to the influence of the body supporting the crystal) will always be the ultimate result. For we cannot imagine a body of the internal structure and external form of a crystal to grow or dissolve by an entirely continuous process, or by a process in the same sense continuous as condensation or evaporation between a liquid and gas, or the corresponding processes between an amorphous solid and a fluid. The process is rather to be regarded as periodic, and the formula (664) cannot properly represent the true value of the quantities intended unless δN is equal to the distance between two successive layers of molecules in the crystal, or a multiple of that distance. Since this can hardly be treated as an infinitesimal, we can only conclude with certainty that sensible changes cannot take place for which the expression (664) would have a positive value.*

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* That it is necessary that certain relations shall be precisely satisfied in order that equilibrium may subsist between a liquid and gas with respect to evaporation, is explained (see Clausius "Ueber die Art der Bewegung, welche wir Wärme nennen," *Pogg. Ann.*, Bd. c, S. 353; or *Abhand. über die mech. Wärmetheorie*, XIV,) by supposing that a passage of individual molecules from the one mass to the other is continually taking place, so that the slightest circumstance may give the preponderance to the passage of matter in either direction. The same supposition may be applied, at least in many cases, to the equilibrium between amorphous solids and fluids. Also in the case of crystals in equilibrium with fluids, there may be a passage of individual molecules from one mass to the other, so as to cause insensible fluctuations in the mass of the solid. If these fluctuations are such as to cause the occasional deposit or removal of a whole layer of particles, the least cause would be sufficient to make the probability of one kind of change prevail over that of the other, and it would be necessary for equilibrium that the theoretical conditions deduced above should be precisely satisfied. But this supposition seems quite improbable, except with respect to a very small side.

The following view of the molecular state of a crystal when in equilibrium with respect to growth or dissolution appears as probable as any. Since the molecules at the corners and edges of a perfect crystal would be less firmly held in their places than those in the middle of a side, we may suppose that when the condition of theoretical equilibrium (665) is satisfied several of the outermost layers of molecules on each side of the crystal are incomplete toward the edges. The boundaries of these imperfect layers probably fluctuate, as individual molecules attach themselves to the crystal or detach themselves, but not so that a layer is entirely removed (on any side of considerable size), to be restored again simply by the irregularities of the motions of the individual molecules. Single molecules or small groups of molecules may indeed attach themselves to the side of the crystal but they will speedily be dislodged, and if any molecules are thrown out from the middle of a surface, these deficiencies

Let us now examine the special condition of equilibrium which relates to a line at which three different masses meet, when one or more of these masses is solid. If we apply the method of page 685 to a system containing such a line, it is evident that we shall obtain in the expression corresponding to (660), beside the integral relating to the surfaces, a term of the form

$$\int \Sigma(\sigma\, \delta T)\, Dl$$

to be interpreted as the similar term in (611), except so far as the definition of σ has been modified in its extension to solid masses. In order that this term shall be incapable of a negative value it is neces-

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will also soon be made good; nor will the frequency of these occurrences be such as greatly to affect the general smoothness of the surfaces, except near the edges where the surfaces fall off somewhat, as before described. Now a continued growth on any side of a crystal is impossible unless new layers can be formed. This will require a value of μ_1'' which may exceed that given by equation (665) by a finite quantity. Since the difficulty in the formation of a new layer is at or near the commencement of the formation, the necessary value of μ_1'' may be independent of the area of the side, except when the side is very small. The value of μ_1'' which is necessary for the growth of the crystal will however be different for different kinds of surfaces, and probably will generally be greatest for the surfaces for which σ is least.

On the whole, it seems not improbable that the form of very minute crystals in equilibrium with solvents is principally determined by equation (665), (*i. e.*, by the condition that $\Sigma(\sigma s)$ shall be a minimum for the volume of the crystal except so far as the case is modified by gravity or the contact of other bodies,) but as they grow larger (in a solvent no more supersaturated than is necessary to make them grow at all), the deposition of new matter on the different surfaces will be determined more by the nature (orientation) of the surfaces and less by their size and relations to the surrounding surfaces. As a final result, a large crystal, thus formed, will generally be bounded by those surfaces alone on which the deposit of new matter takes place least readily, with small, perhaps insensible truncations. If one kind of surfaces satisfying this condition cannot form a closed figure, the crystal will be bounded by two or three kinds of surfaces determined by the same condition. The kinds of surface thus determined will probably generally be those for which σ has the least values. But the relative development of the different kinds of sides, even if unmodified by gravity or the contact of other bodies, will not be such as to make $\Sigma(\sigma s)$ a minimum. The growth of the crystal will finally be confined to sides of a single kind.

It does not appear that any part of the operation of removing a layer of molecules presents any especial difficulty so marked as that of commencing a new layer; yet the values of μ_1'' which will just allow the different stages of the process to go on must be slightly different, and therefore, for the continued dissolving of the crystal the value of μ_1'' must be less (by a finite quantity) than that given by equation (665). It seems probable that this would be especially true of those sides for which σ has the least values. The effect of dissolving a crystal (even when it is done as slowly as possible) is therefore to produce a form which probably differs from that of theoretical equilibrium in a direction opposite to that of a growing crystal.

sary that at every point of the line

$$\Sigma(\sigma\,\delta T) \geqq 0 \tag{671}$$

for any *possible* displacement of the line. Those displacements are to be regarded as possible which are not prevented by the solidity of the masses, when the interior of every solid mass is regarded as incapable of motion. At the surfaces between solid and fluid masses, the processes of solidification and dissolution will be possible in some cases, and impossible in others.

The simplest case is when two masses are fluid and the third is solid and insoluble. Let us denote the solid by S, the fluids by A and B, and the angles filled by these fluids by α and β respectively. If the surface of the solid is continuous at the line where it meets the two fluids, the condition of equilibrium reduces to

$$\sigma_{AB} \cos \alpha = \sigma_{BS} - \sigma_{AS}. \tag{672}$$

If the line where these masses meet is at an edge of the solid, the condition of equilibrium is that

$$\left.\begin{array}{ll} & \sigma_{AB} \cos \alpha \leqq \sigma_{BS} - \sigma_{AS}, \\ \text{and} & \sigma_{AB} \cos \beta \leqq \sigma_{AS} - \sigma_{BS}; \end{array}\right\} \tag{673}$$

which reduces to the preceding when $\alpha + \beta = \pi$. Since the displacement of the line can take place by a purely mechanical process, this condition is capable of a more satisfactory experimental verification than those conditions which relate to processes of solidification and dissolution. Yet the frictional resistance to a displacement of the line is enormously greater than in the case of three fluids, since the relative displacements of contiguous portions of matter are enormously greater. Moreover, foreign substances adhering to the solid are not easily displaced, and cannot be distributed by extensions and contractions of the surface of discontinuity, as in the case of fluid masses. Hence, the distribution of such substances is arbitrary to a greater extent than in the case of fluid masses, (in which a single foreign substance in any surface of discontinuity is uniformly distributed, and a greater number are at least so distributed as to make the tension of the surface uniform,) and the presence of these substances will modify the conditions of equilibrium in a more irregular manner.

If one or more of three surfaces of discontinuity which meet in a line divides an amorphous solid from a fluid in which it is soluble, such a surface is to be regarded as movable, and the particular conditions involved in (671) will be accordingly modified. If the soluble solid is a crystal, the case will properly be treated by the method used on page 490. The condition of equilibrium relating to the line will not in this case be entirely separable from those relating to the adjacent surfaces, since a displacement of the line will involve a displacement of the whole side of the crystal which is terminated at this line. But the expression for the total increment of energy in the system due to any internal changes not involving any variation in the total entropy or volume will consist of two parts, of which one relates to the properties of the masses of the system, and the other may be expressed in the form

$$\delta \Sigma (\sigma s),$$

the summation relating to all the surfaces of discontinuity. This indicates the same tendency toward changes diminishing the value of $\Sigma(\sigma s)$, which appears in other cases.*

General Relations.—For any constant state of strain of the surface of the solid, we may write

$$d\varepsilon_{S(1)} = t\, d\eta_{S(1)} + \mu_2\, d\Gamma_{2(1)} + \mu_3\, d\Gamma_{3(1)} + \text{etc.}, \qquad (674)$$

since this relation is implied in the definition of the quantities involved. From this and (659) we obtain

$$d\sigma = -\eta_{S(1)}\, dt - \Gamma_{2(1)}\, d\mu_2 - \Gamma_{3(1)}\, d\mu_3 - \text{etc.}, \qquad (675)$$

which is subject, in strictness, to the same limitation—that the state of strain of the surface of the solid remains the same. But this limitation may in most cases be neglected. (If the quantity σ represented the true tension of the surface, as in the case of a surface between fluids, the limitation would be wholly unnecessary.)

Another method and notation.—We have so far supposed that we have to do with a non-homogeneous film of matter between two homogeneous (or very nearly homogeneous) masses, and that the nature and state of this film is in all respects determined by the

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* The freezing together of wool and ice may be mentioned here. The fact that a fiber of wool which remains in contact with a block of ice under water will become attached to it seems to be strictly analogous to the fact that if a solid body be brought into such a position that it just touches the free surface of water, the water will generally rise up about the point of contact so as to touch the solid over a surface of some extent. The condition of the latter phenomenon is

$$\sigma_{SA} + \sigma_{WA} > \sigma_{SW},$$

where the suffixes S, A, and W refer to the solid, to air, and to water, respectively. In like manner, the condition for the freezing of the ice to the wool, if we neglect the æolotropic properties of the ice, is

$$\sigma_{SW} + \sigma_{IW} > \sigma_{SI},$$

where the suffixes S, W, and I relate to wool, to water, and to ice, respectively. See *Proc. Roy. Soc.*, vol. x, p. 447; or *Phil. Mag.*, 4th ser., vol. xxi, p. 151.

nature and state of these masses together with the quantities of the foreign substances which may be present in the film. (See page 483.) Problems relating to processes of solidification and dissolution seem hardly capable of a satisfactory solution, except on this supposition, which appears in general allowable with respect to the surfaces produced by these processes. But in considering the equilibrium of fluids at the surface of an unchangeable solid, such a limitation is neither necessary nor convenient. The following method of treating the subject will be found more simple and at the same time more general.

Let us suppose the superficial density of energy to be determined by the excess of energy in the vicinity of the surface over that which would belong to the solid, if (with the same temperature and state of strain) it were bounded by a vacuum in place of the fluid, and to the fluid, if it extended with a uniform volume-density of energy just up to the surface of the solid, or, if in any case this does not sufficiently define a surface, to a surface determined in some definite way by the exterior particles of the solid. Let us use the symbol (ε_S) to denote the superficial energy *thus defined.* Let us suppose a superficial density of entropy to be determined in a manner entirely analogous, and be denoted by (η_S). In like manner also, for all the components of the fluid, and for all foreign fluid substances which may be present at the surface, let the superficial densities be determined, and denoted by (Γ_2), (Γ_3), etc. These *superficial densities of the fluid components* relate solely to the matter which is fluid or movable. All matter which is immovably attached to the solid mass is to be regarded as a part of the same. Moreover, let ς be defined by the equation

$$\varsigma = (\varepsilon_S) - t\,(\eta_S) - \mu_2\,(\Gamma_2) - \mu_3\,(\Gamma_3) - \text{etc.} \tag{676}$$

These quantities will satisfy the following general relations—

$$d(\varepsilon_S) = t\,d(\eta_S) + \mu_2\,d(\Gamma_2) + \mu_3\,d(\Gamma_3) + \text{etc.}, \tag{677}$$

$$d\varsigma = -(\eta_S)\,dt - (\Gamma_2)\,d\mu_2 - (\Gamma_3)\,d\mu_3 - \text{etc.} \tag{678}$$

In strictness, these relations are subject to the same limitation as (674) and (675). But this limitation may generally be neglected. In fact, the values of ς, (ε_S), etc. must in general be much less affected by variations in the state of strain of the surface of the solid than those of σ, $\varepsilon_{S(1)}$, etc.

The quantity ς evidently represents the tendency to contraction in that portion of the surface of the fluid which is in contact with the solid. It may be called *the superficial tension of the fluid in contact with the solid.* Its value may be either positive or negative.

It will be observed that for the same solid surface and for the same temperature but for different fluids the values of σ (in all cases to which the definition of this quantity is applicable) will differ from those of ς by a constant, viz., the value of σ for the solid surface in a vacuum.

For the condition of equilibrium of two different fluids at a line on the surface of the solid, we may easily obtain

$$\sigma_{AB} \cos \alpha = \varsigma_{BS} - \varsigma_{AS}, \qquad (679)$$

the suffixes, etc., being used as in (672), and the condition being subject to the same modification when the fluids meet at an edge of the solid.

It must also be regarded as a condition of theoretical equilibrium at the line considered, [subject, like (679), to limitation on account of passive resistances to motion,] that if there are any foreign substances in the surfaces A-S and B-S, the potentials for these substances shall have the same value on both sides of the line; or, if any such substance is found only on one side of the line, that the potential for that substance must not have a less value on the other side; and that the potentials for the components of the mass A, for example, must have the same values in the surface B-C as in the mass A, or, if they are not actual components of the surface B-C, a value not less than in A. Hence, we cannot determine the difference of the surface-tensions of two fluids in contact with the same solid, by bringing them together upon the surface of the solid, unless these conditions are satisfied, as well as those which are necessary to prevent the mixing of the fluid masses.

The investigation on pages 442–448 of the conditions of equilibrium for a fluid system under the influence of gravity may easily be extended to the case in which the system is bounded by or includes solid masses, when these can be treated as rigid and incapable of dissolution. The general condition of mechanical equilibrium would be of the form

$$-\int p\, \delta Dv + \int g\, \gamma\, \delta z\, Dv + \int \sigma\, \delta Ds + \int g\, \Gamma\, \delta z\, Ds$$
$$+ \int g\, \delta z\, \mathrm{Dm} + \int \varsigma\, \delta Ds + \int g\, (\Gamma)\, \delta z\, Ds = 0, \qquad (680)$$

where the first four integrals relate to the fluid masses and the surfaces which divide them, and have the same signification as in equation (606), the fifth integral relates to the movable solid masses, and the sixth and seventh to the surfaces between the solids and fluids, (Γ) denoting the sum of the quantities (Γ_2), (Γ_3), etc. It should be observed that at the surface where a fluid meets a solid

δz and δz, which indicate respectively the displacements of the solid and the fluid, may have different values, but the components of these displacements which are normal to the surface must be equal.

From this equation, among other particular conditions of equilibrium, we may derive the following—

$$d\varsigma = g\,(\Gamma)\,dz, \tag{681}$$

[compare (614),] which expresses the law governing the distribution of a thin fluid film on the surface of a solid, when there are no passive resistances to its motion.

By applying equation (680) to the case of a vertical cylindrical tube containing two different fluids, we may easily obtain the well-known theorem that the product of the perimeter of the internal surface by the difference $\varsigma' - \varsigma''$ of the superficial tensions of the upper and lower fluids in contact with the tube is equal to the excess of weight of the matter in the tube above that which would be there, if the boundary between the fluids were in the horizontal plane at which their pressures would be equal. In this theorem, we may either include or exclude the weight of a film of fluid matter adhering to the tube. The proposition is usually applied to the column of fluid *in mass* between the horizontal plane for which $p' = p''$ and the actual boundary between the two fluids. The superficial tensions ς' and ς'' are then to be measured in the vicinity of this column. But we may also include the weight of a film adhering to the internal surface of the tube. For example, in the case of water in equilibrium with its own vapor in a tube, the weight of all the water-substance in the tube above the plane $p' = p''$, diminished by that of the water-vapor which would fill the same space, is equal to the perimeter multiplied by the difference in the values of ς at the top of the tube and at the plane $p' = p''$. If the height of the tube is infinite, the value of ς at the top vanishes, and the weight of the film of water adhering to the tube and of the mass of liquid water above the plane $p' = p''$ diminished by the weight of vapor which would fill the same space is equal in numerical value but of opposite sign to the product of the perimeter of the internal surface of the tube multiplied by ς'', the superficial tension of liquid water in contact with the tube at the pressure at which the water and its vapor would be in equilibrium at a plane surface. In this sense, the total weight of water which can be supported by the tube per unit of the perimeter of its surface is directly measured by the value of $-\varsigma$ for water in contact with the tube.

Modification of the conditions of equilibrium by electro-motive force.—Theory of a perfect electro-chemical apparatus.

We know by experience that in certain fluids (electrolytic conductors) there is a connection between the fluxes of the component substances and that of electricity. The quantitative relation between these fluxes may be expressed by an equation of the form

$$De = \frac{Dm_a}{\alpha_a} + \frac{Dm_b}{\alpha_b} + \text{etc.} - \frac{Dm_g}{\alpha_g} - \frac{Dm_h}{\alpha_h} - \text{etc.}, \qquad (682)$$

where De, Dm_a, etc. denote the infinitesimal quantities of electricity and of the components of the fluid which pass simultaneously through any same surface, which may be either at rest or in motion, and α_a, α_b, etc., α_g, α_h, etc. denote positive constants. We may evidently regard Dm_a, Dm_b, etc., Dm_g, Dm_h, etc., as independent of one another. For, if they were not so, one or more could be expressed in terms of the others, and we could reduce the equation to a shorter form in which all the terms of this kind would be independent.

Since the motion of the fluid as a whole will not involve any electrical current, the densities of the components specified by the suffixes must satisfy the relation

$$\frac{\gamma_a}{\alpha_a} + \frac{\gamma_b}{\alpha_b} + \text{etc.} = \frac{\gamma_g}{\alpha_g} + \frac{\gamma_h}{\alpha_h} + \text{etc.} \qquad (683)$$

These densities, therefore, are not independently variable, like the densities of the components which we have employed in other cases.

We may account for the relation (682) by supposing that electricity (positive or negative) is inseparably attached to the different kinds of molecules, so long as they remain in the interior of the fluid, in such a way that the quantities α_a, α_b, etc. of the substances specified are each charged with a unit of positive electricity, and the quantities α_g, α_h, etc. of the substances specified by these suffixes are each charged with a unit of negative electricity. The relation (683) is accounted for by the fact that the constants α_a, α_g, etc. are so small that the electrical charge of any sensible portion of the fluid varying sensibly from the law expressed in (683) would be enormously great, so that the formation of such a mass would be resisted by a very great force.

It will be observed that the choice of the substances which we regard as the components of the fluid is to some extent arbitrary, and that the same physical relations may be expressed by different equations of the form (682), in which the fluxes are expressed with reference to different sets of components. If the components chosen are such as represent what we believe to be the actual molecular constitution of the fluid, those of which the fluxes appear in the equation of the form (682) are called the *ions*, and the constants of the equation are called their *electro-chemical equivalents.* For our present purpose, which has nothing to do with any theories of molecular constitution, we may choose such a set of components as may be convenient, and call those *ions*, of which the fluxes appear in the equation of the form (682), without farther limitation.

Now, since the fluxes of the independently variable components of an electrolytic fluid do not necessitate any electrical currents, all the conditions of equilibrium which relate to the movements of these components will be the same as if the fluid were incapable of the electrolytic process. Therefore all the conditions of equilibrium which we have found without reference to electrical considerations, will apply to an electrolytic fluid and its independently variable components. But we have still to seek the remaining conditions of equilibrium, which relate to the possibility of electrolytic conduction.

For simplicity, we shall suppose that the fluid is without internal surfaces of discontinuity (and therefore homogeneous except so far as it may be slightly affected by gravity), and that it meets metallic conductors (*electrodes*) in different parts of its surface, being otherwise bounded by non-conductors. The only electrical currents which it is necessary to consider are those which enter the electrolyte at one electrode and leave it at another.

If all the conditions of equilibrium are fulfilled in a given state of the system, except those which relate to changes involving a flux of electricity, and we imagine the state of the system to be varied by the passage from one electrode to another of the quantity of electricity δe accompanied by the quantity δm_a of the component specified, without any flux of the other components or any variation in the total entropy, the total variation of energy in the system will be represented by the expression

$$(V'' - V')\,\delta e + (\mu_a'' - \mu_a')\,\delta m_a + (\Upsilon' - \Upsilon'')\,\delta m_a,$$

in which V', V'' denote the electrical potentials in pieces of the same kind of metal connected with the two electrodes, Υ', Υ'', the gravitational potentials at the two electrodes, and μ_a', μ_a'', the intrinsic potentials for the substance specified. The first term represents the increment of the potential energy of electricity, the second the increment of the intrinsic energy of the ponderable matter, and the third the increment of the energy due to gravitation.* But by (682)

$$\delta m_a = \alpha_a \, \delta e$$

It is therefore necessary for equilibrium that

$$V'' - V' + \alpha_a (\mu_a'' - \mu_a' - \Upsilon'' + \Upsilon') = 0. \tag{684}$$

To extend this relation to all the electrodes we may write

$$\begin{aligned} V' + \alpha_a (\mu_a' - \Upsilon') &= V'' + \alpha_a (\mu_a'' - \Upsilon'') \\ &= V''' + \alpha_a (\mu_a''' - \Upsilon''') = \text{etc.} \end{aligned} \tag{685}$$

For each of the other cations (specified by $_b$ etc.) there will be a similar condition, and for each of the anions a condition of the form

$$\begin{aligned} V' - \alpha_g (\mu_g' - \Upsilon') &= V'' - \alpha_g (\mu_g'' - \Upsilon'') \\ &= V''' - \alpha_g (\mu_g''' - \Upsilon''') = \text{etc.} \end{aligned} \tag{686}$$

When the effect of gravity may be neglected, and there are but two electrodes, as in a galvanic or electrolytic cell, we have for any cation

$$V'' - V' = \alpha_a (\mu_a' - \mu_a''), \tag{687}$$

and for any anion

$$V'' - V' = \alpha_g (\mu_g'' - \mu_g'), \tag{688}$$

where $V'' - V'$ denotes the electromotive force of the combination. That is:—

When all the conditions of equilibrium are fulfilled in a galvanic or electrolytic cell, the electromotive force is equal to the difference in the values of the potential for any ion or apparent ion at the surfaces of the electrodes multiplied by the electro-chemical equivalent of that ion, the greater potential of an anion being at the same electrode as the greater electrical potential, and the reverse being true of a cation.

Let us apply this principle to different cases.

(I.) If the ion is an independently variable component of an electrode, or by itself constitutes an electrode, the potential for the ion (in any case of equilibrium which does not depend upon passive resistances to change) will have the same value within the electrode as on its surface, and will be determined by the composition of the electrode with its temperature and pressure. This might be illustrated by a cell with electrodes of mercury containing certain quantities of zinc in solution (or with one such electrode and the other of pure

* It is here supposed that the gravitational potential may be regarded as constant for each electrode. When this is not the case, the expression may be applied to small parts of the electrodes taken separately.

zinc) and an electrolytic fluid containing a salt of zinc, but not capable of dissolving the mercury.* We may regard a cell in which hydrogen acts as an ion between electrodes of palladium charged with hydrogen as another illustration of the same principle, but the solidity of the electrodes and the consequent resistance to the diffusion of the hydrogen within them (a process which cannot be assisted by convective currents as in a liquid mass) present considerable obstacles to the experimental verification of the relation.

(II.) Sometimes the ion is soluble (as an independently variable component) in the electrolytic fluid. Of course its condition in the fluid when thus dissolved must be entirely different from its condition when acting on an ion, in which case its quantity is not independently variable, as we have already seen. Its diffusion in the fluid in this state of solution is not necessarily connected with any electrical current, and in other relations its properties may be entirely changed. In any discussion of the internal properties of the fluid (with respect to its fundamental equation, for example,) it would be necessary to treat it as a different substance. (See page 117.) But if the process by which the charge of electricity passes into the electrode, and the ion is dissolved in the electrolyte is *reversible*, we may evidently regard the potentials for the substance of the ion in (687) or (688) as relating to the substance thus dissolved in the electrolyte. In case of absolute equilibrium, the density of the substance thus dissolved would of course be uniform throughout the fluid, (since it can move independently of any electrical current,) so that by the strict application of our principle we only obtain the somewhat barren result, that if any of the ions are soluble in the fluid without their electrical charges, the electromotive force must vanish in any case of absolute equilibrium not dependent upon passive resistances. Nevertheless, cases in which the ion is thus dissolved in the electrolytic fluid only to a very small extent, and its passage from one electrode to the other by ordinary diffusion is extremely slow, may be regarded as approximating to the case in which it is incapable of diffusion. In such cases, we may regard the relations (687), (688) as approximately valid, although the condition of equilibrium

* If the electrolytic fluid dissolved the mercury as well as the zinc, equilibrium could only subsist when the electromotive force is zero, and the composition of the electrodes identical. For when the electrodes are formed of the two metals in different proportions, that which has the greater potential for zinc will have the less potential for mercury. [See equation (98).] This is inconsistent with equilibrium, according to the principle mentioned above, if both metals can act as cations.

relating to the diffusion of the dissolved ion is not satisfied. This may be the case with hydrogen and oxygen as ions (or apparent ions) between electrodes of platinum in some of its forms.

(III.) The ion may appear in mass at the electrode. If it be a conductor of electricity, it may be regarded as forming an electrode, as soon as the deposit has become thick enough to have the properties of matter in mass. The case therefore will not be different from that first considered. When the ion is a non-conductor, a continuous thick deposit on the electrode would of course prevent the possibility of an electrical current. But the case in which the ion being a non-conductor is disengaged in masses contiguous to the electrode but not entirely covering it, is an important one. It may be illustrated by hydrogen appearing in bubbles at a cathode. In case of perfect equilibrium, independent of passive resistances, the potential of the ion in (687) or (688) may be determined in such a mass. Yet the circumstances are quite unfavorable for the establishment of perfect equilibrium, unless the ion is to some extent absorbed by the electrode or electrolytic fluid, or the electrode is fluid. For if the ion must pass *immediately* into the non-conducting mass, while the electricity passes into the electrode, it is evident that the only possible terminus of an electrolytic current is at the line where the electrode, the non-conducting mass, and the electrolytic fluid meet, so that the electrolytic process is necessarily greatly retarded, and an approximate ceasing of the current cannot be regarded as evidence that a state of approximate equilibrium has been reached. But even a slight degree of solubility of the ion in the electrolytic fluid or in the electrode may greatly diminish the resistance to the electrolytic process, and help toward producing that state of complete equilibrium which is supposed in the theorem we are discussing. And the mobility of the surface of a liquid electrode may act in the same way. When the ion is absorbed by the electrode, or by the electrolytic fluid, the case of course comes under the heads which we have already considered, yet the fact that the ion is set free in mass is important, since it is in such a mass that the determination of the value of the potential will generally be most easily made.

(IV.) When the ion is not absorbed either by the electrode or by the electrolytic fluid, and is not set free in mass, it may still be deposited on the surface of the electrode. Although this can take place only to a limited extent (without forming a body having the properties of matter in mass), yet the electro-chemical equivalents of all substances are so small that a very considerable flux of electricity may take place before the deposit will have the properties of matter in mass. Even when the ion appears in mass, or is absorbed by the electrode or electrolytic fluid, the non-homogeneous film between the electrolytic fluid and the electrode may contain an additional portion of it. Whether the ion is confined to the surface of the electrode or not, we may regard this as one of the cases in which we have to recognize a certain superficial density of substances at surfaces of discontinuity, the general theory of which we have already considered.

The deposit of the ion will affect the superficial tension of the electrode if it is liquid, or the closely related quantity which we have denoted by the same symbol σ (see pages 482–500) if the electrode is solid. The effect can of course be best observed in the case of a liquid electrode. But whether the electrodes are liquid or solid, if the external electromotive force $V' - V''$ applied to an electrolytic combination is varied, when it is too weak to produce a lasting current, and the electrodes are thereby brought into a new state of polarization, in which they make equilibrium with the altered value of the electromotive force, without change in the nature of the electrodes or of the electrolytic fluid, then by (508) or (675)

$$d\sigma' = -\Gamma_{\mathrm{a}}'\, d\mu_{\mathrm{a}}',$$
$$d\sigma'' = -\Gamma_{\mathrm{a}}''\, d\mu_{\mathrm{a}}'';$$

and by (687),

$$d(V' - V'') = -\alpha_{\mathrm{a}}\,(d\mu_{\mathrm{a}}' - d\mu_{\mathrm{a}}'').$$

Hence

$$d(V' - V'') = \frac{\alpha_{\mathrm{a}}}{\Gamma_{\mathrm{a}}'}\, d\sigma' - \frac{\alpha_{\mathrm{a}}}{\Gamma_{\mathrm{a}}''}\, d\sigma''. \tag{689}$$

If we suppose that the state of polarization of only one of the electrodes is affected (as will be the case when its surface is very small compared with that of the other), we have

$$d\sigma' = \frac{\Gamma_{\mathrm{a}}'}{\alpha_{\mathrm{a}}}\, d(V' - V''). \tag{690}$$

The superficial tension of one of the electrodes is then a function of the electromotive force.

This principle has been applied by M. Lippmann to the construction of the electrometer which bears his name.* In applying equations (689) and (690) to dilute sulphuric acid between electrodes of mercury, as in a Lippmann's electrometer, we may suppose that the

* See his memoir: "Relations entre les phénomènes électriques et capillaires," *Annales de Chimie et de Physique*, 5e série, t. v, p. 494.

suffix refers to hydrogen. It will be most convenient to suppose the *dividing surface* to be so placed as to make the surface-density of mercury zero. (See page 397.) The matter which exists in excess or deficiency at the surface may then be expressed by the surface-densities of sulphuric acid, of water, and of hydrogen. The value of the last may be determined from equation (690). According to M. Lippmann's determinations, it is negative when the surface is in its natural state (i. e., the state to which it tends when no external electromotive force is applied), since σ' increases with $V'' - V'$. When $V'' - V'$ is equal to nine-tenths of the electromotive force of a Daniell's cell, the electrode to which V'' relates remaining in its natural state, the tension σ' of the surface of the other electrode has a maximum value, and there is no excess or deficiency of hydrogen at that surface. This is the condition toward which a surface tends when it is extended while no flux of electricity takes place. The flux of electricity per unit of new surface formed, which will maintain a surface in a constant condition while it is extended, is represented by $\frac{\Gamma_a'}{\alpha_a}$ in numerical value, and its direction, when Γ_a'' is negative, is from the mercury into the acid.

We have so far supposed, in the main, that there are no passive resistances to change, except such as vanish with the rapidity of the processes which they resist. The actual condition of things with respect to passive resistances appears to be nearly as follows. There does not appear to be any passive resistance to the electrolytic process by which an ion is transferred from one electrode to another, except such as vanishes with the rapidity of the process. For, in any case of equilibrium, the smallest variation of the externally applied electromotive force appears to be sufficient to cause a (temporary) electrolytic current. But the case is not the same with respect to the molecular changes by which the ion passes into new combinations or relations, as when it enters into the mass of the electrodes, or separates itself in mass, or is dissolved (no longer with the properties of an ion) in the electrolytic fluid. In virtue of the passive resistance to these processes, the external electromotive force may often vary within wide limits, without creating any current by which the ion is transferred from one of the masses considered to the other. In other words, the value of $V' - V''$ may often differ greatly from that obtained from (687) or (688) when we determine the values of the potentials for the ion as in cases I, II, and III. We may, however, regard these equations as entirely valid, when the potentials for the ions are determined at the surface of the electrodes with reference to the ion in the condition in which it is brought there or taken away by an electrolytic current, without any attendant irreversible processes. But in a complete discussion of the properties of the surface of an electrode it may be necessary to distinguish (both in respect to surface-densities and to potentials) between the substance of the ion in this condition and the same substance in other conditions into which it cannot pass (directly) without irreversible processes. No such distinction, however, is necessary when the substance of the ion can pass at the surface of the electrode by reversible processes from any one of the conditions in which it appears to any other.

The formulæ (687), (688) afford as many equations as there are ions. These, however, amount to only one independent equation additional to those which relate to the independently variable components of the electrolytic fluid. This appears from the consideration that a flux of any cation may be combined with a flux of any anion in the same direction so as to involve no electrical current, and that this may be regarded as the flux of an independently variable component of the electrolytic fluid.

General Properties of a Perfect Electro-chemical Apparatus.

When an electrical current passes through a galvanic or electrolytic cell, the state of the cell is altered. If no changes take place in the cell except during the passage of the current, and all changes which accompany the current can be reversed by reversing the current, the cell may be called a perfect electro-chemical apparatus. The electromotive force of the cell may be determined by the equations which have just been given. But some of the general relations to which such an apparatus is subject may be conveniently stated in a form in which the ions are not explicitly mentioned.

In the most general case, we may regard the cell as subject to external action of four different kinds. (1) The supply of electricity at one electrode and the withdrawal of the same quantity at the other. (2) The supply or withdrawal of a certain quantity of heat. (3) The action of gravity. (4) The motion of the surfaces enclosing the apparatus, as when its volume is increased by the liberation of gases.

The increase of the energy in the cell is necessarily equal to that which it receives from external sources. We may express this by the equation

$$d\varepsilon = (V' - V'')\, de + dQ + dW_G + dW_P, \tag{691}$$

in which $d\varepsilon$ denotes the increment of the intrinsic energy of the cell, de the quantity of electricity which passes through it, V' and V'' the electrical potentials in masses of the same kind of metal connected with the anode and cathode respectively, dQ the heat received from external bodies, dW_G the work done by gravity, and dW_P the work done by the pressures which act on the external surface of the apparatus.

The conditions under which we suppose the processes to take place are such that the increase of the entropy of the apparatus is equal to the entropy which it receives from external sources. The only external source of entropy is the heat which is communicated to the cell by the surrounding bodies. If we write $d\eta$ for the increment of entropy in the cell, and t for the temperature, we have

$$d\eta = \frac{dQ}{t}. \tag{692}$$

Eliminating dQ, we obtain

$$d\varepsilon = (V' - V'')\,de + t\,d\eta + dW_G + dW_P, \tag{693}$$

or

$$V'' - V' = -\frac{d\varepsilon}{de} + t\,\frac{d\eta}{de} + \frac{dW_G}{de} + \frac{dW_P}{de}. \tag{694}$$

It is worth while to notice that if we give up the condition of the reversibility of the processes, so that the cell is no longer supposed to be a perfect electro-chemical apparatus, the relation (691) will still subsist. But, if we still suppose, for simplicity, that all parts of the cell have the same temperature, which is *necessarily* the case with a perfect electro-chemical apparatus, we shall have, instead of (692),

$$d\eta \geqq \frac{dQ}{t}, \tag{695}$$

and instead of (693), (694)

$$(V'' - V')\,de \leqq -d\varepsilon + t\,d\eta + dW_G + dW_P. \tag{696}$$

The values of the several terms of the second member of (694), for a given cell, will vary with the external influences to which the cell is subjected. If the cell is enclosed (with the products of electrolysis) in a rigid envelop, the last term will vanish. The term relating to gravity is generally to be neglected. If no heat is supplied or withdrawn, the term containing $d\eta$ will vanish. But in the calculation of the electromotive force, which is the most important application of the equation, it is generally more convenient to suppose that the temperature remains constant.

The quantities expressed by the terms containing dQ and $d\eta$ in (691), (693), (694), and (696) are 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 nor cold is produced by the passage of an electrical current through a perfect electro-chemical combination (except that heat which may be indefinitely diminished by increasing the time in which a given quantity of electricity passes), and that only heat can be produced in any cell, unless it be by processes of a secondary nature, which are not immediately or necessarily connected with the process of electrolysis.

It does not appear that this assumption is justified by any sufficient reason. In fact, it is easy to find a case in which the electromotive force is determined entirely by the term $t\dfrac{d\eta}{de}$ in (694), all the other terms in the second member of the equation vanishing. This is true of a Grove's gas battery charged with hydrogen and nitrogen. In this case, the hydrogen passes over to the nitrogen,—a process which does not alter the energy of the cell, when maintained at a constant temperature. The work done by external pressures is evidently nothing, and that done by gravity is (or may be) nothing. Yet an electrical current is produced. The work done (or which may be done) by the current outside of the cell is the equivalent of the work (or of a part of the work) which might be gained by allowing the gases to mix in other ways. This is equal, as has been shown by Lord Rayleigh,* to the work which may be gained by allowing each gas separately to expand at constant temperature from its initial volume to the volume occupied by the two gases together. The same work is equal, as appears from equations (278), (279) on page 217, (see also page 220,) to the increase of the entropy of the system multiplied by the temperature.

It is possible to vary the construction of the cell in such a way that nitrogen or other neutral gas will not be necessary. Let the cell consist of a U-shaped tube of sufficient height, and have pure hydrogen at each pole under very unequal pressures (as of one and two atmospheres respectively) which are maintained constant by properly weighted pistons, sliding in the arms of the tube. The difference of the pressures in the gas-masses at the two electrodes must of course be balanced by the difference in the height of the two columns of acidulated water. It will hardly be doubted that such an apparatus

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* *Philosophical Magazine*, vol. xlix, p. 311.

would have an electromotive force acting in the direction of a current which would carry the hydrogen from the denser to the rarer mass. Certainly the gas could not be carried in the opposite direction by an external electromotive force without the expenditure of as much (electromotive) work as is equal to the mechanical work necessary to pump the gas from the one arm of the tube to the other. And if by any modification of the metallic electrodes (which remain unchanged by the passage of electricity) we could reduce the passive resistances to zero, so that the hydrogen could be carried reversibly from one mass to the other without finite variation of the electromotive force, the only possible value of the electromotive force would be represented by the expression $t\frac{d\eta}{de}$, as a very close approximation. It will be observed that, although gravity plays an essential part in a cell of this kind by maintaining the difference of pressure in the masses of hydrogen, the electromotive force cannot possibly be ascribed to gravity, since the work done by gravity, when hydrogen passes from the denser to the rarer mass, is negative.

Again, it is entirely improbable that the electrical currents caused by differences in the concentration of solutions of salts, (as in a cell containing sulphate of zinc between zinc electrodes, or sulphate of copper between copper electrodes, the solution of the salt being of unequal strength at the two electrodes,) which have recently been investigated theoretically and experimentally by MM. Helmholtz and Moser,* are confined to cases in which the mixture of solutions of different degrees of concentration will produce heat. Yet in cases in which the mixture of more and less concentrated solutions is not attended with evolution or absorption of heat, the electromotive force must vanish in a cell of the kind considered, if it is determined simply by the diminution of energy in the cell. And when the mixture produces cold, the same rule would make any electromotive force impossible except in the direction which would tend to increase the difference of concentration. Such conclusions as would be quite irreconcilable with the theory of the phenomena given by Professor Helmholtz.

A more striking example of the necessity of taking account of the variations of entropy in the cell in *a priori* determinations of electromotive force is afforded by electrodes of zinc and mercury in a solution of sulphate of zinc. Since heat is absorbed when zinc is dissolved

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* *Annalen der Physik und Chemie*, Neue Folge, Band iii, February, 1878.

in mercury,* the energy of the cell is increased by a transfer of zinc to the mercury, when the temperature is maintained constant. Yet in this combination, the electromotive force acts in the direction of the current producing such a transfer.† The couple presents certain anomalies when a considerable quantity of zinc is united with the mercury. The electromotive force changes its direction, so that this case is usually cited as an illustration of the principle that the electromotive force is in the direction of the current which diminishes the energy of the cell, *i. e.*, which produces or allows those changes which are accompanied by evolution of heat when they take place directly. But whatever may be the cause of the electromotive force which has been observed acting in the direction from the amalgam through the electrolyte to the zinc (a force which according to the determinations of M. Gaugain is only one twenty-fifth part of that which acts in the reverse direction when pure mercury takes the place of the amalgam), these anomalies can hardly affect the general conclusions with which alone we are here concerned. If the electrodes of a cell are pure zinc and an amalgam containing zinc not in excess of the amount which the mercury will dissolve at the temperature of the experiment without losing its fluidity, and if the only change (other than thermal) accompanying a current is a transfer of zinc from one electrode to the other,—conditions which may not have been satisfied in all the experiments recorded, but which it is allowable to suppose in a theoretical discussion, and which certainly will not be regarded as inconsistent with the fact that heat is absorbed when zinc is dissolved in mercury,—it is impossible that the electromotive force should be in the direction of a current transferring zinc from the amalgam to the electrode of pure zinc. For, since the zinc eliminated from the amalgam by the electrolytic process might be re-dissolved directly, such a direction of the electromotive force would involve the possibility of obtaining an indefinite amount of electromotive work, and therefore of mechanical work, without other expenditure than that of heat at the constant temperature of the cell.

None of the cases which we have been considering involve combinations by definite proportions, and, except in the case of the cell with electrodes of mercury and zinc, the electromotive forces are quite small. It may perhaps be thought that with respect to those cells in which combinations take place by definite proportions the electromotive force may be calculated with substantial accuracy from

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* J. Regnauld, *Comptes Rendus*, t. li, p. 778.

† Gaugain, *Comptes Rendus*, t. xlii, p. 430.

the diminution of the energy, without regarding the variation of entropy. But the phenomena of chemical combination do not in general seem to indicate any possibility of obtaining from the combination of substances by any process whatever an amount of mechanical work which is equivalent to the heat produced by the direct union of the substances.

A kilogramme of hydrogen, for example, combining by combustion under the pressure of the atmosphere with eight kilogrammes of oxygen to form liquid water, yields an amount of heat which may be represented in round numbers by 34000 calories.* We may suppose that the gases are taken at the temperature of 0° C., and that the water is reduced to the same temperature. *But this heat cannot be obtained at any temperature desired.* A very high temperature has the effect of preventing to a greater or less extent, the combination of the elements. Thus, according to M. Sainte-Claire Deville,† the temperature obtained by the combustion of hydrogen and oxygen cannot much if at all exceed 2500° C., which implies that less than one-half of the hydrogen and oxygen present combine at that temperature. This relates to combustion under the pressure of the atmosphere. According to the determinations of Professor Bunsen‡ in regard to combustion in a confined space, only one-third of a mixture of hydrogen and oxygen will form a chemical compound at the temperature of 2850° C. and a pressure of ten atmospheres, and only a little more than one-half when the temperature is reduced by the addition of nitrogen to 2024° C., and the pressure to about three atmospheres *exclusive* of the part due to the nitrogen.

Now 10 calories at 2500° C. are to be regarded as reversibly convertible into one calorie at 4° C. together with the mechanical work representing the energy of 9 calories. If, therefore, all the 34000 calories obtainable from the union of hydrogen and oxygen under atmospheric pressure could be obtained at the temperature of 2500° C., and no higher, we should estimate the electromotive work performed in a perfect electro-chemical apparatus in which these elements are combined or separated at ordinary temperatures and under atmospheric pressure as representing nine-tenths of the 34000 calories, and the heat evolved or absorbed in the apparatus as representing one-tenth of the 34000 calories.§ This, of course, would give an electromotive

* See Rühlmann's *Handbuch der mechanischen Wärmetheorie*, Bd. ii, p. 290.

† *Comptes Rendus*, t. lvi, p. 199; and t. lxiv, 67.

‡ *Pogg. Ann.*, Bd. cxxxi (1867), p. 161.

§ These numbers are not subject to correction for the pressure of the atmosphere, since the 34000 calories relate to combustion under the same pressure.

force exactly nine-tenths as great as is obtained on the supposition that all the 34000 calories are convertible into electromotive or mechanical work. But, according to all indications, the estimate 2500° C. (for the temperature at which we may regard all the heat of combustion as obtainable) is far too high,* and we must regard the theoretical value of the electromotive force necessary to electrolyze water as considerably less than nine-tenths of the value obtained on the supposition that it is necessary for the electromotive agent to supply all the energy necessary for the process.

The case is essentially the same with respect to the electrolysis of hydrochloric acid, which is probably a more typical example of the process than the electrolysis of water. The phenomenon of dissociation is equally marked, and occurs at a much lower temperature, more than half of the gas being dissociated at 1400° C.† And the heat which is obtained by the combination of hydrochloric acid gas with water, especially with water which already contains a considerable quantity of the acid, is probably only to be obtained at temperatures comparatively low. This indicates that the theoretical value of the electromotive force necessary to electrolyze this acid (*i. e.*, the electromotive force which would be necessary in a reversible electrochemical apparatus), must be very much less than that which could perform in electromotive work the equivalent of all the heat evolved in the combination of hydrogen, chlorine and water to form the liquid submitted to electrolysis. This presumption, based upon the phenomena exhibited in the direct combination of the substances, is corroborated by the experiments of M. Favre, who has observed an absorption of heat in the cell in which this acid was electrolyzed.‡ The

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* Unless the received ideas concerning the behavior of gases at high temperatures are quite erroneous, it is possible to indicate the general character of a process (involving at most only such difficulties as are neglected in theoretical discussions) by which water may be converted into separate masses of hydrogen and oxygen without other expenditure than that of an amount of heat equal to the difference of energy of the matter in the two states and supplied at a temperature far below 2500° C. The essential parts of the process would be (1) vaporizing the water and heating it to a temperature at which a considerable part will be dissociated, (2) the partial separation of the hydrogen and oxygen by filtration, and (3) the cooling of both gaseous masses until the vapor they contain is condensed. A little calculation will show that in a continuous process all the heat obtained in the operation of cooling the products of filtration could be utilized in heating fresh water.

† Sainte-Claire Deville, *Comptes Rendus*, t. lxiv, p. 67.

‡ See *Mémoires des Savants Étrangers*, Sér. 2, t. xxv, No. 1, p. 142; or *Comptes Rendus*, t. lxxiii, p. 973. The figures obtained by M. Favre will be given hereafter, in connection with others of the same nature.

electromotive work expended must therefore have been less than the increase of energy in the cell.

In both cases of composition in definite proportions which we have considered, the compound has more entropy than its elements, and the difference is by no means inconsiderable. This appears to be the rule rather than the exception with respect to compounds which have less energy than their elements. Yet it would be rash to assert that it is an invariable rule. And when one substance is substituted for another in a compound, we may expect great diversity in the relations of energy and entropy.

In some cases, there is a striking correspondence between the electromotive force of a cell and the rate of diminution of its energy per unit of electricity transmitted, the temperature remaining constant. A Daniell's cell is a notable example of this correspondence. It may perhaps be regarded as a very significant case, since of all cells in common use, it has the most constant electromotive force, and most nearly approaches the condition of reversibility. If we apply our previous notation [compare (691)] with the substitution of finite for infinitesimal differences to the determinations of M. Favre,* estimating energy in calories, we have for each equivalent (32.6 kilogrammes) of zinc dissolved

$$(V'' - V')\,\Delta e = 24327^{\text{cal.}}, \quad \Delta \varepsilon = -25394^{\text{cal.}}, \quad \Delta Q = -1067^{\text{cal.}}.$$

It will be observed that the electromotive work performed by the cell is about four per cent. less than the diminution of energy in the cell.† The value of ΔQ, which, when negative, represents the heat evolved in the cell when the external resistance of the circuit is very great, was determined by direct measurement, and does not appear to have been corrected for the resistance of the cell. This correction would diminish the value of $-\Delta Q$, and increase that of $(V'' - V')\,\Delta e$, which was obtained by subtracting $-\Delta Q$ from $-\Delta \varepsilon$.

It appears that under certain conditions neither heat nor cold is produced in a Grove's cell. For M. Favre has found that with different degrees of concentration of the nitric acid sometimes heat and sometimes cold is produced.‡ When neither is produced, of course

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* See *Mém. Savants Étrang.*, loc. cit., p. 90; or *Comptes Rendus*, vol. lxix, p. 35, where the numbers are slightly different.

† A comparison of the experiments of different physicists has in some cases given a much closer correspondence. See Wiedemann's *Galvanismus*, etc., 2te Auflage, Bd. ii, §§ 1117. 1118.

‡ *Mém. Savants Étrang.*, loc. cit., p. 93; or *Comptes Rendus*, t. lxix, p. 37, and t. lxxiii, p. 893.

the electromotive force of the cell is exactly equal to its diminution of energy per unit of electricity transmitted. But such a coincidence is far less significant than the fact that an absorption of heat has been observed. With acid containing about seven equivalents of water (HNO_6+7HO), M. Favre has found

$$(V''-V')\,\Delta e = 46781^{\text{cal.}}, \quad \Delta\varepsilon = -41824^{\text{cal.}}, \quad \Delta Q = 4957^{\text{cal.}};$$

and with acid containing about one equivalent of water (HNO_6+HO),

$$(V''-V')\,\Delta e = 49847^{\text{cal.}}, \quad \Delta\varepsilon = -52714^{\text{cal.}}, \quad \Delta Q = -2867^{\text{cal.}}.$$

In the first example, it will be observed that the quantity of heat absorbed in the cell is not small, and that the electromotive force is nearly one-eighth greater than can be accounted for by the diminution of energy in the cell.

This absorption of heat in the cell he has observed in other cases, in which the chemical processes are much more simple.

For electrodes of cadmium and platinum in hydrochloric acid his experiments give*

$$(V''-V')\,\Delta e = 9256^{\text{cal.}}, \qquad \Delta\varepsilon = -8258^{\text{cal.}},$$
$$\Delta W_{\text{P}} = -290^{\text{cal.}}, \qquad \Delta Q = 1288^{\text{cal.}}.$$

In this case the electromotive force is nearly one-sixth greater than can be accounted for by the diminution of energy in the cell with the work done against the pressure of the atmosphere.

For electrodes of zinc and platinum in the same acid one series of experiments gives†

$$(V''-V')\,\Delta e = 16950^{\text{cal.}}, \qquad \Delta\varepsilon = -16189^{\text{cal.}},$$
$$\Delta W_{\text{P}} = -290^{\text{cal.}}, \qquad \Delta Q = 1051^{\text{cal.}};$$

and a later series,‡

$$(V''-V')\,\Delta e = 16738^{\text{cal.}}, \qquad \Delta\varepsilon = -17702^{\text{cal.}},$$
$$\Delta W_{\text{P}} = -290^{\text{cal.}}, \qquad \Delta Q = -674^{\text{cal.}}.$$

In the electrolysis of hydrochloric acid in a cell with a porous partition, he has found§

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* *Comptes Rendus*, t. lxviii, p. 1305. The total heat obtained in the whole circuit (including the cell) when all the electromotive work is turned into heat, was ascertained by direct experiment. This quantity, 7968 calories, is evidently represented by $(V''-V')\,\Delta e - \Delta Q$, also by $-\Delta\varepsilon + \Delta W_{\text{P}}$. [See (691).] The value of $(V''-V')\,\Delta e$ is obtained by adding ΔQ, and that of $-\Delta\varepsilon$ by adding $-\Delta W_{\text{P}}$, which is easily estimated, being determined by the evolution of one kilogramme of hydrogen.

† *Ibid.*

‡ *Mém. Savants Étrang.*, loc. cit., p. 145.

§ *Ibid*, p. 142.

$$(V' - V'')\,\Delta e = 34825^{\text{cal.}} \qquad \Delta Q = 2113^{\text{cal.}},$$

whence

$$\Delta \varepsilon - \Delta W_{\text{P}} = 36938.$$

We cannot assign a precise value to ΔW_{P}, since the quantity of chlorine which was evolved in the form of gas is not stated. But the value of $-\Delta W_{\text{P}}$ must lie between $290^{\text{cal.}}$ and $580^{\text{cal.}}$, probably nearer to the former.

The great difference in the results of the two series of experiments relating to electrodes of zinc and platinum in hydrochloric acid is most naturally explained by supposing some difference in the conditions of the experiment, as in the concentration of the acid, or in the extent to which the substitution of zinc for hydrogen took place.* That which it is important for us to observe in all these cases is that there are conditions under which heat is absorbed in a galvanic or electrolytic cell, so that the galvanic cell has a greater electromotive force than can be accounted for by the diminution of its energy, and the operation of electrolysis requires a less electromotive force than would be calculated from the increase of energy in the cell,—especially when the work done against the pressure of the atmosphere is taken into account.

It should be noticed that in all these experiments the quantity represented by ΔQ (which is the critical quantity with respect to the point at issue) was determined by direct measurement of the heat absorbed or evolved by the cell when placed alone in a calorimeter. The resistance of the circuit was made so great by a rheostat placed outside of the calorimeter that the resistance of the cell was regarded as insignificant in comparison, and no correction appears to have been made in any case for this resistance. With exception of the error due to this circumstance, which would in all cases diminish the heat absorbed in the cell (or increase the heat evolved), the probable error of ΔQ must be very small in comparison with that of $(V' - V'')\,\Delta e$, or with that of $\Delta \varepsilon$, which were in general determined by the compar-

* It should perhaps be stated that in his extended memoir published in 1877 in the *Mémoires des Savants Étrangers*, in which he has presumably collected those results of his experiments which he regards as most important and most accurate, M. Favre does not mention the absorption of heat in a cell of this kind, or in the similar cell in which cadmium takes the place of zinc. This may be taken to indicate a decided preference for the later experiments which showed an evolution of heat. Whatever the ground of this preference may have been, it can hardly destroy the significance of the absorption of heat, which was a matter of direct observation in repeated experiments. See *Comptes Rendus*, t. lxviii, p. 1305.

ison of different calorimetrical measurements, involving very much greater quantities of heat.

In considering the numbers which have been cited, we should remember that when hydrogen is evolved as gas the process is in general very far from reversible. In a perfect electrochemical apparatus, the same changes in the cell would yield a much greater amount of electromotive work, or absorb a much less amount. In either case, the value of ΔQ would be much greater than in the imperfect apparatus, the difference being measured perhaps by thousands of calories.*

It often occurs in a galvanic or electrolytic cell that an ion which is set free at one of the electrodes appears in part as gas, and is in part absorbed by the electrolytic fluid, and in part absorbed by the electrode. In such cases, a slight variation in the circumstances, which would not sensibly affect the electromotive force, would cause all of the ion to be disposed of in one of the three ways mentioned, if the current were sufficiently weak. This would make a considerable

* Except in the case of the Grove's cell, in which the reactions are quite complicated, the absorption of heat is most marked in the electrolysis of hydrochloric acid. The latter case is interesting, since the experiments confirm the presumption afforded by the behavior of the substances in other circumstances. (See page 514.) In addition to the circumstances mentioned above tending to diminish the observed absorption of heat, the following, which are peculiar to this case, should be noticed.

The electrolysis was performed in a cell with a porous partition, in order to prevent the chlorine and hydrogen dissolved in the liquid from coming in contact with each other. It had appeared in a previous series of experiments (*Mém. Savants Étrang.*, loc. cit., p. 131; or *Comptes Rendus*, t. lxvi, p. 1231,) that a very considerable amount of heat might be produced by the chemical union of the gases in solution. In a cell without partition, instead of an absorption, an evolution of heat took place, which sometimes exceeded 5000 calories. If, therefore, the partition did not perfectly perform its office, this could only cause a diminution in the value of ΔQ.

A large part at least of the chlorine appears to have been absorbed by the electrolytic fluid. It is probable that a slight difference in the circumstances of the experiment—a diminution of pressure, for example,—might have caused the greater part of the chlorine to be evolved as gas, without essentially affecting the electromotive force. The solution of chlorine in water presents some anomalies, and may be attended with complex reactions, but it appears to be always attended with a very considerable evolution of heat. (See Berthelot, *Comptes Rendus*, t. lxxvi, p. 1514.) If we regard the evolution of the chlorine in the form of gas as the normal process, we may suppose that the absorption of heat in the cell was greatly diminished by the retention of the chlorine in solution.

Under certain circumstances, oxygen is evolved in the electrolysis of dilute hydrochloric acid. It does not appear that this took place to any considerable extent in the experiments which we are considering. But so far as it may have occurred, we may regard it as a case of the electrolysis of water. The significance of the fact of the absorption of heat is not thereby affected.

difference in the variation of energy in the cell, and the electromotive force cannot certainly be calculated from the variation of energy alone in all these cases. The correction due to the work performed against the pressure of the atmosphere when the ion is set free as gas will not help us in reconciling these differences. It will appear on consideration that this correction will in general increase the discordance in the values of the electromotive force. Nor does it distinctly appear which of these cases is to be regarded as normal and which are to be rejected as involving secondary processes.*

If in any case secondary processes are excluded, we should expect it to be when the ion is identical in substance with the electrode upon which it is deposited, or from which it passes into the electrolyte. But even in this case we do not escape the difficulty of the different forms in which the substance may appear. If the temperature of the experiment is at the melting point of a metal which forms the ion and the electrode, a slight variation of temperature will cause the ion to be deposited in the solid or in the liquid state, or, if the current is in the opposite direction, to be taken up from a solid or from a liquid body. Since this will make a considerable difference in the variation of energy, we obtain different values for the electromotive force above and below the melting point of the metal, unless we also take account of the variations of entropy. Experiment does not indicate the existence of any such difference,† and when we take account of variations of entropy, as in equation (694), it is apparent that there ought not to be any, the terms $\frac{d\varepsilon}{de}$ and $t\frac{d\eta}{de}$ being both

* It will be observed that in using the formulae (694) and (696) we do not have to make any distinction between *primary* and *secondary* processes. The only limitation to the generality of these formulae depends upon the *reversibility* of the processes, and this limitation does not apply to (696).

† M. Raoult has experimented with a galvanic element having an electrode of bismuth in contact with phosphoric acid containing phosphate of bismuth in solution. (See *Comptes Rendus*, t. lxviii, p. 643.) Since this metal absorbs in melting 12.64 calories per kilogramme or 885 calories per equivalent ($70^{\text{kil.}}$), while a Daniell's cell yields about 24000 calories of electromotive work per equivalent of metal, the solid or liquid state of the bismuth ought to make a difference of electromotive force represented by .037 of a Daniell's cell, if the electromotive force depended simply upon the energy of the cell. But in M. Raoult's experiments no sudden change of electromotive force was manifested at the moment when the bismuth changed its state of aggregation. In fact, a change of temperature in the electrode from about fifteen degrees above to about fifteen degrees below the temperature of fusion only occasioned a variation of electromotive force equal to .002 of a Daniell's cell.

Experiments upon lead and tin gave similar results.

affected by the same difference, viz., the heat of fusion of an electro-chemical equivalent of the metal. In fact, if such a difference existed, it would be easy to devise arrangements by which the heat yielded by a metal in passing from the liquid to the solid state could be transformed into electromotive work (and therefore into mechanical work) without other expenditure.

The foregoing examples will be sufficient, it is believed, to show the necessity of regarding other considerations in determining the electromotive force of a galvanic or electrolytic cell than the variation of its energy alone (when its temperature is supposed to remain constant), or corrected only for the work which may be done by external pressures or by gravity. But the relations expressed by (693), (694), and (696) may be put in a briefer form.

If we set, as on page 144,

$$\psi = \varepsilon - t\,\eta,$$

we have, for any constant temperature,

$$d\psi = d\varepsilon - t\,d\,\eta;$$

and for any perfect electrochemical apparatus, the temperature of which is maintained constant,

$$V'' - V' = -\frac{d\psi}{de} + \frac{d\,W_{\mathrm{G}}}{de} + \frac{d\,W_{\mathrm{P}}}{de}; \tag{697}$$

and for any cell whatever, when the temperature is maintained uniform and constant,

$$(V'' - V')\,de \leqq -d\psi + d\,W_{\mathrm{G}} + d\,W_{\mathrm{P}}. \tag{698}$$

In a cell of any ordinary dimensions, the work done by gravity, as well as the inequalities of pressure in different parts of the cell may be neglected. If the pressure as well as the temperature is maintained uniform and constant, and we set, as on page 147,

$$\zeta = \varepsilon - t\,\eta + p\,v,$$

where p denotes the pressure in the cell, and v its total volume (including the products of electrolysis), we have

$$d\zeta = d\varepsilon - t\,d\eta + p\,dv,$$

and for a perfect electro-chemical apparatus,

$$V'' - V' = -\frac{d\zeta}{de}, \tag{699}$$

or for any cell,

$$(V'' - V')\,de \leqq -d\zeta. \tag{700}$$

SYNOPSIS OF SUBJECTS TREATED.

SURFACES OF DISCONTINUITY BETWEEN SOLIDS AND FLUIDS.

ELECTROMOTIVE FORCE.

ERRATA.

Page 356, last line but two, for crystalline solid, read solid of continuous crystalline structure.

Page 385, line 13, for M′, read M.

Pages 391, 394, 395, 400, in headings, after *Discontinuity*, add *between Fluid Masses.*

Page 403, line 16, after any other film, add of the same components.

Page 405, line 29, after this, add case.

Page 432, line 15 of foot-note, for H, read H_2.