

## PHOTO-ACTIVE CELLS WITH FLUORESCENT ELECTROLYTES.

BY GEO. E. THOMPSON.

### INTRODUCTION.

THE efforts of previous experimenters to prove a dependence of the photo-electric current on fluorescence, in the case where two metal electrodes immersed in certain fluorescent solutions are unequally illuminated, have not led to definite results. Minchin<sup>1</sup> and Hodge<sup>2</sup> suspected such a relation but Goldmann<sup>3</sup> thought the relation unlikely.

The present work was begun with the idea of securing any possible additional facts which may have a bearing on this subject. Several related facts have appeared during the progress of the work and these are also included in this paper.

### OUTLINE OF EXPERIMENTAL WORK.

Preliminary experiments were performed in order to determine what materials and solvents give the largest effect and are, therefore, most suitable for further study.

Several different metals were used as electrodes.

The fluorescence of fluorescein was increased by dilution and by addition of caustic potash and the change of current on illumination sought for.

The variation of current with wave-length of exciting light was measured in several different substances and with two types of cell.

### APPARATUS.

Two types of cell were used; a "Pt foil cell" and a "Ag film cell." The "Pt foil cell" was a glass box 6 cm. in depth, 1 cm. from front to back, and 4 cm. wide. Two thin strips of platinum foil about .3 cm. wide, reaching nearly to the bottom of the cell and leaving enough foil outside for making the connections to galvanometer leads, were placed about .3 cm. apart. These were held against the front wall of the cell by a piece of hard rubber and a brass spring which pressed against the

<sup>1</sup> Minchin, *Phil. Mag.*, Vol. 31, pp. 207-238, 1891.

<sup>2</sup> Hodge, *PHYS. REV.*, Vol. 28, p. 25, 1909.

<sup>3</sup> Goldmann, *Ann. d. Phys.*, Vol. 27, p. 449, 1908.

back wall. A paraffin stopper was used to prevent evaporation. This type of cell allowed a thin film of liquid to creep in between the electrodes and the front wall of the cell. Fig. 1 shows two views of this cell.

The "Ag film cell" had the same dimensions as the "Pt foil cell." Contact was made with precipitated silver<sup>1</sup> electrodes by pressing a thin sheet of tin plate against each one by means of a spring clasp clothespin. In order for the light to reach the liquid in this type of cell it must first pass through the silver film. These electrodes transmitted from 20 to 30 per cent. of the incident light for all wave-lengths. On account of deterioration probably due to imperfect adhesion of the silver, this cell had to be reconstructed occasionally.

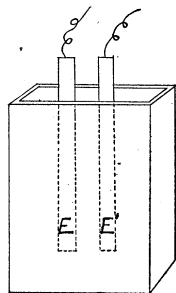


Fig. 1.

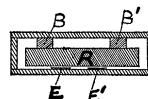


Fig. 1a.

When comparing the sensitiveness of different solutions without regard to the wave-length of the exciting light, a portion of the most active part of the spectrum from the spectrometer, described in the next paragraph, was used, or in cases where stronger illumination was required the arc light was focused upon the slit by means of a lens. A water cell was sometimes interposed to absorb heat rays but this was found to be unnecessary.

In studying the exciting power of various regions of the spectrum, a Nernst glower (110-volt A. C.) which furnished the exciting light was mounted in place of the slit of the spectrometer and an adjustable slit placed at the focus of the telescope lens permitted light of the wave-length desired to fall on one electrode of the sensitive cell. The slit width commonly used was .14 cm. The wave-length of the light used for excitation was varied by swinging the collimator arm with glower attached, the rest of the apparatus remaining fixed in position. The spectrometer arms were each about 60 cm. in length. A lead glass prism gave a visible spectrum about 7 cm. in length.

A Sullivan d'Arsonval galvanometer having a sensibility of  $10^{-9}$

<sup>1</sup> The Rochelle salts method. See Kohlrausch's *Practischen Physik*, p. 36.

ampere per mm. deflection with scale at 130 cm. distance, was used for measuring the current produced by the action of the light. Ordinarily about 20,000 ohms resistance were placed in circuit to diminish the current set up by the natural E.M.F. of the cell, which could not be completely eliminated.

#### METHOD OF OBSERVATION.

The light was allowed to shine on one electrode of the cell until the maximum value of current was approximately attained. This value of current was used in comparing the photo-activity of solutions. In order to obtain data for various wave-lengths of exciting light, one of the electrodes was exposed successively to the various regions of the spectrum and readings of the current taken for each setting of the spectrometer, time enough being allowed at each setting for the current to reach approximately its maximum value for that color. About thirty minutes were usually sufficient for obtaining data for a complete curve; from three to five minutes per point.

#### GROWTH AND DECAY OF CURRENT.

Figs. 2 and 3 show the relation between time in minutes and current when one electrode of a cell is illuminated and also the decay of the current after the light is shut off. Galvanometer deflections, which are proportional to current, have been plotted. Each figure contains curves for growth and decay of current in a strong solution of rhodamin BX in

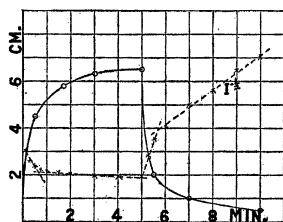


Fig. 2.

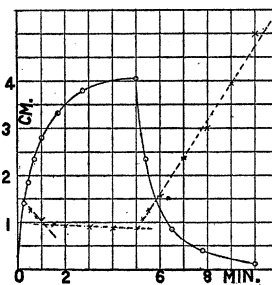


Fig. 3.

Rhodamin BX. Ordinates, galvanometer deflections in cm. Abscissæ, time in minutes.

absolute alcohol with the "Pt foil cell." For obtaining Fig. 2 a strip of electrode .14 cm. wide was exposed to the light; for Fig. 3, .08 cm. in width.

These curves are almost identical in form with those for growth and decay of intensity of phosphorescence in many substances that possess

long time phosphorescence. This similarity is made more evident by the fact that when the reciprocal of the square root of the current is plotted the broken line characteristic of phosphorescence is obtained.<sup>1</sup>

The same general explanation that applies to the growth and decay of phosphorescence is probably also applicable here, namely; that the total effect is the result of two effects, each of which follows a simple law, and which have different rates of growth and decay. In Fig. 3 one of these effects seems to be relatively less prominent as indicated by the more nearly linear character of the curve for  $I^{-\frac{1}{2}}$ .

The data obtained by Goldmann when plotted in the same way also indicate the same linear relation between  $I^{-\frac{1}{2}}$  and time.

#### PRELIMINARY OBSERVATIONS.

In order to work with a comparatively weak source of light such as a Nernst glower where only a narrow portion of the spectrum is used it is desirable to have the most sensitive cell possible. It was found that the most fluorescent substances did not give the largest current under the action of light. Fluorescein, which was most fluorescent of all materials tried, gave a current too small to be measured when excited by the glower spectrum. Rhodamin BX, which possesses a fairly strong fluorescence, gave the largest effect of anything tried. Rhodamin R and rhodamin RRR and tetrabrom-fluorescein were mildly fluorescent and gave measurable effects. Fuchsin is weakly fluorescent but gave no current even when illuminated by the electric arc. The substances<sup>2</sup> tested were in all these cases in concentrated solution and used with the "Pt foil cell."

Among the solvents tried are absolute alcohol, water, grain alcohol, benzine, ether, alkaline and acidulated water and alcohol. Only alcohol dissolved sufficient quantities of the dye-stuffs for purposes of experiment so that the substances finally chosen for further experiment were rhodamin BX, rhodamin R, rhodamin RRR, tetra-brom-fluorescein and fluorescein; all in absolute alcohol.

Ordinarily the current flowed from the illuminated to the dark electrode outside the cell. The only exception noted was an alkaline water solution of fluorescein in which current could be excited only by the intense illumination of the arc. Due to the uncertainties involved in this particular case it is not quite safe to say that the current observed was a photo-electric current due to the fluorescein.

<sup>1</sup> Nichols and Merritt, *PHYS. REV.*, Vol. 27, p. 370, 1908.

<sup>2</sup> The rhodamin BX, tetra-brom-fluorescein, fuchsin, and fluorescein used in these experiments were obtained from Merz & Co. of New York City. The rhodamin R and RRR were kindly furnished by Prof. Orndorff of the Chemistry Department of Cornell University.

The size of the current generated by the action of light was found to be dependent upon the material of the electrodes and upon their condition. Only a few of the metals used as electrodes produced a measurable effect. Of those tried, platinum foil, silver, gold, and oxidized copper were the only ones which gave a measurable current although the more obstinate ones were exposed to the direct illumination from the arc. Zinc, iron, polished copper, lead, tin and aluminum gave no effect. Platinum foil was best and the others followed in the order named.

#### PHOTO-ELECTRIC EFFECT AND FLUORESCENCE.

If the photo-electric current observed is directly connected with fluorescence we should expect that any increase in the fluorescence would be accompanied by an increase in the current. A dilute solution of fluorescein is more fluorescent than a concentrated solution, but repeated trials led to the conclusion that there is a loss of sensitiveness on dilution rather than an increase.<sup>1</sup>

The fluorescence of a fluorescein solution may be increased very markedly by adding a trace of caustic potash. Observation showed no change in the current when this was done. There is a chance here for error, however, unless all of the fluorescein is dissolved before the alkali is put in. The fluorescein is more easily dissolved after the addition of the alkali and an increase of photo-electric current which is really due to an increase of concentration may be wrongly attributed to the increase of fluorescence.

#### VARIATION WITH WAVE-LENGTH OF EXCITING LIGHT.

It has been pointed out by other observers that the maximum effect is produced in the region of maximum absorption, but definite data have not been given. Goldmann<sup>2</sup> found that the light included in the region of absorption produced practically the whole effect, but he did not disperse the light. Hodge,<sup>3</sup> and Rigollot,<sup>4</sup> state that the maximum effect was found on the red side of the absorption band just before entering the band. But as will be shown later this result would have been different had a correction been made for unequal energy distribution in the spectrum used for excitation.

<sup>1</sup> Since this work was done, a paper has been published by Mecklenberg and Valentine which states that the fluorescence of fluorescein is proportional to concentration if the absorption of the excited fluorescent light is corrected for. The above experiment is, therefore, based on a false but common assumption (*Phys. Zeit.*, Vol. 15, p. 267).

<sup>2</sup> Goldmann, l. c., p. 476.

<sup>3</sup> Hodge, l. c.

<sup>4</sup> Rigollot, *Journ. d. Phys.* (3), Vol. 6, p. 520, 1897.

Fig. 4, Curve I., shows the variation of current with wave-length of exciting light, using the "Pt foil cell" with a fairly concentrated absolute alcohol solution of rhodamin BX; width of electrode illuminated, .08 cm. The ordinates of Curve *A* are proportional to the coefficients of absorp-

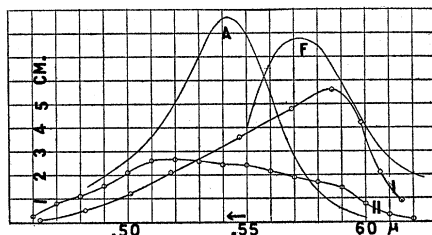


Fig. 4.

Rhodamin BX; "Pt foil cell." Ordinates of curve *A* are proportional to coefficients of absorption. Curve *F*, fluorescence; *I*., observed photo-electric current; *II*., corrected curve.

tion in a dilute alcohol solution. The general shape of the Curve *A* is the same as for a concentrated solution.<sup>1</sup> The fluorescence band for a dilute solution is represented approximately by Curve *F*.

Fig. 5 shows results obtained under similar conditions except that the

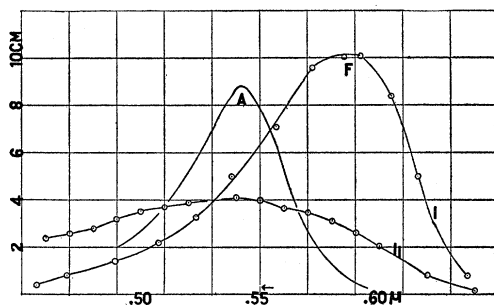


Fig. 5.

Rhodamin BX. *A*; absorption; *I*., photo-electric current; *II*., corrected curve.  
"Pt foil cell."

width of slit was .14 cm. On account of the larger current obtained, this curve is probably the most accurate of any that will be shown.

The results of Fig. 6 were obtained with the "Ag film cell" under similar conditions.

Fig. 7 contains curves for tetra-brom-fluorescein with the "Pt foil cell"; slit width, .14 cm.; absolute alcohol solution.

Fig. 8 shows two curves for rhodamin RRR using the "Pt foil cell";

<sup>1</sup> Nichols and Merritt, *PHYS. REV.*, Vol. 31, p. 376, 1910.

absolute alcohol solution. They were both obtained with the same solution but with different areas of the electrodes exposed in each case; .08 cm. for the lower curve and .14 cm. for the upper.

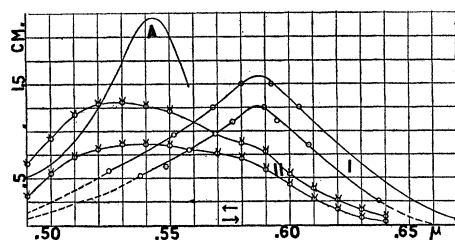


Fig. 6.

Rhodamin BX. Cell No. 2. I., observed curve; II., corrected curve. "Ag film cell."

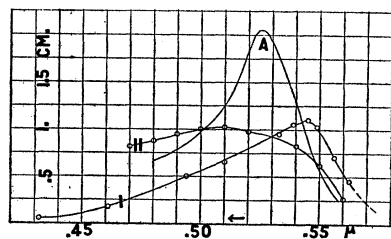


Fig. 7.

Tetra-brom-fluorescein. "Pt foil cell."

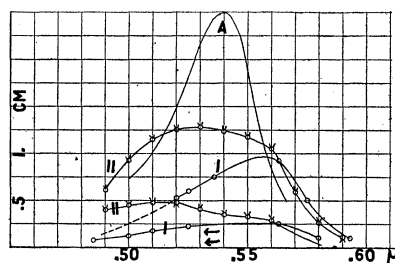


Fig. 8.

Rhodamin RRR. "Pt foil cell."

#### CORRECTIONS TO BE MADE.

The manner in which the photo-electric current depends upon the wave-length of the exciting light is more clearly brought out by correcting for unequal dispersion and unequal energy distribution throughout the spectrum of the glower. The dispersion for a particular wave-length was taken as an arbitrary unit with which the dispersion in other parts of the spectrum could be compared. Then for any wave-length the ratio of the dispersion to this arbitrary unit becomes the correction factor by which each corresponding ordinate of the observed curve must be multiplied in order to correct for unequal dispersion. Column 3 of Table I. gives values of these factors for various wave-lengths.

The intensity of the spectrum from the glower was then compared, wave-length by wave-length, with that of an acetylene flame by means of a spectro-photometer. Six sets of readings were taken throughout the spectrum and the average values used in computing the ordinates of the energy curve of the glower. Column 2 of the table gives the

results of this comparison. The curve given by Coblenz<sup>1</sup> for the energy distribution of the acetylene flame afforded a basis for the computation of energy distribution of the glower from the spectro-photometric comparison. The ordinates of the acetylene energy curve were multiplied by the numbers in column 2 in order to get the energy curve of the glower. The energy of some particular wave-length was taken as the arbitrary unit and correction factors for other wave-lengths found by comparing the ordinates of the glower curve. For example, the correction factor for the wave-length whose energy is one half the arbitrary unit is 2. Column 4 contains these correction factors.

TABLE I.  
DATA FOR FIG. 4.

1	2	3	4	5	6	7
Wave-length.	Ratio of Glower to Acetylene.	Correction Factors for Dispersion.	Correction Factors for Energy Distribution.	Product.	Ordinates of Observed Curve.	Ordinates of Corrected Curve.
.450		1.05	5.08	5.34	0.00	0.00
.460		.92	4.40	4.04	.07	.28
.470	.89	.90	3.66	3.29	.25	.80
.480	.94	.80	3.14	2.51	.45	1.13
.490	.89	.75	2.85	2.14	.75	1.60
.500	.89	.75	2.54	1.85	1.15	2.12
.510	.91	.71	2.20	1.56	1.65	2.57
.520	.95	.70	1.78	1.25	2.20	2.75
.530	1.00	.64	1.53	.98	2.70	2.64
.540	1.04	.60	1.32	.79	3.20	2.53
.550	1.07	.55	1.16	.64	3.80	2.43
.560	1.04	.46	1.06	.49	4.30	2.16
.570	1.01	.38	1.00	.38	4.90	1.87
.580	1.01	.35	.91	.32	5.40	1.73
.590	1.02	.33	.82	.27	5.50	1.48
.600	1.04	.32	.74	.24	3.50	.84
.610	1.08	.30	.66	.20	1.50	.30
.620	1.13	.30	.57	.17	.50	.08
.630	1.17	.30	.51	.15	.10	.02
.640	1.20	.30	.46	.14	.00	.00

The product of the factors in columns 3 and 4 (column 5) gives the number by which each ordinate of Curve I. must be multiplied. The resulting curve represents, therefore, the current which would be produced by a normal spectrum of uniform energy distribution. Column 6 gives the ordinates of the observed curve and 7 those of the corrected curve of Fig. 4.

<sup>1</sup> W. W. Coblenz, Bull. Bur. of Stds., Vol. 7, p. 259, 1910.



#### SOURCES OF ERROR.

It has been recognized that the use of the galvanometer as a measuring instrument permits the polarization of the cell and may influence the results. But since Goldmann<sup>1</sup> has shown that the effect is only slightly diminished by polarization and not changed in character, it seems that results obtained in this way are not invalidated. Attempts were made to avoid this by using an electrometer but a quadrant electrometer (.001 volt sensibility) did not prove sensitive enough to measure the E.M.F. developed by the glower spectrum.

The spectrum had some overlapping of colors on account of the width of the source (about .5 mm.) and all colors were not accurately focused. The focus was accurate in the yellowish green. This impurity of the spectrum would not lead to any serious error.

The fluctuations of voltage on the glower were sometimes considerable but caused no serious disturbance because of the lag of the photo-electric current behind changes in intensity of the exciting light (see Fig. 2). The tendency is, therefore, for the effect to assume a value which corresponds to the average illumination.

The sensitiveness of the cell diminished slightly with each succeeding illumination but recovered somewhat when let stand in the dark. Finally the solution had to be renewed on account of permanent loss of sensitiveness.

It was more difficult to secure data with the "Ag film cell" on account of disturbances due to slight jarring, etc. The two curves shown were the best ones observed. These show an extrapolation in the blue, but several independent observations in this region prove this to be the correct form for the curves. On account of the disturbances, observations had to be made more hurriedly with this cell; hence, the necessity for extrapolation. When the observations were made it was not realized that this was to be the important part of the curve or the extrapolation could have been avoided in this region.

The displacement of the current maximum from the absorption band toward the blue may be due in part to the fact that in those cases the observations were begun in the red. If sufficient time were not given for the current to diminish to its normal value for each color, the values to the left of the maximum on the observed curve would be too large and might shift the maximum of the corrected curve. Sufficient data is not at hand to make this conclusion certain. There is also considerable difficulty in reproducing results.

The arrows at the bottom of the figures indicate the manner in which

<sup>1</sup> Goldmann, l. c., p. 500.

the readings were made; *e. g.*, an arrow pointing toward the blue means that readings were begun in the red and progressed toward the blue.

With the "Pt foil cell" we might expect the maximum to be somewhat diminished by the absorption of the layer through which the light must pass before it strikes the electrode. There is no very noticeable difference, however, between the corrected curves for the two types of cell.

#### SUMMARY OF RESULTS.

The curves for the growth and decay of the photo-electric current are similar to those for the growth and decay of phosphorescence. If  $I^{-\frac{1}{2}}$  be plotted, the characteristic broken line is obtained.

The magnitude of the photo-electric current depends on the metal used as electrodes. Of ten metals tried, only platinum, gold, silver and oxidized copper gave a measurable effect.

The position of the maximum effect does not depend upon the material of the electrodes but upon the material in solution.<sup>1</sup> The effect is not the photo-electric effect of the metal in the liquid.

The experimental results do not show any close connection between the photo-electric current and fluorescence. Two methods of increasing fluorescence did not increase the current. The region of excitation for the current extends further into the red than for fluorescence.

All of the curves show the maximum photo-electric current approximately in the region of maximum absorption.

CORNELL UNIVERSITY,

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<sup>1</sup> Rigollot has mentioned this. Journ. d. Phys. (3), Vol. 6, p. 520, 1897.