

## THE POTENTIAL OF PHOTOACTIVE CELLS CONTAINING FLUORESCENT ELECTROLYTES

BY H. W. RUSSELL

### ABSTRACT

**Variation with time of illumination of the potential of a cell containing rhodamin B dissolved in absolute alcohol.**—A theory of the variation of potential with time has been developed for the photoactive cell. It is assumed that the exciting light produces a chemical change in the electrolyte. Allowing for the effects of diffusion the expression

$$E = K \log (T^{1/2} - t^{1/2} + t/2T^{1/2} - t^2/8T^{3/2} + B/I) - K \log (B/I)$$

where  $E$  is the e.m.f.,  $T$  is time of illumination,  $t$  is time after illumination ceases,  $I$  is the intensity of illumination, and  $K$  and  $B$  are constants, has been derived. By the use of a cell with platinum electrodes containing Rhodamin B in absolute alcohol and illuminated with monochromatic light, results in good agreement with the theory are secured. Diffusion is shown to play an important part. Goldmann's theory is shown to be inadequate. No "limiting potential," independent of the intensity of illumination, was found. No evidence was found which indicated the presence of the Hallwachs photo-electric effect.

### INTRODUCTION

**I**N 1839 Edmund Bequerel<sup>1</sup> noted that if two similar electrodes were immersed in a suitable solution and the region around one was illuminated a difference of electrical potential between the electrodes was produced. Much later Rigollot<sup>2</sup> noted this effect with fluorescent electrolytes. Hodge<sup>3</sup> showed that the apparent change in resistance found by Nichols and Merritt<sup>4</sup> on illumination of fluorescent electrolytes was due to the setting up of an electromotive force. Goldmann,<sup>5</sup> in a very thorough investigation, independently found the e.m.f. and studied its variation with time of illumination.

Goldmann found what he called the "photo-electric potential." The magnitude of this "photo-electric potential" was independent of the intensity of the exciting light. This led him to believe that the potential had its origin in the Hallwachs photo-electric effect. However, E. Bauer<sup>6</sup> and others<sup>7,8</sup> believe that the important process is a photochemical modification of the sensitive substance and that these material compounds give their oxidation or reduction potential to the electrode. Using this theory of the origin of the e.m.f. and taking account of the effect of diffusion, a theory

<sup>1</sup> Bequerel, Comptes Rendus **9**, 144, 561 (1839).

<sup>2</sup> Rigollot, Comptes Rendus **66**, 878 (1893); Jour. d. Physique **6**, 520 (1897).

<sup>3</sup> Hodge, Phys. Rev. **28**, 25 (1908).

<sup>4</sup> Nichols and Merritt, Phys. Rev. **19**, 415 (1904).

<sup>5</sup> Goldmann, Ann. d. Physik **27**, 449 (1908).

<sup>6</sup> Bauer, Zeits. f. Physik. Chemie **63**, 683 (1908).

<sup>7</sup> Staechelin, Zeits. f. Physik. Chemie **94**, 542 (1920).

<sup>8</sup> Murdoch, Proc. Nat. Acad. Sci. **12**, 504 (1926); Faraday Soc. Trans. **23**, 593 (1927).

of the variation of the e.m.f. with time has been developed which involves no unusual assumptions.

#### THEORY

Consider a straight glass tube of great length containing a suitable dye solution as electrolyte. Let the ends be closed by similar semi-transparent electrodes and have the concentration and temperature of the electrolyte uniform. Except for the effect of outside forces there should be no difference of electrical potential between the electrodes. Now admit light to the electrolyte through one of the transparent electrodes. Assume that the dye is changed chemically by oxidation or reduction into a new material. Because of absorption this change takes place largely at the end where the light is admitted and the concentrations of the substance formed will be different at the two electrodes; hence a difference of potential, dependent upon the relative concentrations, is to be expected. If the new substance is produced in a very thin layer near the electrode, the concentration at this electrode should increase quite rapidly during illumination, and the e.m.f. should increase. If the light source is removed diffusion away from the electrode should diminish the concentration of the new substance, and the e.m.f. should decrease.

To determine the effect of diffusion consider a tube of infinite length in which diffusion may occur. At the end let there be a source of material which will diffuse, and let the strength of this source be  $Q$  grams of material per unit time. Now it can be shown that the concentration  $C$  at any time  $T$  and distance  $x$  is given by

$$C = (Q/h\pi^{1/2}) \int_0^T e^{-x^2/4h^2(T-\tau)} (T-\tau)^{-1/2} d\tau$$

where  $h$  depends on the diffusivity.

To solve this make the following substitutions:

$$\alpha = x/2h; \quad A = Q/h\pi^{1/2}; \quad \alpha^2/w^2 = T - \tau;$$

and we get

$$C = 2A \int_{\alpha/T^{1/2}}^{\infty} e^{-w^2} w^{-2} dw.$$

Integrating by parts

$$C = 2AT^{1/2}e^{-\alpha^2/T} - 4A\alpha^2 \int_{\alpha/T^{1/2}}^{\infty} e^{-w^2} dw,$$

giving as the solution

$$C = 2A \{ T^{1/2}e^{-\alpha^2/T} - \alpha\pi^{1/2} [1 - \Theta(\alpha/T^{1/2})] \}$$

where  $\Theta(\alpha/T^{1/2})$  stands for  $(2/\pi^{1/2}) \int_0^{\alpha/T^{1/2}} e^{-w^2} dw$ —the probability integral.

Expressing this in series

$$C = 2AT^{1/2} \left( 1 - \frac{\alpha^2}{T} + \frac{\alpha^4}{2!T^2} \dots \right) - \alpha\pi^{1/2} \left( 1 - \frac{2}{\pi^{1/2}} \left[ \frac{\alpha}{T^{1/2}} - \frac{\alpha^3}{3T^{3/2}} + \dots \right] \right)$$

and approximately

$$C = 2A \left( T^{1/2} + \frac{\alpha^2}{T^{1/2}} - \frac{\alpha^4}{6T^{3/2}} - \alpha\pi^{1/2} \right)$$

This approximation is quite good to  $\alpha = T^{1/2}$ .

After a time  $T$  the source is stopped. The future condition of an infinite tube initially with a concentration  $C = f(x)$  is given by

$$C = (1/\pi^{1/2}) \int_{-\infty}^{+\infty} f(x - 2ht^{1/2}\beta) e^{-\beta^2} d\beta$$

Integrating, for  $x = 0$  this gives

$$C = 2A \left( T^{1/2} - t^{1/2} + \frac{t}{2T^{1/2}} - \frac{t^2}{8T^{3/2}} \right)$$

Now assume that the action of light on the dye produces a new material at a rate proportional to the intensity of the light. The concentration of material produced by illumination, assuming that the light penetrates a short distance, is  $C$ . Now further assume that before illumination the substance which is to be produced is present at a concentration  $c_1$ , the old substance at a concentration  $c_2$ . If these substances give rise to an oxidation-reduction potential obeying the Nernst theory, the electrode potential at the unilluminated end will be

$$E_1 = E_0 + K \log (c_1/c_2)$$

where

$$K = (RT/nF) \log_e 10$$

while at the illuminated end, if we assume that no appreciable fraction of the original material is changed

$$E_2 = E_0 + K \log [(c_1 + C)/c_2]$$

The e.m.f. of the cell is

$$E = E_2 - E_1 = K \log \left( \frac{C}{2A} + \frac{c_1}{2A} \right) - K \log \frac{c_1}{2A}$$

Now assume that the strength of the source  $Q = kI$ , where  $I$  is the intensity of the light and  $k$  is a constant, depending on the wave-length of the light used. Hence,  $c_1/2A = B/I$  where  $B$  is a constant. Putting in the value of  $C$  at the electrode at any time

$$E = K \log \left( T^{1/2} - t^{1/2} + \frac{t}{2T^{1/2}} - \frac{t^2}{8T^{3/2}} + \frac{B}{I} \right) - K \log (B/I)$$

In this  $T$  is the time during illumination and is constant after the illumination ceases, while  $t$  is the time in the dark;  $t=0$  at the instant illumination ceases and at all times before.

#### EXPERIMENTAL CONDITIONS

The experimental conditions consistent with the assumptions of the theory are as follows: The cell should permit diffusion similar to that which would take place in an infinitely long tube; the electrodes should be alike, and should be kept at the same temperature; the exciting light should be absorbed in a thin layer of the dye near the electrode; the concentration of the original dye solution should be constant; the light used should be of known quality and intensity; the potential change should be followed with an instrument of short period, drawing no current.

An inverted U type of cell of the form shown in Fig. 1 was used. Because of the very slow diffusion of the electrolyte and the short time involved, the length of the tube may be considered infinite. The electrodes were

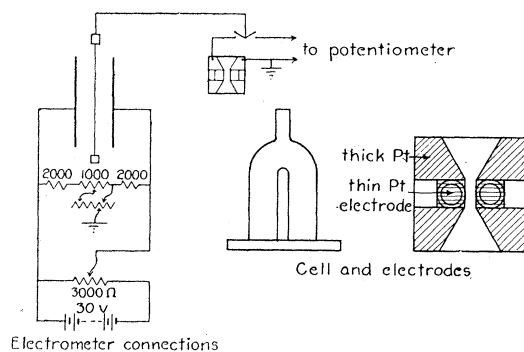


Fig. 1. Electrometer, cell, and electrodes.

of platinum, sputtered in the form shown in the figure, on a single piece of glass. The middle transparent portions had a transmission of greater than 50 percent for all wave-lengths in the visible; the outer portions were thick, almost opaque films of platinum. Copper lead wires were soldered to these thick films. The tube forming the cell was fastened to the base with an alcohol resisting cement: "Gumsol" proved most satisfactory. There was no cement connecting the electrodes so that the resistance between them was very high. Illumination was secured by placing the cell on a reflecting prism, one electrode being covered with black paper.

Rhodamin B in absolute alcohol was chosen as the fluorescent solution. Numerous workers have found it to give a large effect. Goldmann used it for his work. On the basis of Mrs. Jenkins'<sup>9</sup> results a three percent solution was chosen.

<sup>9</sup> Jenkins, Phys. Rev. **18**, 402 (1921).

The light source was a Heraeus quartz mercury arc. Nearly monochromatic light was secured by means of filters. Wratten filter No. 77A isolated the green ( $\lambda 5461$ ) and No. 22 isolated the yellow ( $\lambda\lambda 5791, 5769$ ). A solution of copper sulphate and ammonium carbonate in a 1 cm glass cell was used to isolate the blue ( $\lambda\lambda 4358, 4046, 4078$ ). A 1 cm cell containing a three percent solution of cupric chloride in water was used at all times to absorb the infra-red radiation. Temperature differences between the electrodes should have been small.

The intensity of the illumination was measured with a sensitive Coblenz linear thermopile and a low resistance galvanometer having an all copper circuit. The thermopile was placed in the box with the photoactive cell and could be raised out of the path of the light by a cord. Calibration with a radiation standard showed the system, with the galvanometer scale at 2 meters, to have a sensitivity of  $5.5 \times 10^{-8}$  watt per sq. mm per cm deflection. The intensity will be expressed in centimeters deflection. The intensity of illumination was changed by varying the resistance in series with the mercury arc. About half an hour was allowed for the lamp to reach a steady state, and the intensity was measured with the thermopile before and after each run.

The difference in potential between the electrodes was measured by means of a string electrometer of the Stebbins<sup>10</sup> type. The displacement of the fiber could be made proportional to its change in potential in the range covered by the eyepiece of the observing microscope. A sensitivity of 200 divisions of the eyepiece scale per volt was generally used. To increase stability and to decrease the damping, the entire electrometer was placed under a bell jar and evacuated to a pressure of about 0.1 mm of mercury. The eyepiece was placed outside of the bell jar. The period of the fiber was so short that the electrometer would assume a steady reading in less than a second after the application of the potential causing a deflection of 40 divisions. The calibration was checked before and after each run by means of a potentiometer.

Sulphur was used for insulating the electrical system from ground. The resistance to ground was greater than 20,000 megohms, and the resistance between the electrodes of a cell when empty was of the same order. When filled with the dye solution, the resistance of the cell as measured by an alternating current bridge was a few thousand ohms. The electrical circuit is shown in Fig. 1.

Time was measured with a chronograph. The key was closed the instant the fiber of the electrometer crossed each scale division. Times were read from the record to the nearest tenth of a second.

#### RESULTS

Fig. 2 shows curves of the potential-time relation. The light was yellow of intensity 60. Two runs taken under the same conditions are shown. That the effect is reproducible is apparent. Curves for the same cell with

<sup>10</sup> Swann, J.O.S.A. and R.S.I. 11, 375 (1925).

light of intensity 30 and 15 are shown in Fig. 3. Fig. 4 shows curves taken with green light of intensities 100, 50, and 3.3. Fig. 5 shows curves for yellow, green, and blue light, all at the same intensity.

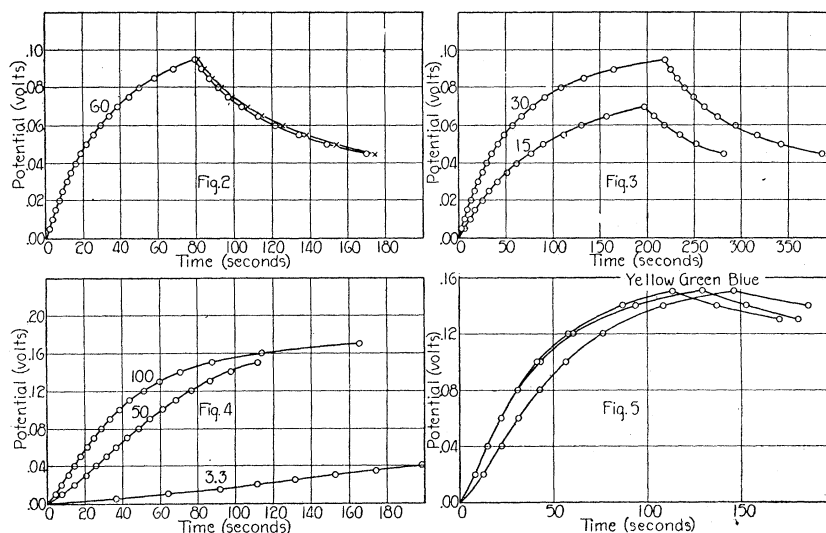


Fig. 2. Potential-time curve. Light off at peak of curve. Yellow light,  $I=60$ . Two runs, second indicated by crosses.

Fig. 3. Potential-time curves. Yellow light,  $I=30, 15$ .

Fig. 4. Potential-time curves. Green light,  $I=100, 50, 3.3$ .

Fig. 5. Potential-time curves. Yellow  $\lambda\lambda 5791, 5769$ ; Green  $\lambda 5461$ ; Blue  $\lambda\lambda 4358, 4046, 4078$ ;  $I=100$

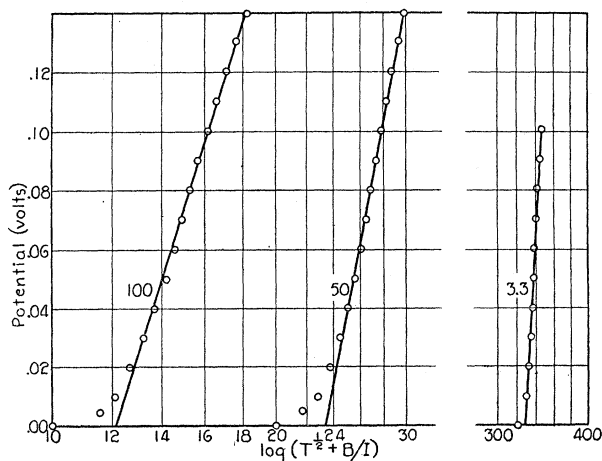


Fig. 6. Potential- $\log(T^{1/2} + B/I)$ . Green light,  $I=100, 50, 3.3$ . Data of Fig. 4.

Value of  $B$  in the theoretical equation developed cannot be found from our knowledge of the properties of Rhodamin B. By trial 1000 was chosen

as the value of  $B$ . Taking the data used in the curves of Fig. 4, the lines of Fig. 6 result. Here values of  $E$  are plotted as ordinates against the logarithm of  $T^{1/2} + B/I$ . These are straight lines as called for by the theory, and are in a rough way parallel. The failure of the points to fall on the line for small

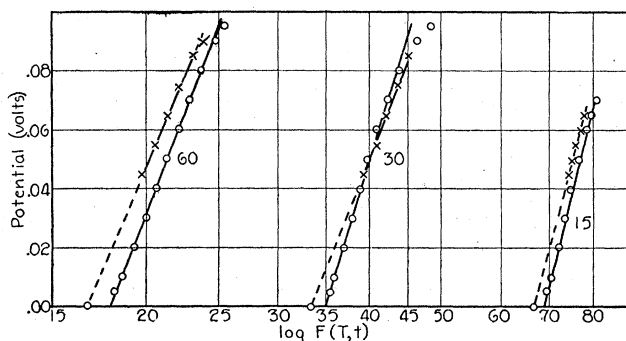


Fig. 7. Potential-log  $F(T, t)$  curves. Yellow light,  $I=60, 30, 15$ . Circles-growth of e.m.f. Crosses decay in dark. Data of Figs. 2 and 3.

values of  $E$  can be accounted for by assuming a small constant negative e.m.f. to be built up in the first moments of illumination. Such an initial e.m.f. has been noted by Wilderman,<sup>11</sup> Grumbach,<sup>12</sup> Rule,<sup>13</sup> and others. Its

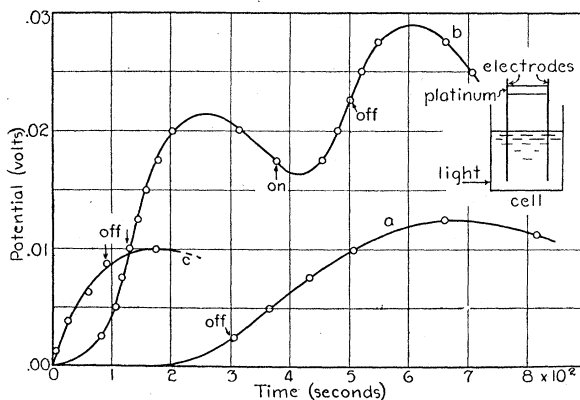


Fig. 8. Potential-time for cell as shown. Curve  $a$ —electrode 0.7 mm from cell wall; Curve  $b$ —electrode 0.1 mm from cell wall; Curve  $c$ —electrode reversed. Light through electrode, then into dye.

explanation may lie in an intermediate compound indicated by the work of Wood.<sup>14</sup>

The decay of the e.m.f. in the dark is shown by Fig. 7 where  $E$  is plotted against the logarithm of  $T^{1/2} - t^{1/2} + t/2T^{1/2} - t^2/8T^{3/2} + B/I$ . The growth

<sup>11</sup> Wilderman, Proc. Roy. Soc. A77. 274 (1906).

<sup>12</sup> Grumbach, Comptes Rendus, 176, 88 (1923); 179, 626 (1924); 180, 1102 (1925).

<sup>13</sup> Rule, Phil. Mag. 1, 532 (1926).; Proc. Nat. Acad. Sci. 14, 272 (1928).

<sup>14</sup> Wood, Phil. Mag. 43, 757 (1922).

curves are also shown. These data are the same as those of Figs. 2 and 3. The results for decay are in better agreement with the theory than the results for growth. This again indicates that during illumination there is present some source of e.m.f. which is not allowed for in the theory.

As a further test of the importance of diffusion, experiments were made with a different type of cell. Two strips of glass bearing sputtered platinum electrodes were immersed in a rectangular glass cell containing a six percent solution of Rhodamin B. First, one electrode was placed 0.7 mm from the wall, and the other electrode was placed 2 cm behind it. Green light of intensity 100 was allowed to fall upon this cell. The results are shown in Fig. 8, curve *a*. Illumination ceased at the time marked "off." Then, placing the electrode closer so that only a thin layer of dye was between the cell wall and the electrode, the curve *b* was obtained. Here, after stopping illumination, it was started again. Curve *c* shows the effect when the electrodes were reversed so that the light passed first through the transparent electrode then into the dye.

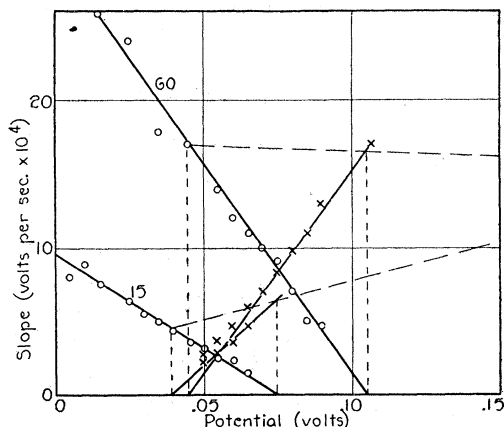


Fig. 9. Goldmann plot;  $dE/dt$  against  $E$ . Circles—growth in light; crosses—decay in dark.

Curves *a* and *b* show a lag between the illumination and the change in potential. This indicates that material formed by the light at the cell wall must diffuse to the electrode before it produces its effect. When the electrode is closer to the wall the time of the lag is, of course, shorter. Curve *c* indicates, however, that this cell when used under a condition similar to that used with the cells previously discussed gives the effect found with those cells. Because the new material is formed at the electrode, it immediately produces its effect. Stirring the cell during the decay caused  $E$  to return to zero.

This experiment indicates that the material which causes the e.m.f. is formed at or near the place where the light enters the dye and that diffusion is an important factor in controlling the potential-time relation.



Fig. 9 shows a check of Goldmann's theory by his method of plotting, using the data of Figs. 2 and 3. The circles indicate the rate of growth of  $E$  plotted against the corresponding  $E$ . The crosses give the same relation for the decay of  $E$ . The dashed lines are the rate of growth corrected for the effects which cause decay. According to Goldmann's theory these dashed lines should intersect the  $E$  axis at the same point. The value of  $E$  at this intercept Goldmann called the "photo-electric potential." Obviously for these data the "photo-electric potential" is not independent of the intensity of the exciting light. Furthermore the points of the growth curve do not show a very good agreement with Goldmann's equation.

A photo-electric limiting potential should increase with increasing frequency of the exciting light. Fig. 5 shows that the blue is far less effective than the yellow. It is probable that only a fraction, dependent upon the wave length, of the absorbed energy is used to produce the chemical change upon which the photo-voltaic effect depends.

The writer wishes to express his indebtedness to Professor C. C. Murdock, who suggested this problem, and to Professor R. C. Gibbs and Professor Ernest Merritt, who gave valuable aid during its progress.

CORNELL UNIVERSITY,  
June 18, 1928.