

value of the integral in (4) or

$$\int_0^{2.40483} x f(x) J_0(x) . dx = 0.6117,$$

and hence by (4), as $J_1(2.40483) = 0.519$,

$$A_1 = \frac{2 \times 0.6117}{(0.519)^2 (2.405)^2} = 0.7852.$$

To find A_2 . The 25 equidistant ordinates of the original curve (straight line) are the ordinates of points in the curve MBLBBP (fig. 2), the abscissæ being taken from Table II. We found it convenient to multiply the abscissæ by 5 and represent in inches. Our ordinates were multiplied by 10 and represented in inches. The actual area was 2.36 square inches and one-fiftieth of this, or 0.0472, is the value of the integral in (4).

Hence, as $J_1(5.5201) = 0.3403$,

$$A_2 = \frac{2 \times 0.0472}{(0.3403)^2 \times (5.5201)^2} = 0.0268.$$

We need not show the curves used in finding A_3 and A_4 . The area of fig. 2 is the positive area MLNOM minus the area LQPNL, but one need not think about whether an area is positive or negative. It is only necessary to start the planimeter-tracer from the point numbered 0 in every case, and go from 0 to M and along the curve in the direction of the increasing numbers to 24, then along the axes of abscissæ, ending at the point 0 from which we started.

XLVIII. *The Relation between the Atom and the Charge of Electricity carried by it.* By J. J. THOMSON, M.A., F.R.S.,
Professor of Experimental Physics, Cambridge*.

IN the electrolysis of solutions, the persistency of the sign of the electric charge carried by an ion is almost as marked a feature as the constancy of the magnitude of the charge. Thus the hydrogen ion always carries a positive charge, the chlorine ion a negative one. In the electrolysis of gases, however, the sign of the charges carried by the atoms of the different elements is much more variable: here an atom of hydrogen does not always carry a positive charge, nor an atom of chlorine always a negative one; each of these

* Communicated by the Author.

atoms sometimes carries a negative charge, sometimes a positive one. But though in the gaseous state the atoms do not restrict themselves to charges of one sign, there are many phenomena which prove that even in this state the atoms of the different elements behave differently with respect to positive and negative charges. v. Helmholtz explained this behaviour of the elements by supposing that there is a specific attraction between the atom and its charge; that the zinc atom, for example, attracts a positive charge more powerfully than it does a negative one, while an atom of chlorine, on the other hand, attracts a negative charge more powerfully than it does a positive one.

The connexion between ordinary matter and the electrical charges on the atom is evidently a matter of fundamental importance, and one which must be closely related to a good many of the most important chemical as well as electrical phenomena. In fact a complete explanation of this connexion would probably go a long way towards establishing a theory of the constitution of matter as well as of the mechanism of the electric field. It seems therefore to be of interest to look on this question from as many points of view as possible, and to consider the consequences which might be expected to follow from any method of explaining, or rather illustrating, the preference which some elements show for one kind of electricity rather than the other.

The following method of regarding the electric field seems to indicate that this effect may be illustrated by simple dynamical appliances. The charges on the atoms are regarded as the ends of Faraday tubes (see J. J. Thomson, 'Recent Researches in Electricity and Magnetism,' p. 2): each unit of positive charge is the origin, each unit of negative charge the termination of such a tube. The magnitude of the unit charge is here taken equal to the charge carried by a monovalent ion. When these tubes spread into the medium they give rise to Maxwell's *Electric Displacement*, and the motion of the tubes through the medium produces a magnetic field.

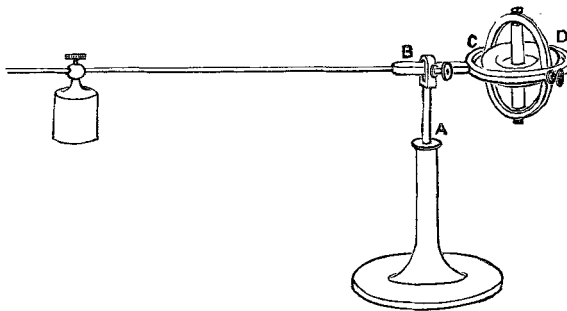
Now suppose that the medium forming these tubes possesses rotatory motion: we may imagine, for example, that the tubes are bundles of vortex filaments, the axis of rotation being parallel to the axis of the tube. The total amount of vorticity which starts from any solid totally immersed in a liquid is zero; to satisfy this condition, we may suppose that there is slipping between the walls of the bundle of vortex filaments and the surrounding liquid, or, what amounts to the same thing, that there is on the surface of the bundle a film

of negative vorticity whose strength is equal and opposite to the positive vorticity of the core. To fix our ideas, let us suppose that the rotation in the core is related to the direction of the axis of the tube (the line running from the origin to the end of the tube) like rotation and translation in a right-handed screw.

Now let us consider the atoms on which these tubes end. Let us suppose that these atoms have a structure possessing similar properties to those which the atoms would possess if they contained a number of gyrostats all spinning in one way round the outwardly drawn normals to their surface. Then one of these atoms will be differently affected by a Faraday tube, and will possess different amounts of energy according as the tube begins or ends on its surface. For if, when the tube starts from the atom, the rotation in the core of the tube is in the same direction as the rotation of the gyrostats, then when a tube ends on the atom the rotation in the tube will be in the opposite direction to that of the gyrostats. Thus in the first case the tube will tend to twist a gyrostat in the same direction as that in which it is already spinning, while in the second case it will tend to twist it in the opposite direction. Now if we try to rotate a gyroscopic system, its behaviour when we try to make it rotate in the direction in which the gyroscopes are spinning is quite different from its behaviour when we try to spin it in the opposite direction.

Thus let fig. 1 represent a balanced gyrostat which can

Fig. 1.



rotate as a whole about the vertical axis AB ; the heavy fly-wheel CD is supported so that its axis can move freely in a vertical plane. Let this fly-wheel be in rapid rotation with its axis vertical; the framework of the gyrostat will not tend to rotate. Now if we set the framework rotating about the

vertical axis, the behaviour of the system, if we make the framework rotate in the direction in which the fly-wheel is spinning, will be very different from its behaviour when we make the framework rotate in the opposite direction. If the framework rotates in the same direction as the fly-wheel, the axis of the wheel remains vertical, and the whole system goes on rotating quietly until stopped by friction. If, however, we attempt to set the framework rotating in the opposite direction to the fly-wheel, the axis of the wheel begins to wobble about, the disturbance gets more violent until finally the fly-wheel topples right over; then the fly-wheel is rotating in the same direction as the framework, and the rotation goes smoothly on. If the axis of the fly-wheel were held in its original position by springs, then in the first case these springs would not be stretched; but in the second case they would, and the axis of the fly-wheel would take up a position inclined to the vertical, the angle it made with the vertical depending on the stiffness of the springs and the moment of momentum of the fly-wheel. Thus in the second case the attempt to make the framework of the gyrostat rotate would be accompanied by the storing up of potential energy in the system due to the stretching of the springs, while there would be no such storage of potential energy in the first case.

Suppose, now, that an atom of hydrogen possesses a structure analogous to this gyroscopic system with springs, the gyrostats rotating in the same direction as the fluid in a Faraday tube *leaving* the atom. Then, since a charge of negative electricity on the atom implies the *incidence* of a tube on the atom, when the hydrogen atom is charged negatively the rotation in the tube connected with the atom is in the opposite direction to that of its gyrostats. The negative charge will thus cause an increase in the potential energy of the atom, whereas a positive charge when the rotation in the tube is in the same direction as that of the gyrostats does not cause any such increase. Thus the internal potential energy of the hydrogen atom will *ceteris paribus* be greater when it has a negative charge than when it has a positive one. In the case of a strongly electronegative element such as chlorine, we suppose that the gyrostats in the atom are rotating in the opposite direction to those in the hydrogen atom, *i. e.* that in the chlorine atom the rotation in the gyrostats is in the *opposite* direction to that of the liquid in a Faraday tube *leaving* the atom: thus the chlorine atom will, *ceteris paribus*, have more internal potential energy when charged with positive electricity than it has when charged with negative.

The existence of the property conferred by these gyrostats

would call into play forces between two charged atoms placed very close together, in addition to those given by the ordinary laws of electrostatics ; it would make, for example, the attraction between a negatively charged hydrogen atom and a positively charged chlorine one less than that between a positive hydrogen atom and a negative chlorine one at the same distance apart. For imagine, in the first case, the atoms to approach a little closer together, then, besides the diminution in the potential energy due to the ordinary electric forces between the atoms, there will be an *increase* in the potential energy from the increase in the effect on the gyrostats due to the rotation in the Faraday tubes ; while in the second case, when the hydrogen is positive and the chlorine negative, this increase will not take place. Thus the diminution in the potential energy due to a given diminution in the distance between the atoms is less in the first case than in the second, and consequently the attraction between them is smaller in the first case than in the second. If we could reach a place where, as the distance between the atoms diminished, the increase in the potential energy due to the effect of the gyrostats was numerically greater than the diminution in the potential energy due to the electrostatic attraction, then the oppositely-charged atoms would repel instead of attracting each other.

Hydrodynamical Illustration.

The following illustration also indicates that the force between two electric charges may be modified by the electrochemical properties of the atoms carrying the charges.

In a cylindrical column of rotating fluid the pressure increases with the distance from the axis of rotation, so that the average pressure over a cross section of the cylinder is less than the pressure at the surface of the cylinder. When a solid is immersed in a liquid where the pressure is uniform, the pressures of the liquid on the solid form a system of forces in equilibrium. Now suppose that a column of the liquid abutting on the solid acquires rotation, the pressure on the part of the solid in contact with the column will be less than the pressure outside, the pressures on the solid will no longer be in equilibrium. The defect in pressure over the cross section of the column will give rise to a tension acting on the solid. This tension is equal to the excess of the pressure over the cross section, when the pressure is uniform and equal to that at the surface of the cylinder, over that actually exerted over the area by the rotating liquid. If the rotating column is a cylinder containing a number of vortex filaments mixed up

with irrotationally moving liquid, the pressure over a cross section of the cylinder will depend upon the distribution of the vortex filaments in the cylinder. Let the cylinder be a right circular one. Let v be the velocity, and p the pressure at a distance r from its axis, ρ the density of the liquid; then we have

$$\rho \frac{v^2}{r} = \frac{dp}{dr}. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The pressure over the cross section of the cylinder is equal to

$$\int_0^b 2\pi r p \, dr,$$

where b is the radius of the cylinder. Integrating this by parts, we find that the pressure Π over the cross section is given by the equation

$$\begin{aligned} \Pi &= P\pi b^2 - \int_0^b \pi r^2 \frac{dp}{dr} \, dr \\ &= P\pi b^2 - \int_0^b \frac{1}{2} \rho v^2 2\pi r \, dr \quad . \quad . \quad . \quad . \quad (2) \end{aligned}$$

by equation (1), P is the pressure at the surface of the cylinder.

The tension Δ exerted by the cylinder on the solid is given by the equation

$$\begin{aligned} \Delta &= P\pi b^2 - \Pi \\ &= \int_0^b \frac{1}{2} \rho v^2 2\pi r \, dr. \quad . \quad . \quad . \quad . \quad (3) \end{aligned}$$

$$= \text{kinetic energy per unit length of the cylinder.} \quad (4)$$

Since

$$2\pi r v = \text{vorticity inside a circle of radius } r,$$

we can, if we know the distribution of vorticity, easily calculate by means of equation (3) the value of Δ .

Let us suppose that if all the vortex filaments were collected round the axis to the exclusion of the irrotationally moving liquid, they would occupy a cylinder of radius a . Let ζ be the rotation in the vortex filament, and let

$$\int_0^b 2\pi r \zeta l \, r = m.$$

Then we find that when the vortex filaments are as close to the axis of the cylinder as possible,

$$\Delta = \frac{\rho m^2}{16\pi} + \frac{\rho m^2}{4\pi} \log \frac{b}{a}.$$

When the vorticity is uniformly distributed over the cross section of the cylinder,

$$\Delta = \frac{\rho m^2}{16\pi}.$$

When the vorticity is all as near to the surface of the cylinder as possible,

$$\Delta = \frac{\rho m^2}{16\pi} \left\{ 1 - 2 \frac{(b^2 - a^2)}{a^2} \left(1 - \frac{(b^2 - a^2)}{a^2} \log \frac{b^2}{b^2 - a^2} \right) \right\}.$$

We may expand the right-hand side of the last equation, and get

$$\Delta = \frac{\rho m^2}{8\pi} \left\{ \frac{1}{3} \frac{a^2}{b^2 - a^2} - \frac{1}{4} \frac{a^4}{(b^2 - a^2)^2} + \frac{1}{5} \frac{a^6}{(b^2 - a^2)^3} - \dots \right\},$$

so that when a is small compared with b ,

$$\Delta = \frac{\rho m^2}{24\pi} \frac{a^2}{b^2}.$$

In this case the tension in the cylinder is very small compared with its value in the two previous cases: the value of Δ in the first case is greater than that in the second; the more the vortex filaments are concentrated at the axis the greater will be the value of Δ . Now let us suppose that a Faraday tube contains a given amount of vorticity distributed among irrotationally moving liquid; the axes of the vortex filaments being parallel to the axis of the tube. The moment of momentum of the fluid in the tube about its axis will depend upon the distribution of vorticity in the tube: the more the vorticity is concentrated near the axis of the tube the greater will be the moment of the momentum. Now suppose we apply a couple to the Faraday tube, the couple acting in such a direction as to increase the moment of momentum; this couple will cause the vortex filaments to concentrate more at the axis of the tube, and will consequently increase the tension in the tube. If, however, the couple on the Faraday tube acts in the opposite direction to the moment of momentum of the fluid in the tube, the action of the couple will cause the vortex filaments to spread out and get nearer the boundary of the tube: this will diminish the value of Δ , and consequently diminish the tension in the tube. If we suppose that the solid on which the tube abuts is an atom containing gyrostats, then when the gyrostats are rotating in

the same direction as the fluid in the tube, we may regard the action between the gyrostats and the tube as equivalent to a couple tending to increase the moment of momentum of the fluid in the tube, and thus to increase the pull exerted by the tube on the atom. When, however, the rotation of the gyrostats is in the opposite direction to that of the fluid in the tube, the action between the atom and the tube will be equivalent to a couple tending to diminish the moment of momentum of the fluid in the tube, and thus to diminish the pull exerted by the tube on the atom. Thus if, as before, we suppose that the gyrostats in the hydrogen atom are rotating in the same direction as the fluid in the Faraday tube of which it is the origin when it carries a positive charge, whereas the gyrostats in the chlorine atom are rotating in the same direction as the fluid in the Faraday tube of which it is the termination when it carries a negative charge, we see that the attraction between a positively charged hydrogen atom and a negatively charged chlorine one will be greater than that between a negative hydrogen and a positive chlorine atom separated by the same distance.

The object of these illustrations is to call attention to the point that when charged atoms are close together, there may be forces partly electrical, partly chemical, in their origin in addition to those expressed by the ordinary laws of electrostatics.

There are one or two points in connexion with the theory of the electric field which can be illustrated by the conception of a Faraday tube as a bundle of vortex filaments, which, though not connected with the main object of this paper, may be briefly pointed out. The first of these arises from equation (4), p. 516, which indicates that the tension exerted by a vortex column is equal to the kinetic energy of the fluid in unit length of the column. Now we know that the forces on a charged body in the electric field are such as would be produced if there were a tension along the lines of force equal per unit area to the electrostatic energy in unit volume of the field. If we suppose the tension to be exerted by the Faraday tubes and the energy to reside in these tubes, this is equivalent to saying that the tension exerted by each of these tubes is equal to the energy in unit length of the tube. This exactly coincides with the result indicated by equation (4), if we suppose that the Faraday tubes are bundles of vortex filaments.

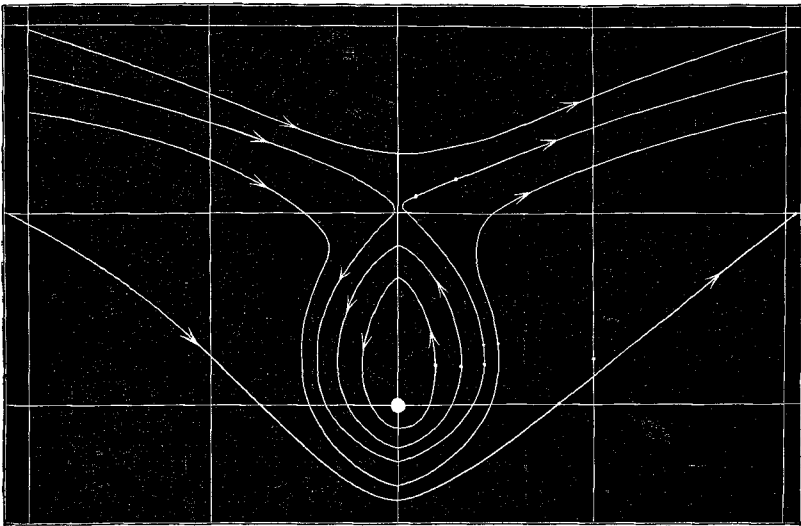
The other point is in connexion with the view that magnetic force is due to the movement of the Faraday tubes: the magnetic force being at right angles to the direction of the

Faraday tubes, and also to the direction in which they are moving, the magnitude of the force varying as the product of the "polarization" and the velocity of the tubes at right angles to their direction (see 'Recent Researches in Electricity and Magnetism,' by J. J. Thomson, p. 8). On this view the energy per unit volume in the magnetic field when the tubes are moving at right angles to themselves is (see 'Recent Researches,' p. 9)

$$\frac{\mu}{8\pi} P^2 V^2,$$

where μ is the magnetic permeability, P the polarization, and V the translatory velocity of the tubes. This expression would represent the kinetic energy due to the translatory motion of the tubes if the expression for the effective mass of the tubes contained a term proportional to the square of the "polarization." Now if we have a vortex column moving about in a fluid which is subject to other disturbances, the following considerations would seem to show that the expression for its effective mass would contain a term proportional to the square of the vorticity in the vortex column. The lines of flow when the vortex column is stationary in a

Fig. 2.



liquid moving so that at an infinite distance its velocity is uniform and horizontal are represented in fig. 2.

We see that some of these lines of flow in the neighbourhood of the column are closed curves ; now the liquid inside any one of these curves will always remain in the neighbourhood of the column, and if the column is moved will move with it : thus the effective mass of the column will be that of the column plus that of the liquid enclosed by the largest of the closed lines of flow. The linear dimensions of the curve are proportional to m/u , where u is the velocity of the fluid at an infinite distance from the column, and m the strength of the vortex ; (the equation to the bounding line of flow is easily seen to be $r = \frac{m}{u} e^{-\frac{u\theta}{m}}$), thus the area enclosed by the line

of flow, and consequently the mass of fluid inside a cylinder of which it is the cross section, is proportional to m^2/u^2 ; thus, as the effective mass is increased by this mass of fluid, the expression for the effective mass of the vortex column will contain a term proportional to the square of the vorticity. Hence, if we regard a Faraday tube as a bundle of vortex filaments, we can by this analogy see that its effective inertia might involve a term proportional to the square of the polarization.

Relation of the preceding Analogies to the Electrochemical Properties of the Atoms.

To return, however, to the relation between the electric charge and the electrochemical properties of the element whose atom carries the charge. The illustration given on page 513 suggests that when an atom is charged with electricity it acquires a certain amount of potential energy depending upon the sign of the charge and also upon the kind of atom carrying the charge. Let us suppose that when an atom of an element A carries unit charge of positive electricity, its potential energy, in consequence of the connexion between the internal motion of the atom and the motion of the fluid in the Faraday tube, is greater by σ_A than when it has no charge, while when the atom has the unit negative charge its potential energy is less by σ_A than that of the uncharged atom. The quantity σ depends upon the nature of the atom ; in 'Recent Researches on Electricity and Magnetism,' p. 64, it is called the Volta potential of the substance, since the difference of potential between two metals A and B when placed in contact can be proved to be equal to $\sigma_A - \sigma_B$.

If the substance A has a charge Q of positive electricity, then in the expression for its potential energy there will be the term $\sigma_A Q$. If we consider this term alone, then if σ_A is positive an increase in the positive charge will involve an

increase in the potential energy, while an increase in the negative charge would diminish the potential energy; if σ_A is negative the converse is true. Now a dynamical system behaves so as to facilitate any change which causes a diminution in the potential energy. Thus those substances for which σ is negative will tend to acquire a charge of positive electricity, while those for which σ is positive will tend to get a charge of negative electricity. Thus the existence of the property expressed by the coefficient σ would produce the same effect as von Helmholtz's specific attraction of the elements for the two electricities.

Suppose, for example, that we have two metals A and B in contact, and that σ_A, σ_B are the values of the Volta coefficients for A and B respectively; let σ_A be greater than σ_B . Then if A acquires a negative charge equal to $-Q$, and B a positive charge equal to Q , the potential energy of the two metals will be diminished by $(\sigma_A - \sigma_B)Q$. If this were the only source of potential energy, the transference of positive electricity from A to B, and of negative from B to A, would go on indefinitely, as each transference would involve a diminution in the potential energy. The separation of the electricities will, however, produce an electric field the potential energy due to which will increase as Q increases, so that the diminution in energy due to the Volta effect will be accompanied by an increase in the energy due to the electrostatic field. Let us suppose, for example, that the two metals form the plates of a condenser whose capacity is C , then when A has a charge $-Q$ and B a charge $+Q$, the energy in the electrostatic field is equal to

$$\frac{1}{2} \frac{Q^2}{C},$$

while the energy due to the Volta effect is

$$-(\sigma_A - \sigma_B)Q.$$

The flow of negative electricity into A and of positive into B will go on until the increment in the energy of the electrostatic field due to an increase δQ in the charge on B is equal to the decrement of the energy due to the Volta effect produced by the same displacement of electricity.

Since the total energy is

$$\frac{1}{2} \frac{Q^2}{C} - (\sigma_A - \sigma_B)Q,$$

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the increment when Q is increased by δQ is equal to

$$\delta Q \left\{ \frac{Q}{C} - (\sigma_A - \sigma_B) \right\};$$

or, if V is the difference of potential between A and B , the increment of the potential energy is equal to

$$\delta Q \{ V - (\sigma_A - \sigma_B) \}.$$

Thus so long as V is less than $\sigma_A - \sigma_B$, an increase in Q will be accompanied by a decrease in the potential energy, so that Q will tend to increase; while, on the other hand, when V is greater than $\sigma_A - \sigma_B$, an increase in Q will be accompanied by an increase in the potential energy, so that Q will tend to diminish: there will be equilibrium when $V = \sigma_A - \sigma_B$.

We see from this that if an atom of A has a unit negative charge, an atom of B a unit positive one, these atoms will retain their respective charges even though connected by a conductor, unless the potential of B exceeds that of A by more than $\sigma_A - \sigma_B$. If, on the other hand, A had a positive charge, B a negative one, they would, if connected by a conductor, interchange their charges unless the potential of B exceeded that of A by more than $\sigma_A - \sigma_B$.

Thus, assuming that σ is positive for chlorine and negative for hydrogen, an atom of hydrogen could retain a positive charge, and an atom of chlorine a negative one, even though the two were immersed in a conductor, provided the potential of the hydrogen atom did not exceed that of the chlorine atom by more than a certain limit; whereas if the hydrogen were negatively electrified and the chlorine positively, they would, if immersed in a conductor, interchange their charges unless the potential of the hydrogen atom exceeded that of the chlorine by the same limit as before.

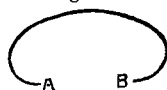
Chemical Combination.

Thus, if we have a number of hydrogen atoms and an equal number of chlorine atoms immersed in a conductor, and if initially half of both the hydrogen and chlorine atoms were positively and half negatively electrified, interchange of charges between the atoms would go on until all the hydrogen atoms were positively and all the chlorine atoms negatively electrified.

For this interchange of charges to go on, however, it would seem necessary that a negatively electrified hydrogen atom

and a positively electrified chlorine one should be connected by a conducting circuit. From the mechanical illustrations previously given, it seems unlikely that the atoms would interchange their charges by coming into contact, the positive charge passing from the chlorine to the hydrogen atom and *vice versd*. From these illustrations we should rather expect that if a negative hydrogen atom came very near to a positive chlorine one, the two, if alone in the field, would tend to repel rather than to attract each other, the Faraday tube connecting the atoms ceasing to be straight, and bulging out into the surrounding medium somewhat in the manner shown in fig. 3.

Fig. 3.

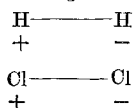


If in addition to the two atoms there were other charged bodies producing a very intense field tending to push the hydrogen and chlorine atoms together, then the interchange of their charges might take place by the ends of the Faraday tube gliding from one atom to the other after these atoms had been forced into contact by the external field. There are indications that the external field would have to be such as to produce a potential difference of a large number of volts between the two atoms before this method of exchanging their charges took place. In the absence of this potential difference, the atoms would not exchange their charges unless the medium into which the Faraday tube spread contained some conductor along which the ends of the Faraday tube could glide from one atom to the other. The necessity for this conducting circuit is perhaps one of the reasons why the presence of a third substance seems necessary for the continuance of many chemical reactions. How much a third substance able to act as a conductor could facilitate chemical combination may be seen from the following example. Suppose we have a mixture of hydrogen and chlorine molecules, and that by some external cause we split up these molecules into atoms; half of the hydrogen atoms produced by the dissociation of the hydrogen molecules will be positively electrified, while the other half will be negatively electrified; the same will also be true of the chlorine atoms. This condition will be permanent if the negative hydrogen atoms have no opportunities of interchanging their charges with the positive chlorine atoms, and a positive hydrogen atom would thus not be limited to combining with a negative chlorine one to form a molecule of hydrochloric acid, but might instead combine with a negative hydrogen atom to form a hydrogen molecule. If, however,

conducting circuits, able to connect atom with atom, were present, the circumstances would be much more favourable to the formation of hydrochloric acid. For if the conducting circuit stretched from a positive hydrogen atom to a negative chlorine one, these atoms would retain their charges; whereas when the circuits stretched from a negatively electrified hydrogen atom to a positively electrified chlorine one, the atoms would interchange their charges. Thus the effect of these conducting circuits would be to cause all the hydrogen atoms to be positively electrified, and all the chlorine ones negatively; this would of course increase the tendency for the hydrogen and chlorine to combine.

In the preceding case we have supposed the molecules to be already split up into atoms; when, however, we consider the case of a mixture of molecules not already decomposed, we see that something more than the stretching of a conductor from one atom to another is required to effect the interchange of their charges. For suppose H, H, Cl, Cl (fig. 4) represent

Fig. 4.



respectively a hydrogen and a chlorine molecule, and suppose that the negative hydrogen atom is connected with the positive chlorine one by a conducting circuit. Then, if the negative charge of the hydrogen and the positive one of the chlorine were interchanged, the diminution in the potential energy due to the Volta effect would be $2(\sigma_{\text{Cl}} - \sigma_{\text{H}})$, where σ_{Cl} , σ_{H} are the Volta coefficients of chlorine and hydrogen respectively, σ_{H} being negative. To set off against this diminution in the potential energy due to the Volta effect, we have the increase in the energy produced by tearing the $-$ charge on the H atom from its proximity to the $+$ charge, and forcing it close to the $-$ charge on the Cl atom. The increase in the potential energy due to this cause will be of the order $2(V_1 + V_2)$, where V_1 and V_2 are the potential differences between the atoms in the hydrogen and chlorine molecules respectively. Thus the diminution in the potential energy when the charges are interchanged is

$$2(\sigma_{\text{Cl}} - \sigma_{\text{H}}) - 2(V_1 + V_2),$$

and the interchange will not go on unless this quantity is positive. Now the potential difference due to the contact of two substances is equal to the difference of their Volta

coefficients, so that the σ 's will not exceed a small number of volts. To estimate the V 's is more difficult, but we may remark that when we produce a spark through a gas, in which case there is strong evidence that we split up some of the molecules into atoms, then, no matter how short the spark may be, or what may be the pressure of the gas, the potential difference between the electrodes must exceed a certain value which is very large compared with the potential differences developed by the contact of heterogeneous substances, amounting in the case of hydrogen to between 190 and 200 volts. This minimum potential difference required to produce a spark is so constant under very varying physical conditions, such as pressure, spark-length, and so on, as to suggest that it represents some property of the molecule; and I am inclined to think, and some experiments recently made at the Cavendish laboratory seem strongly to support the view, that the potential difference between the atoms in a molecule placed so as to be free from the action of other molecules is of the order of the minimum potential difference required to produce a spark. In the few cases where a direct estimate has been made of the work required to split up the molecule into atoms, such as that made by E. Wiedemann of the work required to decompose the hydrogen molecule, and that by Boltzmann for the iodine molecule, the potential difference indicated by these estimates far exceeds that produced by the contact of heterogeneous substances.

It would thus appear that in the case of gases where the molecules are free, the condition

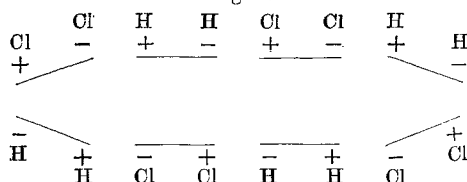
$$2(\sigma_{\text{Cl}} - \sigma_{\text{H}}) > V_1 + V_2$$

is not fulfilled; so that, on the electrical theory, chemical combination would not proceed. To produce chemical combination in such cases there must be some means of lowering the potential difference between the atoms in the molecules. Two methods by which this might take place at once suggest themselves. The first of these is that the combination, instead of taking place between a single pair of molecules, really takes place between aggregates of the molecules, physical aggregation preceding chemical combination.

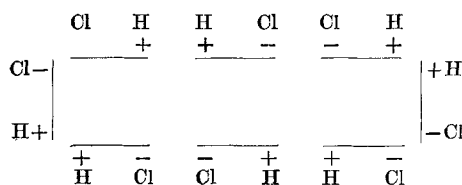
Thus suppose that a number of molecules form themselves into a chain, such as that represented in fig. 5; then, if we consider a $-H$ atom and the adjacent $+Cl$ one, we see that the disposition of the charges on the atoms of the other molecules in the chain will diminish the work required to separate the $-$ charge on the H atom from the $+$ charge on the

neighbouring H atom, and also that required to separate the + charge on the Cl atom from the - charge on the atom with which it is paired. Thus this disposition of molecules, by diminishing the electrostatic attractions, increases the chance for the -H and +Cl to interchange their charges in

Fig. 5.



(a)



(b)

response to the "Volta effect:" after this interchange has taken place the adjacent H and Cl atoms will have respectively + and - charges, *i. e.* charges suitable for the formation of the HCl molecule; if such molecules form, the ring will be disposed as in fig. 5, *b*. This disposition will not be stable, since the lines joining the negative to the positive atoms in the molecule do not all point in one way; the ring will consequently break up into separate HCl molecules.

Thus, on this view the chemical combination consists in the formation of an aggregate of a large number of H and Cl molecules, then the interchange of the charges on some of the atoms, then the formation of an aggregate of HCl molecules, and finally the breaking up of this aggregate into a number of separate molecules of HCl. It will be noticed that there are no atoms set "free" during the whole of the process. The presence of free charged atoms during the progress of chemical combination between gases could be detected by experiments made on the electric conductivity of the mixture whilst the combination is proceeding. If free charged atoms are present they will move under electromotive forces, and will cause the mixture of gases to act as a conductor of electricity. A method of testing the conductivity of gases and the results of experiments made with it are given in a paper

by the author (Proc. Camb. Phil. Soc. vol. viii. p. 258). These experiments showed that when a mixture of H and Cl was combining it did not possess any conductivity, thus proving that in these cases no charged atoms were set free during the combination. Some other cases of chemical combination gave the same result; on the other hand there were a class of cases in which the mixture of gases acted as a conductor whilst chemical combination was going on. The experiments thus proved that in many cases of chemical combination no charged atoms are set free.

I also investigated this point by another method. Let us assume for a moment that free charged atoms are liberated during chemical action. To fix our ideas, let us take the case of a piece of zinc attacked by chlorine; suppose now that we electrify the zinc: if chemical action liberated free ions, or, supposing that an aggregation of atoms is necessary, if the algebraical sum of the charges on the atoms forming this aggregate were not zero, then when the electrified zinc atom enters into chemical combination an atom of chlorine must be set free carrying a charge of electricity of the same sign as that on the electrified zinc atom. Thus, in this case the charge would leak from the metal into the gas and the latter would cease to insulate. If, on the other hand, chemical combination went on between an aggregate of atoms the algebraical sum of whose charges was zero, then, however much the zinc was attacked, there would be no liberation of charged atoms and no transference of electricity from the metal to the gas.

I made an extensive series of experiments to find out whether an electrified metal plate when immersed in a gas by which it was chemically attacked did or did not lose its charge. I was never able to trace any leakage of electricity to this cause, even though two metal plates charged to a great difference of potential, either by a Wimshurst machine or by a battery of 2000 small storage-cells, were placed close together in the gas. The electrified surfaces were zinc, mercury, and electrolytic solutions, the gases chlorine and nitrosyl chloride; but though the conditions of the surfaces showed that active chemical action had taken place, there was no escape of electricity through the gas whether the surfaces were positively or negatively electrified. In these cases the chemical combination went on at the temperature of the room when there was no chance of the gas being dissociated. In the case of combination at very high temperatures, when the gas may be dissociated, we shall see later that there are cases where chemical combination does promote the discharge of electricity.

The aggregation of molecules, as described in the preceding sections, is one method by which the attractions between the oppositely electrified atoms in the molecule might be weakened sufficiently to allow chemical action to proceed. Another method by which the same end might be accomplished would be for the molecules to be immersed in, or to be close to the surface of, a conductor or substance of large specific inductive capacity. The effect of this, as explained in the *Philosophical Magazine*, vol. xxxvi. p. 320, would be to diminish the attraction between the atoms and allow them to be easily separated. The substance which acts as the bridge for the interchange of the charges on the atoms might be the substance which when collected into lumps served by its electrostatic action to diminish the attraction between the atoms. This method of producing chemical change closely resembles the preceding—in each of them the presence of a third substance is necessary, and in each of them the formation of molecular aggregates, but whereas on the first view the aggregates are those of the substances which are combining chemically, on the second they are formed by the third substance.

The hypotheses to which we are led by the preceding considerations may be summed up as follows :—

The forces between charged atoms placed very near together are modified by the electrochemical properties of the atoms. In consequence of this an electronegative atom if positively charged cannot, in the absence of a strong external electric field, interchange its charge with the negative charge on an electropositive atom unless the two are connected by an external conducting circuit.

Chemical action does not (in general) take place between a single pair of molecules alone in the field, but requires the formation of aggregates either of the interacting molecules or of some third substance which is either a conductor of electricity or has a large specific inductive capacity.

In the preceding statement an element is called electropositive or electronegative according as its Volta coefficient is negative or positive.

Thus, on these hypotheses, chemical combination between two elements involves in general two processes :—(1) a process by which all the electropositive atoms, half of which were originally positively and half negatively charged, all become positively charged, while the electronegative atoms become all negatively charged ; (2) the combination of these properly charged atoms to form a molecule of the compound.

In some cases the process of chemical combination seems

only to reach the first stage, that of the interchange of charges between the atoms of the elements. If the process stops at this stage, the electropositive substance will be charged with positive electricity, the electronegative substance with negative electricity. If one of the substances, say the electropositive, is a solid or a liquid, while the other is a gas, then at the surface of the solid or liquid there will be two layers, one of positive electricity on the solid or liquid, the other of negative in the gas. This double layer of electrification will make the electric potential discontinuous at the surface separating the two substances, the potential in the solid just inside the surface of separation exceeding that in the gas just outside the surface by a finite amount. The electrification produced by the splashing of drops is evidence of the existence of this double layer of electrification: when a drop of water or of mercury falls through air and splashes on a plate, the drop itself is positively electrified, while there is negative electrification in the surrounding air. On the view just given, this is an example of incomplete chemical combination: in the case of the water, the electrical interchanges preliminary to the formation of H_2O_2 , the oxygen in the air getting the negative charge, have taken place; the second stage, however, does not go on, or at any rate is not completed during the falling of the drop. Thus the positively and negatively electrified atoms are not bound together so firmly as they are in a chemical compound, and get separated in the great extension of surface produced by the splashing. In the case of mercury the first stage of oxidation, that is the assumption of the negative charge by the oxygen and of the positive by the mercury, occurs, while the second either does not occur or is not completed during the fall of the drop. It would seem from the phenomena of drops that examples of this incomplete chemical action are very frequent, for the splashing of drops of the most widely different substances gives rise to electrification. In fact it seems possible that the existence of this double coat, and on our hypothesis of incomplete chemical action, is almost universal at ordinary temperatures, and that the electrification produced by the friction of heterogeneous substances is due to the partial rubbing off of this coating from one or both of the substances.

We shall now proceed to consider in the light of this hypothesis as to chemical action several simple chemical and electrical phenomena. We shall begin with the case of oxidation. Let us suppose that we have a zinc rod immersed in oxygen, and in order to take a case where the chances of combination are greatest, let us suppose that the oxygen molecules are dissociated by some external agent into atoms.

Suppose that the combination begins, ZnO being formed.

Since a positive charge is withdrawn from the zinc and a negative one from the oxygen, the zinc and oxygen, which were originally electrically neutral, will now be charged negatively and positively, so that at the surface of contact of the zinc and the oxygen a charged condenser will be formed with its negative charge carried by the zinc atoms, its positive charge by the oxygen atoms. According to our hypothesis, zinc and oxygen atoms in these electric states do not combine unless connected by conducting circuits, so that, unless such circuits are present, for each molecule of ZnO formed there will be an increase in the charge on the condenser, and consequently an increase in its potential energy. The charge on the condenser is proportional to the number of molecules of ZnO formed, so that the electrostatic potential energy will be proportional to the square of the number of molecules; the diminution in the chemical potential energy due to the formation of ZnO is only proportional to the number of molecules of this substance. Thus the increase of the potential energy increases faster with the number of molecules of ZnO formed than the diminution in the energy; so that after a certain amount of chemical combination has occurred, any further combination will be attended by an increase in the total potential energy. When this point has been reached chemical combination will stop; so that under these circumstances only a limited amount of chemical combination will occur. Suppose now, however, that in addition to the zinc and oxygen other substances are present which can form conducting circuits between the negative zinc and the positive oxygen atoms, and thus enable these atoms to interchange their charges, so that the zinc becomes positively, the oxygen negatively electrified. In this state they can combine so that the condenser at the surface of the zinc will be discharged. As this condenser is constantly being discharged, there will be no increase in the potential energy due to it, and thus the progress of the chemical action will be accompanied by a diminution in the potential energy, and will therefore proceed until one or other of the substances is exhausted.

Similar considerations will show why but little chemical action goes on if zinc is immersed in acid, while the action proceeds freely when the zinc is connected to the acid by an external conducting circuit.

It is easy to find an expression for the difference of potential reached between the plates of the condenser formed at the surface of the zinc when there is no external con-

ducting circuit. Let us take the case of zinc immersed in acid, suppose we have a rod of zinc immersed in a solution of zinc chloride. We may suppose that in the solution we have positively charged zinc atoms, negatively charged chlorine ones, and molecules of zinc chloride, consisting of a positive zinc atom combined with a negative chlorine one. When a stick of zinc is immersed in the solution, some of its positively charged zinc atoms combine with the negative chlorine ones in the solution and form neutral zinc chloride. This leaves on the zinc rod an excess of negative electricity, while in the solution there will be an excess of positive electricity carried by the zinc atoms. These atoms approach the rod and form one plate of a condenser, the other plate of which consists of the negatively electrified zinc atoms in the rod, the charge in this condenser will be proportional to the number of molecules of zinc chloride formed.

We can find the potential difference between the plates of this condenser when equilibrium is reached in the following way :—When equilibrium is reached the mean Lagrangian function of the system will be stationary.

Now the Lagrangian function consists (1) of a part due to the solvent; as this does not change during the process of chemical combination we may leave it out of account. (2) A part due to the zinc rod; this will be of the form $m_1 Z_1$ where m_1 is the mass of the zinc in the rod, and Z_1 a quantity independent of m_1 . (3) A part due to the zinc chloride in solution; if m_2 is the mass of ZnCl_2 , then this part of the mean Lagrangian function is equal to

$$-m_2 R_2 \theta \log m_2 + m_2 w_2$$

(see ‘Applications of Dynamics to Physics and Chemistry,’ p. 154): here θ represents the absolute temperature, w_2 a quantity independent of m_2 , while $R_2 \theta$ is equal to the pressure exerted by a number of molecules of ZnCl_2 in the gaseous state and obeying Boyle’s law divided by the density of the gas in this state. (4) A part due to the zinc atoms in the solution; if m_3 is the mass of these atoms, this part of the Lagrangian function is equal to

$$-m_3 R_3 \theta \log m_3 + m_3 w_3.$$

(5) A part due to the Cl atoms in the solution; if m_4 is the mass of these atoms, this part is equal to

$$-m_4 R_4 \theta \log m_4 + m_4 w_4.$$

(6) A part due to the condenser formed at the junction of the zinc and the solution; if C is the capacity of this condenser

and Q the charge, this part of the Lagrangian function will be equal to

$$-\frac{1}{2} \frac{Q^2}{C}.$$

Thus the total variable part of the Lagrangian function, which we shall denote by H , is given by the equation

$$H = m_1 Z_1 - \theta(m_2 R_2 \log m_2 + m_3 R_3 \log m_3 + m_4 R_4 \log m_4) \\ + (m_2 w_2 + m_3 w_3 + m_4 w_4) - \frac{1}{2} \frac{Q^2}{C}.$$

When things are in a steady state the value of this function is stationary, hence

$$\frac{dH}{dm_1} \delta m_1 + \frac{dH}{dm_2} \delta m_2 + \frac{dH}{dm_3} \delta m_3 + \frac{dH}{dm_4} \delta m_4 + \frac{dH}{dQ} \delta Q = 0, \quad (1)$$

for all consistent values of $\delta m_1, \delta m_2, \delta m_3, \delta m_4, \delta Q$.

One possible change in the system is for n atoms of zinc in the rod to combine with $2n$ atoms of Cl to form n molecules of ZnCl_2 . Q will, if we take as unit charge the charge carried by a monad atom, be increased by $2n$, since zinc is a dyad.

Hence

$$\delta m_1 = -n, \quad \delta m_2 = +n, \quad \delta m_3 = 0, \quad \delta m_4 = -2n, \quad \delta Q = 2n;$$

so that by (1) we have

$$-\frac{dH}{dm_1} + \frac{dH}{dm_2} - \frac{2dH}{dm_4} + \frac{2dH}{dQ} = 0.$$

Since $\frac{dH}{dQ} = -\frac{Q}{C} = -V$, where V is the potential difference between the plates of the condenser, we have

$$V = \frac{1}{2} \left\{ \frac{dH}{dm_2} - \frac{dH}{dm_1} - \frac{2dH}{dm_4} \right\}. \quad (2)$$

Another change that could take place in the system is for n of the atoms of zinc in the solution to combine with $2n$ of the chlorine atoms to produce n molecules of ZnCl_2 . In this case

$$\delta m_1 = 0, \quad \delta m_2 = n, \quad \delta m_3 = -n, \quad \delta m_4 = -2n, \quad \delta Q = 0.$$

Thus equation (1) becomes

$$\frac{dH}{dm_2} - \frac{dH}{dm_3} - \frac{2dH}{dm_4} = 0; \quad (3)$$

hence from (3) and (4) we have

$$V = \frac{1}{2} \left\{ \frac{dH}{dm_3} - \frac{dH}{dm_1} \right\} (4)$$

Now dH/dm_3 depends solely upon the number of zinc atoms in unit volume of the solution, while dH/dm_1 is independent of the solution altogether. Hence we see that the potential difference between the zinc and the solution depends solely upon the number of free zinc atoms in unit volume of the solution. If this be constant the potential difference is the same whatever salt of zinc is used.

From the value found for H we see

$$V = \frac{1}{2} \{ -R_s \theta \log m_3 + \text{a term independent of } m_3 \} , . . (5)$$

thus

$$\frac{dV}{dm_3} = - \frac{1}{2} \frac{R_s \theta}{m_3} .$$

An expression which shows how the potential difference varies with the strength of the solution.

We see from equation (5) that the magnitude and even the sign of V depends upon the value of m_3 , the number of free zinc ions in the solution. If m_3 is less than a certain quantity V is positive, that is the positive coating of the double layer formed at the zinc surface is in the electrolyte, while the negative is on the zinc; when m_3 exceeds this value, the signs of the coatings are reversed. For infinitely dilute solutions the value of V would be infinite. Though equation (5) enables us to find the value of V when m_3 is known, the equations are insufficient to determine this quantity in such a case, for example, as when a zinc rod is immersed in a solution of HCl : here $ZnCl_2$ may be formed by chemical action and dissolve in the zinc, and then partly be split up into Zn and Cl atoms. In this case we have in the solution molecules of $ZnCl_2$ and HCl , atoms of Zn , H , and Cl . Let m_5 denote the number of atoms of H , m_6 the number of molecules of HCl , the rest of the notation being the same as before. Then to determine the variables we have the equations 2, 3, 4, and since one way in which the system could vary would be by an atom of hydrogen combining with an atom of chlorine to form a molecule of hydrochloric acid, we have

$$\frac{dH}{dm_6} - \frac{dH}{dm_5} - \frac{dH}{dm_4} = 0 (6)$$

Since the total number of hydrogen and chlorine atoms contained in the solution must be equal to N , if N is the number of hydrochloric acid molecules originally taken for the

534 Prof. J. J. Thomson on the Relation between the solution, we have

$$m_5 + m_6 = N, \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$m_4 + 2m_2 + m_6 = N. \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Thus to determine the 6 quantities $m_2 \dots m_6$, V , we have only the five equations (3), (4), (6), (7), (8). The charge on the condenser $Q = 2m_2$, and $V = Q/C$; hence if we know C the capacity of the condenser we have another equation connecting the six quantities, so that they can be determined. To calculate C , however, we should require to know the distance between the plates of the condenser, that is the distance between the positively and negatively charged zinc atoms. We do not know this distance, but if we had a series of measurements of V we should by the preceding equations be able to calculate m_2 , and hence the capacity of the condenser, and from this capacity the distance between the two layers.

The preceding expression gives the potential difference between the zinc and the electrolyte on the supposition that these are not connected by an external conducting circuit; the presence of such a circuit might, however, so modify the conditions as to render the preceding considerations quite inapplicable. Thus, take the preceding case of zinc immersed in dilute HCl , if the solution is exceedingly dilute, we have on the surface of the zinc a number of positive hydrogen atoms. If the Volta effect could come into play there would be a diminution in the potential energy of the whole system, if the $-$ zinc and the $+H$ interchanged their charges: in the absence of the external circuit this on our hypothesis is impossible, but it would take place if such a circuit were present. In this case the negative charges on the zinc atoms would be replaced by positive, the potential of the zinc instead of being lower than that of the electrolyte would be higher. This illustrates the principle that the two causes which tend to produce potential differences between substances in contact, viz. direct chemical combination and the interchange of charges on the atoms, tend to establish potential differences of opposite sign. Chemical combination tends to make the electropositive substance negative to the electronegative one, since the positive atoms combine while the negative ones are left, while the interchange of charges tends to make the electropositive substance positive to the electronegative. Thus, when two substances are placed in contact under varying physical conditions, the sign of the potential difference will depend upon the relative intensity of these two effects. Observation seems to prove that a difference in

the sign of the contact potential difference between two substances does take place when the circumstances are altered in such a way that we might expect great changes in the relative importance of these effects to occur. Thus there are cases where, when the substances are cold, when we should expect the chemical action to be sluggish, the electropositive substance is at a higher potential than the electronegative one, while when the temperature is that of red heat or higher, when chemical action is presumably more vigorous, the sign of the potential difference is reversed. Thus, for example, when a drop breaks off from a column of mercury and falls through oxygen, the mercury is positively, the oxygen negatively electrified: again, when ultra-violet light falls upon a clean metal plate, the metal is positively, the surrounding air negatively electrified. In this case the sign of the potential difference indicates that the effect due to the interchange of charges overpowers that due to the chemical combination. If, however, we have a piece of metal above a red heat surrounded by air, the air will acquire a positive charge, the metal a negative one; so that in this case the effect of chemical combination overpowers any effect that may be due to the interchange of atoms.

The contact of the zinc with the solution in the preceding example thus gives rise to the formation of two layers of atoms, one layer being positively, the other layer negatively electrified. When the solution is very weak, this double layer which is interposed between the zinc and the solution consists of a layer of partly dissociated zinc molecules, the positive atoms being next the solution, the negative atoms next the zinc plate. If the solution is strong, the transition between the zinc and the solution is made by a layer of partly dissociated molecules of the salt, the positive layer, consisting of zinc atoms, being next the zinc, the negative layer, consisting of atoms of the electronegative constituent of the salt, being next the solution. In the case of the contact of a metal and the electrolyte, the work required to produce the double electrical layer which gives rise to the potential difference is in the preceding investigation supposed to be done by the osmotic pressure. There is, however, another source of energy quite adequate to produce potential differences at the surfaces of contact of different substances, and which is available in the case of solids as well as liquids. This source is surface-tension. Every unit of area of the surface of separation of two substances, A and B, contributes an amount of potential energy equal to the surface-tension between A and B. Now Lord Rayleigh has shown (*Phil. Mag.* October 1883, p. 315)

that, if the transition from A to B, instead of being abrupt, takes place through a thin layer (whose thickness need only be commensurable with molecular distance) whose properties are intermediate between A and B, the potential energy due to surface-tension will be diminished. This diminution in the potential energy will produce a tendency for such a transitional layer to be formed, even though the formation of the layer is accompanied by a double layer of electrification. The energy rendered available by a sensible diminution in the surface-tension will be more than sufficient to charge the double layer of electrification up to a potential difference amounting to a large fraction of a volt. For if the distance between the electrified layers is 10^{-8} centim., and their potential difference 1 volt, the energy per unit area of the condenser formed by the double layer will be equal to $10^{16}/8\pi \times 10^{-8} \times 9 \times 10^{20}$, or about 44 ergs. If the surface-tension were the same as that of water, the energy due to it would be 78 ergs per square centimetre, so that if any sensible diminution in this took place, the energy rendered available would suffice to charge up the layer to a potential difference comparable with a volt. Even if the formation of this layer required as a preliminary chemical decomposition to liberate the charged atoms forming the layer, and this decomposition required a supply of energy, there would still be plenty available for this purpose. The thickness of the layer is comparable with the range of molecular forces; thus the quantity of matter in it, and therefore the amount of chemical decomposition, will be exceedingly small, so small as to be quite imperceptible by chemical means, but small as it is it may, in consequence of the enormous electric charges carried by the atoms, be sufficient to produce a finite potential difference between the coats of the double layer.

The amount of energy which would be liberated by a diminution in the abruptness of transition, and the effects which this might be expected to produce, are, I think, much greater than is generally suspected. Thus we should, for instance, expect that the abruptness of transition between, say, a metal like mercury and a gas like oxygen, would be diminished if between the mercury and the gas there was a film of the compound of the two: the tendency to form this compound would be very great, for if the film of oxide only diminished the surface-tension by one per cent., enough energy would be liberated to suffice to raise the temperature of a film of oxygen 10^{-8} centim. thick several hundred degrees Centigrade. With this amount of energy available, it is difficult to avoid the conclusion that even the least oxidizable metals must, when exposed to air, be coated with a thin film of oxide, and though

this film is too thin to be detected, either by chemical or optical means, it may yet, as we have seen, produce appreciable electrical effects. The same effects, too, might be expected to take place between solids: thus, if copper and zinc were brought into intimate contact, there would be a tendency for a layer of brass to form between them, it does not seem impossible that under favourable circumstances the zinc and copper might be cemented together by this film of brass.

This consideration, too, must have an important application to the electrification due to the splashing of drops; this phenomenon requires the existence of a double coating of electricity over the surface of the drop, to provide the atoms which carry the charges on these coatings chemical decomposition may have to take place. The energy for this may come from the lowering of the surface-tension produced by the formation of an intermediate layer, so that at the surface of the drop chemical changes may take place, of which we have at ordinary temperatures no experience from experiments made with large masses of the substances.

Contact-difference of Potential between a Metal and a Coating of Oxide.

If we have a metal plate covered with a film of oxide or other compound of the metal, the transition from the metal to the air will be more gradual if the molecules of the compound in the part of the film near the plate are arranged so that the metal atoms are next the plate, and the oxygen atoms on the far side. In the molecules of the oxide, the metal atoms carry the charge of positive electricity, while the oxygen atoms carry the negative charge: there will thus at the surface of the plate be a double coating of electricity, the positive side of this layer being next the plate, the potential, therefore, will fall as we pass from the metal to the layer of oxide, that is the oxide will be negative to the metal. This agrees with the results obtained by those who have experimented on contact-electricity, and it further appears, as a possible interpretation of their experiments, that the potential difference between a metal and its oxide may amount to a considerable fraction of a volt.

Communication of Electricity from the Electrified Atoms of a Gas to a Conductor.

This is only another aspect of the preceding question. For suppose we have a number of electrified atoms of a gas in contact with a metal, and that the metal is electropositive to the gas, the electricity can go from the gas to the metal in the following ways:—(1) If the atoms of the

gas are negatively electrified, they may combine with positive atoms of the metal to form a neutral compound, leaving an excess of the atoms of the metal negatively electrified. Or, if the atoms of the gas are positively electrified, then, if any substance is present which can form conducting chains between the atoms of the gas and those of the metal, the atoms will interchange their charges, the positive charge going to the electropositive substance and the negative to the electronegative. Those atoms of the gas which were positively charged might unite with those negatively charged to form molecules, so that the gas itself would emerge electrically neutral after contact with the metal.

It will be seen that each of these methods requires something more than mere contact of the gas and metal, this seems borne out by the phenomena exhibited by electrified gases. It was shown by Giese that electrified gases from a flame could pass through wire gauze connected with the earth, and yet retain their charges: this fact is exemplified in a very striking way by Lord Kelvin's electric strainers, as he finds that electrified gases still retain an appreciable fraction of their charges after passing through these strainers which consist of many layers of wire gauze placed one behind the other. In an experiment I described in the B. A. Report for 1894 ("The Connexion between Chemical Combination and the Discharge of Electricity through Gases"), an electrified gas retained its charge though enclosed in a vessel with a large pool of mercury connected to the earth. I have also found that such gases retain a large proportion of their charge after bubbling through a mixture of sulphuric acid and water. In a paper "On the Passage of Electricity through Hot Gases" (Phil. Mag. [5] xxix. p. 444), I showed that when a current is flowing through a hot gas a piece of cold metal interposed between the electrodes completely stops the current, though when the metal gets red hot the current passes through it with ease. In all these cases the charged atoms would be striking against conductors, so that they furnish very strong evidence that this process alone is not sufficient to rob the atoms of their charges.

The first of the processes alluded to above would tend to make a gas lose a negative charge or the metal a positive one, while the second process would make the gas lose a positive charge, the metal a negative one. This is on the assumption that the metal is electropositive to the gas; if it were electronegative, the words positive and negative must be interchanged in the preceding statement.

The first process involves chemical combination, thus anything tending to promote combination, such as a high tem-

perature of the gas or metal, would increase this effect ; we should therefore expect to find evidence of this effect in the case of hot bodies. A very good instance of this effect is the fact, discovered by Guthrie, that a hot ball of iron could retain a negative charge when it could not retain a positive one. The experiments of Elster and Geitel also illustrate this point. Again I found (see Proc. Roy. Inst. April 13, 1894), that if in a vessel containing hydrogen (and probably a little air) at a low pressure, we split up some of the molecules of the gas so as to get a supply of positively and negatively electrified atoms, a red-hot clean copper rod connected with the earth would discharge the negative electricity and leave the positive behind. The negative electricity escapes from the gas, since the negatively electrified gaseous atoms combine chemically with the positive atoms of the metal. If, however, a red-hot copper rod thickly coated with oxide is placed in the gas, the *positive* electricity escapes from the gas through the rod to the earth. This is in accordance with the theory ; the chemical process which now goes on is the reduction of the oxide : and this is effected by the positive hydrogen atoms combining with the negative oxygen atoms, thus the process affords a means of escape to the positive electricity in the gas, but not to the negative.

The second process by which we have explained the escape of electricity from a gas is that of the interchange of charges between oppositely charged atoms. As the tendency for this process to take place arises from the Volta effect, it will be great when we have a number of strongly electropositive atoms charged with negative electricity near a number of electronegative ones charged with positive electricity. Thus we should expect the effect to be great when one of the substances is an electropositive metal, as when this is in an electrically neutral state half the strongly electropositive atoms are charged with negative electricity, and on account of the Volta effect there is a great tendency for them to lose their charges. When, however, we have an electrolyte instead of the metal, we should expect the effect to be much smaller, as in an electrolyte the electropositive element has the positive charge, the electronegative one the negative ; it might, however, still exist to some extent if, for example, the electrified gas in contact with the electrolyte were more electronegative than the negative element of the electrolyte, and if the gas carried a positive charge.

This difference between metals and electrolytes may perhaps be the explanation of the fact that, whereas a sheet of metal when illuminated by ultra-violet light rapidly loses a negative charge while it can retain a positive one, this effect being

most pronounced the more electropositive the metal, an electrolyte, on the other hand, when exposed to ultra-violet light does not lose its charge, whether this be positive or negative.

Another example of the discharge of electricity by the second process, is that in the glow-discharge from a metal where the temperature is low the negative discharge occurs more easily than the positive, *i. e.* the potential difference between the point from which the electricity escapes and the nearest large conductor is less when the point is negatively electrified than when it is positively. It would be interesting to see whether this difference would still persist if the point from which the discharge takes place were made of an electrolyte and not of metal. On the hypothesis we have just been describing, we should expect the difference to be much reduced by the substitution of an electrolyte for the metal. Some recent experiments by Prof. S. P. Thompson show that the conditions of discharge are modified when lead peroxide is substituted for metal.

When a glow-discharge takes place from a metal point connected directly with a Ruhmkorff coil or a Wimshurst electrical machine the surrounding gas gets negatively electrified. This, however, is not always the case if we connect the point from which the discharge takes place to an instrument producing potential differences greatly exceeding those given by a Ruhmkorff coil. A very convenient form of such an instrument is the one described by Prof. Elihu Thompson, which is a transformer whose primary is a coil connecting the outside coatings of two Leyden jars, while the secondary is a coil with a large number of turns carefully insulated from the primary. When the oscillating current produced by discharging the jars passes through the primary, the electromotive force induced in the secondary is able to induce sparks of great length. Using a transformer of this kind instead of the Ruhmkorff coil, Harvey and Hird (*Phil. Mag.* vol. xxxvi. p. 45) and Himstedt (*Wied. Ann.* lii. p. 473) found that when the point discharged in oxygen, the gas was *positively* electrified, while when it discharged in hydrogen, the hydrogen was negatively electrified, just as when the Ruhmkorff is used. The very intense field produced by the transformer would split up the molecules of the gas and promote direct combination between the metal and the gas; this, as we have seen, would cause the gas to be positively, the metal negatively electrified, and this, as we have seen, is what happens in the case of oxygen, though not in that of hydrogen. In the case of the electrification of the

air in a vessel into which a point is discharging, we have to consider not only the communication of electricity from the point to the gas, but also the diffusion of the electrified atoms of the gas from the neighbourhood of the point through the vessel. Any difference in the rate of diffusion would, even though the communications of + and - electricity from the point to the jar were made with equal ease, give rise to an electrification of the gas. Imagine, for example, that negatively electrified atoms diffuse through the gas more quickly than positively electrified ones; then, if the rates of emission of + and - electricity were the same, the negatively electrified atoms would get further from the point than the positive, so that the outlying regions would get a charge of negative electricity; the region round the point would be charged with positive electricity, part of this would leak back into the point, leaving the gas as a whole negatively charged. Several phenomena, which I shall now proceed to describe, have led me to the conclusion that the effects due to the communication of the electricity from the metal to the gas are masked in many cases by the difference in the rates at which the electrified atoms diffuse, the negative atoms in all my experiments diffusing more rapidly than the positive ones. In the case of oxygen, where the gas gets a positive charge, the strong tendency for the oxygen to combine with the metal is sufficient to overcome the more rapid diffusion, whereas with such gases as hydrogen and carbonic acid, where the tendency to combine is weaker, diffusion gets the upper hand.

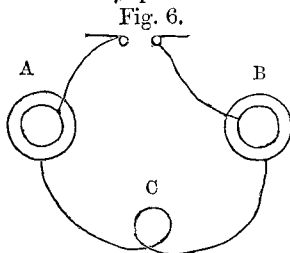
I made several experiments with chlorine, using different materials for the discharging point. The first substance I tried was silver chloride which had been fused into a solid mass; when this point was connected to one of the terminals of the high tension transformer, the chlorine was negatively electrified. I then used a zinc point, protecting the zinc before the experiment began by covering it with a glass tube, through which it was pushed just before the discharge began; in this case, again, the chlorine was negatively electrified to a slight extent. I then replaced the zinc point by a sodium one, protecting this in the same way as the zinc by a glass tube; when the discharge passed from the sodium point, the chlorine was *positively* electrified. Thus by using a substance such as sodium, which has a very great affinity for chlorine, we are able to overcome the effect of diffusion, and get a positive charge in the gas, just as when the discharge passes from a copper point into oxygen.

The following experiments seem to show that a negatively

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electrified hydrogen or oxygen atom moves more quickly under equal electric intensities than a positively electrified one.

The outside coatings of two Leyden jars, A, B (fig. 6), were connected by a wire wound into a coil C. In this coil an exhausted bulb was placed and a platinum wire fused into the bulb; this wire was connected with an electrometer. The inside coatings of the jar were connected with the terminals of an induction-coil through the primary of which the alternating current used for lighting the laboratory passed. This caused an arc-discharge to pass between the terminals of the induction-coil, and produced a potential difference between the insides of the jars. This potential difference can be very greatly increased by directing a blast of air on the space between the terminals of the induction-coil, and so blowing out the arc. If we now examine the electrical state of the platinum wire in the bulb, we shall find that, when the blast is on, the wire acquires a positive charge when placed near the equator of the bulb (by the equator of the bulb we mean the region inside the bulb adjacent to the coil which encircles it), and a negative charge when placed near the pole. If, however, after the blast has been on for some time, it is suddenly stopped and the arc allowed to pass between the terminals of the induction-coil, the sign of the electrification is reversed, the platinum wire now acquiring a positive charge when placed at the pole and a negative charge when placed at the equator. Both these results are, I think, explicable if we suppose that the negative atoms diffuse more rapidly than the positive ones. For, take the case when the arc is blown out. Here there is a great potential difference between the electrodes, and the coil surrounding the bulb is raised to a high potential. This causes a brush-discharge to start from the glass into the rarefied gas in the bulb, the discharge starting from the part of the glass nearest the coil, *i. e.* from the equator. If, now, the negative atoms travel faster through the bulb than the positive, then, even though the same number of the two kinds of atoms start from the glass, the negative atoms will be in excess in the region remote from the origin of the discharge, while near this origin the positive atoms will be in excess: thus we shall have positive electrification at the equator, negative electrification at the poles. Let this go on until a number of positive and negative atoms are dispersed through the bulb. Then stop the blast. This at once



greatly diminishes the potential difference between the terminals of the induction-coil, and lowers the potential of the coil surrounding the bulb to such an extent that the brush discharge no longer takes place from the glass: the electric intensity in the bulb is lowered, so that no further decomposition of the gas takes place, and the bulb now does not show any luminosity. The charged atoms produced by the previous discharge linger for some time in the bulb before recombining, and move under the electric intensity due to the oscillating currents in the coil; the lines of electric intensity arising from the induction due to these currents are circles, with the line joining the poles of the bulb for their axis. Under these forces the atoms will tend to describe these circles; and since the negative ones move more quickly than the positive ones, the negative atoms will be revolving round the axis of the bulb with greater rapidity than the positive ones: hence, on account of centrifugal force, there will be an excess of negative atoms at the equator, and consequently an excess of positive ones at the pole: thus the equator will be negatively, the poles positively electrified. This electrification is, however, only transient, as the opposite charged atoms soon recombine.

If the negative atoms move more quickly than the positive ones, then in a discharge-tube in a steady state the pressure at the positive electrode must be higher than that at the negative. For at any part of such a tube where there is no excess of positive electrification, the number of negative atoms which in unit time cross a section of the tube is greater than the number of positive ones. There will thus be a stream of atoms towards the positive electrode: to keep the pressure in the tube constant, we must compensate this by a stream of molecules from the positive to the negative electrode.

To calculate this pressure, let us suppose that the discharge-tube is cylindrical of radius a . Let i be the current through the tube, u the velocity of the negative ions, v the velocity of the positive; then in unit time the number of atoms lost by the side of the tube next the negative electrode and gained by the side of the tube next the positive is equal to

$$\frac{i}{e} \frac{u-v}{u+v},$$

where e is the charge carried by one of the atoms.

To keep the pressure constant, the positive side of the tube must lose, and the negative side gain this number of molecules. If P is the pressure-gradient, μ the coefficient of

viscosity, ρ the density of the gas, and m the mass of a molecule, then the number of molecules which in unit time cross a section of the tube is

$$\frac{\rho}{m} \frac{P\pi a^4}{8\mu}$$

Hence we have, when the pressure is steady,

$$\frac{\rho}{m} \frac{P\pi a^4}{8\mu} = \frac{u-v}{u+v} \frac{i}{\epsilon},$$

or

$$\frac{P\pi a^4}{8\mu} = \frac{1}{\rho} \frac{u-v}{u+v} \cdot \frac{im}{\epsilon}.$$

Thus the potential gradient will vary inversely as the pressure of the gas, and the ratio of the pressure at the positive electrode to that at the negative will depend upon the square of the reciprocal of the pressure.

Taking the case of a tube 1 millim. in diameter, 10 centim. in length, filled with hydrogen at a pressure of one ten-thousandth of an atmosphere, and conveying a current of one ten-thousandth of an ampere, I find from the preceding formula that, supposing u much greater than v , the pressure at the positive electrode would exceed that at the negative by about twenty per cent.

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GEOLOGICAL SOCIETY.

June 19th, 1895.—Dr. Henry Woodward, F.R.S., President,
in the Chair.

[Continued from p. 395.]

THE following communications were read:—

3. ‘The Chalky Clay of the Fenland and its Borders : its Constitution, Origin, Distribution, and Age.’ By Sir Henry H. Howorth, K.C.I.E., M.P., F.R.S., F.G.S.

The distribution of the Clay (so often termed Chalky Boulder Clay) is noticed, and it is stated that it is surrounded on all sides by country occupied by different deposits, being mainly separated from the sea on the east and north-east by sandy and pebbly materials, while on every other side it is clearly and sharply defined. The paucity of foreign stones is noted as compared with natives, and the similarity of the matrix of the Chalky Clay to the material of the older deposits of the neighbourhood. The author maintains that the contents of the Clay indicate movement of material from west to east