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# XXV. Experiments in photoelectricity

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Experiments upon which I have been engaged since the above paper has been in type fully confirm these expectations. Preliminary measurements show that the force with which the glass suspended in water tends to move toward the weaker parts of the field is several times greater than that with which it tends to move toward the stronger parts of the field in air, and that, other things being the same, this force is proportional to the square of the electric force.

A conductor, on the contrary, tends to move toward the stronger parts of the field *for all media*, with a force many times greater in water than in air or oil. Increasing the conductivity of the water does not appreciably alter the force.

A new piece of apparatus is being constructed, and when finished accurate measurements will be made of the force on the suspended body in these several cases. The preliminary results are of interest, however, as confirming the conclusions of the foregoing paper that water and other conducting liquids have a true specific inductive capacity.—E. B. R.

XXV. *Experiments in Photoelectricity*. By GEORGE M. MINCHIN, M.A., *Professor of Mathematics in the Royal Indian Engineering College, Coopers Hill\**.

NEAR the beginning of the year 1877 I commenced a long series of investigations in Photoelectricity, and I was not then aware that M. Becquerel had previously worked at this subject and had obtained some results which I also obtained independently. In the spring of 1880 I made a verbal communication to this Society, illustrated by experiments, on the generation of electric currents by the action of light on silver plates which were coated with collodion and gelatine emulsions of bromide, chloride, iodide, and other salts of silver, as well as with eosine, fluoresceine, and various aniline dyes. A short summary of these results appears in the Report of the meeting of the British Association that year at Swansea. The chief object which I had then in view in prosecuting such experiments was the solution of the problem of producing a photographic image of an object at a distance by means of an instrument which is still imaginary and which I proposed to call a *telephotograph*.

As these experiments have never been published in adequate detail, I propose to begin this paper with an account of them.

\* Communicated by the Physical Society: read January 16, 1891.

*Silver Plates.*

Let two strips of cleaned silver foil be each fastened on a plate of glass, by means of pitch or other suitable substance ; take some finely powdered chloride of silver and shake it up well in a test-tube containing collodion, the emulsion being, of course, screened from light by a covering of black paper on the test-tube ; pour a thin coating of the emulsion over both silver plates in the dark ; and when the films have set, immerse both plates in a glass vessel containing distilled water with a few grains of common salt ; screen one plate completely ; and then connect the plates with the terminals of a Thomson galvanometer. A disturbing current will, of course, be produced ; but if the plates are very nearly alike, this current will be small and will soon almost disappear.

Now, on exposing the unscreened plate to light, a current will be produced, and the exposed plate is *negative* to the unexposed (*i. e.*, as copper to zinc).

The direction of the disturbing current is not in any way related to the direction of the current produced by light—as is, indeed, *à priori* evident.

If the plates are coated with an emulsion of bromide of silver, the liquid being distilled water with a few grains of bromide of potassium, the exposed plate is made also *negative* with respect to the unexposed by the action of light.

If the plates are coated with iodide of silver by first pouring a layer of iodized collodion over them, and then immersing them in a nitrate of silver bath, the liquid being water with a few grains of iodide of potassium, we obtain a reversal of the nature of the exposed plate ; *i. e.* the action of light makes the exposed plate *positive* with respect to the unexposed.

By placing coloured glasses in front of the exposed plate in each of these cells, it was found that the red rays produced comparatively feeble currents, while the currents produced by the blue and violet rays were very great ; but the directions of the currents were the same for all rays.

A somewhat different result was obtained when the plates were coated with an emulsion of sulphide of silver, the liquid being water with a few grains of sulphate of potash. The exposed plate is, as in the case of iodide of silver, *positive*. In this cell the directions of the currents were the same for rays passing through all the coloured glasses ; but the strength of the current was very much less for rays passing through the green glass than for the rays at each side of the green.

When the plates were coated with an emulsion of nitrate of silver and gelatine, the water containing a few grains of

nitrate of barium, the exposed plate was positive, the effect of the red rays being exceedingly small and that of the blue very great.

*Photographic Effect of the Current.*—A fact of very great importance in this subject is that which relates to the action of an electric current which passes through a photographic layer on a plate.

Two silver plates, each coated with a film of Liverpool emulsion (bromide of silver), were immersed in a tumbler containing distilled water and a few grains of bromide of potassium. One of these plates was connected with the zinc and the other with the carbon pole of a bichromate cell. The current was allowed to pass through the plates for a few seconds, with the following results:—

(1) The plate connected with the carbon pole was, without the employment of any developer, visibly blackened in its immersed part.

(2) No *visible* change took place on the other plate; but when the plate was developed, by pouring over it the usual pyrogallie acid developer, its immersed portion was also blackened.

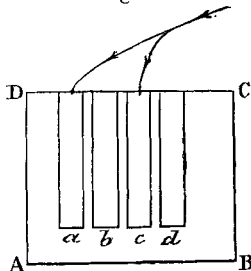
The photographic result was also obtained when the bichromate cell, which originated the current, was replaced by a photoelectric cell exposed to light. A vessel containing distilled water and a small quantity of bromide of potassium was placed in a dark room; in this vessel were immersed (or partially immersed) two silver plates S', V', the first coated with a film of Liverpool emulsion, the second uncoated. These plates were connected by insulated wires with the plates, S, V, of a glass cell containing water and a small quantity of common salt, the plate S being coated with a layer of a chloride of silver emulsion, and the plate V being uncoated. Magnesium light was then allowed to fall on the plate S of this latter cell for a few minutes. Now, whether S' was connected with S or with V, the plate S' when taken out of the vessel and developed was very sensibly blacker on its immersed portion than on the unimmersed. The action on the plate S' was assisted by exposing it for about ten seconds to gaslight before the photoelectric current of the exposed cell was passed through it. The effect is undoubtedly due to the action of the current, because when the plate S' was left immersed in its cell for twenty hours and then developed, no blackening effect was produced.

Not only is this photographic effect of the current important, but it is also important to prove that the effect on a sensitized plate is strictly confined to those portions of it

through which a current passes ; and to establish this fact more fully the following experiment was made :—

On a glass plate, ABCD, were cemented, close together but not in contact, several strips of silver foil,  $a, b, c, d, \dots$ , the whole plate being uniformly coated with a film of Liverpool emulsion ; two or more of the silver strips,  $a, c$ , were put into the circuit of a bichromate cell, the other strips,  $b, d$ , being left out of the circuit. This glass plate with its strips was half immersed in a vessel of water in presence of another silver plate, and the current was passed for a few seconds. On removing the sensitized plate from the vessel and applying the developer, the blackening took place only on those strips which were metallically thrown into the circuit, and only on the immersed portions of those strips.

Fig. 1.



I made use of this principle in an attempt to transmit an image of a simple figure to a distance ; but the arrangements were so difficult that the success attained was small, and I must leave the matter for renewed trial.

*Eosine*.—Comparatively strong currents are obtained by coating a silver plate with an emulsion of eosine and gelatine, and the currents are strengthened by allowing the film to set thoroughly on the plate. But such a plate has the drawback that the eosine readily leaves the film and comes into the liquid. This passage of the eosine may be delayed by pouring a layer of collodion over the dry gelatine film. By the action of light, this plate is rendered *negative* to the unexposed plate.

When daylight was allowed to fall on this plate, any variation of the light caused by a passing cloud, or the interposition and withdrawal of the hand in front of the cell, was at once accompanied by a variation of the current strength ; and the same thing is true for all the cells previously described ; but no variations of sufficient rapidity are produced to affect a telephone, although the make and break of the current itself is, of course, amply sufficient to do so.

The photographic action on a bromide-of-silver plate placed in a cell in a dark room and connected with one of the poles of an eosine cell was effected by the current generated by daylight in the latter without any preliminary exposure of the bromide plate to gaslight.

A very curious case of *inversion of the current* produced by

light was observed in a cell containing eosine in solution ; and as the same effect was occasionally observed in cells of other kinds employed in experiments made long afterwards, I shall draw attention to the phenomenon here.

Two clean silver plates were immersed in a glass cell containing distilled water and a very small quantity of eosine. One of these plates was screened and the other exposed to light, both being connected with the galvanometer. Immediately on exposure of the plate to light, there was generated a current in which the exposed plate was *positive* to the other. This current, however, lasted for only a second, and it was then (the exposure continuing) succeeded by a steady and much stronger current in the opposite direction, this latter being the current which would exist if the plate had been coated with an eosine-gelatine film in the usual way, any variation in the intensity of the light being answered by a corresponding variation in the strength of the photoelectric current. Now when the light was suddenly shut off from the plate, the instantaneous effect was to *increase* the existing current—the effect being merely impulsive—after which (the plate being screened) the current gradually disappeared. This result was again and again reproduced, and exactly the same result was found if the water in the cell contained a small quantity of fluoresceine instead of eosine, except that the initial and final impulsive currents were much smaller with fluoresceine than with eosine.

The plates of this cell having been left in the liquid and kept in the dark for a fortnight, the action of light was again tried ; and it was then found that, while the inverse currents were produced as before, the initial current on exposure was enormously increased both in magnitude and in duration. It now disappeared gradually, and was succeeded by a current in the reverse direction.

When one of these plates was removed from the cell and immersed in water in presence of a clean silver plate, it was at once, on exposure to light, *negative*, like a silver plate coated in the ordinary way with an emulsion of eosine.

M. Becquerel, in the course of his experiments on the electric action of light on plates coated with salts of silver, made the observation that in the case of *silver* plates coated with bromide, chloride, and iodide of silver, the nature of the exposed plate (whether positive or negative) depends on the *thickness* of the layer deposited on the surface of the plate. Thus, he says (*La Lumière*, vol. ii. p. 129):—" By depositing on one of these plates a *thin* layer of iodide, obtained by the action of the vapour of iodine at the ordinary temperature,

and then exposing this plate to light, it was found that it took *positive* electricity from the liquid. . . . With a *thick* layer of iodide on the surface of the silver, there is, on the contrary, a current the inverse of the preceding ; that is to say, the plate exposed to light took *negative* electricity. This result shows that, in this case, iodine acts on silver under the influence of light." He then gives a table of deflexions obtained when various coloured glasses were placed in front of a silver plate coated with a thick layer of iodide, the greatest effect being produced by violet rays, and the least by red, the former being 22 times the latter.

M. Becquerel continues :—"Thus, whilst with chloride and bromide of silver precipitated, placed on plates of platinum, there is always produced a current of the same sense, the exposed plate being positive, with a layer deposited on silver, there is an effect depending on the thickness of this layer. These two inverse effects indicate that there should be necessarily a thickness for which the electric effect is almost nothing."

These observations of M. Becquerel may possibly explain the above inverse effects in the eosine-silver cell ; but his last conjecture would not be practically verifiable, unless, when the critical thickness was reached, the state of the sensitive surface was one of stability. One result, however, would pretty evidently follow, viz., that if on the same plate a portion of the layer was below the critical thickness, while the remainder was above it, the plate, on exposure, might be, on the whole, positive, negative, or inert. In the case of photoelectric cells to be subsequently described, it is possible that the observed results are due to this cause.

Certain mordants were tried for the purpose of preventing the eosine from leaving the film. The sensitized plate was washed with a solution of borax, which had the effect of keeping the film on the plate, but almost completely destroyed its sensitiveness to light. A similar effect followed from the employment of a solution of chloride of aluminium. The best effect was produced when a silver plate coated with an emulsion of eosine and photographic gelatine was immersed for a few minutes in a strong solution of alum.

Naphthalene red, a substance soluble in alcohol and only slightly soluble in water, was also used in place of eosine. A little of this was dissolved in alcohol and then emulsified with gelatine. It was then poured on a silver plate, and the film was allowed to set thoroughly. The photoelectric currents produced were not quite so strong as those obtained with eosine. The effect is much greater in the blue than in any

other part of the spectrum, the exposed plate being positive ; and, apparently, with strong red rays, there is a reversal of the sign of the E.M.F.

Various other substances were used, among which I may mention iodine green, which gives rather strong currents with daylight, the exposed plate being negative.

In all these cells the E.M.F. is feeble compared with the electromotive forces which I have obtained by other means, to be presently described ; but in the case of silver plates coated with iodine green, an E.M.F. of about  $\frac{1}{20}$  volt can be observed with sunlight.

Fluoresceine used like eosine on silver or platinum plates gives poor results.

A few experiments with a solution of sulphate of quinine and some other fluorescent liquids were made with a view to connecting fluorescence with electric effect ; but the observed results were comparatively small, and the subject has been left for further trial.

#### *Other Metals.*

Many experiments were made with other metals, but the currents produced by most of them were smaller than those given by silver plates. Thus, I have on record an experiment in which bismuth was melted into thin plates which were fixed on glass, and then immersed in a cell containing water. When light fell on one of these plates, a considerable current was generated, the exposed plate being positive ; but on adding a solution of chloride of bismuth to the water, the current generated by light was reversed. On taking them out of the cell and washing them with distilled water, and then immersing them again in a water-cell, when the plate was exposed to light, there was an impulsive current corresponding to a negative nature of the plate, but this was promptly succeeded by a very large current in the opposite direction—just as in the cases previously mentioned.

Copper, antimony, and other metals were also tried, but the results are not of sufficient importance to demand any detailed record. In particular, iron plates coated with the magnetic oxide and immersed in water yielded photoelectric currents.

#### *Tin Plates.*

A glass cell containing a solution of fluoresceine in distilled water, in which two silver plates had been immersed, was taken for trial with other than silver plates. Almost the first metal that I used in this cell was tin. Two plates of tin foil whose surface had not been in any way prepared,

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but which was in the state in which it was obtained from the manufacturers, were fixed on plates of glass and placed in the cell. One of them being screened from light and the other exposed, a very strong current was the result. When the tin plates were replaced by copper, a current, but of less strength, was also produced. Gold plates gave no current at all. It was found, however, that the fluoresceine was unnecessary, and that when common tap-water was used in the cell, the currents produced by light seemed to be no weaker than before. If the hand or any other screen were moved rapidly in front of the exposed plate, the spot on the galvanometer-scale moved correspondingly. A telephone was put into the circuit with a view to the production of sound by variations in the incident light, but the alterations were not sufficiently rapid to produce this result. A battery of three cells in series was then formed, but no sound was produced in the telephone, and, moreover, the current indicated by the galvanometer was no greater than when only one cell was used. This latter fact seemed most extraordinary; but, on examining the cells separately, I found that one of the cells was producing a current in a sense opposed to that of the current given by the other two. Of this more presently.

When the liquid in the cell was distilled water, currents were still produced by the action of light on the tin. When a drop of sulphuric acid was added to the water, the currents ceased.

In nearly every cell that I used with tin plates—whose surfaces, as stated above, had not been treated in any way—the exposed plate was *positive* to the unexposed; but, after a time varying from a few minutes to a few hours, it was found that this positive current died out and was replaced by an apparently stronger current, in which the exposed plate was *negative*. Thus there was a change in the sign of the E.M.F. produced by the continuous action of light. This again reminds us of M. Becquerel's observation about the thickness of sensitive layers. There seemed to be almost no exception to the rule that the exposed plate begins by being positive and ends by being negative, the negative regime lasting for many days of prolonged exposure to light.

It was also found that when the chloride of any substance was dissolved in the distilled water of the cell, all photoelectric action ceased. Again, if the tin foil is cleaned by immersion in sodic hydrate and then in hydrochloric acid, or by immersion in a solution of either of the chlorides of tin,

the plate becomes completely insensitive to light. Thus the photoelectric result is obviously due to some layer on the surface.

In connexion with the change of sign of the E.M.F. produced by continuous exposure, the following remarkable experiment was made. Round the outside of a cylindrical porous pot was fixed a coating of tin foil; inside the pot was placed a strip of tin foil, these two strips being the exposed and unexposed plates of the cell respectively. The porous pot was filled with water and immersed in a glass beaker also containing water, the diameter of the beaker being very slightly greater than that of the porous pot. The strip of foil inside the pot was completely covered from light and connected with one terminal of a galvanometer; the foil outside the pot being connected with the other terminal. Outside the glass beaker, and fitting round it very closely, was a cylinder of black paper with a vertical slit cut in it, the breadth of the slit being about half an inch, while the diameter of the cylinder was about 3 inches. Thus, by rotating the black paper cylinder round the beaker, different strips of the tin foil on the outer surface of the porous pot could be successively exposed to light.

The slit in the paper occupying a given position, the corresponding portion of the tin foil was exposed to sunlight. The current indicated that the plate was positive, and the exposure was continued until the current changed its direction, *i. e.*, the plate became negative. The slit was then moved opposite another and distant portion of the tin foil, which, by the same process, was finally rendered negative; and so on all the way round. Thus the surface of the tin foil was divided into a number of strips, which were alternately negative and positive in their electromotive forces when exposed to light; and by rotating the black paper continuously round the beaker, a series of currents in contrary directions were obtained from the action of light on one and the same metallic plate—a result which, at first sight, sounds very strange. It is easily understood, however, when we remember the different conditions into which the various strips of the surface of the plate—*i. e.*, some very thin stratum on the tin—were put in the preliminary process; and, moreover, it prepares us for cases in which different portions of a tin plate which has been sensitized by a special process give, on exposure, electromotive forces of different signs.

I have not yet spoken of any process for producing a sensitive layer on the surface, and a long time elapsed before I discovered one. The tin foil hitherto spoken of is pure

tin foil as it is obtained from the maker ; and, as must be expected, not only were some pieces on exposure to light observed to be at once negative while others (the great majority) were positive, but there were various degrees of sensitiveness. Occasionally, also, the curious jerks immediately on exposure and immediately on screening, which were observed in the case of silver and eosine, were observed with these plates.

Then succeeded a series of experiments in which a quadrant electrometer was used instead of the galvanometer, *i. e.*, the E.M.F., and not the current, was measured.

A curious result was very soon observed with the thin tin foil which is wrapped inside small packages of tobacco. The two sides of this foil are notably different in appearance, one being somewhat dull, while the other has a bright silvery aspect. Two strips of this were cemented on opposite sides of a small glass plate, the dull surface of one and the bright surface of the other being fixed to the glass. This plate was immersed in a glass cell containing absolute alcohol, the two pieces of tinfoil being connected with the poles of the electrometer. When the bright surface was exposed to daylight, a small deflexion was obtained which showed the plate to be negative ; when the dull surface was exposed, the deflexion was more than doubled, the plate being, like the other, also negative, and the magnitude of its E.M.F. being about  $\frac{1}{16}$  volt.

A tin-foil plate, which at once on exposure to light is negative, is produced by thoroughly cleaning a piece of foil and coating it with *sulphide* of tin, either by exposing it to  $\text{SH}_2$  or by rubbing a little "mosaic gold" over the surface.

When distilled water was used instead of alcohol, the E.M.F. produced by light was in all cases diminished ; and the same result always happened when any salt whatever was dissolved in the alcohol with a view to diminishing its resistance.

This unfortunate result is characteristic of every photo-electric cell that I have employed. It is unfortunate, because it seems to preclude the possibility of obtaining really strong and practically useful *currents* by the action of light, and it appears to indicate some essential connexion of *resistance* and *electromotive force*.

The liquid is, of course, an essential element of the cell, and a very large number of liquids was tried in these experiments. Thus, for example, the two tobacco-foil plates when immersed in peroxide of hydrogen were absolutely insensitive. The alcohols are much the best liquids when tin

plates are used. Large electromotive forces have been obtained with all of them: but they are not all of quite equal value. As has been already stated, if any substance containing chlorine is put into the liquid, the E.M.F. of light completely ceases.

If a small quantity of nitrate of potassium is dissolved in the alcohol, a Thomson high-resistance galvanometer will be very easily and strongly affected by the photoelectric currents of these cells.

Among liquids an aqueous solution of pyrogallic acid is one which presents itself as worthy of trial, since pyrogallic acid is a greedy absorber of oxygen; and I have on record a striking result of its employment. A small plate of tin foil, the surface of which had been cleaned, was covered over with a thin layer of water, with which a drop of nitric acid had been mixed; the foil was placed on a glass plate, under which was applied a gas-flame until the liquid had quite evaporated, and the tin foil remained coated with some salt of tin. Whatever this salt was, when this plate was immersed in a cell containing absolute alcohol in presence of a cleaned tin-foil plate, the first was, on exposure to light, strongly *negative* to the second. The sensitive plate was then taken out of this cell and immersed in another containing a clear aqueous solution of pyrogallic acid. It was now absolutely insensitive to light. Taken out of this cell, and dried with blotting-paper, it was again put into the alcohol; and now, on exposure to light, it was found to be strongly *positive*. Here, then, is a case of complete reversal. This change was accompanied by a slight jerk or kick in the E.M.F., such as has been already described in connexion with silver and eosine; that is, on exposing the plate for the second time in alcohol, the initial indication of the electrometer was a very slight kick indicating a negative E.M.F., but this was immediately followed by a large deflexion in the opposite direction. This result was repeated many times; the plate was taken out of the alcohol and dried in the dark for about two hours, and when replaced in the alcohol cell the jerk and large contrary deflexion were obtained.

A similar experiment has been recently tried with a tin-foil plate sensitized by the process which I now adopt, and which will be presently described, and the result obtained was not the same as the above. In the new process the plate *appears* to be coated with the white oxide of tin,  $\text{SnO}_2$ ; but whether it really is so or not, I cannot say. However, such a plate which had been in a cell with methyl alcohol for two years was taken out, together with the back or unexposed plate,

and immersed in a cell with an aqueous solution of pyrogallie acid. On exposure to light in this cell, the plate was about half as sensitive, and of the same sign (positive) as in the methyl alcohol; and on replacing it in the alcohol cell, its indication was less than it had been originally. Thus, there was merely a falling off, but not an absolute destruction, of the E.M.F. caused by the pyrogallie acid, the sensitive surface having assumed a yellowish appearance.

The conjecture of M. Becquerel, that the sign of the E.M.F. developed by light depends on the *thickness* of the sensitive layer on the plate, has been already mentioned; but it may be allowable to put forward another conjecture—that when there are two, three, or any number of salts of a metal, any one of which may be on the plate, the result depends on the particular salt, and that the series may be alternately positive and negative on exposure to light according to the amount of oxygen (suppose) that they contain. A reducing agent may convert one of these into an adjacent one, and so alter the sign of the E.M.F. The question is not one with which I am competent to deal; it is for the chemist. And it might also be worth while to investigate whether there is any connexion between the sign and magnitude of the E.M.F. generated by the action of light on a metallic salt and the effect produced on the salt by electrolysis.

*Production of the Sensitive Surface.*—After trying a very great number of processes for producing a sensitive tin surface which is *positive* on exposure to light, the following is that which I have found to be most efficacious.

Take a strip of *pure* tin foil, say 1 inch long and  $\frac{1}{8}$  inch broad, and about as thick as a stiff sheet of note-paper (the very thin foil is not suitable; but the exact thickness is not of much consequence): clean it first in sodic hydrate, and then in dilute hydrochloric acid, or in hydrofluoric acid, until the surface presents a bright crystalline appearance. Having thoroughly washed it in distilled water until every trace of acid disappears from the water, place it horizontally, at *p*, on a bent plate of glass of the shape *gg* in fig. 2, this plate of glass being held by a clamp *C* supported by an ordinary retort-stand, which is not represented in the figure; under the tin plate *p* and the

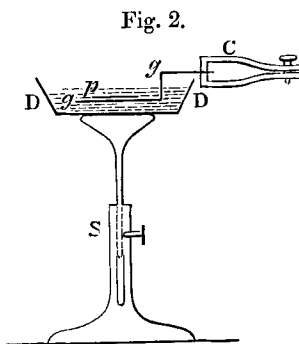


Fig. 2.

glass place a dish, D D, supported by a stand S, which allows the dish to be raised or lowered; the dish being raised until it nearly touches the glass *g*, pour into it, until the tin plate *p* is completely covered, a portion of the following mixture :—

500 c. c. of distilled water,  
3 c. c. of pure nitric acid,  
15 grammes of nitrate of ammonia.

If the tin *is pure* and has been *thoroughly cleaned*, the moment the plate *p* is covered by the solution, a whitish deposit is thrown down on its surface. The plate may be left in the solution for 3 or 4 minutes, and then the dish D D is lowered and removed. The deposit on the tin should be uniform and must not be allowed to form for more than 4 minutes. When the dish D D has been removed, the under surface of the glass plate *g g* should be dried by blotting-paper. Then a process of heating must take place. The flame of a spirit-lamp must be applied uniformly to the under surface of the glass plate, *i. e.* moved backwards and forwards until the whole of the liquid on its upper surface is evaporated. Great care must be taken not to melt the tin plate *p*.

Continuing the heating process, the upper surface of the tin passes through a series of appearances. At first (*i. e.*, when the water has just been evaporated) the deposit has a dull slaty look; as the heating goes on, this changes to a whitish aspect, a gas with a nitrous smell coming off; as the heating is continued, this whitish surface undergoes a rapid change to a dark colour with, apparently, a tinge of green, which travels like a shadow from one end of the plate to the other; the heating being still continued, this dark surface changes to a strong white, and the flame ought to be kept under it until the gas is completely driven off.

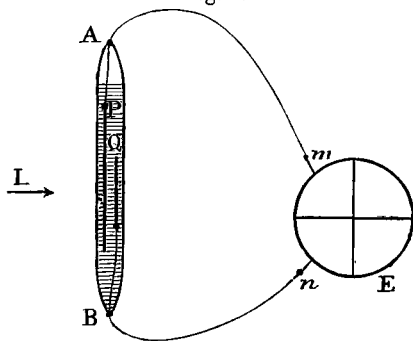
The plate should then be plunged into alcohol. It is now in the most sensitive condition. I have found that if the heating is stopped at the end of the penultimate stage—*viz.*, that in which the dark greenish colour has been reached—the plate will be very fairly sensitive to light. It may be suspended from a platinum wire fixed through a pin-hole at one end of the plate, and when placed in an alcohol cell in front of a clean tin plate similarly suspended, these plates being connected with the poles of an electrometer while the cell is screened from light, a small difference of potential will be observed, the sensitized plate being positive to the unsensitized; but this difference of potential will usually disappear after a short time.

Many liquids can be used in the cell; but I have found that the best results are obtained from *methyl alcohol prepared from oil of wintergreen*. With methyl alcohol prepared from wood-spirit I failed to obtain anything like the maximum E.M.F. on exposure to light. A plate so prepared is, on exposure to light, positive to the clean plate in the cell. In some liquids the plate is almost quite insensitive to light, but on replacing it in methyl alcohol its sensitiveness reappears.

It is remarkable that the plate while immersed in the cell (and unexposed) takes a considerable time—about five hours—to develop its maximum sensitiveness; that is, the cell should be left in the dark for this time to allow the plate to develop. Moreover, shortly after the plate has been formed, it is much more rapid in its response to light and shade than it is subsequently; not that there is any falling off in the final indications of E.M.F., but that the indications are more slowly produced.

Fig. 3 represents a cell connected with the electrometer. AB is a small glass tube nearly full of the liquid; P and Q are the sensitized and unsensitized plates, two fine platinum

Fig. 3.



wires being either soldered to them or passed through minute holes in them, these wires being sealed into the glass tube at A and B, and connected with the poles *m*, *n*, of a quadrant electrometer, E; the arrow L represents the incident light.

After forming the sensitive plate, it should be tried in the cell before the cell is sealed up completely; if it is not satisfactorily sensitive, it should be taken out and re-heated either on the glass plate in fig. 2 or over the chimney of a paraffin lamp. This further heating will often convert a partially sensitive plate into a very sensitive one.

The cell is usually fixed in a piece of cork by means of which it may be held in a support.

*Dispersion of the Residual Effect.*—On the withdrawal of the light, the fall of E.M.F. in the cell is usually much slower than the rise of E.M.F. on exposure ; and this fact would constitute a grave inconvenience if there were no speedy remedy. The effect of the light can, however, be quickly and satisfactorily overcome by connecting the exposed plate with the copper, and the unexposed with the zinc pole of a Daniell cell for a few seconds—the time of connexion being longer as the time of exposure of the plate to light was longer. In fact, a series of three or four impulsive contacts with the poles of the Daniell, followed by a few seconds' short-circuiting, will suffice to remove the residual effect of light, and to leave the spot on the electrometer-scale at the point from which it started.

This result is important, because when feeble light, such as that of a candle, falls on the cell, the maximum E.M.F. takes some minutes to develop, and the return of the spot on the scale would occupy a long time.

*Variation of the Effect with the Distance of the Source of Light.*—Six cells connected in series were placed on circles of varying radius, and a candle was in each case placed at the centre of the circle. The E.M.F. developed by the light of the candle was, with fair accuracy, found to be inversely proportional to the distance of the candle from the cells. As the intensity of the light varies inversely as the square of the distance, it follows that the square of the electromotive force is proportional to the intensity of the light.

*Curve of Rise of E.M.F.*—The law of increase of E.M.F. during exposure was studied by placing a "standard" candle at a distance of 6 inches from 6 cells connected in series, the poles of the series being connected with a Thomson quadrant-electrometer. The deflexions on the scale were noted every quarter minute, and a curve was traced having the deflexions for ordinates and the times for abscissæ. The maximum E.M.F. attained was .566 of that of a Minotto cell, giving for each cell .094 of this amount.

If we denote by  $A$  the maximum E.M.F. developed, and by  $\eta$  the E.M.F. at any time  $t$ , it would appear to be legitimate to assume the equation

$$\frac{d\eta}{dt} = k(A - \eta),$$

where  $k$  is a constant. This gives, by integration,

$$\eta = A + Be^{-kt},$$

where  $B$  is another constant. The curves actually traced in



the experiments closely satisfy an equation of this form, which is, of course, that of a logarithmic curve.

The curve of fall is probably of the same nature, but the rate of fall is much slower than that of rise, as is evident by an inspection of the diagram exhibited to the Society.

*Unhomogeneous Surfaces.*—To produce a homogeneous surface on the sensitive plate, it is manifestly necessary to satisfy two conditions : the deposit produced by the oxidizing solution must be uniform, and so must the heating by the spirit-lamp. It is obvious, then, that if these conditions are not fulfilled, we must be prepared to find some part of the plate positive and another part negative on exposure to light ; and such has actually been found to be the case in many experiments. But a much more extraordinary result of quite common occurrence is that described under the next head.

*Impulsion-Cells.*—It often happens that, a few days after a cell is mounted and found to be duly sensitive to light, an exposure produces no E.M.F. at all. But if a slight tap (sometimes scarcely audible) is given either to the support of the cell or to the table on which this support rests, a change, indicated by the motion of the spot on the electrometer-scale, takes place in the cell, and it is as sensitive to light as it was originally. Another tap given to the base throws the cell again into the insensitive state ; another tap will restore the sensitive state ; and so on indefinitely.

These results are not due to any defect in the contact of the platinum wires with the plates ; these wires are tightly pinched to clean parts of the plates, and often soldered to them.

It might be conjectured that these results are due to the formation of some gas in the cell ; but how can one tap replace the gas which has been displaced by another tap ?

I believe the sensitive and insensitive states to be due to some molecular alteration, either in the sensitive surface or in the liquid, or in their layer of contact—a sort of polarity in the medium which, as in the case of magnetic bodies, can be produced or destroyed by vibrations. Thus the E.M.F. due to light may be simply due to strain and not accompanied by any actual chemical combination.

A most remarkable instance of these impulsion-effects may be cited to show that they are not due to any defective contact. Referring to fig. 3, which represents the sensitive plate completely submerged in the liquid, let the plate be only partially submerged, and let the liquid surface be at a point C, about midway between B and A, the portion CA of the cell being occupied by vapour alone. This will be the state of

affairs in a cell which was under experiment. It was found that on exposing the upper portion, CP, of the plate and screening the lower, a *negative* deflexion on the scale was observed—that is, a deflexion which indicated that the exposed plate was negative; while if the upper portion was screened and the lower exposed, a *positive* deflexion resulted. Then on giving a slight tap to the support of the cell and exposing the portion CP, while screening the lower, a *positive* deflexion was observed; and on exposing the lower portion alone, a *positive* E.M.F. resulted, as before. Thus the effect of the vibration was to alter the nature of the upper portion while leaving the lower unaltered.

In another cell, which I now exhibit to the Society, the sensitive plate was completely immersed, and there was, as in the last case, a certain portion, CP, at the upper end which was rendered alternately positive and negative by vibrations, while the lower portion remained unaltered. These facts seem to be quite inconsistent with a want-of-contact theory. Before citing another experiment, in which a Thomson galvanometer is employed, to disprove such a theory, it is well to mention a remarkable method of producing the sensitive state from the insensitive.

While investigating the effect of static charges communicated to the plates on the sensitive and insensitive states, I found that if a Voss machine, not in any way connected with the cell or the electrometer, was worked in the room while the cell was in the insensitive state, *the moment a spark passed between the poles of the Voss, the insensitive state was altered to the sensitive*, whether the cell was connected with the electrometer or not. The same effect was produced at a much greater distance from the cell by the inductive action of the spark passing between the two poles of the secondary coil of an induction-coil, as in a Hertz oscillator arrangement. In fact when a Hertz oscillator was taken into the grounds outside the laboratory in which I worked, the induction-coil being actuated by a battery of 4 or 5 Grove cells, no wires whatever passing from this machine near the laboratory, the insensitive cell inside the room at a distance of 81 feet was instantly rendered sensitive by the inductive action of the Hertz arrangement.

Impulsion-cells differ much from each other in the readiness with which they undergo the change from one state to the opposite; but the most obstinate can be thrown from the insensitive into the sensitive state by leading a wire connected with either pole into the vicinity of a Hertz or a Voss machine.

I am not able to produce the reverse effect—the change from the sensitive to the insensitive state—by electromagnetic induction; dull taps administered to the base of the cell constitute the only way in which this change can be produced with certainty. On very rare occasions the change has been effected by the inductive action of strong sparks from a Leyden jar; but the result is quite exceptional. There appears to be some reason for supposing that this change—from sensitive to insensitive—is produced by vibrations of slow period, or very dull taps. I have produced it by dropping very small pieces of cork on the base of the iron retort-stand in which the cell is held, and even by gently drawing a piece of paper across the retort-stand.

Nearly all these tin-foil cells will develop the impulsion character a few days, or weeks, after they have been formed, *provided that the alcohol in them has not been thrown out and replaced by fresh alcohol*. Three years ago I formed a battery of 30 of these little cells, testing each before adopting it in the battery, and connected them in series, hoping thereby to obtain a very large E.M.F. on exposure to light. To my disappointment, however, I found a comparatively small result; and on examining the cells individually, I found some of them insensitive. Their sensitiveness was restored by renewing the alcohol, but it might have been restored by impulses if I had known the fact.

One of this battery in which the impulsion results appeared was taken out and its alcohol renewed on 4 or 5 days successively, with a view to ascertaining whether the impulsion results could be got rid of by renewing the liquid. After six renewals the cell ceased to give impulsion-effects, and it has been since under trial from time to time for about three years.

Impulsion-cells are very strongly influenced if they are kept in a room in which powerful sparks are being produced from a Holtz machine. A box of them which had been put by, for exhibition before this Society, in a cupboard about six feet distant from a Holtz which was put in action, was found during the process to have had nearly every cell affected in such a manner that no impulsion-effects could be produced for several hours after the Holtz ceased to be worked; and a strikingly good example of an impulsion-cell which I was very anxious to preserve acquired a strong tendency to revert from the sensitive to the insensitive state, and to remain in the latter; at the same time it lost its extreme sensitiveness to impulses.

The experiment with a galvanometer, previously men-

tioned, to show that in neither state of an impulsion-cell is there a want of contact, is as follows:—An impulsion-cell in which both plates hang from the top of the cell, and in which the liquid did not rise nearly to the level of the junction of either platinum wire with the plate, was made part of the circuit of a galvanometer and a Daniell cell by means of a key; its poles were connected with the electrometer, and before pressing down the key which put the cell into the galvanometer circuit, it was made insensitive by an impulse. On pressing down the key, the needle of the galvanometer was deflected, and this could not have happened if either contact were broken. In fact, the indication of the galvanometer was the same whether the cell was in the sensitive or in the insensitive state.

In two or three cells in which the alcohol had partially evaporated, leaving a portion of the sensitive plate above the liquid, it was found that, the whole plate having been originally positive, the portion in the vapour gave a negative E.M.F., while the lower portion continued positive.

Among the numerous liquids tried in these cells was butyric acid, which is efficacious; but after a few days it acts on the tin plate and tends to destroy the sensitive surface. A plate which had been kept in a cell containing butyric acid for some days was removed into one containing propylic alcohol. The effect was that the upper portion of the plate exhibited impulsion-effects—being alternately positive and negative with impulses—while the lower portion remained positive.

In acetone, nitrate of amyl, and glycerine these plates are also sensitive—as indeed in water also; but the E.M.F. in these liquids is less than in methyl alcohol.

It was found also that if the cell contained only the vapour of alcohol, an E.M.F. was generated by light, but less than that in the liquid. In aldehyde no E.M.F. due to light was observed.

Hydroxyl has the effect, after about twenty-four hours, of giving to the plate a yellowish colour, and also of changing the sign of the E.M.F. which exists in the dark.

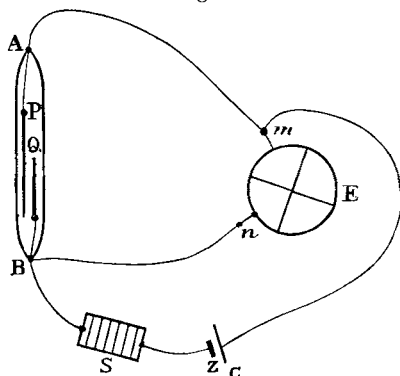
It has been found many times that one effect of removing a sensitive plate from an alcohol cell to a cell filled with hydroxyl or other liquids and then replacing it in the alcohol, was to develop impulsion results; and this fact shows that these results cannot be due to any induced electrification on the glass of the cell and an action of light on this electrification—such an action as has been the subject of recent experiment by a Russian physicist.

If, then, I am right in supposing that the development of electrical charges on these sensitive plates is in some way connected with molecular disturbances produced by electromagnetic induction or mechanical vibration, it must be admitted that the result is possibly a very important one, and that it may play a large part in the economy of nature. Thus, the mode in which solar energy is taken up in the cells of plants may be largely dependent on such disturbances in the atmosphere or in the earth. And in this connexion a somewhat wild conjecture may be pardoned.

The microradiometer of Prof. Boys works wonders in the measurement of very minute changes of temperature. If, then, we imagine a beam of light to be incident on the sensitized plate of an impulsion-cell from which it is, in part, reflected to a microradiometer, when the cell is in its insensitive state the incident energy is not taken up electrically and statically, and a greater portion of it would be sent to the radiometer than would be sent if the cell were in the sensitive state, so that a mechanical tap or an electromagnetic impulse, in altering the cell from electrical insensitiveness to sensitiveness, should produce an effect on the radiometer.

*Connexion with the Daniell Cell.*—It has been already stated that the residual effect when light is withdrawn from the cell is got rid of by connecting the cell with a Daniell cell in such a way that the deflexion caused by the latter is opposed to that produced by light—*i. e.*, the sensitive plate, P (fig. 4), is connected with the copper pole of the Daniell.

Fig. 4.



A very curious result of this arrangement deserves to be mentioned, inasmuch as it may possibly afford a clue to the nature of the action of light on the sensitive plate. Between the Zn pole of the Daniell and the plate Q interpose a very

great resistance,  $S$ , of the same order of magnitude as the resistance,  $R$ , of the photoelectric cell itself—*i.e.*, several megohms. This resistance  $S$  is composed of lead lines traced carefully on glass and then covered with shellac, and is, in my experiments, something like 10 megohms. The poles,  $A$ ,  $B$ , of the cell being connected with the electrometer, if  $e$  is the (disturbing) E.M.F. of the cell in the dark (which may be zero or very small), and  $E$  that of the Daniell, we shall obtain a deflexion,  $\Delta$ , given by the expression

$$\Delta = \pm e + \frac{R}{R+S}(E \mp e),$$

the signs  $\pm$  being taken according as  $e$  produces a deflexion in the same sense as  $E$  or in the opposite sense. This is on the assumption that  $e$  is not modified by  $E$ , which is possibly false, but not material to the result. Whether  $e$  is or is not modified by  $E$ , it is clear that if  $S$  is very small compared with  $R$ , the deflexion on the scale will simply indicate  $E$ , no matter how great  $e$  may be; and hence if light is allowed to fall on the cell with this arrangement, *there will be no indication of its effect on the scale*. But taking  $S$  of the same order of magnitude as  $R$ , we obtain, when the cell is in the dark, a deflexion of, say, half the amount produced by the Daniell alone. When the connexions are those indicated in fig. 4, *i.e.* when the Cu pole is connected with the sensitive plate, if light is allowed to fall on the cell a very large deflexion of the spot (of course in the direction opposed to  $\Delta$ ) is produced. If after this we reverse the connexions, *i.e.* connect the Zn pole with the sensitive plate, and allow the spot to settle to its position of rest in the dark, and then let the light fall on the cell, the deflexion produced by light is *very much smaller than before*. To quote a particular case—when the Cu pole was connected with the sensitive plate and the spot came to rest, the spot was deflected from this point through 260 divisions on the scale; and when the connexions were reversed and the spot again allowed to come to rest, it was deflected from the point of rest through only 50 divisions.

From the above expression it is obvious that, in the first mode of connexion with the Daniell, the deflexion from the zero produced by light is  $e - \lambda + \frac{R}{R+S}(E - e + \lambda)$ , where  $\lambda$  is the E.M.F. due to light, on the supposition that  $R$  is constant, so that the observed deflexion on the scale from the point of rest due to the Daniell is

$$\lambda \left(1 - \frac{R}{R+S}\right), \text{ or } \frac{S}{R+S} \lambda;$$

and if  $\lambda$  were the same in the second mode of connexion, the deflexion would be also of this value ; but since the deflexion is very notably less in the second case, it is almost certain that  $\lambda$  is also less.

Observe that in the first mode of connexion the action, or possibly only the tendency, of the Daniell is to deposit a layer of oxygen on the sensitive plate ; and if light tends to reduce oxygen at the surface, its action would be increased owing to the additional layer due to the Daniell ; while with the reverse connexions, the reducing action of light would obviously be lessened.

The electrolytic action of a Daniell battery on one of these cells is not permanent ; it disappears rapidly, and, indeed, it is not certain that anything more than a strain tending to electrolysis is produced.

The current of a Daniell cell, or any battery, if passed through an impulsion-cell, does not influence the state of the cell—*i. e.*, this current does not alter the sensitive to the insensitive state, or *vice versa*.

Supposing S, and therefore  $\Delta$ , to be such that when (in the first case) light falls on the cell, the spot on the scale is brought back just to the zero from which it started, if the Daniell is suddenly removed the light will then cause a further deflexion—which is the normal amount due to the light. This fact agrees perfectly with the theory of a reducing action, because, in the position of equilibrium of the spot when both light and the opposing Daniell act, the rate at which light tends to reduce is equal to that at which the Daniell tends to deposit oxygen ; and therefore in this particular case the plate is really in its normal state, so that when the Daniell is removed, light finds the plate in the condition in which it would be if no Daniell cell were connected with the photoelectric cell.

*Action of Different Colours.*—In a sensitive tin-foil cell, the action of the blue part of the spectrum is very much greater than that of any other part ; but measurable results can be obtained all through, as will be seen by the diagram exhibited to the Society. The spectrum was that of lime-light passed through a prism of bisulphide of carbon, a single cell being used in the experiment. This cell has been, from time to time, under experiment for more than four years, and its action is now exhibited to the Society. It has not appreciably deteriorated, but the time of any one exposure has never been more than a few minutes.

*Seleno-Aluminium Cells.*

In the year 1880 Mr. A. Graham Bell utilized the property of conductivity possessed by a modification of selenium which had been previously found to be a conductor, and also the property of variable conductivity when light of variable intensity falls upon it. These properties, as is well known, were utilized in the reproduction of sound by means of a telephone and a battery in the external circuit of which was placed a sensitive selenium conductor. This selenium arrangement is usually called a "selenium cell," but a *selenium conductor* or a *selenium resistance* is a much more appropriate term.

When the photophone was announced, selenium resistances were made in this country first, I believe, by Mr. Shelford Bidwell, who showed some of them at the last meeting of this Society, and by means of them produced two results of striking beauty, which I shall presently endeavour to reproduce by different means.

Last year I set about constructing selenium cells, properly so called—that is, cells in which electromotive force is produced by the action of light. The method adopted was to take two small clean plates of any metal, to spread a thin layer of the already recognized sensitive selenium on the surface of one of them, and, connecting each with a fine platinum wire, to immerse them in presence of each other in a small glass cell containing a liquid. Thus a large number of metals and a large number of liquids had to be tried for the best result. Plates of platinum, silver, tin, copper, zinc, bismuth, mica, glass, and other substances were tried with various liquids. With copper the E.M.F. produced by light was almost, if not quite, zero. All the others gave considerable results; but much the best result was obtained with plates of aluminium; and for some time the liquid used was one of the alcohols—preferably methylic. In the course of a few days, however, the aluminium plates in alcohol were found to be covered with a kind of gelatinous deposit, which, I am told, is an aluminate of alcohol. This liquid was, therefore, abandoned; and the best result of all was found to be produced with *acetone*.

The process of forming the sensitive plate is as follows:—On an iron tripod is supported a porcelain plate which is heated from below by a Bunsen flame; the little strip of cleaned aluminium is placed on this plate, and when it has got hot, one end of it is held in a forceps, while a drop of melted selenium placed at the end of a very hot glass rod is

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rapidly smeared over the aluminium plate. This selenium layer should be of uniform thickness, and the thickness must be neither very great nor very small. When the layer is deposited, the aluminium plate is quickly removed from the porcelain plate by the forceps and rapidly moved up and down in the air for a few seconds, the gas-flame being, at the same time, removed from under the porcelain plate. Both plates having now become slightly cooler, the aluminium plate is replaced on a comparatively cool part of the porcelain plate, and any tendency of the selenium to become liquid is checked by blowing over its surface. Working the gas-flame now rapidly backwards and forwards under the porcelain plate and occasionally blowing over the selenium surface, a series of changes—very much resembling those presented in the preparation of a sensitive tin surface—are observed. The appearances are as follows :—

1. The originally jet-black selenium surface gradually assumes a bluish-white appearance.

2. As the process is continued, this latter surface becomes a grey which may be of several shades. It may be a light grey, or a grey with a violet tinge, or a grey with some glossy spots or streaks. None of these surfaces is to be accepted. They are the final forms which most readily present themselves; and when they do, the selenium must be melted afresh and again spread over the aluminium plate—the whole process being repeated with its gradual heatings and coolings, until finally—

3. The surface of the selenium assumes a very dark brown colour.

This is the most sensitive surface that can be obtained. At first, accepting too literally the statement that “the grey modification of selenium is the sensitive one,” I accepted every plate which finally assumed a grey appearance, and constructed a large number of cells for a battery. By accident, however, a plate with the brownish colour was formed, and it proved to be so much superior to the others, that they were all rejected.

The glossy spots and streaks which sometimes exist on the grey surfaces are, I think, due to an indefinitely thin layer of the black selenium which has escaped the necessary transformation; and to observe them, it is well to look at the plate almost in the plane of its surface. The dark brown surface is devoid of them, and is in appearance quite homogeneous.

When the plate has assumed this appearance, it may be screened from light and left on the porcelain plate to get

cool, for which about ten minutes will suffice. When the plate has cooled, it can, apparently, be kept in the dark, un-immersed in any liquid, for any length of time before being put into the acetone cell. A plate was thus kept for sixteen days, and then, on being placed in the acetone cell, it was as sensitive as if it had been immersed immediately after formation. It is a marked peculiarity of the seleno-aluminium cell that, immediately after it has been set up, it is wonderfully rapid in its response to light, and that on the withdrawal of the light the E.M.F. at once disappears; but after a few days it is much slower in both respects—particularly the latter—while its sensitiveness as regards the magnitude of the E.M.F. developed is unimpaired.

The dispersion of the residual effect is produced by the means before described for the tin cells, viz., connexion with a Daniell cell, the sensitive plate being now, of course, connected with the Zn pole of the Daniell.

No sensitive and insensitive states due to vibrations, mechanical or electromagnetic, have, so far, been observed in the seleno-aluminium cells.

*Sign of the E.M.F. due to Light.*—Unlike the tin-foil plates described, the sensitive plate in a seleno-aluminium cell is strongly *negative* towards the insensitive plate when the cell is exposed to light.

*Effects of Different Colours.*—The seleno-aluminium cells differ from all other photoelectric cells that I have constructed in their great sensitiveness to all parts of the spectrum, the maximum effect being produced in the yellow near the borders of the green.

No very accurate experiment has yet been made on this subject, because the Thomson quadrant-electrometer at my disposal happens to be out of order; but with Clifton's form of the instrument, in which great sensitiveness has been aimed at rather than accuracy or constancy, the following numbers represent the relative electromotive forces produced by the spectrum of an albocarbon light formed by a bisulphide-of-carbon prism :—

Red . . . . .	109
Border of red and yellow . .	117
Yellow . . . . .	130
First edge of green . . . .	113
Last edge of green . . . .	101
Middle of blue . . . . .	104
End of blue . . . . .	102

The E.M.F. of a Daniell was represented by 408, and the

cell was about one metre from the prism. Most probably, of course, the number 101, corresponding to the border of green and blue, is less than it should be.

All other photoelectric cells may almost be said to be sensitive to the blue alone.

*Effect of Continuous Exposure to Light.*—The effect of exposing a seleno-aluminium cell continuously to daylight depends on whether the cell is left on open or on closed circuit. A cell left on open circuit for many hours, and then kept in the dark until its E.M.F. settles down, will be found to have fallen to one fifth of its original value; but if then kept during the night and observed in the morning, the E.M.F. produced by exposure to light will have quite recovered its first magnitude. Not so with the cell on closed circuit; its E.M.F., on fresh exposure, will be reduced to nearly one half its original value.

A cell which had been exposed to daylight for five days (with, of course, the advantage of each night's resuscitation) is now shown to the Society, and its action can be compared with that of a fresh cell.

*Connexion with a Daniell during Exposure.*—When a Daniell with a very great resistance interposed, as described in connexion with the tin cells, is connected with a seleno-aluminium cell, so that the Zn pole is first connected with the sensitive plate, and then with the insensitive, the E.M.F. developed by light is much greater in the first case than in the second—a result which is the same as before, since the seleno-aluminium plate is the negative one in the cell, and therefore the effect of this connexion with the Daniell is to develop between the poles of the photo cell a difference of potential opposed in sign to that which light produces.

*Mechanical Effects.*—The E.M.F. generated by light in a photoelectric battery can be utilized for ringing electric bells, lighting or extinguishing electric lamps, and possibly other things, although the materials of the battery are never used up in producing currents. The method which I have employed consists in utilizing the motions of an electrometer needle (due to the E.M.F. of the photoelectric battery) for making a contact and completing the circuit of an ordinary voltaic battery, whose current, thus completed, rings a bell, lights a lamp, &c.

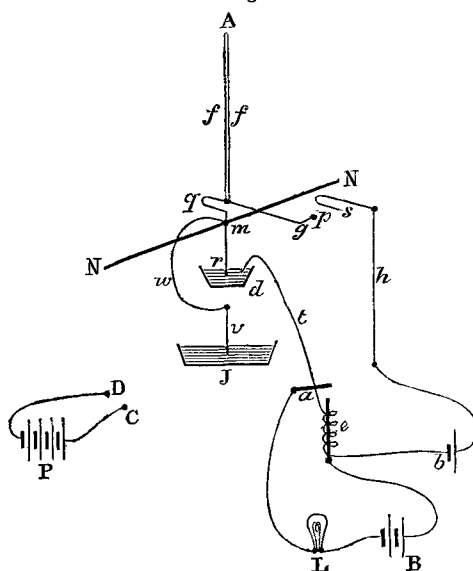
The first arrangement which I employed for this purpose was as follows:—At the middle of the aluminium needle of a quadrant-electrometer, and at right angles to the length of the needle, is fixed a very fine glass tube about  $1\frac{1}{4}$  inch long; a platinum wire traverses the interior of this glass

tube and, coming out at its ends, this wire terminates in two little spheres of platinum. Over the quadrants were fixed two small mercury-cups which were completely insulated from the quadrants and which were permanently connected with the poles of an external battery which had an electric bell in its circuit. When light shone on the photoelectric battery (whose poles were connected with those of the electrometer), the needle was deflected and, carrying the little glass tube with it, brought the platinum points into contact with the mercury in the cups; thus the circuit of the voltaic battery was completed, and the bell rung. This arrangement was unsatisfactory, owing to the difficulty with which the platinum points separated from the mercury, and it has been replaced by a much more satisfactory plan devised by Mr. Appleyard, to whom I beg to express my thanks for the untiring perseverance which he devoted to the perfecting of the apparatus.

The improved arrangement is as follows :—

In the figure *NN* represents the needle of the quadrant-electrometer, the quadrants of which are not represented ;

Fig. 5.



*g q m* is a very fine glass tube passing down through the middle point, *m*, of the needle; a platinum wire, *p g q m r*, traverses this tube, the portion *g q* lying at right angles to

the long diameter,  $NN$ , of the needle, and terminating in a sphere,  $p$ ; the portion  $mr$  of the wire dips into a shallow dish,  $d$ , of mercury which is supported below the quadrants by an arm not represented; a platinum wire,  $t$ , dips into the dish  $d$ , and, passing outside the case of the electrometer, is connected with one end of the coil of a small electromagnet,  $e$ , whose armature is  $a$ ; the other end of this coil is connected with one pole of a weak voltaic cell,  $b$ , whose other pole is connected with a small platinum plate,  $s$ , through a support,  $h$ , which is fixed inside the case of the electrometer, and, of course, insulated from the needle and the quadrants; the platinum plate  $s$  is fixed tolerably close to the position of rest of the platinum point  $p$ ; and when the needle is deflected by the E.M.F. of a photoelectric battery,  $P$ , connected with the poles,  $C, D$ , of the electrometer, the point  $p$  comes into contact with the plate  $s$  and completes the circuit of the voltaic cell  $b$ , and thus brings the armature  $a$  into contact with the magnet of the coil  $e$ : this connexion completes the circuit of a voltaic battery,  $B$ , in whose circuit is an incandescent lamp,  $L$ , or an electric bell, which is then set in action. The needle is connected with the sulphuric acid jar,  $J$ , by means of a fine platinum wire,  $w$ , bent into a semicircular form so as to avoid contact with the dish  $d$  when the needle moves, the wire  $w$  terminating in a vertical length exactly under the centre of the needle; thus, since the wires  $r$  and  $v$  are in the vertical axis of rotation of the needle, no appreciable friction hinders the motion of the needle.

The needle is suspended by two fine silk fibres,  $f, f$ , from a support  $A$  inside the case of the electrometer. Instead of the *two* external voltaic batteries,  $B, b$ , *one* would theoretically suffice; but it is found that, to prevent sparking and "stiction" between  $p$  and  $s$  when the current is made, it is preferable to have a very weak current traversing this portion of the arrangement—one which is just sufficient to work the electromagnet  $e$ .

In this way, by means of a few seleno-aluminium cells,  $P$ , I have found no difficulty in ringing a bell by the light of a taper or that of a match held at a distance of a few feet from the battery  $P$ . Observe that by this method we never draw on the materials of the photo-battery, because no current ever passes through it; it is simply connected with the poles of the electrometer, and its E.M.F. alone is employed.

### *The Problems of Photoelectricity.*

Three prominent problems in this subject deserve to be signalized. The first, and least pretentious, is the construc-

tion of a really scientific photometer. It cannot be said that the comparison of two lights by means of a spot of grease is a very satisfactory procedure ; but in the seleno-aluminium cell we have, on account of its great sensitiveness and range in the spectrum, an approximation to the possibility of an electrophotometer—at least so far as the *comparison* of lights is concerned. For, assuming that, by means of such a cell, we take, as it were, each light to pieces, and note the intensities of the different colours—which are directly proportional to the squares of the corresponding electromotive forces—we could then apply the principle of Newton's chromatic circle to determine the value of the resultant light. The second problem—and that which in 1877 induced me to work at this subject—is the electrical transmission of an image to any distance ; in other words, the construction of a telephotograph. The problem seems to be one of exceedingly great difficulty—much more difficult than the problem of the telephone—because the parts of an image are *simultaneous* and not, like the sounds of the voice, *successive* ; and, indeed, we have also to deal with a quick succession if we are to transmit a living moving image, such as Homer depicted on the shield of Achilles. The early attempt which I made consisted in the construction of a cable, somewhat on the model of the optic nerve. The optic nerve consists of a bundle of fibres, each a conductor of electricity and each separated from its neighbour by being surrounded by a medium. One set of ends of this nerve abuts on the retina, which is its sensitized plate, and the other in the brain. It is well known that light incident on the eye causes a photographic decomposition on the retina ; and I believe that images have been seen on the retina of a rabbit which was immediately killed after a strong light had been presented to its eye. The images, then, of external objects are transmitted along the optic-nerve cable to the brain, where by some means or other they result in a process of thought. Possibly thought is an equivalent of at least a part of the originally incident energy. No satisfactory solution of this problem will be attained by any slow and painful mechanical process of tracing out in succession the various portions of a picture ; and it does not now seem that we are near any true solution of the problem, whatever startling stories the newspapers may from time to time report.

The third problem is the direct transformation of the radiant energy of the sun into work useful to us, without the consumption (at least on any large scale) of materials on the earth—in other words to get rid of that terrible waster of

energy, the steam-engine. I usually find two objections made against any investigation in this direction. The first is, that the attempt is contrary to the principle of the conservation of energy. The objection, however, does not seem to be well founded; because it is conceivable that a photo-electric battery may yet be found which will simply act as a transformer of the energy which it receives from the sun, while its own materials, being merely the implements used in the process, may be almost wholly unmodified. The energy thus taken out of the sun may finally be radiated out into space from the earth in the form of heat, if it is true that all forms of energy must ultimately pass into this form—a proposition which, being a very wide generalization from our experience on the earth, it may be permitted to doubt in the universal necessity claimed for it.

The second objection is that there is not energy enough in the solar rays at the distance of the earth to supply the work desired. This objection is founded on the experiments of Pouillet, Violle, and others, who have estimated the solar energy incident per square foot per second on the surface of the earth. Let us see how much energy, according to the assumptions based on these experiments, is at our disposal.

The quantity of solar energy, assumed to be measured in metric thermal units, which is incident, normally, every minute on a square centimetre at the distance of the earth is given by the expression

$$A a^{\epsilon},$$

where, according to Pouillet,  $A$  (the solar constant) is 1·7633 calories,  $a$  (the atmospheric constant) is something between ·7244 and ·7888—let us say that  $a = \cdot 75$ ; and  $\epsilon$  is the ratio of the thickness of atmosphere traversed to the normal thickness of the atmosphere measured from the place of observation. M. Violle employs a formula of this form, but, according to him,  $\epsilon$  involves the height of the barometer and the pressure of aqueous vapour present in the air, and  $A = 2\cdot54$  calories. At the superior limit of the atmosphere  $\epsilon$  is, of course, zero, and at the surface of the earth, for normal rays,  $\epsilon = 1$ . Taking this latter value of  $\epsilon$ , and converting the thermal units into ergs, the quantity of energy incident per square centimetre per minute is

$$1\cdot3224 \times 42 \times 10^6 \text{ ergs}$$

according to Pouillet, and

$$1\cdot905 \times 42 \times 10^6 \text{ ergs}$$





(whatever that may mean) into one huge dark inert mass of uniform temperature in which no life is possible, this much, at least, is included in what we *do* know—viz., that we shall not have then got rid of the static energy of gravitation; and I strongly suspect that if we journeyed out to Antares or to Aldebaran, we should meet with intelligent beings who would express the utmost astonishment that we could ever have framed a principle leading to such a universal catastrophe.

XXVI. *On Gold-coloured Allotropic Silver.*—Part I.

By M. CAREY LEA \*.

[Plates I.-III.]

THE object of the present paper (which may be considered as a continuation of that published in the *American Journal of Science* for June 1889) will be:—

1st. To describe the reactions of gold-coloured allotropic silver.

2nd. To show that there exists a well-characterized form of silver intermediate between the allotropic silver previously described and ordinary silver, differing in a marked way from both.

3rd. To prove that all the forms of energy act upon allotropic silver, converting it either into ordinary silver or into the intermediate form. Mechanical force (shearing stress) and high-tension electricity convert it directly into ordinary silver. Heat and chemical action convert it first into the intermediate form, then into ordinary silver. The action of light is to produce the intermediate form only, and even the most prolonged action at ordinary temperatures does not carry it beyond this.

4th. To show that there exists a remarkable parallelism between the action of these forms of force on allotropic silver and their action on the silver haloids, indicating that it is not improbable that in these haloids silver may exist in the allotropic condition.

REACTIONS.

The most characteristic reactions of gold-coloured allotropic silver are those with the strong acids. When normal silver reduced with milk sugar and alkaline hydroxide is left in contact with strong hydrochloric acid even for several hours, there is no

\* From an advance proof communicated by the Author, to whom we are also indebted for the beautiful Plates illustrative of the paper.—W. F.