seems to bear no relation to the solubility of the metal, considering the group as a whole. That is, the reducing strength of the metal in going to the dichloride is not the major factor in determining its solubility in its dichloride.

It is not possible from the phase diagrams alone to decide on the nature of the solutions of metals and salts; however, the data do show that the mixtures are true solutions because the melting points of the pure substances are lowered by the admixture of the conjugate component. It is further of interest to note the relatively high solubility of salt in metal. This phenomenon must then be considered in the production of pure metals from their halides.

The authors are indebted to Dr. Leo Brewer for valuable suggestions and comments.

Summary

The temperature–composition diagrams for the systems: calcium–calcium chloride, strontium–strontium bromide, strontium–strontium iodide, barium–barium chloride, and barium–barium bromide were determined in the range of about 500 to 1000°. The diagrams are remarkably similar in form. The two liquid components are mutually soluble to a limited extent—the mutual solubility being roughly greater the greater the cation radius.

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[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Imaginary Contact Angles and the Jones–Ray Effect

BY ALBERT SPRAGUE COOLIDGE

When the surface of a liquid forms a concave meniscus in a cylindrical tube or between parallel plates, it is usually stated that it must either be tangent to the walls[1] (perfect wetting) or meet them at an angle of contact α, accordingly as the free energy of the solid–vapor interface is equal to or less than the sum of those of the solid–liquid and liquid–vapor interfaces. Let these energies be denoted by s', s, and σ, respectively, in the case of the first two adopting Gibbs's[2] definition [676] which ignores the unknown but constant energy of the material of the tube or plates. Then

$$\cos \alpha = (s' - s)/\sigma \qquad (1)$$

This gives real values to α only if $s' \leqslant s + \sigma$. The possibility that $s' > s + \sigma$ appears to be excluded by the imaginary contact angle, which can be interpreted as meaning that the meniscus and the wall would nowhere be in contact, and also by energetic considerations, which suggest that the solid–vapor interface would be completely invaded by a thick layer of liquid. Now, Langmuir[3] has recently proposed an explanation of the Jones–Ray effect based precisely on the theory that in dilute electrolytic solutions the meniscus in a capillary rise tube has a sensibly smaller radius than that of the tube itself, because of the presence above it of a wetting film which reduces by its own thickness the effective radius of the tube. According to the strict thermodynamic analysis of Gibbs, however, such a film is merely adsorbed at the solid–vapor surface, and does not constitute a separate bulk phase with a determinable thickness. Hence it is legitimate to say that in the Langmuir model the meniscus and wall do not meet and there is an imaginary contact angle. It is the purpose of this investigation to show that such an imaginary angle of contact is in harmony with mechanical and thermodynamical requirements, but that Langmuir's method of calculating the resulting correction to the apparent surface tension of a liquid is incorrect.

As a simple basis for discussion let us take a system in which all phase boundaries are normal to a common plane, which they intersect in one of the patterns shown in Fig. 1. The heavy lines represent a pair of parallel plane walls, and the circular arcs show the cylindrical portions (hereafter called menisci) of free surfaces separating masses of an involatile liquid from effectively empty space. We shall presently see that these free surfaces must be expected to depart from their cylindrical figure in the immediate neighborhood of the walls, as indicated qualitatively in the right-hand halves of the figures. The left-hand halves are drawn differently in order to show the geometrical relations, but do not imply any asymmetry in the actual systems. We shall ignore gravity, making the orientation immaterial, but for definiteness in future references we shall picture the walls and the common normal plane (the paper) as vertical. In each of the six cases shown, let R be the radius of the meniscus, reckoned positive for a concave surface, and let Δ be the distance from one wall to the nearest vertical plane which can be drawn tangent to the complete cylinder of which the meniscus forms a part, reckoned positive if this plane lies between the walls. Furthermore, let α be a parameter, called the contact angle, and defined as the number whose cosine is equal to $1 + \Delta/R$ in cases (a), (b) and (c), or to $-1 + \Delta/R$ in cases (d), (e) and (f). In the first and last cases α

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[1] In this paper the word "wall" will be used for brevity to indicate the inside surface of the tube or plate.

[2] All references to Gibbs are from "The Collected Works of J. Willard Gibbs," Vol. I, Longmans, Green and Co., New York, N. Y., 1928. Equation numbers in [ ] are from the paper "On the Equilibrium of Heterogeneous Substances."

[3] I. Langmuir, *J. Chem. Phys.*, **6**, 873 (1938).

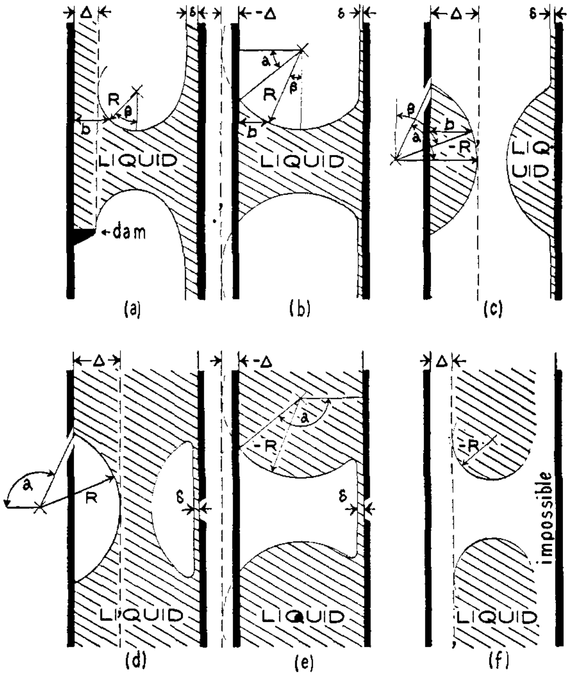

Fig. 1.

is imaginary; in the others it will be seen to be just the angle at which the cylinder intersects the wall, acute in cases (b), (c) and obtuse in cases (d), (e). The special cases in which $\alpha = 0$, $\alpha = \pi/2$, $\alpha = \pi$, or $R = \infty$ are not shown but can be readily derived from the others.

Let us formulate the conditions for the balance of vertical forces in these systems. The equations derived from the first three and from the last three cases will differ in certain signs owing to the difference in the definition of α, and it will be sufficient for our purposes to consider only cases (a), (b) and (c), since the others would yield nothing essentially different. We may regard the surface energies s, s' and σ as tensions at the interfaces, while the liquid is the seat of an ordinary hydrostatic pressure p. The value of σ is necessarily positive, but the other quantities may have either sign. In each of our three cases it is a condition of mechanical equilibrium that the vertical component of the force resulting from the combined action of the pressure and the tensions must be the same across every horizontal plane. Let this force be reckoned positive when it is an attraction between the parts of the system on opposite sides of the plane. For definiteness let us limit our consideration to a section of the system contained between two planes parallel to the paper and at unit distance apart; then for any plane wholly above or below the liquid the force is $2s'$. For a plane intersecting the meniscus at a distance b inside each wall it is $2(s + \sigma \sin \beta - pb)$, where β is the angle between a vertical radius and one drawn to the intersection. Now by geometry $b = \Delta + R(1 - \sin \beta)$, and the condition that the result be independent of β requires that $p = -\sigma/R$. Hence we may write the condition for force balance

$$s' = s + \sigma \sin \beta + (\Delta + R - R \sin \beta)\sigma/R \qquad (2)$$

Putting $\beta = \pi/2 - \alpha$ reduces this to (1), which for cases (b) and (c) has its familiar interpretation in terms of the forces acting on the line in which the surfaces meet, but remains purely formal for case (a). Putting $\beta = 0$ gives

$$s' = s + (\Delta + R)\sigma/R \qquad (3)$$

which can be obtained directly for cases (a) and (b) by considering the forces across a plane between the two menisci, while for case (c) it remains purely formal. Finally, putting $\beta = \pi/2$ gives

$$s' = s + \sigma + \Delta\sigma/R \qquad (4)$$

which in all three cases can be regarded as the condition for force balance in an imaginary similar system in which the walls have been displaced toward each other by the distance Δ, becoming tangent to the free surface (extrapolated if necessary), while the tension at the solid–liquid surface has been increased by the amount $\Delta\sigma/R$. The formal significance of this interpretation will appear later.

In case (a) a useful alternative interpretation is possible. Instead of moving the walls and altering their tensions, let us imagine the gaps closed by little dams attached to the walls in such a way that they can slide freely up and down but cannot tip over. Then with regard to translation they will be in equilibrium under the opposing tensions s' and s acting at their bases, the tension σ at their crests, and the pressure $-\sigma/R$ acting on their faces from the liquid side, while the torques due to these forces are automatically absorbed by the rigid wall.

It is clear that the condition for force balance can be satisfied for any values of s, s' and σ. But case (a) does violence to the notion of surface energies as forces residing in the interfaces and capable of being balanced only by other similar forces in interfaces having edges in common, a fact which may seem to rule out the possibility that $s' > s + \sigma$. Yet simple thermodynamic reasoning shows that this inequality must be expected to hold whenever a perfectly wetting liquid forms a concave meniscus, as a result of the pressure differential produced by the curvature of the interface. Consider a pure liquid wetting a plane wall, and suppose that the three surfaces satisfy $s' = s + \sigma$ when liquid and vapor are under the same pressure. The explanation of this equality is presumably that when the bare solid surface is exposed to the saturated vapor of the liquid, it picks up an adsorbed film which cannot come to thermodynamic equilibrium with bulk liquid under a plane surface, *i. e.*, have the normal chemical potential μ_0 of the saturated liquid–vapor system at the given temperature, until it has grown so thick that its outer layers are out of range of the molecular field of the wall; it will then be actually a normal liquid phase and the combined tension of its two surfaces will be just $s + \sigma$. There will thus be much stronger positive adsorption at the solid–vapor surface than at either of the liquid boundaries, where no such local variation of density is to be expected in comparison with the adjacent bulk phases. Now if the liquid has a concave free surface the potential will be less than μ_0, and the interfacial tensions will increase by amounts proportional to the adsorption at each, in accordance with the familiar Gibbs equations [508], [678]. Hence, s' will become greater than $s + \sigma$.

This seeming contradiction between the requirements for mechanical and for thermodynamic equilibrium can be traced to neglect of the finite thickness of the layer in which the surface forces actually operate. It is, of course, generally realized that such a spread does in fact exist, but Gibbs has established conventions by which, for certain purposes, it may be ignored. Thus, in a system of fluid phases the exact values of the pressures in the homogeneous parts, and of the forces transmitted across imaginary planes normal to the interfaces and extending into the homogeneous regions on both sides, can be calculated by supposing the phases to have everywhere their normal bulk properties, and to be separated by infinitely thin tense membranes located at the "surfaces of tension" defined on page 229. Moreover, eq. [508] holds exactly when this surface is made the basis for calculating the adsorption. For a plane solid surface Gibbs prefers another convention, which is not uniquely specified by his statement that the mathematical surface (plane) of reference is to be "determined in some definite way by the exterior particles of the solid" (p. 328). Apparently he did not notice that the value of s defined by [676] (but not of s') depends on the choice of reference plane, in contrast to that of σ which, for a plane interface, does not; for he states that s and σ (for the same interface) differ only by a constant term, namely, the surface tension of the solid in a vacuum. It will be shown in the Appendix that this is true only for the special choice of reference plane which makes equal to zero the calculated adsorption of the material of the solid phase. However, [678] holds exactly for any reference plane provided this same plane is used in calculating the adsorption, and the total force across a plane perpendicular to the wall can be correctly calculated as the algebraic sum of a tension s in a membrane exactly at the reference plane and the pressure (if any) in a layer of normal liquid extending exactly up to this plane. Hence consideration of the finite spread of the seat of surface forces leads to no modification of eqs. (1) to (4) provided R be taken as the radius of the surface of tension; they remain exactly valid for any choice of a mathematical plane to represent the physical surface of the wall, including that which makes the contact angle vanish (see next paragraph) and that which makes the adsorption of solid vanish. The latter is, of course, a much better approximation to the "real" surface, and it is to values of s and α calculated on this basis that the reasoning of the preceding paragraph applies.

But it cannot be concluded without further investigation that in all possible cases the conditions for equilibrium can be accurately obtained from the membrane model; for in the first place the moment of the actual forces about the surface is not the same as though they were concentrated at the surface of tension (for proof in a particular case see eq. (10) below), and in the second place the very definition of this surface breaks down in a region where three phases are in close proximity. In the Appendix it is shown that when the three phases are fluids under the same pressure, the surfaces of tension, in those regions where they are defined, lie in three planes which, when produced, intersect in a common line at the exact angles required by the membrane model, and the limitation to plane interfaces does not seem to be essential to the method of proof. But this method cannot be applied to a solid wall, as is evident from the arbitrariness in choice of the reference plane (which indeed could be chosen differently for the two parts of the wall in contact with the two other phases). Moreover, the value of the angle of contact depends upon this choice. In fact, whether real or imaginary according to any natural location of the reference plane, this angle can always be made to vanish by choosing a new plane at a distance Δ from the natural one. To be sure, this displacement, and the corresponding alteration in s, will depend inconveniently upon the curvature of the free surface of the liquid; but this does not involve any contradiction, for with reference to the displaced plane there will appear to be a large positive or negative adsorption of liquid, causing s to be very sensitive to the changes in μ accompanying alterations in curvature. It appears, then, that cases in which the meniscus and the wall, as naturally defined, fail to meet cannot be excluded as inconsistent with the strict application of accepted principles. As a useful geometrical model it seems best to select a reference plane approximating the physical wall, and to accept the fictitious sliding dam as replacing the actual properties of the inhomogeneous region between the three phases, just as the fictitious membrane replaces those of the region between two phases.

To get a more realistic picture we must abandon the membrane model and recognize explicitly the thickness of the wetting layer. Let us suppose that the wall has a well-defined physical surface which we will take as the plane of reference in calculating s, and that the bulk liquid has a similar physical surface which closely corresponds to the surface of tension. Over that part of the wall which is not immersed in bulk liquid let us imagine material of the liquid phase spread to a small variable thickness δ, measured from the wall itself to a free surface similar to that of the liquid in bulk. (Two specific models meeting these requirements will presently be examined in detail.) The tension s' (which need not be assigned to any plane) will depend upon δ in a way which can be calculated for any molecular model, and so will the potential μ. We may identify the phase boundaries of Fig. 1 with the physical surfaces of the wall and the bulk liquid. Then three conditions must be met. First, μ must have the same value for the film as for the meniscus. Second, s, s', σ and α must satisfy the equation of force balance, which it will be remembered has been derived without any reference to conditions in the special region near all three phases. Third, this special region must constitute a transition zone in which the physical surface of the wetting film goes over continuously and smoothly into that of the meniscus. If we take δ as the independent variable, then the first condition determines R and the second α, the two together fixing Δ, while the third condition must be automatically capable of being satisfied.

Among the many ways in which μ may depend upon δ, let us select the four indicated schematically in Fig. 2, in which $\mu - \mu_0$ is plotted against δ. Only small absolute values of $\mu - \mu_0$ will occur in practice, since the radii of experimental surfaces are always much greater than the range of molecular forces. Moreover, no film can be internally stable unless $d\mu/d\delta > 0$, for in the opposite case the slightest disturbance would cause it to break up into thicker and thinner sections. We need therefore consider only two types of film, corresponding to the heavily inked parts of the curves marked (1) and (2). A film of type (1) may be said to be stabilized by its thinness, and can be in equilibrium with bulk liquid only if the latter is equally stabilized by the concavity of its surface. The transition zone is therefore one in which the cause of stability goes over continuously from thinness to concavity. The simplest assumption is that the respective effects of the local thickness and the local curvature are additive and equal respectively to their values for plane films of the same thickness and for cylindrical menisci of the same radius of curvature. This should be a good approximation if the effects are small and their variation gradual, which is precisely the conclusion to which the assumption leads, thus justifying itself *a posteriori*. For as the thickness increases from its lower limit δ, the resulting stability decreases monotonically from its original small value to zero; the compensating stability and the curvature which produces it must therefore increase monotonically from zero to their small limiting values in the meniscus. The only possibility is that shown on the right side of Fig. 1(a), from which it can be seen that the smallness of the local curvature ensures the gradualness of the change of thickness near the wall, and hence of the variation in the separate causes of stability. The angle of contact is imaginary; not only does the extrapolated curve of the meniscus fail to meet the wall, but it fails to meet the extrapolated inside surface of the wetting film (as Langmuir unjustifiably assumes), so that $\Delta > \delta$.

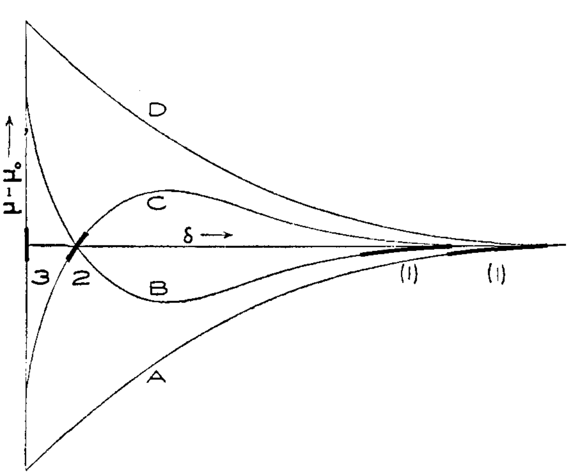

Fig. 2.

A film of type (2) can be in equilibrium with either a concave or a convex meniscus (or with a plane surface). On the basis of our previous assumption, the surface in the transition zone must now be sharply concave in order to offset the high instability corresponding to thicknesses somewhat greater than δ, resulting in a finite contact angle as indicated in Figs. 1(b), (c), (d) and (e). The reasoning has now only qualitative validity since the conditions justifying the assumption are not well fulfilled (unless the contact angle is very small), but it seems clear that in a general way the angle at which the surface emerges from the transition zone will be the greater, the bigger is the hump in the μ,δ curve which must be compensated by concavity. It should, of course, be possible to establish this relationship without discussing the transition zone at all, since the angle of contact depends only on the properties of the three interfaces. It will therefore hold even in the limiting case obtained by allowing the rising portion of the μ,δ curve to coincide with the μ-axis, so that $\mu - \mu_0$ is positive for all positive values of δ. This case is represented in Fig. 2 by the heavily inked region numbered (3). There is now no real film and the previous train of reasoning cannot be carried through. But in general it must be expected that the surface of the liquid will become sharply curved, either concave or convex, very near the wall, in order to offset the perturbation which the proximity of the wall must produce in the value of μ.

It will be noticed that no instance of a situation like Fig. 1(f) has been found. It can be shown that such a system can arise only if there is an actual repulsion between liquid and wall, resulting in an "antiwetting film" or empty space between them; the surface of the liquid then goes through a convex transition zone between the meniscus and the plane part facing the wall. Cases analogous to

Figs. 1(e), (d), (c) and (b) can also be constructed with anti-wetting films and convex transition zones, but have no bearing on the present problem and will not be discussed further.

It is illuminating to develop the theory along the lines devised by Laplace and summarized, for example, by Maxwell,[4] from whose article much of the following material and nomenclature is taken. The liquid is treated as continuous, incompressible, and bounded by perfectly sharp surfaces. For simplicity its density may be taken as unity and that of its vapor as negligible. Between every two elementary masses $\mathrm{d}m_1$, $\mathrm{d}m_2$ (or $\mathrm{d}v_1$, $\mathrm{d}v_2$) at a relative distance r there is assumed to be an attractive force $\phi(r)\mathrm{d}m_1\mathrm{d}m_2$; the attractions of the several parts are additive and can be represented by a force field characterized by a potential function $\chi(x, y, z)$ such that $-x\mathrm{d}m$ is the work required to remove to infinity a particle of mass $\mathrm{d}m$ located at x, y, z. (More briefly, χ is the potential energy of a unit particle at x, y, z.) Thermal effects being ignored, the energy of the whole mass of liquid is

$$\epsilon = \tfrac{1}{2}\int\int\int \chi \mathrm{d}v$$

the integration being over the whole volume. (By a curious lapse, Maxwell omits the factor $^1/_2$, so that his formula (27) is twice too large.)

The relation between χ and $\phi(r)$ is conveniently expressed in terms of the following integrals:

$$\Pi(z) = \int_z^\infty \phi\,(z)\mathrm{d}z \qquad \psi(z) = \int_z^\infty z\Pi(z)\mathrm{d}z$$

$$\theta(z) = \int_z^\infty \psi\,(z)\mathrm{d}z \qquad \xi(z) = \int_z^\infty z\psi(z)\mathrm{d}z = z\theta(z) + \int_z^\infty \theta(z)\mathrm{d}z$$

$$2\pi\theta\,(0) = K \qquad 2\pi\xi\,(0) = H$$

It is assumed that the law of force is such that these integrals converge for $z = 0$ and are effectively zero for z greater than some assignable small distance q. It is found that $2\pi\psi(z)$ and $-2\pi\theta(z)$ give, respectively, the force on a unit particle and its potential energy when it is at a distance z outside the plane surface of a mass of liquid of depth greater than q, so that the potential at such a surface is $-K$ and that at any point deep in the interior is $-2K$.

It can be shown, most simply by energetic considerations, that the surface tension is $\pi\xi(0) = \frac{1}{2}H$ and that in a plane layer of liquid of thickness c less than q the total tension is $2\pi[\xi(0) - \xi(c)]$. Now these and other similar results may also be obtained by the method of force balance, which, though less elegant, yields a much clearer picture of the mechanism involved. Since the liquid does not collapse under the mutual attraction of its parts, we deduce the presence of an additional repulsion, which exactly balances the attraction when there is no external pressure. To explain the postulated incompressibility we have to suppose that the repulsion has a negligible range, acting only between infinitely thin layers of matter in immediate contact, and automatically adjusting itself to maintain equilibrium without sensible changes in density. Such a repulsion will contribute nothing to the energy because of its vanishing range, but will enter the force balance in the form of a variable internal hydrostatic pressure p_i. At equilibrium the body and surface forces acting on every elementary volume $\mathrm{d}v$ must add to zero; hence

$$\nabla p_i \mathrm{d}v = -\nabla \chi \mathrm{d}v$$

Integrating with the boundary condition that p_i must vanish everywhere over a free surface, we obtain

$$p_i = \chi_0 - \chi \qquad (5)$$

where χ_0 is the common value of the potential at all points of the surface. At a point in the interior of a thick layer with a plane surface, p_i reduces to Laplace's "intrinsic pressure" K. In general it is not the same as the measured pressure p, or total force per unit area upon a solid plane wall, but differs by a term arising from the adhesion.

Let us now attempt to describe the interplay of attractive and repulsive forces by associating them with elementary areas instead of volumes. For the repulsion this is always possible. For the attraction it proves possible in regions remote from boundaries, and also near a plane or cylindrical boundary for elementary areas oriented parallel or perpendicular to the first or perpendicular to the axis of the second. Let the elementary area form the base of a perpendicular column extending away at least for a distance q from the plane on which it stands, unless cut off by a boundary. Then this column will be attracted by all the matter on the other side of the plane, with a force proportional to the area of its base. Under the conditions stated, it is easily established that the component of this force perpendicular to the plane will be equal in magnitude and opposite in direction to the corresponding force upon a column similarly constructed on the other side of the plane, and can therefore be treated as the result of a tension acting across the plane. Its magnitude is evidently equal to the work which would be done on a particle of mass numerically equal to the elementary area in moving it over the length of the column against the attraction of all matter beyond the plane. The tension across this plane is therefore equal to the potential difference between the ends of the column, in the field of the matter beyond the plane. For any plane deep in the interior it will have the value K, but near boundaries it will be smaller and will depend on the orientation of the plane.

Let a deep body of liquid have a horizontal surface which we may take as the x,y plane, with z measured down into the liquid; then the tensions across horizontal and vertical planes at any depth can be defined as above and denoted by $t_z(z)$ and $t_x(z) = t_y(z)$, respectively. Upon a vertical column extending from the level z up to the surface the

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[4] J. C. Maxwell, "Encyclopedia Britannica," 11th ed., 1910, Vol. V, p. 256.

only forces which do not cancel out by symmetry are the pressure and the tension on its base; hence $t_z = p_i$ for every z, both ranging in magnitude from K in the interior to zero at the surface. In the interior, likewise, $t_x = p_i = K$, but t_x falls only to half this value at the surface, near which therefore $t_x > p_i$. Thus, contrary to frequent statements, there exists a real contractile force in the surface layer, any portion of which would collapse if not supported in some way at the edges.

To calculate this force we observe that at an interior point near any boundary the potential differs from its value deep inside by an amount equal to the potential which an infinite mass beyond the boundary would produce at the given point. Hence in the present case $\chi(z) = -2K + 2\pi\theta(z)$, and putting $\chi_0 = -K$ into (5) gives

$$p_i(z) = K - 2\pi\theta(z) \qquad (6)$$

To find $t_x(z)$ we must consider a horizontal column based upon the y,z plane at a depth z, and extending indefinitely to the left (negative x) as shown in Fig. 3. The matter to the right of the plane produces the potential $\frac{1}{2}\chi(z)$ at the plane and zero at a great distance beyond it to the left. Hence

$$t_x(z) = K - \pi\theta(z) \qquad (7)$$

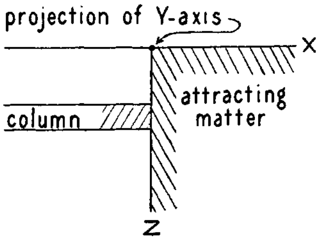

Fig. 3.

and the net contractile force per unit area is

$$f_x(z) = t_x(z) - p_i(z) = \pi\theta(z) \qquad (8)$$

Upon integrating over z from the surface to a great depth we obtain the surface tension

$$\sigma = \pi\xi(0) = \tfrac{1}{2}H \qquad (9)$$

as before. It is apparent that the force across a vertical plane is not for all purposes equivalent to one of equal magnitude concentrated in the surface. For this latter would exert no torque about the line in which the plane intersects the surface, whereas the actual force system produces such a torque equal, per unit length of the line, to

$$\pi \int_0^\infty z\theta(z)\mathrm{d}z = \tfrac{1}{2}\pi \int_0^\infty z^2\psi(z)\mathrm{d}z$$

corresponding to an equal force concentrated in a plane below the surface at the depth

$$\bar{z} = \int_0^\infty z^2\psi(z)\mathrm{d}z \Big/ 2\int_0^\infty z\psi(z)\mathrm{d}z \qquad (10)$$

Now it will shortly appear that in Laplace's model the physical surface is identical with the surface of tension. It is clear, then, that the membrane model is not automatically applicable to problems involving torques.

If the free surface is concave with principle radii R_1, R_2, then p_i and χ will be altered by correction terms which, if small enough, will be linear in $1/R_1$ and $1/R_2$. To this approximation, the potential at a point distant z outside the surface is given by Maxwell as $-2\pi\theta(z) - \pi(1/R_1 + 1/R_2)\xi(z)$, and it is easy to show that for a convex surface the correction merely changes sign. Hence, reasoning as before, the potential at a point z inside a concave surface is

$$\chi(z) = -2K + 2\pi\theta(z) - \pi(1/R_1 + 1/R_2)\xi(z) \qquad (11)$$

and putting

$$\chi_0 = -K - \tfrac{1}{2}H(1/R_1 + 1/R_2) \qquad (12)$$

gives

$$\rho_i(z) = K - 2\pi\theta(z) - (1/R_1 + 1/R_2)[\tfrac{1}{2}H - \pi\xi(z)] \qquad (13)$$

Deep in the interior this reduces to

$$\rho_i(\infty) = K - \tfrac{1}{2}H(1/R_1 + 1/R_2) \qquad (14)$$

The first term is just balanced by the attraction, while the second term constitutes a deficit which, in the case of a large body in contact with a plane wall, would have to be balanced by an outward pull on the wall, and therefore constitutes a negative measured pressure $\sigma(1/R_1 + 1/R_2)$. Now, this is just the result given by the membrane model and at first sight appears to establish the identity of the physical surface with the surface of tension. Inspection shows, however, that it is necessary to examine higher approximations in the expression for the potential, for if R_1 and R_2 were measured from a slightly different surface the resulting changes in $1/R_1$ and $1/R_2$ would be quadratic in these quantities and would not be detected by the linear approximations. At least in the spherical case it is easily shown that the exact form of (13), so long as $R > q$, is

$$\rho_i(z) = K - 2\pi\theta(z) - H/R + \frac{2\pi}{R+z}\xi(z) \qquad (13')$$

This reduces exactly to (14) in the interior, completing the demonstration.

Let us now consider a cylindrical concave free surface, of radius R, tangent to the x,y-plane along the y-axis, and calculate the force between the parts separated by the y,z-plane, per unit length along the y-axis. As this is not one of the allowed cases, the previous method will need to be modified. We may find the x-component of the attractive force per unit cross-section on a long column extending to the left of the y,z-plane (Fig. 4).

$$t_x(z) = -\tfrac{1}{2}\chi(z) = K - \pi\theta(z) + (\pi/2R)\xi(z) \qquad (15)$$

Subtracting $p_i(z)$ gives the net contractile force

$$f_x(z) = \pi\theta(z) + (1/2R)[H - \pi\xi(z)] \qquad (16)$$

If we integrate this from the surface down to some large distance b, we obtain

$$\tfrac{1}{2}H(1 + b/R) - (\pi/2R)\int_0^\infty \xi(z)\mathrm{d}z$$

where the term in b is just the contribution from the measured negative pressure. The remainder

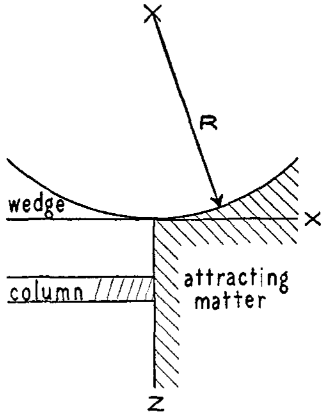

Fig. 4.

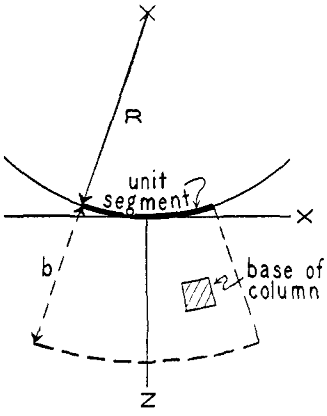

Fig. 5.

gives the additional force on the matter in the lower left-hand quadrant, but neglects the force on the hollow wedge above it, which cannot be represented as acting across any surface. Disregarding the attraction between the two wedges, which is quadratic in $1/R$, it is easily shown that the attraction between the left-hand wedge and the matter in the right-hand lower quadrant just cancels the last term in the expression above, so that the total force exchanged across the y,z-plane is the same as though the measured pressure acted just up to the physical surface and an additional tension $\frac{1}{2}H$ acted exactly in it, according to the membrane model. The value of σ is the same as for a plane surface, for the additional attraction due to the wedges is just compensated by the fact that there is a smaller drop in the internal pressure in going from the interior to the surface. In accordance with the Gibbs adsorption equation, the invariance of σ with the (measured) pressure, *i. e.*, with μ, requires that there be no adsorption at the surface; this is evidently true with reference to the physical surface of an incompressible liquid, and confirms the identification of this with the surface of tension.

The torque about the y-axis can be found by multiplying (16) by z and integrating from 0 to b, the wedge correction being omitted because (to the first approximation) the force involved has no leverage about the axis. The result is

$$\tfrac{1}{2}Hb^2/2R + \frac{\pi}{2}\int_0^\infty z^2\psi(z)\,\mathrm{d}z - (\pi/4R)\int_0^\infty z^3\psi(z)\,\mathrm{d}z$$

The first term comes from the measured pressure, and the last term represents the effect of the curvature on that part of the torque which is associated with the surface of discontinuity.

Let us now find the force exchanged across the x,z-plane, taking columns based upon that plane and extending on the side of negative y, as in Fig. 5. The y-component of the contractile force per unit area is again (16), and there is now no wedge correction, since the columns fill the entire region upon which the force is to be calculated. But in comparing this force with an imaginary tension in the surface, we must ascribe to each unit segment of the latter (measured in the x,z-plane) the actual force across a fan-shaped area spreading out radially from it to some great distance b, diminished by the contribution from the measured pressure. The area of the fan is $b + b^2/2R$, and the total force across it is

$$\int_0^b f_x(z)\frac{R+z}{R}\,\mathrm{d}z = \tfrac{1}{2}H[1 + b/R + b^2/2R^2] - \frac{\pi}{2R^2}\int_0^\infty z\xi(z)\mathrm{d}z \quad (17)$$

The terms in b come from the measured pressure and the last term is quadratic in $1/R$ and can be neglected, so that the equivalent tension on the surface is again $\sigma = \frac{1}{2}H$. The reduction in internal pressure drop is now compensated half by the extra attraction arising from the curvature and half by the increase in area counted because of the fanning.

Spherical or ellipsoidal surfaces can be treated similarly. Taking both wedge and fan effects into account, the standard formulas are readily obtained.

The proximity of a wall (or other homogeneous phase) can be treated by introducing quantities ψ',θ',ξ',K',H', derived exactly as before from the function $\phi'(r)$ which gives the attractive force between a unit particle of the liquid and one of the wall material. Suppose a layer of liquid of thickness δ spread upon a thick plane wall, and let z be measured from the wall into the liquid. Then

$$\chi(z) = -2K + 2\pi\,[\theta(z) + \theta(\delta - z) - \theta'(z)] \quad (18)$$

$$\chi_0 = \chi(\delta) = -K + 2\pi[\theta(\delta) - \theta'(\delta)] \quad (19)$$

$$p_i(z) = K + 2\pi[\theta(\delta) - \theta(z) - \theta(\delta - z) - \theta'(\delta) + \theta'(z)] \quad (20)$$

$$t_x\,(z) = K - \pi[\theta(z) + \theta(\delta - z)] \quad (21)$$

$$f_x\,(z) = \pi[\theta(z) + \theta(\delta - z) - 2\theta(\delta) + 2\theta'(\delta) - 2\theta'(z)] \quad (22)$$

The wall contributes nothing to t_x since, by symmetry, it can exert no tangential force on any particle of liquid. Its sole effect is to increase p_i, which must support the weight of the layers of liquid above in the extra field of the wall. Integration from 0 to δ gives the total tension in the layer

$$\mathfrak{s}' = H - H' - 2\pi[\xi(\delta) - \xi'(\delta)] = -2\pi \int_0^\delta z\psi''(z)\mathrm{d}z \quad (23)$$

where ψ'' is an abbreviation for $\psi' - \psi$. For a thick layer this reduces to

$$\sigma + \mathfrak{s} = H - H' \quad (24)$$

whence

$$\mathfrak{s} = \tfrac{1}{2}H - H' \quad (25)$$

Putting these values into (1) gives for the contact angle

$$\cos \alpha - 1 = (4\pi/H) \int_\delta^\infty z\psi''(z)\mathrm{d}z = (4\pi/H)\xi''(\delta) \quad (26)$$

where ξ'' is an abbreviation for $\xi' - \xi$.

In order to construct the μ,δ curve we must identify the thermodynamic potential of a mass of liquid having the properties postulated. Suppose the mass has a free surface of any configuration, to which we may suppose added an infinitesimal layer of liquid, of mass dm; then the energy of the system is increased by the amount $\mathrm{d}\epsilon = \chi_0\mathrm{d}m$ (actually negative). Comparing this with the general thermodynamic relation $\mathrm{d}\epsilon = t\mathrm{d}\eta - p\mathrm{d}v + \sigma\mathrm{d}s + \mu\mathrm{d}m$, and observing that in a purely mechanical model the entropy η is zero and p and ds vanish in the process described, we see that μ is to be identified with the mechanical potential at the surface, χ_0 (or, more generally, with the constant value of $\chi + p_i$ everywhere in the liquid). For a plane wetting film of thickness δ, (19) then gives

$$\mu - \mu_0 = -2\pi \int_\delta^\infty \psi''(z)\mathrm{d}z = -2\pi\theta''(\delta) \quad (27)$$

where θ'' is an abbreviation for $\theta' - \theta$. In view of (12), the radius of the meniscus in thermodynamic equilibrium with this film is given by

$$1/R = (4\pi/H)\theta''(\delta) \quad (28)$$

For systems like Fig. 1(a), (b) or (c), we find, using (4), (23), (24), (25) and (28)

$$\Delta = \xi''(\delta)/\theta''(\delta) \quad (29)$$

whence

$$\Delta - \delta = \int_\delta^\infty (z - \delta)\psi''(z)\mathrm{d}z \Big/ \int_\delta^\infty \psi''(z)\mathrm{d}z \quad (30)$$

The relation between the angle of contact and the μ,δ-curve can now be given exactly (for this particular model). The integral in (26) can be written in the form

$$\int_\delta^\infty \theta''(z)\mathrm{d}z + \delta\theta''(\delta)$$

Combining with (27), we obtain

$$1 - \cos \alpha = \frac{2}{H}\left[\int_\delta^\infty (\mu - \mu_0)\mathrm{d}\delta + \delta(\mu - \mu_0)\right] \quad (31)$$

The left side varies in the same sense as α. On the right side, the integral is just the area under the $\mu - \mu_0$ curve for values of δ greater than the thickness of the film, while the second term vanishes exactly for a plane free surface and approximately for the slightly curved menisci which always occur in practice. Thus the qualitative relation inferred from consideration of the transition zone is verified.

We may assume that both $\psi(z)$ and $\psi'(z)$ are positive, monotonically decreasing functions. If $\psi'(z) \geqslant \psi(z)$ for all values of z, then ψ'', θ'' and ξ'' will necessarily be positive and the μ,δ-curve will be of type A, Fig. 2, giving imaginary contact angles. The major contributions to the integrals $\theta''(\delta)$ and $\xi''(\delta)$ will come from the values of the integrands $\psi''(z)$ and $z\psi''(z)$ for z just larger than δ. Hence, by (29), Δ will be of the order of magnitude of δ, and ordinarily below the range of observation, but (30) shows that it must be greater than δ, as anticipated. Similar results will follow if the μ,δ-curve is of type B owing to $\psi'(z)$ being greater than $\psi(z)$ for large z and smaller for small z. In the contrary case $\psi''(z)$, $\theta''(z)$ and $\xi''(z)$ will all be negative (or zero) for large z, but as z decreases the first function must, and the other two may, change sign at certain values z_1, z_2, z_3, respectively, where necessarily $z_1 > z_2 > z_3$. This gives a μ,δ-curve of type C, with real contact angle and δ very nearly equal to z_2. In this region $\xi''(\delta)$ is negative and ordinarily much larger absolutely than $\delta\theta''(\theta)$, so that Δ will in general be much greater absolutely than the range of molecular forces. By (26) the contact angle will be acute or obtuse accordingly as $\xi''(\delta)$ is smaller or greater absolutely than $\frac{1}{2}\xi(0)$. It would again become imaginary, as in Fig. 1(f), if the absolute value of $\xi''(\delta)$ exceeded $\xi(0)$, but it can be readily shown that this is impossible unless $\psi'(z)$ is negative at least somewhere in the range $z > \delta$. Finally, if $\psi'(z) \leqslant \psi(z)$ for all z the μ,δ-curve is of type D and no wetting film can form; $\xi''(\delta)$ reduces to $\xi''(0)$, which is negative and gives a real contact angle independent of the curvature of the meniscus.

The Laplace model is admittedly only a rather crude approximation to the nature of an actual liquid. Nevertheless the results to which it leads are extremely suggestive, and should be a fairly reliable picture of the true state of affairs near the surface of a real liquid in bulk, or of wetting layers thick enough to have nearly the properties of liquid in bulk, such as those giving imaginary contact angles For thinner layers, or for no layer, the method is more questionable. Thus, if the stability of a single molecule of the liquid in contact with the wall is positive, but less than that of a molecule at a normal free surface, the mechanical model predicts that the wall will be completely bare, while actually the Boltzmann principle ensures the presence of at least some adsorbed molecules, as in the case of mercury on a carbon wall.[5] These, of course, must modify $\mathfrak{s}'$ and make it, at least in principle, dependent upon the curvature of the meniscus.

We shall now consider the wetting of a charged wall by a dilute solution of an electrolyte, which

(5) A. S. Coolidge, THIS JOURNAL, **49**, 1949 (1927).

for simplicity we shall take to be of the valence type 1–1. According to Langmuir's theory, the wetting film has a thickness of the order of magnitude of $1/\kappa$ (his λ), which is so much greater than the range of ordinary molecular forces that it is permissible to treat the solvent as a continuous medium having its ordinary large-scale properties. These are assumed to be wholly unchanged by the presence of the ions; the liquid is subject to the normal mechanical (non-electrostatic) forces due to its hydrostatic pressure p_m, its surface tensions σ and s, and the thrust of the containing wall. The thermal motion of its molecules is not explicitly considered, but its effects are included in p_m, which is the total rate at which momentum is transferred from the solvent on one side of a plane to that on the other. (It differs from p_i of the previous section by including repulsion as well as attraction.) For simplicity the density and the dielectric constant D will be taken as invariant. The ions are imagined as dimensionless particles whose Brownian movement simulates a thermal pressure

$$p_t = \Sigma n_j \, kT \qquad (32)$$

where n_j is the local concentration of ions of species j. Except at the boundaries (that is, much nearer than $1/\kappa$) they experience no mechanical forces, the exchange of momentum between particles of different species averaging out.

Both solvent and ions experience electrical forces in the prevailing field. The average force on the solvent is of course that corresponding to the average field, and the basic simplifying assumption is that the same is true for the ions. This overlooks the activity coefficients of the ions, which arise from the perturbations which they produce in the average field in their neighborhood. In the interior of the solution (including the interior of the wetting film) the average force systems acting on the different species of particles must be separately in equilibrium. For the solvent, the electrostatic force is balanced by the pressure gradient, from which it follows[6] that

$$p_m = p_0 + (D - 1)E^2/8\pi \qquad (33)$$

where E is the absolute magnitude of the electric field intensity and p_0 is an integration constant. For the ions, the electric force is balanced by the concentration gradient, which is one way[7] of deriving the Boltzmann law. Using Langmuir's abbreviation $\eta = \epsilon\psi/kT$, we may write

$$n_+ = n_0 \, e^{-\eta}, \; n_- = n_0 \, e^{+\eta} \qquad (34)$$

where n_0 is the concentration of the solution far from the wall. In conjunction with (32) this gives

$$p_t = 2n_0 \, kT \cosh \eta \qquad (35)$$

and when combined with the Poisson equation it yields

$$\nabla^2 \eta = \kappa^2 \sinh \eta \qquad (36)$$

To determine p_0 and the boundary conditions for the solution of (36) we must consider the phase boundaries. It is assumed that the wall is charged to a uniform ζ-potential, represented by $\eta_1 = \epsilon\zeta/kT$. For definiteness we may picture the wall charge as a layer of positive ions in the medium, held very close to the wall in sufficient concentration to maintain the constant potential postulated by means of some mechanism which need not be further specified. At the free surfaces of the solution no such layer of charge exists; the escape of ions approaching the surface is in some way prevented and their momentum transferred to the solvent without any modification of the local concentrations specified by (34). (It will be seen that this approximation overlooks the local depletion of both kinds of ions which Onsager and Samaras[8] have shown must result from image forces and from the distortion of the normally symmetrical ionic atmospheres, giving rise to an increase in the surface tension. This defect is not serious, however, for at low concentrations the neglected theoretical increase is much smaller than the apparent decrease due to the Jones–Ray effect.)

For our purposes we need consider only those regions of the system which lie, respectively, well above and well below the transition zone. The upper region is the wetting film, at the surface of which the potential is η_M (in Langmuir's notation) and the field is zero, while the lower region is bounded by the meniscus, where field and potential both vanish. Upon either of these field-free boundaries the pressure p from within the liquid is simply $p_m + p_t$, which (neglecting the vapor pressure) must be zero at the film surface and must balance the tension in the meniscus. Hence, using (33) and (35), we have

$$p = p_0 + 2n_0 \, kT \cosh \eta_M = 0 \quad \text{(for film surface)} \qquad (37)$$

$$p = p_0 + 2n_0 \, kT = -\sigma/R \quad \text{(for meniscus)} \qquad (38)$$

These are evidently just the measured pressures in the two regions, for, regardless of the specific interaction between wall and solution, they must be held in balance by equal external forces applied to each unit area of the wall (or supplied by its rigidity). When n_0, σ and R are assigned, p_0 is determined by (38) and can be substituted into (37) to find η_M. Now, in both the regions considered the electric field is effectively horizontal everywhere, and (36) reduces to the one-dimensional form

$$\mathrm{d}^2 \eta/\mathrm{d}x^2 = \kappa^2 \sinh \eta \qquad (39)$$

where x may be taken as the perpendicular distance from the wall. For the upper region the boundary conditions are $\eta = \eta_1$ where $x = 0$ and $\eta = \eta_M$ where $\mathrm{d}\eta/\mathrm{d}x = 0$; the value of x for which the second condition is fulfilled gives the thickness δ of the film. For the lower region (assuming $R >> 1/\kappa$) we may take as the second condition $\eta \longrightarrow 0$ as $x \longrightarrow \infty$. The corresponding solutions of (39) may be found in Langmuir's paper,

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[6] See for example Leigh Page, "Introduction to Theoretical Physics," D. Van Nostrand Co., New York, N. Y., 1935, second edition, p. 384.

[7] Coolidge and Juda, THIS JOURNAL, 68, 608 (1946).

[8] Onsager and Samaras, *J. Chem. Phys.*, 22, 528 (1934).

and from them may be found E^2, p_m and p_t as functions of x.

Instead of identifying Δ with δ as Langmuir does, we must now determine it separately by considering the balance of vertical forces acting on the contents of a region bounded by the same imaginary surfaces as before, taking into account the electrostatic body forces and the various mechanical forces which act across the boundaries of the region. Among the latter we must include that exerted by the mechanism which regulates the wall charge, since in our picture this charge lies within the region considered. Now, the function of this force is to balance the electrical force upon the wall charge, which is known to be horizontal since by hypothesis the wall is an equipotential surface even in the transition zone. (It should be noted, however, that the part of the field which originates outside the considered region need not be horizontal.) The balancing force is therefore also horizontal and may be neglected for our purpose, and the same is true of the wall thrust which balances the mechanical and thermal pressures. The mechanical and thermal interactions with adjacent portions of the system across the boundaries parallel to the plane of the paper are likewise without vertical components. The only non-electrical forces to be considered are therefore those due to the pressures and surface tensions acting across the upper and lower bounding planes. Reckoned as pulls, they are

$$2[s + \sigma - \int_0^{\delta} (p_m + p_t)\mathrm{d}x] \quad \text{(for upper plane)} \quad (40a)$$

$$2[s - \int_0^{R+\Delta} (p_m + p_t)\mathrm{d}x] \quad \text{(for lower plane)} \quad (40b)$$

Now the electrostatic force upon the contents of any closed surface, plus that due to the variable part of the mechanical pressure in the medium acting across the surface, can be expressed as a surface integral by means of the familiar electrostatic stress tensor.[6] In our case, the field is zero at the walls and the tensor vanishes. Across the planes parallel to the paper the stress is horizontal and can be neglected, since the field is parallel to the planes. For the same reason the stress across the top and bottom planes is vertical, consisting of a pressure of magnitude $DE^2/8\pi$. To get the total force, therefore, we need only replace the integrands in (40a) and (40b) by $p_0 + p_t + DE^2/8\pi$. The actual calculation can be somewhat shortened by the following device. We first observe that, except in the transition zone, the total horizontal force on a vertical slab of liquid parallel to the wall can be derived from a pressure $p_0 + p_t - DE^2/8\pi$ acting on its faces, since the electric stress across a plane perpendicular to the field is a tension. Wherever the field is zero this is just the mechanical hydrostatic pressure, and is equal to the field-free-surface pressure p of eqs. (37) and (38). But equilibrium requires that within either upper or lower region separately the total force across all vertical planes be the same, the effects of variations in field intensity and ion concentration cancelling instead of adding as for horizontal planes. We may therefore put $DE^2/8\pi = p_0 + p_t - p$ for all values of x, replacing the integrands in (40a) and (40b) by $p + 2(p_0 + p_t - p)$. For the upper plane we put $p = 0$, and using (37) and (35) we obtain for the total force across it

$$2\left[s + \sigma - 2\delta p_0 - 2\int_0^{\delta} p_t\,\mathrm{d}x\right] = 2(s + \sigma) + 8n_0kT\left[\delta \cosh \eta_M - \int_0^{\delta} \cosh \eta\,\mathrm{d}x\right] \quad (41)$$

For the lower plane $p = -\sigma/R$, which, together with (38) and (35) gives the force

$$2\left[s + (R + \Delta)\sigma/R - 2\int_0^{R+\Delta} (p_t + p_0 - p)\,\mathrm{d}x\right] = 2(s + \sigma + \Delta\sigma/R) - 8n_0\,kT\int_0^{\infty} (\cosh \eta - 1)\mathrm{d}x \quad (42)$$

the infinite upper limit being permissible when, as always in practice, R is large in comparison with the range of the wall field. Now, Δ must be determined by the condition that the two forces are equal; hence

$$\Delta\sigma/R = 4n_0\,kT[\delta \cosh \eta_M + \int_0^{\infty} (\cosh \eta - 1)\,\mathrm{d}x - \int_0^{\delta} \cosh \eta\,\mathrm{d}x] \quad (43)$$

To facilitate further discussion we shall use Langmuir's notation $\theta = \kappa x$, $\theta_1 = \kappa\delta$, and introduce the abbreviations

$$M = 2(\cosh \eta_M - 1) = 4 \sinh^2 (\eta_M/2) \quad (44)$$

$$E = 2(\cosh \eta_1 - 1) = 4 \sinh^2 (\eta_1/2) \quad (45)$$

$$G = \theta_1 \cosh \eta_M + \int_0^{\infty} (\cosh \eta - 1)\,\mathrm{d}\theta - \int_0^{\theta_1} \cosh \eta\,\mathrm{d}\theta \quad (46)$$

Then the right side of (43) becomes $4n_0kTG/\kappa = F_e$ and gives the net electrical and thermal force acting upon unit width of the junction between wetting film and massive liquid, while in view of (38) and (37) the left side can be written $n_0kTM\Delta = P\Delta$, where P is the difference in the measured pressures at the two planes, and acts over the area Δ in excess of the area R which it requires in order to balance the pull of the surface tension σ. For further use, this relation may be most simply written

$$\kappa\Delta = 4G/M \quad (47)$$

The functions $\eta(\theta)$ in the two integrands in G are different, but both satisfy (39). If we put $-\mathrm{d}\eta/\mathrm{d}\theta = \eta'$, this equation becomes

$$\mathrm{d}^2\eta/\mathrm{d}\theta^2 = -\mathrm{d}\eta'/\mathrm{d}\theta = \eta'\mathrm{d}\eta'/\mathrm{d}\eta = \tfrac{1}{2}\mathrm{d}(\eta')^2/\mathrm{d}\eta = \sinh \eta \quad (48)$$

Integration with respect to η, starting at the point where η' vanishes, gives

$$\eta' = \sqrt{2(\cosh \eta - 1)} \quad \text{for the lower plane} \quad (49)$$

$$\eta' = \sqrt{2(\cosh \eta - \cosh \eta_M)} \quad \text{for the upper plane} \quad (50)$$

(The positive root is the appropriate one.) A second integration gives $\eta(\theta)$, the form depending upon the value of η_M in the case of the upper plane, for which it can be expressed analytically only in terms of elliptic integrals. Langmuir has discussed and illustrated the properties of the η, θ curves, of which three typical examples are shown in Fig. 6. Curve A applies to the lower plane and curve B to the upper when $M = 8$ (giving practically the same curve as ABGH in Langmuir's Fig. 3 except that it has been drawn so that the minimum falls at $\theta = 0.5$ instead of its maximum possible value 1, thus making $\eta_1 = 3$ instead of infinity). The general expression for the initial negative slopes of such curves is found by putting η_1 into (49) and (50) to be

$$\eta_1' = \sqrt{E} \qquad \text{for the lower plane} \qquad (51)$$

$$\bar{\eta}_1' = \sqrt{E - M} \qquad \text{for the upper plane} \qquad (52)$$

For future reference a third curve C is shown, constructed by displacing B to the right (by 0.1 unit in this special case) so that it shall have the same initial negative slope as A (namely, η_1') and the same minimum value as B (namely, η_M), and consequently a higher initial potential than either, which we may call $\bar{\eta}_1$. This is evidently simply the value which must be given to η in (50) in order to make $\eta' = \eta_1'$; hence, by (51) and (44)

$$E + M = 2(\cosh \bar{\eta}_1 - 1) = 4 \sinh^2(\bar{\eta}_1/2) \qquad (53)$$

The first integral in G involves curve A. Taking η as the variable of integration and making use of (49) we readily find

$$\int_{\eta_1}^{0} (\cosh \eta - 1)(\mathrm{d}\theta/\mathrm{d}\eta)\mathrm{d}\eta =$$
$$\int_0^{\eta_1} 2 \sinh^2 (\eta/2)\mathrm{d}\eta/\eta' = 2 \int_0^{\eta_1/2} \sinh (\eta/2)\mathrm{d}(\eta/2) =$$
$$2 \cosh (\eta_1/2) - 2 = \sqrt{E + 4} - 2 \qquad (54)$$

For the second integral, involving curve B, this short cut is not available. However, if we write the integrand in the form $\sinh \eta + e^{-\eta}$, we observe that the first term preponderates for all values of η greater than 0.55, and in most cases will make by far the greater contribution to the integral. In view of (48), this contribution is

$$\int_0^{\theta_1} \sinh \eta \mathrm{d}\theta = -\int_0^{\theta_1} (\mathrm{d}\eta'/\mathrm{d}\theta)\mathrm{d}\theta = \bar{\eta}_1' = \sqrt{E - M} \qquad (55)$$

Using the identity $\sqrt{E + 4} - \sqrt{E - M} = \sqrt{E + 4}[1 - \sqrt{1 - (M + 4)/(E + 4)}]$ and replacing E and M by their definitions, we finally obtain

$$G = \theta_1 \cosh \eta_M - 2 + 2 \cosh (\eta_1/2)[1 -$$
$$\sqrt{1 - (\cosh^2 (\eta_M /2))/(\cosh^2(\eta_1/2))}] - \int_0^{\theta_1} e^{-\eta}\, \mathrm{d}\theta \qquad (56)$$

If $\cosh(\eta_1/2) > 3 \cosh(\eta_M/2)$, the third term in G is given within 3% by $(\cosh \eta_M + 1)e^{-\frac{1}{2}\eta_1}$, and tends to zero for any given η_M as η_1 becomes infinite. In evaluating the last term it will be an adequate approximation, provided η_M is not too small, to replace η in the integrand by the approximate solution of (48) obtained by putting $\sinh \eta \approx \frac{1}{2}e^{\eta}$. This solution is given implicitly in Langmuir's Eq. (43), which can be written

$$\theta = 2e^{-\frac{1}{2}\eta_M} \tan^{-1}\sqrt{e^{\eta - \eta_M} - 1} \qquad (57)$$

where now θ is measured in the opposite direction, from the free surface of the wetting film toward the wall. Introducing the new variable $\xi = \frac{1}{2}\theta e^{\frac{1}{2}\eta_M}$, we readily find $e^{-\eta} = e^{-\eta_M} \cos^2 \xi$. Now, the error in η, as compared to the exact solution of (48), is zero at the origin of ξ and increases without limit as ξ approaches $\pi/2$, for which value the approximate η becomes infinite; but in this neighborhood the exact and approximate values of $e^{-\eta}$ are both extremely small. The integral will therefore be practically insensitive to the upper limit of integration with respect to ξ provided that θ_1 is of the order of magnitude of $\pi e^{-\frac{1}{2}\eta_M}$ (Langmuir's Eq. (44)), which is usually the case. Allowing ξ to run to $\pi/2$, we obtain the estimate

$$\int_0^{\theta_1} e^{-\eta}\, \mathrm{d}\theta \approx 2e^{-\frac{1}{2}\eta_M} \int_0^{\pi/2} \cos^2 \xi\, \mathrm{d}\xi = (\pi/2)e^{-\frac{1}{2}\eta_M} \qquad (58)$$

For small η_M the term can be estimated graphically. Collecting the various approximations gives

$$G \approx \theta_1 \cosh \eta_M - 2 + e^{-\frac{1}{2}\eta_1} (\cosh \eta_M + 1) -$$
$$(\pi/2)e^{-\frac{1}{2}\eta_M} \qquad (59)$$

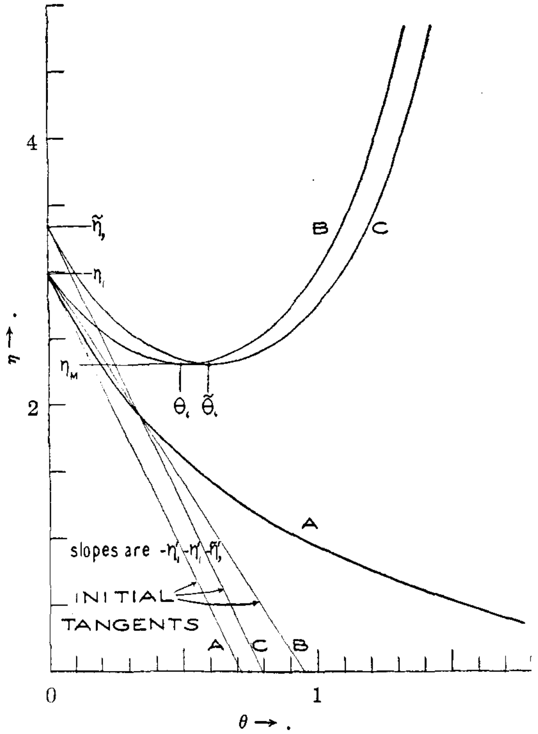

Fig. 6.

The assumption of constant wall potential has not been critically discussed by Langmuir, and appears to be recommended principally by its convenience. An equally convenient alternative assumption is that of constant surface density of charge on the wall, and indeed Langmuir makes this assumption for the air–solution surface, which he takes to be uncharged at all values of the local potential η_M. Consideration of the relations between wall charge and wall potential suggest that neither assumption is likely to be correct, the truth presumably being that for thin wetting layers the wall potential is higher, the wall charge lower, than for walls immersed in the liquid. Let ρ be the charge density on the wall, equal by a familiar relation to $D/4\pi$ times the difference between the normal components of the field intensity on the two sides of the surface. It may be assumed that the material of the wall is so thick that there is no sensible potential gradient in it; then the wall charge is proportional to the initial negative slope of the potential curve in the solution, and is lower for curve B than for curves A and C. Now, whatever may be the mechanism controlling the wall charge, it would be expected to be governed by the local concentrations of the ions, and hence by the local potential (for a given composition of bulk solution). A decrease in wall charge should result only from an increase in potential and consequent increase in the local concentration of ions of opposite sign to that of the wall charge, some of which would tend to react with the wall layer and partially neutralize it. Thus the abnormally low wall charge of curve B (compared to curve A) is incompatible with its normal wall potential. Likewise the abnormally high potential of curve C is incompatible with its normal wall charge. The true curve probably lies somewhere between, but its precise location must await an adequate theory of the mechanism of wall charges. Meanwhile it is of interest to investigate both liming cases.

For the case of uniform wall charge, several modifications must be made in our calculation of the total force on the contents of the selected region. Since in the upper plane the potential curve is now C instead of B, we must replace θ_1 by $\bar{\theta}_1$, the new value of $\kappa\delta$, in (46). Moreover, there is now an upward component of the force from the mechanism regulating the wall charge, which must now equilibrate the downward force exerted upon this charge by the vertical component of the electrostatic field prevailing at the wall in the transition region. If we measure z upward, then the force per unit area is $\rho\partial\psi/\partial z$, and the total force on a strip of unit width extending from the lower to the upper plane is simply ρ times the difference in the wall potential. Since $\rho = DkT\kappa\eta_1'/4\pi\epsilon$ and $\kappa^2 = 8\pi n_0\epsilon^2/DKT$, the required force (including both walls) is $4\kappa^{-1}n_0kT\eta_1'(\bar{\eta}_1 - \eta_1)$, giving an additional term $\frac{1}{2}\eta_1'(\bar{\eta}_1 - \eta_1)$ in G. Finally, we must consider the contribution from the electrostatic tensor acting across the plane of the wall, for in the transition layer the field is oblique to this plane and the tensor gives a shearing stress. The force per unit area will be proportional to the square of the field just outside the wall charge. Now, for a given distance between upper and lower planes, this stray field may be taken as proportional to the total potential difference, at least in the first approximation, since it vanishes when the potential difference is zero. Therefore the shearing force per unit area and the total shearing force will vary as the square of the potential difference, and may be neglected in comparison with those forces which, like that due to the regulating mechanism, are directly proportional to this difference. We have, therefore, to replace G in (46) by

$$\tilde{G} = \bar{\theta}_1 \cosh \eta_M + \int_0^\infty (\cosh \eta - 1)d\theta - \int_0^{\bar{\theta}_1} \cosh \eta \, d\theta + \tfrac{1}{2}\eta_1'(\bar{\eta}_1 - \eta_1) \qquad (46')$$

The integrals can be handled exactly as before except that in (55) we get $\eta_1' = \sqrt{\bar{E}}$, with the result that in (56) the factor $(\cosh^2 (\eta_M/2))$ under the radicle must be replaced by unity. Under the conditions specified, the third term in (56) reduces to $2e^{-\frac{1}{2}\eta_1}$. To get a useful expression for the last term in (46′), we first observe that we may ordinarily replace the hyperbolic functions by exponentials in (45) and (53), obtaining $e^{\bar{\eta}_1 - \eta_2} = 1 + M/(E + 2)$ and $\eta_1'(\bar{\eta} - \eta_1) = e^{\frac{1}{2}\eta_1} \log [1 + M/(E + 2)]$. Now, if $\cosh \eta_1 > 16 (\cosh \eta_M - 1)$, the logarithm may be replaced by $M/(E + 2)$ with an error not greater than 3%, giving

$$\tfrac{1}{2}\eta_1'(\bar{\eta}_1 - \eta_1) \approx \mathrm{e}^{-\frac{1}{2}\eta_1} (\cosh \eta_M - 1) \qquad (60)$$

Collecting the approximations, we obtain

$$\tilde{G} \approx \bar{\theta}_1 \cosh \eta_M - 2 + e^{-\frac{1}{2}\eta_1} (\cosh \eta_M + 1) - (\pi/2)e^{-\frac{3}{2}\eta_M} \qquad (59')$$

From (47) and either (59) or (59′) we obtain

$$\kappa\Delta \approx 2\kappa\delta \frac{\cosh \eta_M}{\cosh \eta_M - 1} - \frac{4 - 2e^{-\frac{1}{2}\eta_1} (\cosh \eta_M + 1) + (\pi/2)e^{-\frac{3}{2}\eta_M}}{\cosh \eta_M - 1} \qquad (61)$$

If we now let both e^{η_M} and $e^{\eta_1 - \eta_M}$ increase without limit, the first term on the right approaches $2\pi e^{-\frac{1}{2}\eta_M}$ and the second approaches $2e^{-\frac{1}{2}\eta_1}$ and becomes negligible in comparison with the first. In this limiting case, then, Δ is equal to twice δ instead of to δ as Langmuir assumes. The limiting form approached by both G and $\tilde{G}$ is found to be

$$G_\infty = \tfrac{1}{2}\pi e^{\frac{1}{2}\eta_M} - 2 \qquad (62)$$

the relative error being of the order of $e^{-2\eta_M}$: In terms of the pressure difference P this becomes, to the same order of accuracy

$$G_\infty = \tfrac{1}{2}\pi[\sqrt{P/n_0kT} + \sqrt{n_0kt/P}] - 2 \qquad (63)$$

When κ is given its value $\sqrt{8\pi n_0\epsilon^2/DkT}$, the corresponding limiting expression for the electrical and thermal junction force is

$$F_e = \sqrt{2D(kT)^3/\pi\epsilon^2}\sqrt{n_0}\, G_\infty = (kT/\epsilon)\sqrt{\pi D/2}[\sqrt{P} + n_0 kT/\sqrt{P} - (4/\pi)\sqrt{n_0kT}] \qquad (64)$$

In the foregoing calculation of the forces acting across a pair of planes, it has for simplicity been assumed that the lower plane lies below the bottom of the meniscus, but this is not essential for the final result. The plane may lie higher, provided that the lines in which it cuts the meniscus are out of range of the field of the wall charge. Then, just as in the standard elementary theory, the vertical component of the surface tension at the intersection will compensate the reduction in the area over which P acts. Our result remains valid, therefore, even in a gravitational field, for the two planes can be taken so close together that the weight of the enclosed matter is negligible. Suppose, however, that we take the lower plane at "sea level," where the measured pressure vanishes, and the upper plane at any arbitrary height h. Then in (38) we must put zero instead of $-\sigma/R$, and in (39) we must replace p_0 by $p_0 - \rho g h$, (ρ being here the density of the solvent, the mass of the ions being ignored). We can then write $n_0 k T M = \rho g h = P$, the pressure difference between the film and a portion of massive liquid in equilibrium with it at the same gravitational potential. G can be calculated exactly as before, and the corresponding force F_e then gives the weight of liquid raised to heights between 0 and h, per unit width of a single wall, in excess of that supported by the normal surface tension.

In the case of the film above the meniscus in a cylindrical tube, we may calculate the balance of forces acting upon the contents of the tube between two horizontal planes, respectively well above and well below the meniscus. To facilitate comparison with the previous results, we may take the radius of the tube as $R + \Delta$ and that of the free surface of the wetting film as $R + \Delta - \delta$. We may neglect any term of order of magnitude Δ/R or δ/R relative to other non-vanishing terms. Thus, since the meniscus is now spherical and the film cylindrical, we replace (37) and (38) by

$$p = p_0 + 2n_0\, kT \cosh \eta_M = -\sigma/(R + \Delta) \qquad (37')$$

$$p = p_0 + 2n_0\, kT = -2\sigma/R \qquad (38')$$

The tensions in the surfaces of the film act across the upper plane with the force $2\pi[(R + \Delta)(s + \sigma) - \delta\sigma]$. To the proposed approximation, the curvature may be neglected in calculating the body forces, giving for the total force

$$2\pi(R + \Delta)\left\{s + \sigma - \frac{\delta}{R + \Delta}\sigma - \delta\,(2p_0 - p) - 2\int_0^\delta p_t\, \mathrm{d}x\right\} = 2\pi(R + \Delta)\left\{s + \sigma + 4n_0kT\left[\delta \cosh \eta_M - \int_0^\delta \cosh \eta\, \mathrm{d}x\right]\right\} \qquad (41')$$

Across the lower plane the surface tension gives the force $2\pi(R + \Delta)$. We may again neglect the curvature in dealing with the part of the liquid near the wall, where alone the term $2(p_0 + p_t - p)$ in the integrand differs appreciably from zero; but the constant term $p = -2\sigma/R$ acts across the whole cross section of area $\pi(R + \Delta)^2$. Hence the total force is

$$2\,\pi(R + \Delta)\left\{s + (R + \Delta)\,\sigma/R - 2\int_0^{R+\Delta}(p_t + p_0 - p)\mathrm{d}x\right\} = 2\pi\,(R + \Delta)\left\{s + \sigma + \Delta\sigma/R - 4n_0\, kT\int_0^\infty (\cosh \eta - 1)\mathrm{d}x\right\} \qquad (42')$$

Except for the factor $\pi(R + \Delta)$, these expressions are identical with (41) and (42), and lead to the same equations for Δ.

The most reliable quantitative experimental test of Langmuir's theory is that carried out by Jones and Wood[9] on the original data of Jones and Ray.[10] To the "apparent relative surface tension" they apply a correction factor $(r - \Delta r_c)/(r - \Delta r_0) \approx 1 + (\Delta r_0 - \Delta r_c)$, where r is the radius of the capillary, and Δr_0 and Δr_c are the thicknesses of the wetting film (δ in the present notation) for pure solvent and for solution, respectively. According to the foregoing analysis these latter must be replaced by Δ. Assuming constant wall potential, the corresponding values of Δ have been computed for potassium chloride solutions of concentrations 10^{-5}, 10^{-4} and 10^{-3} normal in a tube of radius 0.0136 cm., using the data of Jones and Wood's Table X. (In this table the value of $K = e^{-\eta_M}$ for $c = 0.0001$ should be 0.25764.) For comparison, the separate terms in G are shown as computed both by the exact formula (56) and by the approximation (59). Jones and Wood show that when the values of δ are used in the correction factor, the Jones–Ray anomaly is almost exactly eliminated. Since the Δ values change more rapidly with the concentration, their use will obviously over-compensate the anomaly and leave an unexplained discrepancy in the opposite sense.

VALUES OF Δ FOR POTASSIUM CHLORIDE SOLUTIONS AT 25°
CAPILLARY RADIUS 0.0136 CM.

c	10^{-5}	10^{-4}	10^{-3}
η_1	5.8	5.3	4
Cosh η_M	11.7	2.07	1.107
θ_1	0.536	1.47	2.60
$2 \cosh (\eta_1/2) \times \left\{1 - \sqrt{1 - \frac{\cosh^2(\eta_M/2)}{2 \cosh(\eta_1/2)}}\right\}$	.71	0.218	0.234
$e^{-\frac{1}{2}\eta_1}(\cosh \eta_M + 1)$	.70	.217	.233
$\int_0^{\theta_1} e^{-\eta}\, \mathrm{d}\theta$	.01	.211	.951
$(\pi/2)e^{-\frac{3}{2}\eta_M}$	.01	.206	.790
G (Eq. (56))	4.99	1.06	.161
G (Eq. (59))	4.98	1.06	.32
Δ (A)	895	605	289
δ (A)	516	449	250

It remains to examine the effect of the electrical and thermal terms in the weight of solution lifted above sea-level in the wide tube of Jones and Ray's capillarimeter (their W_0''). Since this quantity is subtracted from the total weight of the

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(9) Jones and Wood, *J. Chem. Phys.*, **13**, 106 (1945).

(10) Jones and Ray, THIS JOURNAL, **59**, 187 (1937).

solution in determining the capillary rise, a positive correction to it will produce a positive correction to the calculated value of the surface tension, as can be verified by Jones and Ray's equations. The correction will be greatest at the lowest concentrations, and being of opposite sign must be subtracted from the correction due to Δ, thus tending to diminish the discrepancy noted above. Definite values cannot be calculated without some assumption as to the total height of the wetting film. To get a plausible upper limit we may take this as 5 cm., giving $P = 5 \times 10^3$, and put $n_0 = 0$. Then, for a tube of radius 2.15 cm., eq. (64) gives a total lifting force equivalent to 0.9 mg. According to Jones and Ray's precision analysis, a difference in weight of 1.55 mg. produces a change of 0.001% in the relative surface tension. It is clear, then, that the effect here considered is below the limit of measurement, and cannot account for the outstanding discrepancy.

Appendix

Proof that the value of s for a liquid in contact with a flat solid surface depends upon the choice of the reference plane (dividing surface), except when the pressure is zero; and that when the pressure does not vanish, the difference between σ, the surface tension of the interface, and s is not equal to σ_0, the value of σ for the solid in a vacuum, unless the reference plane is chosen so as to make Γ_1, the superficial density of the solid, equal to zero.

The definitions given by Gibbs are

$$s = (\epsilon_s) - t(\eta_s) - \mu_2(\Gamma_2) - \mu_3(\Gamma_3) - \text{etc.} \quad [676]$$
$$\sigma = \epsilon_s - t\eta_s - \mu_1\Gamma_1 - \mu_2\Gamma_2 - \mu_3\Gamma_3 - \text{etc.} \quad [507]$$

For the special case that the liquid is replaced by a vacuum, we may write [507] as

$$\sigma_0 = \epsilon_{s0} - t\eta_{s0} - \mu_{10}\Gamma_{10}$$

The meanings of the terms in the right sides of these equations are explained in words. To reduce them to symbols, let us choose the mass M of page 220 so as to include unit area of the surface of the solid, and let its thickness be everywhere $D = \lambda' + \lambda''$, where λ' and λ'' are the thicknesses ascribed to the solid and liquid phases by the arbitrary choice of the reference plane. Let ϵ, η, m_1, m_2, etc., be the actual energy, entropy and masses of M. For the vacuum case, ϵ and η reduce to ϵ_0 and η_0, m_1 remains constant, and the other masses vanish. Let ϵ'_{v}, η'_{v}, γ'_1 be the bulk densities of energy, entropy and mass in the solid; since its state of strain is supposed unaffected by the presence of the liquid these quantities will be constants. Let the corresponding densities for the liquid phase be ϵ''_{v}, η''_{v}, γ''_2, γ''_3, etc., at the given pressure. Then

$$(\epsilon_s) = \epsilon - \epsilon_0 - \lambda''\epsilon''_{\mathrm{v}};\ \epsilon_s = \epsilon - \lambda'\epsilon'_{\mathrm{v}} - \lambda''\epsilon''_{\mathrm{v}};\ \epsilon_{s0} = \epsilon_0 - \lambda'\epsilon'_{\mathrm{v}}$$
$$(\eta_s) = \eta - \eta_0 - \lambda''\eta''_{\mathrm{v}};\ \eta_s = \eta - \lambda'\eta'_{\mathrm{v}} - \lambda''\epsilon''_{\mathrm{v}};\ \eta_{s0} = \eta_0 - \lambda''\epsilon$$
$$\Gamma_1 = m_1 - \lambda'\gamma'_1 = \Gamma_{10}$$
$$(\Gamma_2) = m_2 - \lambda''\gamma''_2 = \Gamma_2, \text{ etc.}$$

Substituting these values into the previous equations, we readily find

$$\partial s/\partial\lambda'' = -\epsilon''_{\mathrm{v}} + t\eta''_{\mathrm{v}} + \mu_2\gamma''_2, \text{ etc.} = p$$

by virtue of [93]. This establishes the first proposition. To prove the second, we first notice the relations

$$\epsilon_s - (\epsilon_s) = \epsilon_{s0};\ \eta_s - \eta_s\,(\eta_s) = \epsilon_{s0}$$

Then we easily find

$$\sigma - s = \epsilon_{s0} - t\eta_{s0} - \mu_1\Gamma_1$$

This differs from σ_0 by the term $(\mu_{10} - \mu_1)\Gamma_1$. Now, unless the pressure of the liquid is zero, the potential of the solid will not be the same in its presence as in a vacuum, and the term will vanish only if Γ_1 is made to vanish by suitable choice of the plane of reference.

Proof that when the interfaces separating three fluids at the same pressure are not all parallel, the surfaces of tension, in the regions where they are defined, lie in planes which meet in a common line when produced, and which, with respect to any plane of reference containing this line, make angles such that the products of their cosines and the corresponding surface tensions add to zero.

It will always be possible to find a line which, if not common to the three planes, is the axis of a small cylinder (f in Fig. 7) to which all three are tangent. Let the outer boundary of the physical system considered to be a much larger cylinder with this line as axis (too large to show in Fig. 7, but indicated by k in Fig. 8, which is supposed to be drawn on a much smaller scale). Let the system be divided into inner and outer portions by a triangular prismatic surface (t in both figures) lying entirely outside the region where the influence of all three phases is appreciable, circumscribed about another coaxial cylinder (g in Fig. 7), and with faces perpendicular to the surfaces of tension AB, BC, AC. Then the thermodynamic properties of the outer part are exactly reproduced by the membrane model, and for any variation

$$\delta\epsilon = t\delta\eta + \mu\delta m - p_{\mathrm{A}}\delta v_{\mathrm{A}} - p_{\mathrm{B}}\delta v_{\mathrm{B}} - p_{\mathrm{C}}\delta v_{\mathrm{C}} + \sigma_{\mathrm{AB}}\delta s_{\mathrm{AB}} + \sigma_{\mathrm{BC}}\delta s_{\mathrm{BC}} + \sigma_{\mathrm{AC}}\delta s_{\mathrm{AC}}$$

where ϵ, η and m refer to the whole outer part and the other quantities are self-explanatory. This will also be the variation of the whole system for any variation which does not distort the inner part in any way nor destroy the perpendicularity between its boundaries and the surfaces of tension. We now show that if the configuration does not satisfy the conditions of the first paragraph, then a variation can be carried out which meets the requirements just stated and which, without altering η, m, v_{A}, v_{B} or v_{C}, will so change s_{AB}, s_{BC} and s_{AC} as to make $\delta\epsilon$ negative; the given configuration cannot, therefore, be in thermodynamic equilibrium.

Suppose first that the planes do not meet in a common line, but are tangent to a common cylinder of finite radius as in Fig. 7. Imagine still another concentric cylinder like h, and let the entire physical contents of this cylinder be rotated with-

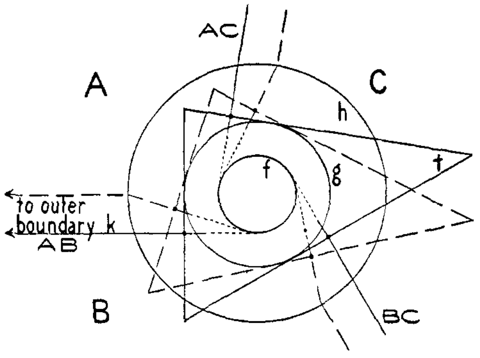

Fig. 7.

out any internal distortion (clockwise in the figure), while the matter outside is rearranged in such a way that the surfaces of tension remain continuous, though bent, at their intersections with *h*. The new positions of these surfaces and of the prism are shown by dashed lines. (It does not matter if the corners of the prism project beyond *h*, since they lie wholly in the homogeneous regions.) It is clear from the geometry of the figure that the distance from *h* to the outer boundary is shorter along the new positions of the surfaces of tension than along the old, while that between *t* and *h* is unchanged; the quantities s_{AB}, s_{BC} and s_{AC} have therefore been made smaller. They can be made still smaller by easing away the sharp bends at the intersections with *h*. By the fundamental property defining the surface of tension, the gentle curvature so introduced does not affect the surface energy; hence the total energy has been reduced by the variation described.

Now suppose that, for some choice of reference plane (Fig. 8), the condition

$$\sigma_{AB} \cos \gamma_{AB} + \sigma_{BC} \cos \gamma_{BC} + \sigma_{AC} \cos \gamma_{AC} = 0$$

is not satisfied. Let the prism and its contents be given a small bodily displacement parallel to the reference plane, the matter outside being so rearranged that the surfaces of tension remain attached to the prism at the original points. The changes in s_{AB}, s_{BC} and s_{AC}, respectively, will be proportional to $\cos \gamma_{AB}$, $\cos \gamma_{BC}$ and $\cos \gamma_{AC}$. In Fig. 8 the new positions of the surfaces of tension are shown as planes; without altering the positions of their extremities, let these surfaces now be slightly distorted in such a way as to make them again perpendicular to *t* and *k* and to make the volumes of the bulk phases the same as at first. (The second provision is not essential to the argument here, but if the method were extended to the case of different pressures it would be convenient to exclude energy changes arising from the terms $p\delta v$.) By the fundamental property of a straight line, the consequent changes in the distance from *t* to *k* are small of the second order; hence the energy change is proportional to $\sigma_{AB} \cos \gamma_{AB} + \sigma_{BC} \cos \gamma_{BC} + \sigma_{AC} \cos \gamma_{AC}$, and can be made negative by the proper choice of the direction of motion.

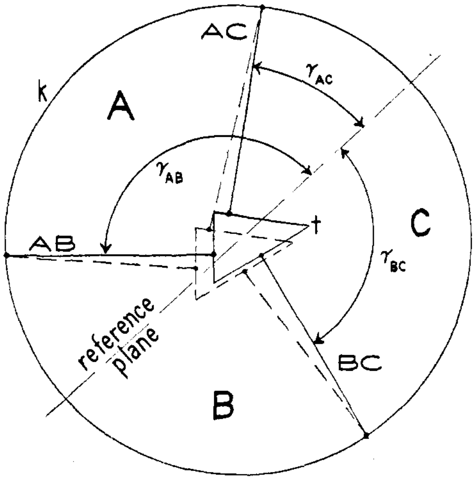

Fig. 8.

Summary

Let two fluid phases be in equilibrium in contact with each other and with the plane surface of a rigid solid, and let the contact angle be calculated from the three surface tensions by means of the usual relation. It is shown that if one of the fluids forms a wetting film of finite thickness upon the solid, and if the surfaces in which the tensions are supposed to act are defined as specified by Gibbs, then the value of the contact angle must be expected to be imaginary when the wetting fluid is under a lower pressure than the other, as in a capillary rise device. The Gibbsian surface of tension between the fluid phases is not defined at points within the molecular field of the wall, and if extrapolated into that region will not meet the wall. In order to describe the situation in terms of a fictitious tense membrane of zero thickness exactly at the Gibbsian surface, the membrane must be conceived as attached to the crest of a rigid dam closing the gap. The height of this dam, Δ, is greater than δ, the thickness of the wetting film, instead of equal to it as assumed by Langmuir in explaining the Jones–Ray effect.

The interplay of forces near phase boundaries and in wetting films is investigated in detail on the alternative bases of Laplace's model of an incompressible liquid and of the Debye–Hückel model of a dilute electrolytic solution. It is demonstrated that the surface tension may not for all purposes be assumed to act exactly in the Gibbsian surface of tension. Explicit formulas are found for the relation between Δ and δ. In the limiting case of high ζ-potentials, the Langmuir correction to the measured surface tension must be doubled.

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