AN EXPERIMENTAL STUDY OF PHOTO-ACTIVE
CELLS WITH FLUORESCENT
ELECTROLYTES. I.¹

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THE effect of light on the electrical conductivity of cells containing a fluorescent electrolyte has been studied by several experimenters, with somewhat conflicting results.

Cunningham² observed a small increase of conductivity in the case of uranyl nitrate when illuminated by the light from an arc lamp, but he states that no precautions were taken to protect the cell from the heat of the arc, and that therefore his results are not trustworthy.

Regner³ also experimented upon solutions of eosin and fluorescein in water. His cell was so arranged that the liquid was in constant motion past the electrodes, and thus the danger of error from heating of the electrodes or liquid was largely eliminated. He was unable to obtain a change of conductivity as great as 0.1 per cent. in either case.

Nichols and Merritt⁴ tried the effect of light upon five different fluorescent compounds, using, instead of water, absolute alcohol as the solvent, and obtained effects ranging from 0.05 per cent. increase of conductivity in the case of naphthalin-roth, to 1.1 per cent. in that of eosin.

Still more recently Camichael⁵ has obtained a series of entirely negative results, and suggested that the precautions taken by the last named experimenters against heat effects were not sufficient, and that the change of conductivity observed by them was probably due to this cause.

¹ A summary of the work described in this paper was presented to the Physical Society at the Washington meeting, April 24, 1908, and an abstract was published in the *PHYSICAL REVIEW*, Vol. 26, p. 540, June, 1908.

² J. A. Cunningham, *Proc. Camb. Phil Soc.*, Vol. 11., 1902.

³ V. K. Regner, *Phys. Zeit.*, Vol. 4, 1903.

⁴ *PHYS. REV.*, Vol. 19, 1904.

⁵ M. C. Camichael, *Jour. de Phys.*, Vol. 4, 1905.

As the question seemed still to be an open one it was suggested to the author by Professor Nichols and Professor Merritt that he undertake a series of experiments which would, if possible, give conclusive evidence as to whether there is a conductivity change accompanying the phenomenon of fluorescence or not.

The author's experience in this line of work had been very slight indeed, up to the time of undertaking the above problem. Therefore he thought it advisable to first repeat, as nearly as possible, some of the experiments of Nichols and Merritt, and afterward to go on from that point to a systematic and thorough study of the subject.

The substance first chosen for experiment was eosin, and nearly all the results to be described in the following paper were obtained with this substance. As solvent absolute alcohol was used, and in most cases the solution was saturated at room temperature.

Fig. 1.

The apparatus used by Nichols and Merritt, and described by them in their article, was copied by the author as nearly as possible in the first experiments, various modifications being made from time to time as the work proceeded.

The essentials of the apparatus are shown in Fig. 1. The source of light *A* was a Schuckert arc lamp enclosed in the light tight cover which is used with the lamp for projection. After passing through a pair of condensers the beam of light illuminated the slit *S*, then went to a water cell *W*, and thence to a lens and crown glass prism, finally forming a spectrum on the front of the light tight box *D*, containing the cell *C*. *D* was provided with a sliding front by which the light could be admitted to the cell *C*.

For measuring the change of resistance an ordinary Wheatstone bridge was used, the cell being placed in one arm, and the source

of current being a battery of gravity cells, the number of which was varied as will be seen later. A very sensitive Sullivan d'Arsonval galvanometer was used with the bridge, the resistance of which was 1,100 ohms. The galvanometer was fitted with a concave mirror of four feet focus, and its constant with the scale at that distance was 90×10^{-11} per mm. deflection.

The cell used to contain the solution was a small rectangular glass cell 6 cm. deep and 1 cm. from front to back on the inside. In this were placed side by side, and at a distance of approximately a millimeter apart, two strips of platinum foil 0.1 mm. in thickness, 5 cm. long, and 3 mm. wide. Behind these in the cell was placed a piece of plate glass, holding the electrodes pressed against the front wall of the cell, and itself held in place by brass springs between it and the rear wall of the cell. A section of the cell is shown in Fig. 2, the thickness of the electrodes and other dimensions of the cell being considerably exaggerated. The dispersion of the prism used gave a visible spectrum at the point where the cell was placed about 4 cm. wide. Thus the portion of the spectrum illuminating the narrow space 1 mm. wide between the electrodes was quite small, and it was easy to select the part of the spectrum producing maximum fluorescence without including the rays of longer wave-length which would be likely to produce heat disturbances. In the case of the eosin cell the light used was at the infra edge of the green.

Fig. 2.

The fact was recognized, as had been done by Nichols and Merritt, that polarization effects would make it impossible to obtain the true resistance of the cell, and would at the same time greatly reduce the sensitiveness of the indications of change of conductivity due to light. Nevertheless the method in which a direct current was used was found to give much greater sensibility than any of the alternating current methods, and was therefore used, as an indication of a change of resistance was the chief thing to be looked for.

When the cell was first set up great difficulty was experienced in obtaining a balance, the drift toward higher values of the resistance being quite rapid and continuing for several hours. This was

at first thought to be due entirely to polarization, but it was found that if the top of the cell was covered so tightly that evaporation was prevented the drift lasted for only a short time, after which a comparatively steady condition was reached, and quite accurate measurements were possible. At no time was the cell absolutely free from a very slow drift, always toward higher resistance, and probably due partly to polarization and partly to a very gradual decomposition of the electrolyte. Evidence of the latter was seen in a very narrow strip of colorless liquid which was observed along the inner edge of the anode after several hours of application of the current. On account of this decomposition most of the tests were made with cells which had been freshly set up, the electrodes being removed and carefully cleaned between each two of the sets of tests.

The method of the experiment was as follows. After the apparatus had been set up and the cell placed in its dark box the slide was raised and the cell so adjusted in the spectrum that the liquid between the electrodes became brilliantly fluorescent. The slide was then dropped, shutting off the light, and a balance obtained with the bridge. In the measurements to be described in the first part of this paper the resistance of R_1 (see Fig. 1) was in nearly every case 10,000 ohms, that of R_3 was 50,000 ohms, and R_4 was adjusted to suit the resistance to be measured. As it was impossible to set the electrodes at exactly the same distance from each other when the cell was set up at various times the apparent resistances differed from each other greatly during different sets of readings. Also the polarization E.M.F. in the case of eosin was found to be over two volts. Therefore when two gravity cells were used the resistance was much higher than when four were used. When the applied E.M.F. was two volts the resistances ran between two and three thousand ohms. The sensibility of the bridge, of course, varied with the magnitude of the cell resistance, and when readings were being taken the sensibility was frequently tested by reading the deflection of the galvanometer produced by changing the variable arm by a known amount.

After the cell had stood in darkness long enough to obtain a fairly steady condition of the bridge, the slide was suddenly removed and the cell illuminated.

With two volts as the applied E.M.F. the result was an immediate and very large decrease of resistance, the amount of resistance change required in the variable arm to restore a balance indicating as high as ten or fifteen per cent. increase of conductivity. When the light was shut off the cell returned immediately to nearly the same resistance which it had before illumination. The test was repeated many times and on different days, and always with about the same results. As the effect was vastly larger than any that had been anticipated it seemed advisable to see if it could in any way be due to heating of the liquid. With this end in view the temperature coefficient of the solution was determined in the following manner. A balance was obtained at the temperature of the room. Then the cell was surrounded with ice water and a balance again obtained. Lastly the ice water was drawn off and the cell allowed to regain the temperature of the room. The first and last values of the apparent resistance were in turn subtracted from the second and then averaged. The result showed a temperature coefficient between zero and 20 degrees of not more than 1.5 per cent. per degree. The effect of the light was also tried while the cell was in ice water and found to be apparently about as large as at room temperature. These tests seemed to preclude the possibility of any considerable portion of the effect being attributable to heat. An additional reason why the effect should not be attributed to heat was mentioned by Nichols and Merritt in their article, namely, the fact that the change of conductivity took place within an exceedingly short time after the light was thrown on the cell, and after the light was shut off the cell immediately resumed its former state. This fact was confirmed by the author's experiments, the time required for the change to take place being apparently considerably less than a second, and the decay of the effect taking about the same time.

The next step in the work was a series of tests with the same cell and solution, but using four gravity cells in series as the source of E.M.F. A difference of effect from that obtained with two cells was expected, as with two cells only a very small current could possibly have passed through the cell since the applied E.M.F. was not equal to the E.M.F. of polarization, while with four volts the current flowing was of considerable magnitude. The effect anticipated

was one similar to the first but of smaller magnitude. When the light was thrown on the cell, however, the surprising result was obtained of a large *increase* of resistance instead of a decrease as in the former experiments. The effects were produced as promptly as those of the preceding experiments and died away nearly as quickly.

Here was something quite puzzling, and which apparently contradicted any theory that might be advanced in regard to the first effect. If the remarkable decrease of resistance observed in the first experiments was due to electrons set free by ionization of the solution accompanying the phenomenon of fluorescence it seemed highly improbable that an increase of resistance would be produced by light under any conditions whatever. Further, both effects were entirely too large to be satisfactorily accounted for by any theory analogous to that applied to the ionization phenomena in gases, phenomena which it might be supposed would very probably accompany fluorescence.

Again, if the decrease of resistance in the first case were due to ionization of the nature of that produced in gases, it should be greater in dilute solutions than in concentrated, since, owing to the greater penetration of the light into a dilute solution the number of molecules affected would be as great as in a concentrated solution, while, owing to the greater distance between the molecules, the mean free path of the ions would be greater and therefore recombination less rapid. A number of experiments were made by diluting the saturated solution with two, four and six parts by volume of alcohol, and the effects were found to be diminished, even in the solution with two parts of alcohol, to not above a change of 1 per cent. in resistance.

In order to vary the conditions it was thought worth while to try next a cell in which, as in Regner's experiments, the liquid could be kept moving past the electrodes while being illuminated. All possible heat effects would be in this way eliminated, and some light might be thrown upon the nature of the phenomena which would not be brought out when the liquid was at rest. A cell was therefore prepared in the following manner, again copying the design of one used by Nichols and Merritt.

A glass tube of 5 mm. internal diameter was drawn down at its

middle point to a capillary about a millimeter in outside diameter and 1.5 cm. in length. Into the larger parts of the tube, at either end of the capillary were led platinum wires in the form of spirals to serve as electrodes. The upper end of the tube was attached to a tubulated bottle to serve as a reservoir for the liquid. To the lower end of the tube was attached a capillary tube to hold the liquid back and keep the capillary full. With this apparatus the liquid could be illuminated while flowing through the capillary at any rate desired. A number of tests were made with the apparatus, and in all cases the results were entirely negative. The form of the cell was such, however, that its resistance was much larger than that of any of the cells previously tried, and as the sensitiveness of the bridge was much less under these conditions than when the resistance was less, the results were looked upon with some suspicion.

Fig. 3.

Another form of circulation cell was therefore devised which was free from the above objection.

A piece of glass tubing was obtained from the Taylor Thermometer Co. of Rochester, whose internal cross-section was almost that of a figure 8, except that where the two loops of the eight would cross one another there was an opening between them about 0.3 mm. in width. In a short length of this tubing were placed two No. 16 platinum wires, each having a length of five centimeters. The wires were parallel to one another in the two loops of the 8, and from the end of each a small platinum wire was led out through the walls of the tube. There was thus left (see Fig. 3. which shows an enlarged cross-section of the cell) a narrow space between the electrodes through which the liquid could flow, the electrodes themselves almost filling the loops of the 8. Below the electrodes the tube was drawn down to a coarse capillary to make it possible to keep the space between the electrodes filled with liquid, and the upper end of the tube was attached to a tubulated bottle as in the last experiment. By illuminating the contracted part of the tube between the electrodes a moving strip of liquid about 0.3 mm. wide and 0.1 mm. from front to back could be excited to fluorescence, while the current flow was from side to side of the strip at right angles to its length.

Upon connecting the cell to the bridge it was found that its resistance reached a steady value almost immediately after the current was turned on, and retained the same value as long as the motion of the liquid continued.

The movement of the liquid was quite rapid, the time required to empty the 400-c.c. reservoir being about ten minutes. As the whole space between the electrodes could not have held more than 0.1 c.c. a complete change of liquid between the electrodes could not have occupied more than a fifth of a second.

Numerous tests were made with this apparatus, but in no case was there any evidence of a change of conductivity while the liquid was in motion. When, however, the lower end of the tube was stopped the effects reappeared, though they were not as marked as in the original type of cell. The sensibility of the bridge as used in these tests was at least 0.01 per cent. Therefore it seems fair to conclude that there could not have been any appreciable effect due to electrons set free at the instant fluorescence began in any part of the liquid, unless this effect required a considerable time to make itself known. Unless the free electrons traveled very slowly indeed it would seem likely that some of them at least would reach the electrodes and produce greater conductivity, even when the liquid was moving as fast as in the above experiments.

Attention was next given to the study of the effects at the two electrodes separately and to the liquid between them, to find out, if possible, just where the phenomena took place which caused the conductivity changes.

As nothing but negative results were to be obtained from a circulation cell the original type of cell was again adopted, and in the front of the box *D* of Fig. 1 was placed a screen with a vertical slit cut in it about 4 mm. wide. By placing the cell behind this screen in such a manner that only one electrode could be seen from the front of the box through the slit, it was possible to observe the effect of illuminating one electrode at a time, the other being in darkness behind the screen. With this arrangement and two gravity cells the effect was tried on anode and kathode in turn. When the anode was exposed the effect was very small, while on the contrary when the kathode was exposed the effect was found

to be about as large as when both were exposed. As some of the liquid between the electrodes was illuminated in either case it was not certain whether the effect was produced only at the electrode or whether the liquid at a distance from the electrode also played its part in it. Therefore the question as to what would happen when the electrodes were both covered and the liquid between them exposed had next to be settled.

To this end several different arrangements of the cell were tried. The first tests were with the same electrodes which had been used in the earlier type of cell, but in front of each of them was placed a thin strip of hard rubber 0.15 mm. thick, projecting just beyond the platinum strip so as to completely screen it from the light, but so as to leave about eighty per cent. of the liquid between the electrodes exposed to the light.

With this arrangement no effect could be obtained by illumination. However, it was felt that the test was not very conclusive as the total thickness of the film of liquid acting as conductor between the electrodes was that of both the electrode and the rubber strip, and as the absorption coefficient of a saturated solution of eosin is very large it was not at all certain that the whole thickness of the layer was illuminated, so as to be fully excited to fluorescence.

In order to overcome this difficulty another type of cell was constructed after the following manner :

A block of hard rubber was sawed of such shape and size as nearly to fit the rectangular cell used in most of the experiments.

Fig. 4.

Fig. 5.

The block was then clamped to another block of ebonite and with a $\frac{3}{8}$ -inch drill two holes were bored between the blocks in such a manner as to leave in each block a pair of grooves of semi-circular cross-section, and separated from each other by a narrow strip approximately 2 mm. wide. The block that had been sawed to fit the cell was then placed in the cell and two L-shaped electrodes placed in the grooves in the positions shown in Fig. 5, which illustrates a

section of the cell with block and electrodes in place. It will be seen from the figure that the electrodes hold the ebonite block back from the front wall of the cell so as to leave a film of liquid of the thickness of the platinum strips between the two grooves when the cell is filled with liquid. The electrodes themselves in this cell offered a broad conducting surface, while being entirely away from the thin film of liquid between the grooves. This film could be perfectly illuminated, was isolated from the electrodes, and at the same time included a large part of the total resistance between the electrodes.

Careful tests were made with this cell and the results were entirely negative, though the resistance of the cell was quite low compared with others that had been tried, averaging about 40,000 ohms with saturated solution, and the sensibility of the bridge was as high as 0.005 per cent. Also the condition of the cell within a few minutes after it was set up was very steady indeed, and a slight change of conductivity would have been readily detected.

In addition to the saturated solution a solution of five parts alcohol to one of saturated eosin solution was tried with both two and four volts E.M.F., but likewise with entirely negative results. From the results of these last experiments the author was convinced that a change of conductivity in the liquid itself, except at or very near the electrodes, did not take place when fluorescence was produced.

Attention was therefore given to the phenomena at the electrodes themselves.

It had frequently been observed that, however smooth the strips of platinum were when they were placed in the cell, and however tightly they were clamped against the front wall, when the solution was poured in a thin film of liquid immediately crept up between the electrodes and the front wall of the cell. There seemed, therefore, to be two regions in which the effects might be produced, either at the inner edges of the electrodes or in the region in front of the electrodes or in both places at once.

From a variety of minor indications which had been noticed from time to time the author was convinced that the main effect was to be looked for in the thin film and not at the edges of the electrodes. In order to test the matter the effect was first tried of placing thin

strips of ebonite in front of the electrodes as in one of the previous experiments, but instead of covering the electrodes the ebonite strips were only allowed to cover the extreme outer edges of the platinum strips, thus leaving nearly the whole of the electrodes exposed to the light, but behind a layer of liquid a number of times as thick as the capillary film formed when the electrodes were against the front wall of the cell. The change of conductivity, though still present, was found to be very greatly diminished.

As mentioned in connection with a previous experiment, the reduction of the effect might easily have been due to the absorption of the light by the thick layer of liquid in front of the electrodes so that fluorescence did not occur very near the surface of the platinum strips.

A second arrangement was then tried in which the platinum strips were separated from the front wall of the cell by strips of lantern slide cover glass a millimeter in thickness. The inner edge of each electrode (see Fig. 5) was allowed to project slightly beyond the edge of the glass.

Thus the capillary film between the electrode and strip of cover glass could be illuminated while the inner edge of the electrode was completely screened from the light by a thick layer of liquid. When the light was turned on this cell the effects were found to be present in as great a degree as when the whole of the electrode had been illuminated.

Lastly the platinum strips were again placed against the front wall of the cell and the inner edges covered while the rest of the electrodes was illuminated. Again the effect was present, as was to be expected.

The conclusion arrived at from the various tests was that, in the first place, no effect is produced by light upon the conductivity of a fluorescent solution unless a region very near the electrodes is illuminated and that further, this effect at the electrodes is only produced in a very thin film of the liquid immediately in contact with the surface of the plates.

It may be well to state at this point that, while no reference has thus far been made to a variation of the effects in different parts of the spectrum, frequent tests were made in all of the experiments

described, to see if the effects could be produced by parts of the spectrum which did not produce fluorescence. In all of these tests the effects obtained were either very feeble or entirely lacking. Thus, in the red, where the energy of the arc is the greatest, but where no fluorescence was to be detected, no effects were observed which were as great as 0.2 per cent. either way. Thus the frequent references to fluorescence in connection with the effects observed seem entirely justified.

The next step undertaken in the investigation was a study of the variation of the effects at anode and cathode with varying potential difference at the terminals of the cell.

For this purpose the original form of cell was adopted, with electrodes 0.15 mm. thick and 3 mm. wide, placed next to the front wall of the cell and 3 mm. apart. The greater distance between the electrodes was adopted so that while one of the plates was being illuminated no stray light could reach the other electrode. The greater thickness of the electrodes was necessary in order to keep the resistance of the cell as low as possible, and in view of the results of previous work could not materially affect the sensibility of the cell.

The screen in the front of the light tight box *D* was so arranged that the cell could be moved into a position to expose either electrode to the light without having to raise the slide in the front of the box to make the adjustment.

As a source of E.M.F. a set of four sal-ammoniac cells was first used, but as these were found to drop slightly in voltage during a run, a pair of storage cells was substituted for them. The cells were connected to the ends of a rheocord, consisting of ten meters of manganin wire, and sliding contacts were arranged so that any desired potential difference could be obtained at the bridge terminals, up to the limit of the cells.

To the bridge terminals were also attached leads from a large Weston milli-voltmeter, a resistance being placed in a series with the meter, and the whole calibrated to a total range of 15 volts. With this arrangement it was found easy to obtain the potential difference between the terminals of the bridge with an accuracy of .01 of a volt, and any given value of the potential difference could

be maintained constant throughout the time needed for the readings.

For greater simplicity in computation, and to make it possible to maintain the potential difference between the terminals of the cell at a constant ratio to the voltmeter reading, the bridge arms were arranged as follows (see Fig. 1): R_3 62,500 ohms, R_4 10,000 ohms, and R_1 a 100,000-ohm box to be used as the variable resistance. Thus, unless in a case where the resistance of the cell was so great that the 10,000-ohm box had to be varied, the fall of potential across the cell terminals was nearly 86 per cent. of the voltmeter reading.

The change of resistance due to the illumination was estimated in two different ways, depending on the magnitude of the effect. If the galvanometer reading remained on the scale when the cell was illuminated, a reading of the deflection was taken, then the illumination stopped and a second reading taken and the two averaged. A plug was then inserted in the 10,000-ohm box, the change of galvanometer reading obtained, then the plug was removed, a second reading taken and the two averaged. Assuming that the galvanometer deflection was proportional to the change of resistance in the 10,000-ohm box, the number of scale divisions corresponding to a change of one ohm or one part in ten thousand was easily obtained. As increase or decrease in the apparent resistance of the cell would produce the same change in the potential difference at the galvanometer terminals as the same percentage decrease or increase of the resistance in R_4 , it was easy to get quite satisfactory estimates of the change produced by the illumination. If the effect of the light was great enough to throw the galvanometer off the scale, a balance was restored by changing the resistance in R_1 . The light was then shut off and a second balance was obtained, and from the average of the two changes in R_1 the change of resistance of the cell was calculated.

Curves were plotted, using potential differences at the cell terminals as abscissas, and change of conductivity, *i. e.*, reciprocals of resistance changes, as ordinates. Eight curves are shown in the accompanying figures. Each value of the conductivity change is the average of at least two readings, taken at intervals of five minutes

time. These curves are typical of a large number that were obtained in a similar manner.

Fig. 6.

Owing to the variation in the intensity of the arc light used, and to the difficulty of setting up the cells in exactly the same manner each time, the magnitude of the effects obtained varies considerably in different curves. Nevertheless the character of the effects obtained did not vary greatly.

In curves 1 and 2, 3 and 4 (Figs. 6 and 7) the kathode and

Fig. 7.

anode were illuminated alternately throughout the experiment. Each value of the change of conductivity is the average of at least two measurements, made at intervals of five minutes from the end of one measurement to the beginning of the next. It will be noticed that the kathode shows at low voltage a large decrease of resistance due to the light, followed by a considerable increase of resistance as the voltage rises. On the anode the effect at low voltage is just the opposite to that on the kathode and changes sign as the voltage rises as in the case of the kathode.

It will be noticed that the change of sign of the effect occurs considerably earlier in the case of the anode than in that of the kathode. The result of this is that for a considerable range of voltage both electrodes show a decrease of resistance with the light. As this region happens to include the voltage obtained when two gravity cells were used as the source of current, it is not surprising that a large decrease of resistance was observed in the first experiments, when both electrodes were exposed to the light at once.

As the curves showed that the effects on the two electrodes were in general of opposite sign, it was thought advisable to arrange a cell so that one electrode could be studied at considerable length, and with a certainty that no complications would be introduced by stray light reaching the other electrode.

In order to have the electrodes as far apart as possible, and still to keep the resistance of the cell within reasonable limits, the electrode to be exposed was alone fixed in the front of the cell, clamped to the front wall in front of and very near the edge of a narrow strip of glass. The other electrode was made L-shaped, nearly a centimeter being the length of each leg of the L cross-section. This electrode was placed in the main part of the cell with the base of the L toward the side of the cell away from the light source. This arrangement insured a very large electrode surface and also an average cross-section of the liquid between the electrodes sufficient to make up for the greater distance between them. It also served to concentrate the greater part of the resistance at the electrode to be illuminated.

As the kathode effect seemed the most promising for further study the current was sent through the cell from the large electrode to the one to be exposed.

A number of runs were made with this cell and from the results curves were plotted, of which 5, 6, 7 and 8 are typical specimens (Figs. 8, 9 and 10). It will be seen that the effects are considerably greater than those obtained in the former experiments, and also that

Fig. 8.

the form of curve obtained is in general more regular than the others. The peculiar rise of the effect after the large decrease shown in the first part of the curve does not appear to be accidental, but is common to almost all the curves plotted for the kathode effect.

Fig. 9.

Curves 7 and 8 were made to ascertain the effect which the previous history of the cell might have on the action of the light. Curve 7 was obtained in the usual way, and immediately after a run was made, without changing the cell, but beginning with high voltage and reducing the voltage by the same steps that had been used in going up,

Fig. 10.

It will be noticed that the curves are very much alike, the one taken on decreasing voltage showing a slight shift toward the right. Also for the last two points on the return curve it was found impossible to obtain a balance of the bridge, the condition of the cell appearing very unstable. At the three voltages 1.03, 1.21 and 1.38 of the first of these two curves a phenomenon was observed which occurred frequently throughout the experiments, at the point where the effect reversed. When the cell was first exposed the galvanometer showed an immediate decrease of resistance, followed in a few seconds, with the light still on, by a large increase. When the light was shut off the cell showed the two changes in the reverse order.

This would seem to indicate, at least in this region, a combination of two effects, one growing to a maximum more rapidly than the other, and dying away more slowly.

A few experiments were made with fluorescein in absolute alcohol,

a trace of caustic soda being added to produce fluorescence. The effects obtained were very similar to those with the eosin, but not nearly as marked.

Rhodamin was also tried, with somewhat doubtful results, except that the effects with very low voltages were fully equal to those with the eosin.

Since there seemed to be no doubt that the seat of the effect was the thin film of liquid in front of the electrode, and since the current could not be supposed to flow only to and from this film and to neglect the opportunity to enter the edge of the electrode, it did not seem possible to account for the changes in resistance observed, except by the actual creation of an electromotive force at the surface of the electrode or near it, by the action of the light. If such an effect did exist it would account for the change of resistance when either anode or kathode was illuminated, so long as low voltages were used. For suppose the E.M.F. produced to be such as to tend to make the exposed plate positive to the unexposed one. Then if the exposed plate were made the kathode with regard to the outside E.M.F., the E.M.F. due to illumination would act with the original E.M.F., producing a greater current through the cell and making its apparent resistance, as measured on the bridge, less.

If, on the contrary, the direction of the impressed E.M.F. were reversed, the photo-E.M.F. would oppose the passage of the current and the apparent resistance of the cell be increased.

The reversal of the effects when the voltage was raised is not easy to account for. From a number of tests of the polarization E.M.F. of eosin cells, made by comparing the E.M.F. with that of a standard cell by means of a condenser, the effect of maximum polarization appears to be a back E.M.F. of over two volts. This value determines the point where any considerable current begins to traverse the cell, and hence it would be most natural to expect that just here would occur any marked change in resistance phenomena, such as the reversal of the illumination effect. This, however, does not seem to be the case, for it will be noticed from the curves that the reversal in the case of the kathode occurs at very nearly 1.7 volts, while at the anode the voltage is much lower. That the effects at high voltages are connected in some way with the polarization of the

cell seems, nevertheless, most probable, though in what manner the author has not as yet been able to determine. If the light effect, through reduction of the electrolyte, is able to produce free hydrogen and thus increase the amount of polarization, it is still difficult to explain why the duration of such an effect should be only that of the illumination, dying away almost immediately when the light is shut off. Further work on that part of the problem has been postponed for the present.

Assuming that the effect at low voltage is due, as has been suggested, to a photo-E.M.F. similar to those which have frequently been observed in cells containing silver salts and many other electrolytes, the author next turned his attention to testing the effect of light on the cell when no external E.M.F. was applied.

The same type of cell was used as had been used for all of the experiments on the kathode alone. The terminals of the cell were connected directly to the Sullivan galvanometer which had been used with the bridge in all the previous experiments.

Very considerable effects were produced by the action of the light, ample in magnitude to account for the phenomena observed with the bridge at low voltages.

A series of experiments was then undertaken to find if in any way this photo-electric effect was intimately connected with fluorescence.

In the first place tests were made throughout the visible spectrum, and curves plotted showing the variation of the current produced in the galvanometer as a function of the wave-length of the exciting light. The effect was found to increase regularly from the edge of the visible spectrum in the violet to a pronounced maximum just before the absorption band was left in going toward the red, namely, just at the infra edge of the green. The decrease of effect from this point on toward the red was very sudden indeed, and the effect was entirely lost before the edge of the visible spectrum was reached. Three other substances, namely, rhodamin, fluorescein and naphthalin-roth were found to give similar effects, and in each one the maximum results were obtained at the infra edge of the absorption band. In rhodamin the effects were found to be enormously greater than with the eosin, but with the other two substances the results were less satisfactory.

With rhodamin tests were made by a condenser method to test the magnitude of the E.M.F. produced, and it was found to be as high as 0.2 of a volt. In eosin it is probable that the maximum was not over half that amount.

Dilute solutions of rhodamin were also tried with very good effects. The maximum dilution thus far tested is that of one part saturated solution to ten of alcohol.

With dilute solutions of eosin, however, the effects were greatly reduced.

The extremely thin capillary film was found to be unnecessary, either in eosin or rhodamin, though the effects produced when the electrodes were more than 0.02 mm. back from the front of the cell were very small.

Tests were made of the absorbing power of both of the substances in saturated solution, and it was found that practically no light penetrated to a depth of 0.02 mm. in the region of the absorption band. Thus, if the effect is produced at the surface of the platinum plate itself, a film of this thickness or greater would completely screen the electrode from the action of the light.

While the author feels that he has wandered much in the dark, among a most confusing and complicated set of phenomena, he believes that the results thus far obtained are not entirely without value, and he hopes in the future to throw more light on the meaning of the effects. Also he believes it quite possible that he will be able to prove a definite connection between the photo-electric effects in fluorescent liquids and the phenomenon of fluorescence itself.

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