XLIV. On the molecular theory of galvanic polarization

J. Larmor

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All sources produced the same result.
The mean of all experiments performed was

1 Siemens unit = 0·94356 ohm;

or, one ohm is equivalent to the resistance of a mercury-column having a section of 1 square millim. and a length of 105·98 centim. at 0° Centigrade.
Of the values determined,

the lowest was 1 Siemens unit = 0·94323 ohm,
the highest was 1 Siemens unit = 0·94380 ohm.

XLIX. *On the Molecular Theory of Galvanic Polarization.*
By J. LARMOR, *Fellow of St. John's College, Cambridge* *.

1. IT was first pointed out by Varley and Sir W. Thomson that the polarizing action of a galvanic cell may be explained by considering the cell to act as an electrical condenser of very large capacity. The mechanism of this action has since been examined in detail, especially by Helmholtz †.

In the polarization of a water-voltameter with platinum plates for electrodes, the action according to Clausius's well-known molecular theory consists in the transfer through the fluid of the temporarily dissociated hydrogen and oxygen constituents under the action of the electric force ; so that in the course of time a layer of hydrogen particles with their positive charges accumulates in the immediate neighbourhood of the kathode plate, and the complementary layer of oxygen particles with their negative charges at the anode.

Each of these layers will form a sheet, with positive or negative charge, lying close to the metal plate. On the plate will therefore appear an equal and opposite charge by induction. There is thus a double electric layer formed at each electrode ; the charged particles forming one side of it being prevented from coming up to and discharging themselves in contact with the metal, in obedience to the electrical attraction, by chemical forces of repulsion.

A double layer of this kind forms an actual condenser, whose capacity is inversely proportional to the distance between its faces. And Gauss's well-known theorem relating to magnetic shells shows, when applied to this case, that the effect of such a condenser is to cause a sudden rise or fall of potential in passing through it without producing any change in the distribution of the electric force in the neighbourhood.

* Communicated by the Author.
† See his *Wissenschaftliche Abhandlungen*, vol. i., section *Galvanismus*, and his Faraday Lecture, in the Journal of the Chemical Society for 1882.

The notion of a condenser, therefore, gives a complete account of the principal feature of the galvanic polarization.

Direct measures of the charge by Kohlrausch showed that on dividing this polarization-fall of potential equally between the anode and kathode plates, the distance between the faces of the condenser comes out to be about the fifteen-millionth part of a millimetre; while more careful observations by Helmholtz on cells in which absorbed gases have been removed from the fluid, give the greater value of a ten-millionth of a millimetre. And Helmholtz makes out the very important fact that for all electromotive forces which do not exceed a certain moderate value, the capacity, and therefore the distance of the surface-layers, is very sensibly constant*.

2. The most accurate and convenient method of observing the polarization at the common surface of two liquids is probably the electro-capillary method invented and applied by Lippmann.

When a surface of separation can persist between the fluids, the energy, reckoned as potential, of pairs of particles close to the surface must exceed that of the same particles when in the interior of their respective fluids. The difference may, as Gauss pointed out, be reckoned as surface-energy, and specified by its amount per unit area of surface. If T represent this amount, it follows, as is well known, that the forces which arise from it may be represented by a surface-tension equal to T across each unit of length, tending to contract the surface in all directions.

Now, if the common surface is polarized with constant charges $+Q$ and $-Q$ on its two faces, there will exist an additional *electrical* energy, which is also reckoned by its amount per unit surface, and whose total value is

$$E = \tfrac{1}{2}QV,$$

or, what is the same,

$$E = \tfrac{1}{2}\frac{Q^2}{CS};$$

where S is the area of the surface and C is its electrical capacity per unit area.

The effect of this surface-energy will therefore, the system being conservative, be represented by a surface-tension T′, where

$$T' = \frac{dE}{dS},$$

$$= -\tfrac{1}{2}\frac{Q^2}{CS^2},$$

$$= -\frac{E}{S};$$

* Faraday Lecture, p. 296; *Wissen. Abh.* i. p. 858.

2 H 2

i. e. is equal to the electrical surface-energy per unit area of the surface, with negative sign.

The effect of the galvanic polarization will therefore be to diminish the capillary surface-tension by this amount $\dfrac{E}{S}$.

In the actual case in which the polarization is maintained by a battery, the difference of potential V between the faces of the condenser is what remains constant; and the system is no longer conservative, because the battery can be drawn upon; we have then

$$E = \tfrac{1}{2} CSV^2,$$

and

$$\frac{dE}{dS} = \tfrac{1}{2} CV^2,$$

$$= \frac{E}{S};$$

therefore $dE = -T'dS$;

i. e. this force T' now acts so as to *increase* the total energy of electrification E, and is measured by its *rate of increase* per unit extension of area; for the work done by the contractile force T' in an extension of surface dS is equal to $-T'dS$, which is now the increment of the energy, but under the previous conditions was its decrement.

It follows that under these circumstances the battery is drawn upon for an amount of energy equal to *twice* that required to do the electrical work of extension, viz. the energy required to do this work together with the equal amount used up in increasing E, as has just been found. This is a particular case of a general theorem of Sir W. Thomson's. We have gone into the matter here to show the consistency of the propositions which make the capillary surface-tension equal to the rate of increase of the *ordinary* surface-energy per unit extension, while the electric surface-tension is equal to the rate of decrease of the electrical surface-energy per unit extension.

Once the surface-tension becomes negative, a free surface becomes unstable, and therefore practically impossible. We notice therefore that, as the polarization is made stronger and stronger, this state of affairs would finally supervene were not the polarization previously relieved by electrolytic separation of the charged layer.

3. We have proved that the surface-tension is diminished by galvanic polarization by an amount equal to $\tfrac{1}{2} CV^2$, where C is the electric capacity of the surface per unit area.

The polarization-charge is therefore zero when T is a maximum, and the surface is then most curved.

The method that we have employed to determine the capil-

lary effect of the polarization-charge is different from that used by Lippmann and by Helmholtz. In their mode of procedure the variation of the energy of the system is expressed in terms of the variations of the surface-area and the surface-density, and it is claimed that this expression is an exact differential, *i. e.* that any series of operations whereby the area or density, or both, are changed so as finally to come back to the original values, will also bring back the energy of the system to its original value. This assumption seems to require justification when it is remembered how complex such a series of changes really is, and what a number of other variations besides those of volume and density may enter into it. Helmholtz appeals to Lippmann's experiments on the influence of extension of the surface-film on its electrification and *vice versâ*, and to his capillary engine, as pointing in a general way to the truth of the assumption.

In the method adopted above, we have proved the general theorem that the mechanical action of two layers of positive and negative electricity of equal amounts, spread over the two faces of a flexible sheet, may be represented by a negative surface-tension of amount numerically measured by the energy of the electrification per unit area. It follows, then, on this representation of the phenomenon, that no matter what other changes are taking place, the effect of the existing surface-charges is to diminish the surface-tension of the sheet by the amount just mentioned.

The case contemplated in the present application of this general proposition is that of a sheet of uniform thickness; but we can clearly extend the result to flexible condensers of variable thickness of dielectric, provided always that the thickness be small compared with any radius of curvature of the surface at the place considered. In this case the mechanical effect on the condenser of a charge to potential V is to produce a negative surface-tension, numerically equal to $KV^2/8\pi t$, K being the dielectric constant and t the thickness of the sheet; this surface-tension varies from point to point of the sheet, and is at any place inversely proportional to its thickness.

This result may also be at once deduced from the expression for the stress transverse to the lines of force in the dielectric on Maxwell's well-known theory.

4. Lippmann's original form of capillary electrometer consists of two mercury electrodes in contact with acidulated water. One of the electrodes is in an extremely fine capillary glass tube, so that the surface of contact is very small; and the other is of considerable area. It follows that when a battery is applied, all the polarization and consequent change

in the surface-tension practically takes place at the fine electrode, as the corresponding charge at the other electrode is spread over so much greater area. The change in the capillary constant is measured by the column of mercury whose pressure is required to restore the meniscus to its former position.

Lippmann has given a series of observations with this instrument in his paper in the *Annales de Chimie*, vol. v. p. 507, the electrolyte being water containing one sixth part by volume of sulphuric acid. He finds that the maximum surface-tension is attained when the applied electromotive force is ·905 of a Daniell's cell. This value, therefore, corresponds to absence of polarization at the electrode meniscus. The following Table, calculated from his results, gives δe the excess (positive or negative) of the electromotive force above this value, δp the excess of the pressure required to neutralize its effect over its value when $e = ·905$ D, and $(\delta e)^2/\delta p$, which is proportional to the capacity of the electrode, and therefore inversely to the distance between the two electrified layers,—on the supposition that the condensing arrangement remains analogous to an ordinary condenser, viz. consists of two infinitely thin layers separated by a dielectric sheet.

δe.	δp.	$\dfrac{(\delta e)^2}{\delta p} \propto$.
− ·89 D	343¼	23·07
− ·88	337	23·0
− ·86	318½	23·07
− ·805	269½	23·4
− ·76	247½	23·3
− ·71	210¼	24·0
− ·63	170	23·3
− ·54	123¼	23·6
− ·405	70	23·26
− ·32	44½	23·01
− ·07	2	24·05
+ ·35	57½	21·3
+ ·43	79¾	23·3
+ ·54	119¾	24·4
+ ·81	230½	28·5
+ ·93	248½	34·8
+ ·98	254¼	34·2
+1·10	264¼	45·8

The pressure supported by the tension of the meniscus when $e = ·905$ D was 1108½ millim. of mercury, which is therefore proportional to the maximum surface-tension of the film. The surface-tension, as ordinarily measured, corresponds to $e = 0$, and is therefore proportional to the pressure, which was then 750 millim.

The last column of this table is in good agreement with Helmholtz's result, that for electromotive forces from zero up

to a limit of considerable magnitude the capacity of the condensing arrangement remains constant.

As δp is measured from a minimum value, it follows that in the immediate neighbourhood of that value $(\delta e)^2$ *must* vary as δp ; so that the discrepancies for small values of δp in the third column are merely to be attributed to the special difficulty of the observations in that part of the series.

Taking the second line of the table to give the average value of this constant, we may calculate the thickness of the dielectric, supposed to have the properties of vacuum, and therefore to have unit specific inductive capacity, on the supposition that the arrangement acts as an ordinary condenser. When $e=0$, Lippmann found by direct measurement that the surface-tension was ·304 × 981 C.G.S. units, which therefore corresponds to $p=750$ millim. When $e=·024$ D, we have $\delta e=-·88$, $\delta p=337$; therefore the change of the surface-tension corresponding to δe is

$$\delta T = \frac{337}{750} \times ·304 \times 981.$$

This, as we have seen, is equal to the energy of the polarization charge per unit area. Now, taking a Daniell to be 1·1 volts, *i. e.* 1·1 × 10⁸ C.G.S. electromagnetic units, which is the same as 1·1 × 10⁸ ÷ (2·98 × 10¹⁰) C.G.S. electrostatic units of potential, we have,

$$\delta T = \frac{(\delta e)^2}{8\pi . \text{ thickness}} \; ;$$

therefore thickness of dielectric

$$= \frac{(\delta e)^2}{8\pi . \delta T},$$

$$= \left(\frac{1·1 \times ·88}{298}\right)^2 \div \left(8\pi . \frac{337}{750} \times ·304 \times 981\right),$$

$$= \frac{(·00325)^2}{3370},$$

$$= ·313 \times 10^{-10} \text{ metre.}$$

This calculation has already been made by Lippmann (*Comptes Rendus*, 1882, quoted in Thomson and Tait's 'Natural Philosophy,' 2nd edit., Appendix, " On Size of Atoms "). It gives an estimate of a molecular distance, viz. that at which the two electrified layers are held by molecular chemical forces, which, notwithstanding the very rough suppositions on which it is founded, ought to be of the true order of magnitude ; and Lippmann has pointed out that it agrees sufficiently with the estimates assigned by Sir W. Thomson and others from different considerations.

It is a satisfactory verification of the general notions in-

volved in this discussion to find that, notwithstanding the large factors occurring in the calculation, such as the ratio of the electrostatic and electro-magnetic units, it yet agrees so closely in order of magnitude with the result 1×10^{-10} metre, obtained by Helmholtz from actual measurement of the polarization capacity of platinum plates.

5. But, on the principles we have been following, we may carry the analysis of the phenomenon still further. The polarization consists in the transfer of charged particles towards the electrode under the action of the electromotive force, and they are finally brought to equilibrium at a distance from the electrode, whose order of magnitude has just been determined. As these equally charged particles repel one another, they will tend to settle down in equidistant positions along the electrode surface. Instead therefore of two electrified sheets analogous to an ordinary condenser, we have really two sheets, one consisting of equidistant electrified particles, and the other of the charges brought opposite to them on the electrode by induction. Each charged particle and its corresponding induced charge will be brought by their mutual attraction so close together that this attraction will just be balanced by the chemical forces which hold them apart.

For polarizations of sufficiently small amount, the sidelong action of the neighbouring particles will be so small as to have no appreciable effect on the distance of any one particle from the electrode surface ; because, in the first place, the distances of neighbouring particles must be at first large compared with the distance of two opposed charges, and, in the second place, the smaller forces exerted by these neighbouring particles must be resolved along the normal to the surface, in which direction they have no appreciable component. The radii of curvature of the surfaces are of course extremely great compared with the distance between opposed charges.

It follows that as the polarization is increased the number of charged particles over unit area of electrode increases in the same proportion, and these particles all come to rest at the same distance from the electrode surface, whatever be the amount of the polarization. And we can clearly expect this uniformity of distance to hold good until the neighbouring particles come within a distance of one another which is of the *same order* as the distance of a pair of the opposed charges.

The pair of opposed surfaces which is thus arrived at, not uniformly charged, but each with a system of equal isolated point-charges arranged uniformly all over it, does not, of course, act as an ordinary condenser in the sense of producing a constant fall of potential in crossing it at all points, in positions whose distances from it are of the same order as

the distance between neighbouring particles. But when we compare two points on opposite sides at distances from it great compared with this latter distance, it is immaterial whether the distribution is supposed to be in isolated points or uniformly spread over the surfaces. Therefore, as regards points not in the immediate molecular neighbourhood of the electrode, the effect of this polarization is still to produce simply a difference of potential on the two sides, which is just the same as if the charges were uniformly spread over the surfaces at the actual distance apart.

These considerations, then, give a reason for the fact which is brought out by the table given above, deduced from Lippmann's experiments with the capillary electrometer, and also independently by Helmholtz from direct measurement of the capacity of platinum electrodes in fluid with no dissolved gas (which would disturb the action); viz. that the polarization capacity is constant for all values of the applied electromotive force up to limits of considerable magnitude.

6. In order to form an estimate of the nearness of the neighbouring molecules on a face of the double sheet when they begin to exert an influence on one another comparable with that exerted by the opposite charges, we must assign a limit to the interval of potentials within which the capacity remains constant. The table in § 4 shows that we shall attain the correct order of magnitude by taking it to be, say, 1 volt in the case there considered.

We may now make the following calculation, bearing in mind that the sign $=$ is to be interpreted as meaning that the quantities are of the same order of magnitude.

Let t be the thickness of dielectric layer;

d the distance between neighbouring atoms when their effective mutual action becomes comparable to that between opposed atoms (the important part of this action being that between any atom and the neighbours of its opposed charge);

t' the mean molecular distance in the electrolyte;

e the constant aggregate charge of a single atom or radical;

so that

$t'^{-3}e =$ the electro-chemical equivalent of 1 cubic centim. of water,

$= \dfrac{10^5}{9}$ coulombs, approximately,

$= \dfrac{10^5}{9} \times 3 \cdot 10^9$ electrostatic C.G.S. units,

and $d^{-2}e =$ surface density.

We have, then, for the condensing sheet,

$$d^{-2} = \frac{V}{4\pi t},$$

where $V = 1$ volt,

$$= 10^8 \div (3 \times 10^{10}) \text{ electrostatic C. G. S. units.}$$

Therefore

$$\frac{1}{3} \cdot 10^{14} t'^3 d^{-2} = \frac{1}{3 \cdot 10^2 \cdot 4\pi t};$$

therefore

$$t'^3 d^{-2} t = \frac{1}{12} \cdot 10^{-16}.$$

If now we write for t the value found above, $\cdot 3 \times 10^{-8}$, and put t' and d equal to each other, both being molecular distances of the same kind, we obtain for either the value

$$\frac{4}{15} \times 10^{-8} \text{ centimetres,}$$

which is very exactly of the same order as the value for molecular intervals obtained already from the other considerations.

On looking through this calculation it will be seen that quantities which we have designated as of the same order of magnitude do not differ nearly so much as in the ratio ten to one.

7. The two estimates of molecular distance which have thus been found on independent considerations connected with galvanic polarization therefore agree within very close limits; and they come very close to the third value determined by Helmholtz on the same theory of galvanic polarization, viz. 1×10^{-8} centim. ; and they are also just below the superior limit assigned by Sir W. Thomson to molecular intervals from various considerations connected with different physical phenomena, viz. 10^{-8} centim., his inferior limit being $\frac{1}{20} \times 10^{-8}$ centim.

Sir W. Thomson's different arguments lead to the following superior and inferior limits of the average distance of molecules from one another in solid and liquid substances :—

	centim.	centim.
Contact electricity	1×10^{-8}	$\frac{1}{4} \times 10^{-8}$
Surface-tension	$\frac{1}{2} \times 10^{-8}$	
Kinetic theory of gases		$\frac{1}{5} \times 10^{-8}$
Solids and liquids	$\frac{7}{10} \times 10^{-8}$	$\frac{1}{5} \times 10^{-8}$

to which we may now add

Helmholtz . . . . 1×10^{-8};

while Lippmann's method places the mean at $\frac{3}{10} \times 10^{-8}$ centim. ; and the other method here given places it at $\frac{4}{15} \times 10^{-8}$ centim., with as small limits of error as any of the methods given above.

8. The chief value of this discussion seems, however, to be not so much that it gives an estimate of molecular distance, but that its very close agreement with the other independent estimates derived from considerations connected with the same phenomenon of galvanic polarization is strong evidence of the substantial and ultimate truth of that representation of the phenomenon which has formed the basis of the discussion.

This argument seems to derive very great weight from the wide variety and very different magnitudes of the physical constants employed in the three calculations, one depending on the direct measurement of the polarizing charge, another on the direct measurement of change in the capillary constant, and the third involving, in addition, the knowledge of the quantity of electricity required to decompose a gramme of water; while they all involve in different ways a constant of such large numerical magnitude as the ratio of the two electrical units of quantity.

9. The critical value ·905 D in § 4 appears to have an important bearing on the much discussed question of contact electrification.

As was pointed out by Helmholtz, a discontinuous change of potential in crossing a surface can only be produced by the existence of an electrical double layer on that surface ; so long as we look upon electrification or electric distribution as the cause of electrical phenomena, this is the only explanation open to us.

It has been seen that this electrification represents a distribution of purely surface-energy ; and if its properties are to

be investigated, it is to be expected that much light will be thrown upon them by their relations to other purely surface-distributions of energy, of which the best known is that leading to capillary phenomena.

We are not required to explain the manner in which this double layer at the surface of contact of two dissimilar substances is brought about. We may illustrate it by the rather crude hypothesis that each molecule of an electrolyte consists of a positively charged cation radical and a negatively charged anion radical held together by electrical forces, but partly also by their forces of chemical affinity, so as to be analogous to a magnetic molecule with north and south poles; that along the surface of the electrode these molecules are all turned into the same direction (polarized) by reason of the greater chemical affinity of one of their constituents for the matter of the electrode ; and that they thus form a double sheet analogous to a magnetic shell. This illustration will at any rate show that it is possible to give an account of the matter which shall be in unison with the commonly received ideas of electrical and chemical action, without having to speculate on the deeper question of the relation of the material atom to its electrical charge.

The electro-capillary observations of Lippmann quoted above, and the later ones of Koenig for various electrolytic fluids, show that, for one definite amount of polarization, each of these fluids in contact with mercury shows a maximum surface-tension. As we have seen that the existence of an electrical double layer on the surface must diminish the surface-tension, it follows that the critical value ·905 D for Lippmann's acidulated water is that difference of potential which, applied from without, just neutralizes the naturally existing double electrical layer on the surface. It would seem therefore that the natural contact-difference of potential between Lippmann's mercury and acidulated water is ·905 D, and that an absolute measure of a contact electromotive force has thus been obtained.

Appendix.

The result that the mechanical effect of the electrification on a charged condenser with thin uniform dielectric, whether flexible or not, is equivalent to a uniform negative surface-tension, has been derived in § 2 from the Principle of Energy without the use of any analysis.

The same result will of course follow from direct calculation of the mutual forces exerted by the charged elements of the surfaces on one another. As it forms a good example of the

theory of surface-energy which Gauss has made the founda-
tion of the doctrine of capillary action, in a case in which all
the circumstances of the forces are known, and as it also
illustrates some other points, the direct calculation is here
appended.

Consider, first, an infinite plane electrified surface, and
imagine a straight line drawn across it. The mutual repulsion
of the electrified parts on the two sides of this line will result
in a tension tending to tear the parts of the surface asunder
along the line, and whose intensity, measured across unit length,
we can calculate as follows.

Imagine a unit of electricity situated at a point distant ξ
from the line of division; the repulsion exerted on it by the
other half of the electrification is easily expressed in polar
coordinates, r, θ; θ being measured from the shortest distance
to the line of separation.

It will, however, be more convenient to take this unit charge
at a distance h from the plane, and to measure r, θ from its
projection on the plane as pole. The repulsion exerted on it,
resolved parallel to the plane, is

$$2\int_{\xi}^{\infty} dr \int_{0}^{\phi} d\theta \, r \, \frac{r}{(h^2+r^2)^{\frac{1}{2}}} \cdot \frac{\rho \cos \theta}{h^2+r^2},$$

where ρ is the surface-density of the electrification, and
$\cos \phi = \xi/r$.

Therefore the repulsion

$$= 2\rho \int_{\xi}^{\infty} dr \frac{r(r^2-\xi^2)^{\frac{1}{2}}}{(r^2+h^2)^{\frac{3}{2}}}.$$

To integrate this, write

$$r^2 - \xi^2 = (r^2 + h^2)z^2;$$

therefore

$$r\,dr = \frac{r^2+h^2}{1-z^2} z\,dz;$$

and the integral

$$= \int_{0}^{1} \frac{z^2}{1-z^2} \, dz$$

$$= \left[\tfrac{1}{2} \log \frac{1+z}{1-z} - z \right]_{z=0}^{z=1}.$$

This quantity becomes infinite at the upper limit; so that
for an infinite plane sheet the tearing-force due to the electri-
fication would be infinite; a result which would also follow
readily from simple consideration of the dimensions of the
variable involved in the integral.

Suppose, however, we take a finite sheet bounded on the

further side by the circular arc $r = r_0$; the repulsion now is

$$R \equiv 2\rho \log \{(r^2_0 + h^2)^{\frac{1}{2}} + (r^2_0 - \xi^2)^{\frac{1}{2}}\} - \rho \log (h^2 + \xi^2)$$

$$- 2\rho \left(\frac{r^2_0 - \xi^2}{r^2_0 + h^2}\right)^{\frac{1}{2}}.$$

As we have seen, this expression increases indefinitely as r_0 increases. But if now, instead of a single electrical sheet, we had a double electrical layer with an intervening vacuum dielectric of thickness t, the repulsion exerted by it on the unit charge in the plane of the positive face will be equal to

$$t \frac{d R}{d h}.$$

But on differentiating the expression for R, it is obvious that the first and last terms give parts which become zero when r_0 is infinite; so that the repulsion of the infinite double layer on the unit charge is finite, and is equal to

$$\frac{2 t \rho h}{h^2 + \xi^2}.$$

The repulsion exerted on a strip of unit breadth of density ρ and extending from $\xi = 0$ to $\xi = \infty$ therefore

$$= \rho \int_0^\infty \frac{2 t \rho h}{h^2 + \xi^2} d\xi$$

$$= \pi \rho^2 t,$$

which is independent of h.

The repulsion exerted on a strip of the same *double* sheet is therefore

$$2 \pi \rho^2 t,$$

i. e. it is the electrical energy of the distribution per unit area. And this quantity that we have thus calculated is clearly the surface-tension required.

It is clear also that the stress across any line drawn on the sheet is wholly tangential, and has no component normal to the sheet; so that this surface-tension is its complete specification.

The calculation just made has been only for the case of an infinite plane double sheet. For a single sheet the distant parts exert a finite effect; and we have seen that the stress increases indefinitely when the size of the sheet increases. But for a double sheet the parts very distant relatively to the thickness no longer contribute sensibly to the result, and the integrals converge. Thus, if the double sheet be of sensible but finite curvature, we may calculate the integrals either

from the sheet itself or from the portion of the sheet which coincides sensibly with the tangent plane at the place considered, or from an infinite plane sheet coinciding with that tangent plane. This is on the assumption that the part of the sheet which coincides sensibly with the tangent plane is of large dimensions compared with the thickness of the dielectric, *i. e.* that the latter is small compared with any radius of curvature of the sheet.

The result obtained therefore holds for curved double sheets as well as plane ones.

Now, if a curved sheet be under a uniform surface-tension T, it is well known that the stress experienced by any element δS of its surface is along the normal, and equal to

$$T\left(\frac{1}{R_1} + \frac{1}{R_2}\right)\delta S,$$

R_1, R_2 being the principal radii of curvature where δS is situated. When we apply this to the electrical double layer, we obtain the same result as comes from the direct expression, on Green's theory, of the force exerted by the electrical system on the two charged faces which belong to the element δS.

For a single curved electrified layer of finite dimensions, open or closed, the surface-tension is different at different points, and at the same point across different lines on the surface; except in the case of an electrified spherical sheet, in which it is easily seen to be constant and equal to $-\pi\rho^2 a$, where a is the radius of the sphere.

September 11, 1885.

L. *On the Influence of Pressure on certain cases of Electrical Conduction and Decomposition. By* J. W. CLARK, *Assistant Professor of Physics in University College, Liverpool**.

A S the subject of electrolysis is to be brought prominently before the next Meeting of the British Association, the following short outline of an investigation, commenced some years ago, may not be without interest at the present time.

The subject properly divides itself into three branches, viz.:— the influence of pressure on the electrical conduction and decomposition of—

I. Dilute sulphuric acid (products of electrolysis occupying much greater volume than when combined to form the electrolyte).

II. A solution of (*e. g.*) $CuSO_4$ (products of electrolysis
* Communicated by the Author.