VII. *On the Electro-Chemical Polarity of Gases.*

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THE different effect of electricity upon gases and liquids has long been a subject of interest to physical inquirers. There are, as far as I am aware, no experiments which show any analogy in the electrization of gases to those effects now commonly comprehended under the term electrolysis. Whether gases at all conduct electricity, properly speaking, or whether its transmission is not always by the disruptive discharge, the discharge by convection, or something closely analogous, is perhaps a doubtful question; but I feel strongly convinced that gases do not conduct in any similar manner to metals or electrolytes.

In a paper published in the year 1849*, I have shown that hydrogen or atmospheric air intensely heated, showed no sign of conduction for voltaic electricity even when a battery of very high intensity was employed.

In the Eleventh, Twelfth and Thirteenth Series of Faraday's Experimental Researches, the line of demarcation between induction across a dielectric and electrolytic discharge is repeatedly adverted to; induction is regarded as an action of contiguous particles, and as a state of polarization anterior to discharge, whether disruptive, as in the case of dielectrics, or electrolytic, as in electrolytes. See §§ 1164—1298—1345—1368, &c.

Mr. Gassiot, in a paper published in the year 1844†, has shown that the static effects, or effects of tension, produced by a voltaic battery, are in some direct ratio with the chemical energies of the substances of which the battery is composed; in other words, that in a voltaic series, whatever increases the decomposing power of the battery when the terminals are united by an electrolyte, also increases the effects of tension produced by it, when its terminals are separated by a dielectric.

In none of the above papers, and in no researches on electricity of which I am aware, is there any experimental evidence that the polarization of the dielectric is or may be chemical in its nature, that, assuming a dielectric to consist of two substances having antagonist chemical relations, as for instance, oxygen and hydrogen, the particles of the oxygen would be determined in one direction, and those of the hydrogen in the other; the only experimental result bearing on this point with which I am acquainted, is the curious fact which was observed by Mr. Gassiot and

* Philosophical Transactions, 1849, p. 55.

† Philosophical Transactions, 1844, p. 39.

some other electricians who experimented with him in the year 1838, viz. that when two wires forming the terminals of a powerful battery were placed across each other, and the voltaic arc taken between them, the extremity of the wire proceeding from the positive end of the battery was rendered incandescent, while the negative wire remained comparatively cool; it was at that time believed that there was some effect exhibited here *extra* the voltaic circuit. Shortly afterwards I showed that with all, or at all events a great number of metals, the positive terminal was more heated than the negative, and that the portion of the crossed wire which was positive became more incandescent than that of the negative, from the greater heating effect developed at the point when the disruptive discharge took place. I suggested as an explanation of this phenomenon, the possibility that in air, as in water, or other electrolyte, the oxygen or electro-negative element was determined to the positive terminal, and that from the union of the metal with that oxygen a greater heating effect was developed. This, with some other impressions, I mentioned in a letter to my friend Dr. SCHÖNBEIN, not intended for publication, but which shortly afterwards found its way into print*.

Though by no means thinking that this explanation was in every respect satisfactory, there were many arguments in its favour, and the fact strongly impressed my mind as evincing a very striking difference in character between the effect of the discharge at the positive and negative terminals, and as presenting, as far as it went, a distant analogy to the effect of electrolysis.

In the year 1848, while experimenting with Mr. GASSIOT with a nitric acid battery consisting of 500 well insulated cells, I made the following experiment:—Two wires of platinum $\frac{1}{40}$th of an inch in diameter, forming the terminals of the battery, were immersed in distilled water; the negative wire was then gradually withdrawn until it reached a point a quarter of an inch distant from the surface of the water. A cone of blue flame was now perceptible, the water forming its base, and the point of the wire its apex; the wire rapidly fused, and became so brilliant that the cone of flame could be no longer perceived, and the globule of fused platinum was apparently suspended in air and hanging from the wire; it appeared sustained by a repulsive action like a cork ball on a *jet d'eau*, and threw out scintillations in a direction away from the water. The surface of the water at the base of the cone was depressed, and divided into little concave cups, which were in a continual agitation. When the conditions were reversed and the negative wire immersed, the positive wire being at the surface, similar phenomena ensued, but not nearly in so marked a manner; the cone was smaller, and its base much more narrow in proportion to its height.

This experiment, the beautiful effect of which requires to be seen to be appreciated, indicates a new mode of transmission of electricity partaking of the electrolytic and disruptive discharges. Not possessing a battery of this enormous intensity, I have not been able to examine this phenomenon more in detail; but I have from time to time

* Philosophical Magazine, 1840, p. 478.

made many other experiments on the voltaic arc taken in various gaseous media, with the view of ascertaining the state of the intervening media anterior to, during, and after the discharge; these experiments have hitherto given me no results of any value. In the voltaic arc, the intense heat developed so affects the terminals and so masks the proper electrical effect, that the difficulty of isolating the latter is extreme; and I have latterly sought for some modified form of electric discharge which should be intermediate between the voltaic arc and the ordinary Franklinic discharge, or that from the prime conductor of a frictional machine; for something, in short, which should yield greater quantitative effects than the electrical machine, but not dissipate the terminals, as is done by the voltaic arc.

An apparatus, to which M. Despretz was kind enough to call my attention recently at Paris, seemed to promise me some aid in this respect. It was constructed by M. Ruhmkorff, on the ordinary plan for producing an induced current, viz. a coil of stout wire round a soft iron core, with a secondary coil of fine wire exterior to it, having an ingenious self-working contact breaker attached; from the attention paid to insulation in the construction of this apparatus, very exalted effects of induction could be procured. Thus in air rarefied by the air-pump, an aurora or discharge of 5 or 6 inches long could be obtained from the secondary coil, and in air of ordinary density a spark of one-eighth of an inch long.

I procured one of these apparatus from M. Ruhmkorff; the size of the coil portion of the apparatus is 6·5 inches long, 4 inches diameter; the length of the wires forming the coils are (I give M. Ruhmkorff's measurements) stout wire, 30 metres long, 2 millimetres diameter, 200 convolutions; fine wire, 2500 metres long, $\frac{1}{4}$ metre diameter, 10,000 convolutions. These measurements will only be taken as approximative, and indeed the exact size is immaterial to the consideration of the experiments which I am about to detail. I will not give my experiments in the order in which I made them, as I should have to describe many fruitless ones, but I will place first that which I consider the most important and fundamental.

1st. On the plate of a good air-pump was placed a silvered copper plate, such as is ordinarily used for Daguerreotypes, the polished silver surface being uppermost. A receiver, with a rod passing through a collar of leathers, was used, and to the lower extremity of this rod was affixed a steel needle, which could thus be brought to any required distance from the silver surface; a vessel containing potassa fusa was suspended in the receiver, and a bladder of hydrogen gas was attached to a stop-cock, another orifice enabling me to pass atmospheric air into the receiver in such quantities as might be required*. A vacuum being made, hydrogen gas and air were allowed to enter the receiver in very small quantities, so as to form an attenuated atmosphere of the mixed gas: there was no barometer attached to my air-pump, but from separate experiments I found the most efficient extent of rarefaction for my purpose was that indicated by a barometric height of from half to three-quarters of

* See a figure and description of the apparatus at the end of this paper.

an inch of mercury; and except where otherwise stated, a similarly attenuated medium was employed for all the following experiments.

Two small cells of the nitric acid battery, each plate exposing 4 square inches of surface, were used to excite the coil machine, and the discharge from the secondary coil was taken between the steel point and the silver plate. The distance between these was generally $=0{\cdot}1$ of an inch, but this may be considerably varied. When the plate formed the positive terminal, a dark circular stain of oxide rapidly formed on the silver, presenting in succession yellow, orange and blue tints, very similar to the successive tints given by iodizing in the ordinary manner a Daguerreotype plate. Upon the poles being reversed and the plate made negative, this spot was entirely removed, and the plate became perfectly clean, leaving, however, a dark, polished spot occasioned by molecular disintegration, and therefore distinguishable from the remainder of the plate.

The experiment was repeated a great many times, and with varying proportions of gas, and I found that with proportions varying from equal volumes of hydrogen and air to those of one volume of the former to two and a half of the latter, the experiments succeeded; better, I should say, when there was rather an excess of hydrogen as compared with the equivalent of oxygen in the atmospheric air; about one volume of hydrogen to one and a half of air succeeded well; when excess of air was present, oxidation took place whether the plate was positive or negative, and when excess of hydrogen was present no oxidation took place.

2nd. I experimented with an air vacuum (to borrow an expression of Dr. Faraday), and found that oxidation took place whether the plates were positive or negative, but in different degrees; when the plate was positive, a small circular spot was rapidly formed, quickly deepening in colour, and apparently eating into the plate; when the plate was negative, a large diffuse spot was formed, the oxidation was more slow, and the plate not so rapidly corroded.

3rd. I now operated with a hydrogen vacuum; when the plate was clean no discoloration took place, the plate retained its polish, though after a long continuance of the discharge a molecular change was perceptible, producing a frosted appearance similar to the mercurialized portions of a Daguerreotype.

When the plate had been previously oxidated by the discharge in an air vacuum, the oxidation was rapidly and beautifully cleared off by the discharge in the hydrogen vacuum, and this whether the plate was positive or negative, the effect being, however, better and more rapidly produced in the latter case.

4th. I substituted respectively for the steel needle, wires of copper, silver and platinum, and found the effect produced by all and with nearly equal facility; if there were any difference, the platinum point was the least efficient; this may be due to the peculiar effect of platinum in itself combining the gases, or to its inoxidable character, the oxygen being thrown off from its surface, and not uniting with it as with the more oxidable metals; the flame or luminous appearance which

surrounded the wire when the platinum was negative, was larger and more diffuse than with the other metals.

5th. As air, notwithstanding its containing a great excess of nitrogen, gave an effect of oxidation at both electrodes, though different in degree, I increased the proportion of nitrogen by passing into the receiver nitrogen which had been formed by the slow combustion of phosphorus, the phosphorous acid having been well washed away, and potash being always in the receiver; no more air was allowed to be present than the very small quantity contained in the apertures of the stopcock; with this mixture, viz. a maximum of nitrogen and a minimum of oxygen, and rarefied as before, a similar effect was produced to that shown in the mixture of air and hydrogen, the positive plate being oxidated by the discharge, and the spot when made negative being reduced. The effect of reduction was not so rapid or so readily produced as when hydrogen was used, but was very decided.

6th. With nitrogen, as much deprived of oxygen as I could procure, the colours of oxidation were not exhibited, but a dark spot apparently due to disintegration was produced, which was not removed by the plate being made negative; if, however, the coloured spot was produced by the plate being made positive in an air vacuum, they were removed by the plate being made negative in a nitrogen vacuum, leaving, however, a darker spot than that which was exhibited when they were reduced in hydrogen. Even when produced in an air vacuum, and then a very perfect exhaustion effected, such as would reduce the mercury in the barometer to the height of $\frac{1}{20}$th of an inch, the spot was partially reduced when the plate was made negative.

7th. An oxyhydrogen vacuum was formed, the gases being in the proportion in which they form water; and thanks to the attenuated atmosphere, it was easy to take the discharge in this mixture without producing detonation or any sudden combination of the gases, a possibility pointed out by Grotthus*. With this mixture the effect took place as with the mixture of atmospheric air and hydrogen. I expected it to have been more efficient, but it was rather less so than the mixture of air and hydrogen; whether it be that the presence of nitrogen lessens the tendency to combine of the gases oxygen and hydrogen, and thus enables the electrical polarization and discharge to operate more efficiently, whether the nitrogen has a specific effect in aiding the electro-chemical effect, as I have shown it has in one peculiar case†, or whether any unknown effect of nitrogen is concerned, I do not undertake to pronounce; I can only say that in several repetitions of the experiment, it appeared to me that the mixture of atmospheric air and hydrogen was more efficient in exhibiting this phenomenon than that of oxygen and hydrogen.

8th. Different proportions of oxygen and hydrogen were employed, and here also I found that within a tolerably wide margin I could vary the proportion of the gases; three volumes of hydrogen to one volume of oxygen I found to be a very efficient mixture.

* Annales de Chimie, vol. lxxxii.

† Philosophical Transactions, 1843, pp. 110, 111.

9th. I now substituted for the silver plate, plates of the following metals:—bismuth, lead, tin, zinc, copper, iron and platinum, the former three metals being burnished, the latter polished.

Bismuth showed the effect nearly, if not quite as well as silver; it was oxidated in an air vacuum, reduced in a hydrogen vacuum, and oxidated or reduced in the mixed gas according as it formed the positive or negative terminal.

Lead oxidated easily, but the spot of oxide could with difficulty be reduced. Tin, zinc and copper required the admission of a great quantity of air to produce oxidation; and I could not succeed in reducing the oxide by the electrical discharge, at least so as to restore the polish of the plate; a blackening effect was in some degree produced. Iron was not oxidated until the receiver was nearly filled with air, and then a small spot of rust was formed which I could not reduce. With all the metals a slight whitish film like the mercurialized portion of a Daguerreotype was visible beyond the circle marked by the discharge when the plate was rendered positive, which film was removed by negative electrolization in a hydrogen vacuum; it seemed to me that this film, as well as others among those I have described, was affected by light, but I did not turn aside to examine this effect. Platinum showed no effect either of oxidation or reduction.

10th. As it was impossible to operate with an atmosphere of chlorine with the apparatus which I possessed, and wishing to vary the electro-negative element, I iodized a silver plate by the vapour of iodine to a deep blue colour, and then made it negative in an atmosphere of hydrogen; the iodine was beautifully removed in a circle or disc opposite the point which formed the positive terminal.

11th. I now substituted for the coil apparatus a very good electrical machine, the cylinder of which was 16 inches diameter, and the prime conductor of which, when the machine was properly excited, gave a spark of 8 inches long. With this machine, and in an attenuated atmosphere of one volume hydrogen plus two of atmospheric air, I produced the effects of oxidation and reduction very distinctly, the plate being in turn connected with the conductor and with the ground; but the comparative minuteness of the spot after many turns of the machine, showed the great superiority of the coil machine for producing quantitative effects over the ordinary electrical machine; and I question whether I should have detected the phenomenon with the latter, had I not become previously well acquainted with it by the former apparatus. Probably an extensive series of the water battery or a steam hydro-electric machine would succeed equally well, or better than the coil machine.

12th. A solution of hyposulphite of soda removed the spots formed by electrization from the silver plate just as it removes the iodine from an iodized plate.

13th. In some of the above experiments I remarked a tendency in the spots produced by the discharge, to show circles or zones of oxidation in different degrees, and in a more marked manner than would be accounted for by the different colours of the thin films of oxide formed. I determined to examine this effect, and selected,

after some experiments, an atmosphere of one volume oxygen mixed with four volumes of hydrogen, and attenuated by the air-pump as in the previous experiments. The plate was made positive, and the point was placed successively opposite different portions of the silver plate, at distances of $\frac{1}{50}$th, $\frac{2}{50}$ths, $\frac{3}{50}$ths, $\frac{4}{50}$ths and $\frac{5}{50}$ths of an inch. The results are given, as nearly as I can copy them, in the accompanying Plate, figs. 1 to 5.

The colour of the central spot was a yellow-green in the centre, surrounded by a blue-green, then a clear ring of polished silver, then an outer ring crimson, with a slightly orange tint on the inner side, and deep purple on the outer; the exterior portion of the spot was, as far as my eye could judge, of a colour complementary to the interior of the external ring, and the central portion of the spot of a colour complementary to the exterior portion of the ring. The colours varied with the time, density of gas and other conditions, but generally showed this complementary tendency. Symptoms of a faint polished ring were visible beyond the outer ring, and could be rendered more distinct by breathing on the plate. As the distance between the point and the plate was increased the colours became fainter, and the rings more diffuse, and beyond the distance I have given nearly lost their defined character; but the first three distances, or those of $\frac{1}{50}$th, $\frac{2}{50}$ths and $\frac{3}{50}$ths of an inch, gave very beautifully defined rings. The luminous appearance on the needle in these experiments extended from three-fourths of an inch to an inch from the point. Frequently a small polished speck was visible, exactly opposite the point of the needle. See fig. 6. When the plate was made negative, the other conditions being the same, a polished space appeared opposite the point of the needle, surrounded by a dusky and ill-defined areola; its colour, when regarded from a point opposite the incident light, was brown tinged with purple; and when in the same direction as the light, a greenish white, similar to the tint seen on mildew or on some of the lichens: these spots were very different from the positive spots, and in some degree the converse of them; but they were not nearly so well defined or capable of being produced with the same uniformity. I have endeavoured to represent one of them at fig. 7.

14th. In order to ascertain whether the polished ring intervening between the oxidated central spot and oxidated external ring were a mere negation of effect or an antithetic polar effect, such as would occasion reduction, I formed in an air vacuum two large spots on a silver plate, with one the plate being made negative, and with the other positive, oxidating them until they began to pass from deep orange to purple. I then perfectly exhausted the receiver, swept it with the gas employed in the last experiment, and then took the discharge in a vacuum of that gas, viz. one volume oxygen+four hydrogen; the plate being positive and the needle $\frac{2}{50}$ths of an inch over the centre of each spot in turn, a ring of clear polish was formed rapidly in both the dark discs, just at the distance where the ring of polish appeared in the last experiment. I then exposed a clean portion of the plate to the needle without

any other change, and on allowing the discharges to pass, formed the rings just as in the last experiment.

15th. I examined some of the spots with an achromatic microscope, magnifying 200 diameters; I could not, however, discover any feature which the naked eye did not show, or any peculiar molecular state; the polishing scratches on the plate were highly magnified, but the electrized spots only showed more dimly the colours or the lights and shadows which they exhibited to the naked eye.

16th. I took the discharge on a silver plate in vacua of the following gases respectively:—Oxygen, protoxide of nitrogen, deutoxide of nitrogen, carbonic acid, carbonic oxide and olefiant gas.

The first four gases presented nothing remarkable, the plate was oxidated whether positive or negative, as in a vacuum of atmospheric air. In the protoxide of nitrogen the colour of the discharge was a beautiful crimson on both terminals.

In deutoxide of nitrogen a greater tendency to reduction was shown when the plate was negative than in the other three gases, and there was also a tendency to the formation of rings. In carbonic oxide the plate was oxidated when positive, and the oxide reduced when negative, just as with a vacuum of air and hydrogen, but rather more slowly; with a mixture of five volumes of carbonic oxide and one volume of oxygen, the rings were formed very distinctly, particularly if the plate was made negative first, and then positive. The luminous spot on the plate, when positive in this gas, was coloured green.

When the plate was negative in olefiant gas it darkened, showing the rings of colour produced by thin plates, and very distinct from the other rings of which I have spoken. After a short time a pulverulent deposit was formed on the plate, giving brilliant sparks or stars of light which were not shown by any other gas.

This deposit was too minute for analysis, but I have no doubt, from the gas used and the appearances presented, it was carbon.

I have given in the above experiments the conditions under which they succeeded best; but upon repetition, although the exact volumes of gases and other conditions were carefully attended to, they sometimes required a slight alteration to succeed, variations taking place from causes which I could not detect; thus it was sometimes necessary to add a little more hydrogen, sometimes a little more oxygen or air, to alter slightly the state of attenuation in the gas, &c.

The necessarily varying condition of the battery, and the state of the contact breaker, slight impurities in the gases or on the surface of the plates would be quite sufficient to account for these irregularities. I mention them for the guidance of any one who may wish to repeat the experiments; a very little practice will enable any electrician to have the results at his command. When there is too great a proportion of air or oxygen, oxidation takes place at both poles; when too much hydrogen, reduction takes place at both; and to effect oxidation or reduction by reversing the

direction of the discharge, an intermediate condition is requisite; so if the gas be not sufficiently attenuated the oxidation is too rapid, and the plate too much corroded to bring out the effects clearly; if too much attenuated, too long a time is required and the effect is feeble and indistinct.

I have above selected all the experiments which I consider material in this, I believe, new class of phenomena. The spots produced by electrical discharges, both on conducting bodies and on electrics, have been before noticed and experimented on, one class by PRIESTLEY*, and another class by KARSTEN† and others, but as far as I am aware no distinct electro-chemical action in dry gases, depending upon the antithetic state of the terminals and presenting a definite relation of the chemical to the electrical actions in gaseous media, has been pointed out. I now proceed to consider the relation which these results bear to other electrical phenomena.

As may be gathered from my opening remarks, the experiments above detailed appear to me to furnish a previously deficient link in the chain of analogy connecting dielectric induction with electrolysis. The only satisfactory rationale which I can present to my own mind of these phenomena is the following. The discharges being interrupted (as is evident from the nature of the apparatus, and may be easily proved by agitating a mirror near them and regarding their reflected images in the moving mirror), the gaseous medium is polarized anterior to each discharge, and polarized not merely physically, as is generally admitted, but chemically, the oxygen or anion being determined to the positive terminal or anode, and the hydrogen or cation being determined to the negative terminal or cathode; at the instant preceding discharge there would then be a molecule or superficial layer of oxygen or of electro-negative molecules in contact with the anode, and a similar layer of hydrogen or of electro-positive molecules in contact with the cathode, in other words, the electrodes in gas would be polarized as the electrodes in liquid are. The discharge now takes place, by which the superficial termini of metal or of oxide, as the case may be, are highly ignited or brought into a state of chemical exaltation at which their affinities can act; the anode thus becomes oxidated, and the cathode, if an oxide, reduced. I have elsewhere‡ shown strong reasons for assuming that the electric or voltaic discharge, the moment polarity is subverted, may be regarded as an intensely heated state of the electrodes, and of the intermedium across which it passes; and my present explanation is perfectly consistent with and derivable from my previous views of the disruptive discharge.

Two other theories might be proposed to account for the phenomena I am considering; the one, that the disruptive discharge itself is analogous to the electrolytic, and that the oxygen and hydrogen are reciprocally transferred by the discharge itself; this would not, I think, be consistent with the generally known facts connected with the discharge, and is entirely ineffectual in explaining the experiments

* History of Electricity, 2nd edition, p. 624.

† Archives de l'Electricité, vol. ii. p. 647; vol. iii. p. 310.

‡ Philosophical Transactions, 1847, pp. 10, 16, 21. Correlation of Physical Forces, p. 50, 2nd edition.

2nd and 3rd, where either the positive or negative terminal can be made either to oxidate or reduce, according to the nature of the chemical medium present, while these experiments are entirely in accordance with, and the results of them flow as a necessary consequence of, the view first advanced. The other theory which may be advanced is, that by dielectric induction the gases may be bodily separated, a layer, not molecular, but corporeal or voluminous, if I may be allowed these expressions, of oxygen being developed on the side next the anode, and one of hydrogen next the cathode, the gas intervening between the terminals being thus divided, as it were, into two halves: this would certainly be a most curious phenomenon, but I believe it to be so inconsistent with the vast mass of accumulated facts in electrical science, and likely to have produced in cosmical phenomena so many results which, if existing, must long ere this have been detected, that I will not do more than advert to it.

I have adopted the views which I have first stated as being the least removed from ordinary theories or modes of regarding electrical phenomena, and because in the present instance I can present the phenomena in no other way which is in the least degree satisfactory to my own mind, while this view to me well accounts for them. Assuming then for the present this view, we get a close approximation, I may say an identity of the state of polarization in gaseous non-conducting dielectrics, and in electrolytes anterior respectively to discharge or to electrolysis.

Faraday observes, Experimental Researches, 1164, "In an electrolyte induction is the first state, and decomposition the second." My present experiments show, I believe, that in induction across gaseous dielectrics there is a commencement, so to speak, of decomposition, a polar arrangement not merely of the molecules, irrespective of their chemical characters, but a chemical alternation of their forces, the electro-negative element being determined or directed, though *not travelling* in one direction, and the electro-positive in the opposite direction.

This arrangement is only evidenced at present, as it is in electrolysis, by the action at the polar extremities or termini of the dielectric; possibly future reasearches may show, by the action of polarized light, by magnetism or some other means of analysis, that the polarity extends, as we theoretically believe it does, through the whole intervening matter.

In the Experiment No. 5 with oxygen and excess of nitrogen, reduction takes place by the effect of negative electricity and heat, at least there seems every reason from analogy to believe that the effect of the nitrogen is only negative, protecting the plate from oxygen, or at furthest catalytic, aiding the reduction as sulphuric acid aids the electrolysis of water. Upon the state of association of the gases in what is generally called mixture, I venture an opinion with the greatest diffidence. I have always inclined to the opinion that the difference between physical admixture, as it is termed, of gases and chemical union, is one of degree, and the views of Dalton ever presented to my mind grave difficulties*. My present results seem to me in favour of

* Philosophical Transactions, 1843, p. 112.

the chemical view, as otherwise we can scarcely imagine electricity as effecting in the instances given a merely physical separation; it may indeed be said that there is composition and decomposition produced by the same discharge, but this is very difficult to conceive, and can hardly apply to the cases of oxygen with nitrogen and of carbonic oxide.

In the experiments I have detailed, the flame or visible effect of the electric discharge coincided with the chemical effect; when the plate was positive, a small globule of flame of a purple colour was visible on the part of the plate attacked, and a bluish flame extended over an inch or more of the needle. When the plate was negative, a wider and less defined disc of blue flame extended over the part of the plate opposed to the positive point, like a splash of liquid thrown upon it, and a pencil of light appeared on the point. Sometimes, but not always, this flame avoided the oxidated portion, probably from its inferior conducting power; and when this was the case reduction took place in a much slighter degree, or not at all; sometimes, and I observed this particularly with bismuth, the flame attached itself to the oxidated portion, and then reduction immediately followed. Here, as in all the electrical phenomena that I can call to mind, we get the visible effects of electricity associated with physical changes in the matter acting, changes of state in the terminals, polarization of the intervening medium, or both*. These experiments furnish additional arguments for the view which I have long advocated, which regards electricity as force or motion, and not as matter or a specific fluid†.

The chemical polarity of gases shown, as I believe, in this paper, associates itself with an experiment which I made known in a lecture at the London Institution in the year 1843‡, and which was subsequently verified by Mr. Gassiot§ with more perfect apparatus than I possessed, viz. that when discs of zinc and copper are closely approximated, but not brought in contact, and then suddenly separated, effects of electrical tension are exhibited, the one disc making the electroscope diverge with positive, and the other with negative electricity, showing that the effects ascribed by Volta to contact can be produced without contact, and by mere approximation, the intermediate dielectric being polarized, or a radiation analogous, if not identical, with that which produces the images of Moser taking place from plate to plate.

The present experiments also associate themselves with the gas battery, where, though an electrolyte is used as the means of making the action continuous, or producing what is called current electricity, the initiating effect is gaseous polarity, the films of gas in contact with the respective plates of platinum having antithetic chemical and electrical states.

* Gases at present believed to be elementary, probably undergo a *quasi* chemical polarization by electricity; thus portions of oxygen are changed to ozone, &c. See a recent paper by MM. Fremy and E. Becquerel, Comptes Rendus, Paris, March 15.—Note added to the Proof, W. R. G.

† Printed Lecture at the London Institution, 1842, p. 28. Correlation of Physical Forces, p. 48.

‡ Literary Gazette, 1843, p. 39.

§ Philosophical Magazine, October, 1844.

The results detailed in Experiment 13th, appear to open a new field of research. PRIESTLEY observed concentric circles produced by the electrical discharge from a powerful Leyden battery, which he describes as consisting of minute cavities and globules of fused metal*. In my experiments there is an alternation of oxidation and reduction, a medium capable of producing both being present; the lateral effect and complementary colours have to my mind something closely resembling the phenomena of interference in light, although from the polar character of the force, it is difficult to imagine any precisely analogous condition of electricity. The discharge taking place from different parts of the needle and extending from its point to a considerable distance over its surface, would give different lengths for the lines of polarization and discharge to the different parts of the disc on the silver plate affected by the discharge; and assuming electricity to be propagated by undulations, there would be interference; but instead of alternations of light and darkness we get alternations of positive and negative electricity. The ring of polished metal between the central spot and the exterior ring, quite distinguishes these rings from the ordinary colours of thin plates, *i. e.* colours, the annular succession of which depends only on the different thicknesses of the film; here doubtless the colours of the oxidated portions are colours of thin plates. Experiment 14 shows clearly that the action by which the polished ring is formed is a polar action of the discharge, and not a mere absence of action.

When the plate is negative, the effect is, as I have observed, less marked and more uncertain; but in this case it should be recollected that the visible discharge issues from the point, and does not extend, or extends to a very small degree, over the surface of the needle.

If the phenomena were such that the central portion were always clear, while around it was one, and one only circle of oxide, it might be accounted for by the hypothesis, that the lines of polarization and discharge between a point and flat surface, assume the form of a hollow cone; but a cone of negative bounded by cones of positive action, still gives the idea of some lateral fits or phases of undulation.

The high rarefaction of the medium by the discharge, and its intermitting character, might occasion pulsations by the inrushing of the surrounding gas, and thus vacua in circles might be formed at the places where the action of oxidation is rendered null; but this view is, I think, inadmissible; it does not account for the effects obtaining only in certain mixtures, it does not account for the reducing action, the plate being positive, and presents other difficulties. The point involved in Experiments 13 and 14, though not perhaps the least valuable one given in this paper, presents apparently a wide field of inquiry; I therefore will not further dilate on it at present, and hope to make it the subject of future investigation.

* History of Electricity, 2nd edition, p. 624.

December 27, 1851.

Postscript, April 24th.

I may, I trust, be permitted to add to this paper one or two experiments on the subject last discussed. Assuming that the alternations of oxidation and reduction were produced by interference in consequence of the discharge proceeding from successive points of the terminal or terminals, a difference of effect might be anticipated if the electricity passed from a point only, and not from a line as was the case in Experiment 13. I therefore sealed a platinum wire $\frac{1}{60}$th of an inch in diameter into a piece of glass tubing, and then ground the extremity to a flat surface, so that the section only of the wire was exposed; this wire was placed opposite, and at 0·07 of an inch distance from the polished silver plate, in a mixture of one volume of oxygen with five volumes of hydrogen attenuated until the barometer stood at half an inch; discharges from the secondary coil were then passed, the plate being positive, and a round dark spot of oxide formed represented at fig. 8; the platinum sealed in glass was then removed and the steel needle substituted for it, all else, viz. plate, gas, barometer height, &c., being the same: the system of rings represented at fig. 9 was now produced.

Another experiment was made, directed to the same point: a wire of copper 0·04 inch diameter, and a thread of glass of the same diameter were attached by sealing-wax at their extremities in a horizontal position 0·025 of an inch from different parts of a silver plate, being insulated from the silver by the wax interposed at the extremities. The gaseous mixture and barometric height being the same as in the last experiment, and the silver plate made positive, when the platinum wire sealed in glass was brought near the plate, and the discharges passed, a spot similar to fig. 8 was formed; but when the coated point of platinum was brought over the copper wire at 0·02 inch distance, a figure consisting of two separated semicircles was formed, having spots in the bisection of the chords, as shown at fig. 10, the portion between the spots and the semicircular line of oxide being of polished silver. With the glass thread the effect was the same, but produced with greater difficulty and not so well defined.

In many repetitions of these experiments which I have made, I have invariably produced the alternately polished and oxidated rings from the bare wire, and have not procured them from the coated wire, except to a very slight degree, and under certain circumstances, which, as far as I could trace, were as follows:—

1st. When the extremity of the wire was very near the plate, so that it had a sensible magnitude with reference to the intervening space, a slight formation of minute rings could be detected at the commencement of the experiment.

2nd. When the experiment was long continued, or when the coated platinum wire had been used for previous experiments, a set of rings, not consisting of an alternation of oxidated and polished rings, but of annuli of different degrees of oxidation, were formed.

When the experiment is continued for some time, a dark deposit is formed on the glass around the extremity of the platinum wire, giving an extended conducting surface; and this may be the reason why such rings are formed, though these rings, in all the cases which I have observed, differ broadly from the rings formed by the bare needle or wire, not having the interposed spaces of perfectly bright silver; and in all the cases the difference of effect produced by the coated and the bare wire is very marked; in by far the greater number of experiments, when proper precautions are taken, not the slightest formation of rings takes place with the coated wire; with the bare wire, in the gaseous mixture last mentioned, I have always seen them formed.

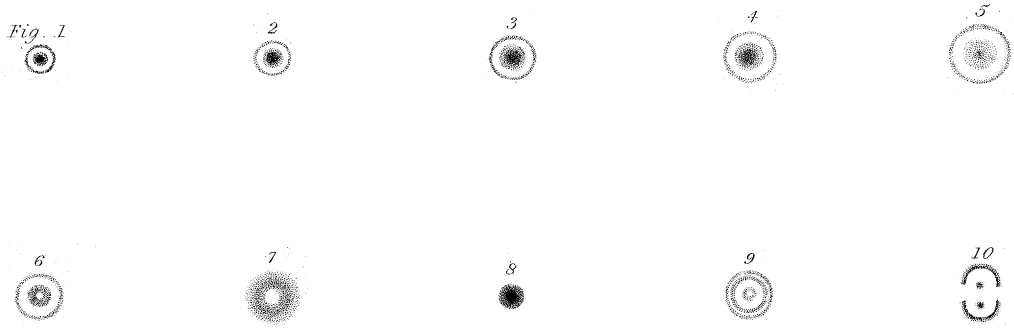
Thus there are three systems of rings which may be formed by the discharge. First, rings such as those seen in the ordinary cases of thin plates; these I have only observed with olefiant gas, though probably there are many other conditions in which they may be produced. Secondly, rings formed by the superposition of layers of oxides, possibly arising from the fact that at certain definite periods portions of the plate become by oxidation inferior conductors, and other portions are attacked, and being at a different distance undergo a different molecular change by oxidation. Thirdly, and to me far the most interesting set of phenomena are presented by the rings alternately bright and oxidated, showing effects of oxidation and reduction by the same current on the same plate, and which only take place in certain gaseous mixtures, of which, up to this time, one volume oxygen+five volumes hydrogen is the most efficient which I have obtained.

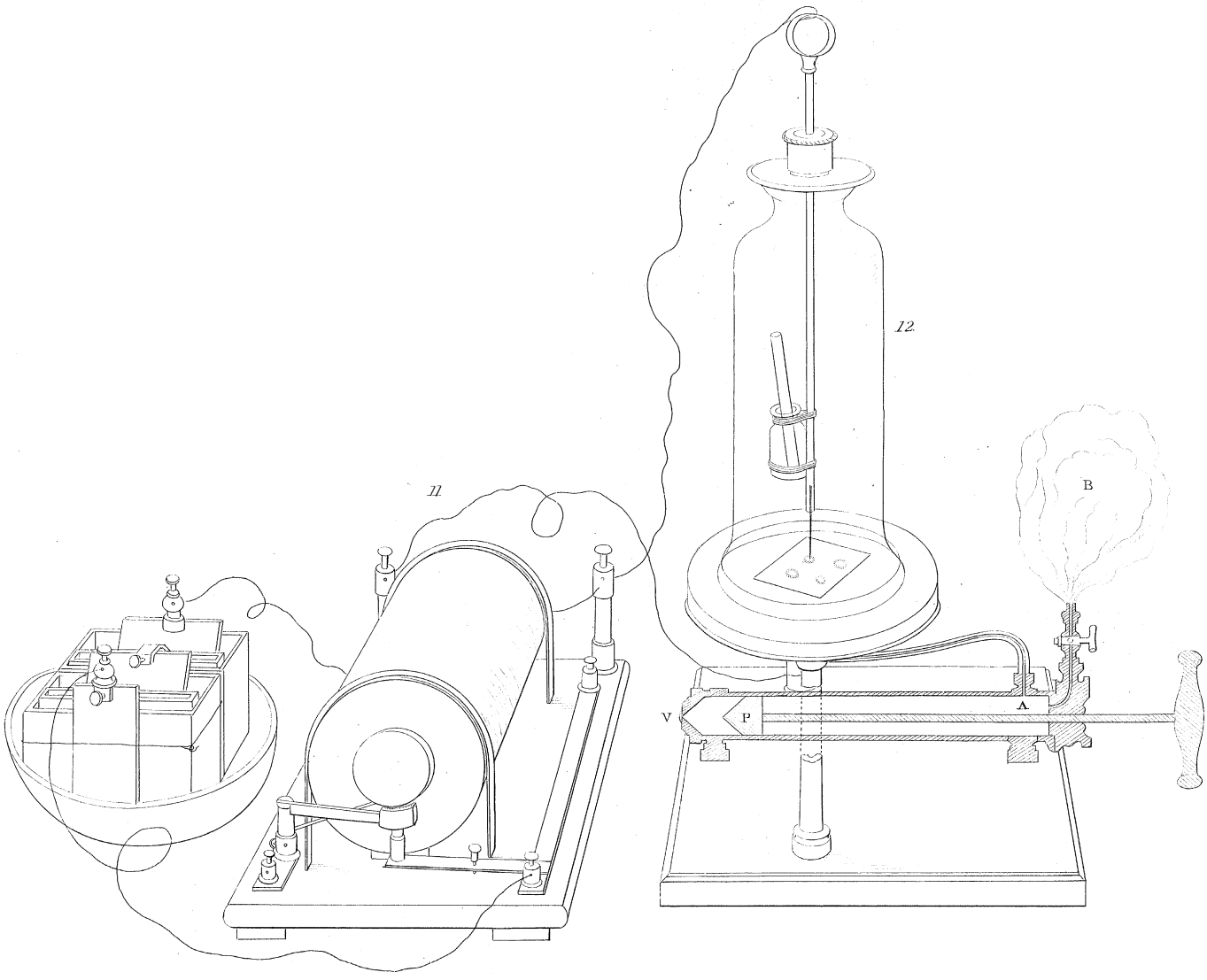
I cannot at present see any better mode of explaining these phenomena than by regarding them as analogous to the phenomena of interference in light, though doubtless if this be a right view, the very different modes of action of light and electricity would present very numerous phenomenal distinctions. Alternations of opposite polar electrical actions in the discharges passing in the same direction are, I think, very clearly shown in these experiments, and this appears to me a result worthy of attention.

Though acquainted with Nobili's beautiful experiments on the formation of coloured rings by deposition in electrolyzed liquids, yet as I was working on gases it did not occur to me to refer to his memoirs*; I have done so since making the experiments given in this Postscript, and find that with regard to the rings so formed by electrolysis, he suggests interference as a possible explanation.

The dark space in the discharge to which Faraday has called attention, may possibly be connected with these phenomena. I have observed, that in a well-exhausted receiver containing a small piece of phosphorus, the discharge is throughout its course striated by transverse non-luminous bands, presenting a very beautiful effect, and a yellow deposit, which, as far as I have yet examined it seems to be allotropic phosphorus, is deposited on the plate of the air-pump and on the neigh-

* Ann. de Ch. et de Phys. vol. xxxiv.





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bouring substances; to show this effect well the needle should be positive and the plate negative, and the distance between them about an inch.

I could dilate much further on these experiments, but have already trespassed perhaps too far for a Postscript. Variations in the form of the terminals, in the nature of the gas, vapour, or gaseous mixture, in the density of the gas, in the intensity and quantity of the discharge, in the nature of the plate, &c. will occur to those who may feel inclined to repeat these experiments, and if I am not over-sanguine, promise results of much interest.

Description of Plate.

PLATE VIII.

Figures 1 to 10 show the spots and rings in the order referred to: it should be observed that printed figures give but a very imperfect notion of the actual effects.

Fig. 11 is the coil apparatus, the contact breaker being in front.

Fig. 12. The air-pump, of a construction which I proposed many years ago, and have found most useful for electrical or chemical experiments on gases.

P. An imperforate piston, with a conical end, which, when pressed down, fits accurately the end of the tube, the apex touching the valve V, which opens outwards.

A. Aperture for the air to rush from the receiver when the piston has been drawn beyond it.

B. Bladder containing the gas to be experimented on.

The piston-rod works air-tight in a collar of leathers, and the operation of the pump will be easily understood without further description.

If it be required to examine the gas after experiment, a bladder, or tube leading to a pneumatic trough, can be attached at the extremity over the valve V.