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The photogalvanic effect

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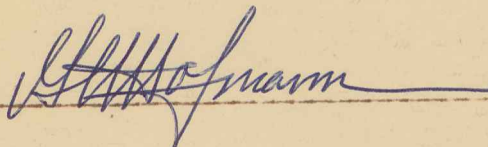
THE PHOTO GALVANIC EFFECT

by

George Henry Hofmann UC1959

A thesis presented to the Department of Chemistry
of Union College in partial fulfillment of the require-
ments for the degree of Bachelor of Science with a Major
in Chemistry.

By



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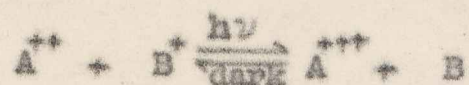
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Introduction

The photogalvanic effect has been studied by relatively few people. Perhaps the largest contribution to the study of this effect has been by E. Rabinowitch while at Massachusetts Institute of Technology and terminated in 1940. At this time Rabinowitch indicated the possibilities in the utilization of solar energy by the photogalvanic effect (1).

Presented here is a study of the effect using a modified form of the apparatus used by Rabinowitch. An attempt is made at explaining the results obtained, the advantages and disadvantages of the apparatus used and suggestions are given for improvement.

The photogalvanic effect is observed in photosensitive redox systems. It is produced in aqueous solutions of reversibly reducible dye salts (B^+) together with an inorganic oxidation-reduction pair (A^{++}/A^{+}). The following equilibrium is established:



The equilibrium is forced to the right through the photosensitive dye molecule ($B \xrightarrow{h\nu} B^+$) (2) under the influence of light. In the dark the equilibrium proceeds to the left.

The photogalvanic effect has been studied for its usefulness in converting light energy into electrical energy. If the photochemical changes caused by light energy, which are transfers of electrons from one molecule to another, are "uphill", light energy will be stored. The problem is how to reverse the process, without wasting the accumulated energy. This can be done by the construction of a photogalvanic cell.

The forward dye-reducing reaction is easily carried out in the electrolyte of the cell. The reversed or "dark" reaction also proceeds easily in this medium. Forcing the transferring electrons of the dark reaction through an external circuit is the main problem. It is known, however, that the back or dark reaction is not instantaneous (3), i.e., the oxidation and reduction products do not immediately retransfer the electrons back to original positions. A chance, therefore, is given to conduct the back reaction as a galvanic process.

Upon placing two electrodes into the electrolyte, one being surrounded by illuminated electrolyte, though not illuminated itself, the other in the dark (or may be a reference electrode), the oxidation and reduction products come into contact with the external circuit. Electrons are given up to the electrode in the illuminated solution by the reduced or bleached dye products (B) which run via the external circuit to the electrode in the dark solution and thence to the oxidation products (A^{++}). As the electrons run through this easier path, to their position of stable equilibrium, electrical work can be extracted from this external circuit.

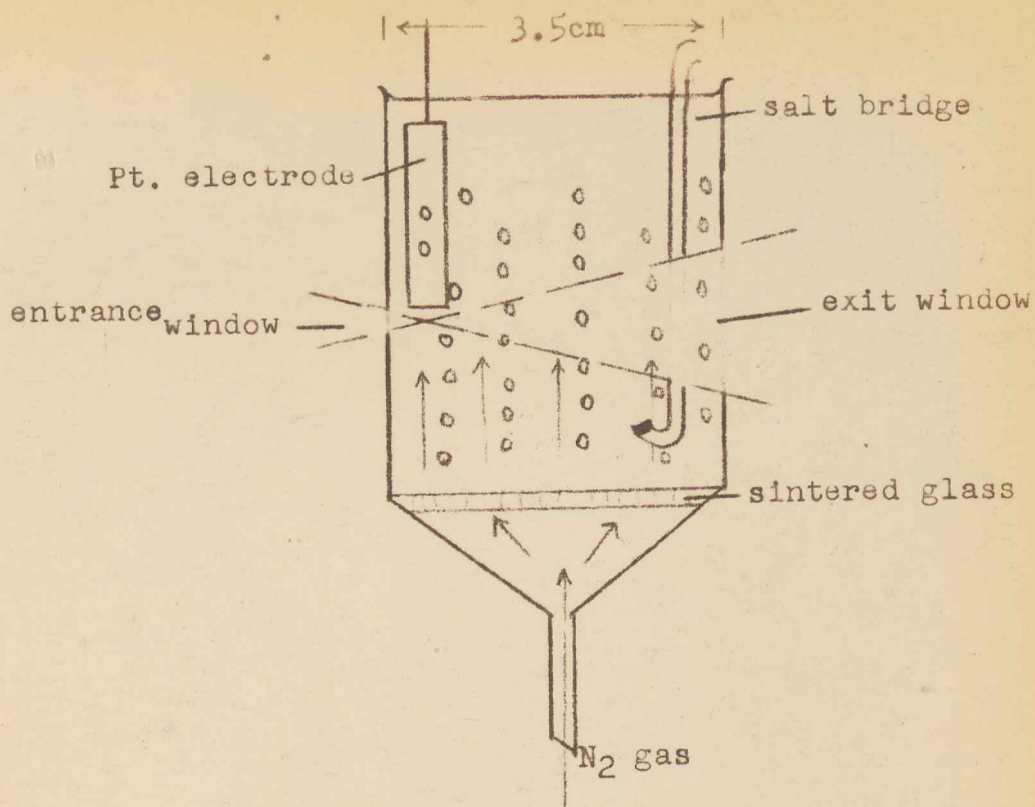
A specific photogalvanic system of high efficiency containing a reversibly reducible organic dyestuff (thionine) together with an inorganic oxidation-reduction pair (Fe^{++}/Fe^{+++}) was thoroughly investigated by E. Rabinowitch (4).

Apparatus

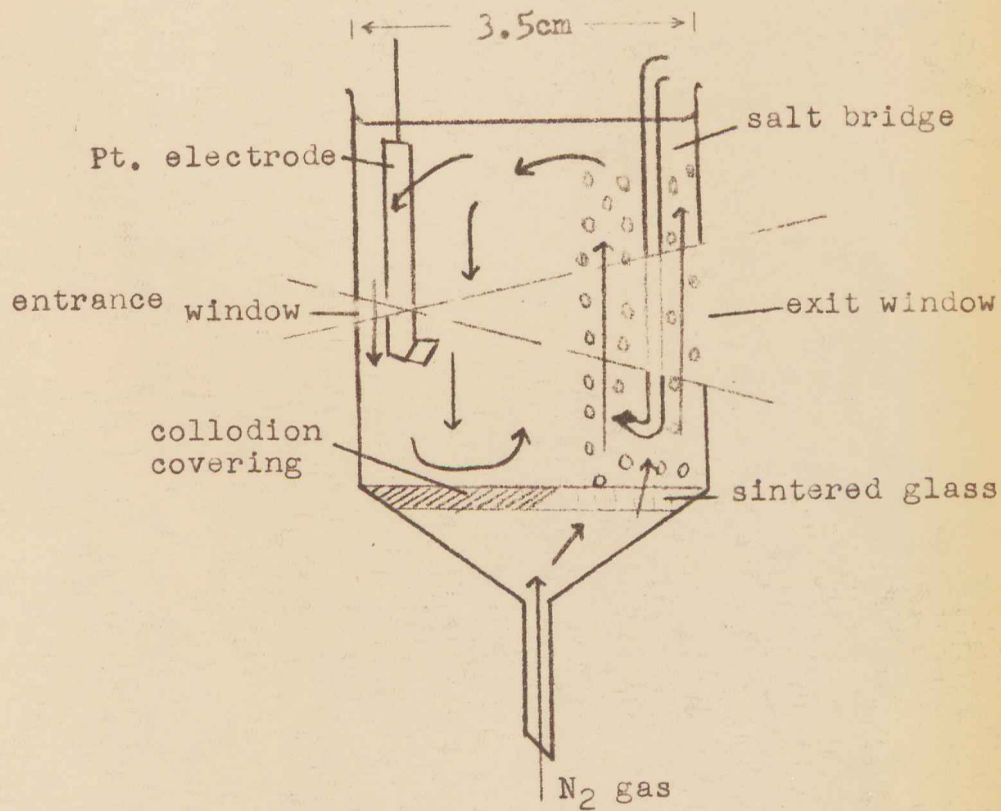
The photosensitive half-cell consisted of a sintered glass Pyrex filtration funnel which was 4 cm deep. It was painted black with flat black paint to reduce the entrance of spurious light. Two opposing windows were left unpainted. One was .8cm x .8cm and the other 1.5cm x 1.5cm : the smaller of the two allowed the entrance of the light beam and acted as a slit while the larger permitted the exit of the beam. The platinum electrode was placed parallel to the incoming beam to minimize shadows but was not placed directly in the beam thereby reducing the Becquerel Effect.* At first the electrode was placed above the incoming beam and commercial nitrogen gas was bubbled up into the solution (Scheme A, p. 6). This was modified, however, to Scheme B which incorporated oxygen free nitrogen gas which bubbled up through half the sintered glass floor of the cell which was half covered with collodion. The electrode in Scheme B was so bent at the bottom that it actually was below the focal point of the incoming beam of light. The portion of the sintered glass bottom that was uncovered by the collodion was farthest away from the small entrance window i.e., directly below the exit window. As the oxygen-free nitrogen gas was allowed to bubble

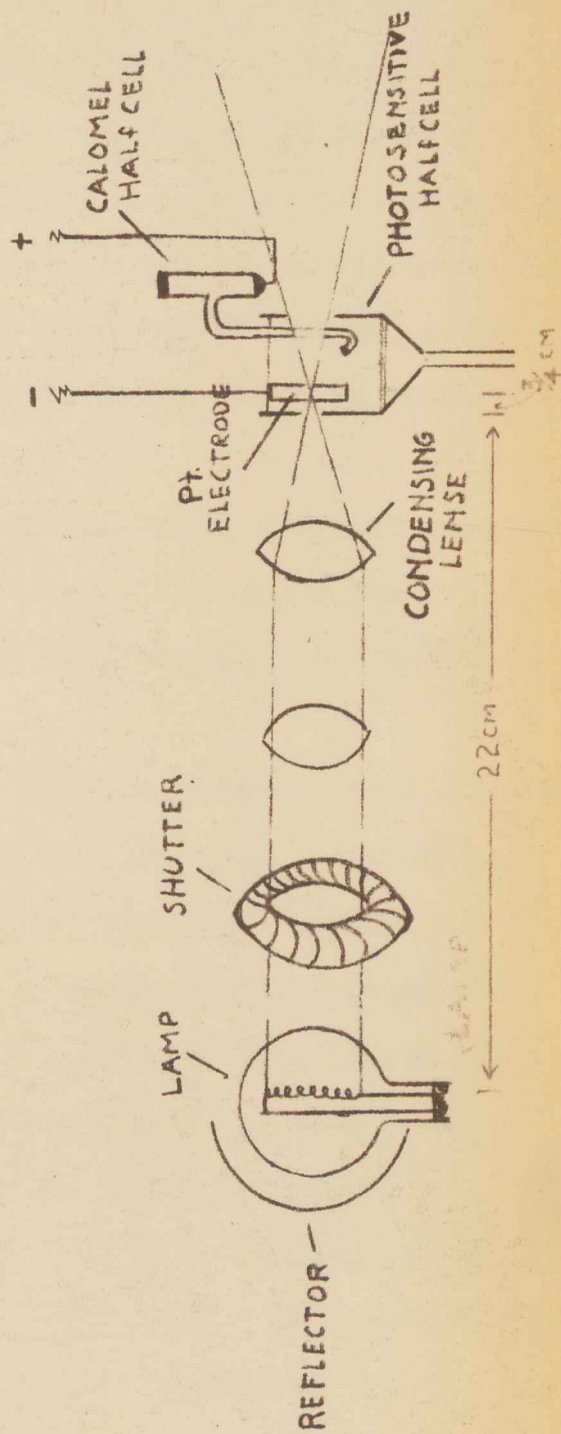
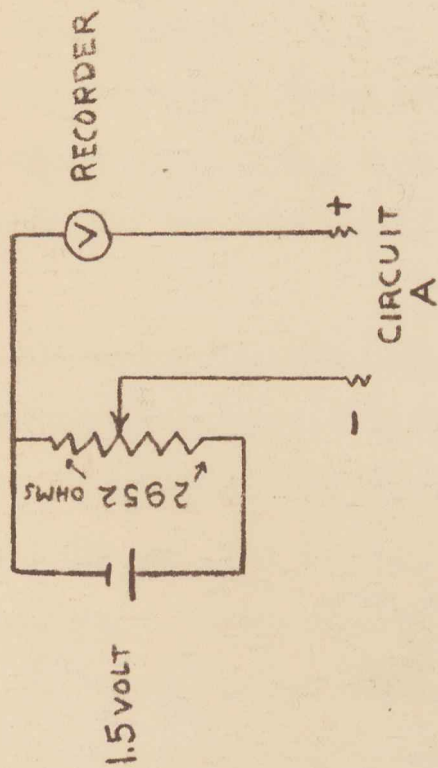
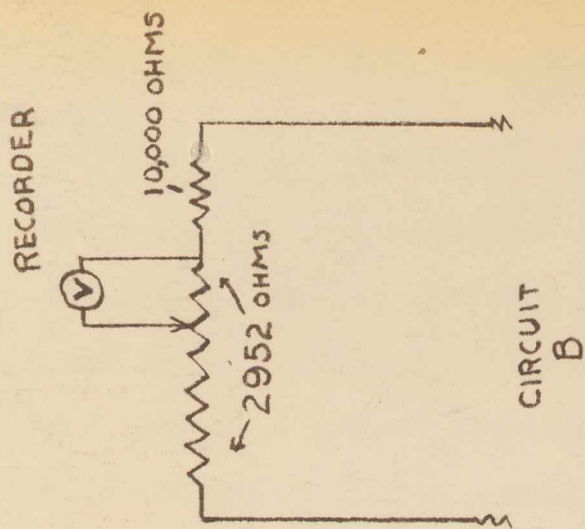
* The not too understandable Becquerel Effect is observed when an electrode in a solution of ions and reversibly reducible dye molecules is excited by light producing an electrical potential. (5)

Scheme A



Scheme B





up through this portion of the cell, stirring was induced thereby by circulating the solution so that the reduced dye molecules would flow down out of the beam of light and onto the platinum electrode. Both schemes incorporated a saturated KCl calomel reference electrode which acted as the unsensitized or dark electrode. The bridge contained an agar gel saturated with KCl. The end of the bridge which dipped into the photosensitive half-cell had a sintered glass tip. This fine guage sintered glass junction minimized the diffusion of potassium and chloride ions into the electrolyte.

The electromotive force was recorded using a Weston Single Point recorder Model 6701, type #1, range 1-10 mv, which was placed in either of the two circuits A or B as shown in the diagram on page 7.

The source of illumination was a 400 watt tungsten filament lamp behind which a parabolic mirror was situated. A shutter was placed in front of the source along with collimating and condensing lenses. The shutter was used to turn the excitation beam on and off instead of turning the bulb on and off with a switch. The filament was thereby allowed to warm up to steady-state before the beam was directed into the solution.

The focal point of the incoming beam was situated as close as possible to the entrance window of the cell. This permitted maximum excitation to take place above the electrode before the

intensity of the beam was decreased by absorptions caused during its passage through the solution.

Rabinowitch's apparatus was much more refined in that he incorporated various filters to limit the wavelength of the entering radiation. He also made colorimetric measurements on his reaction solution. Rabinowitch's apparatus was designed primarily to collect data which would aid in enabling him to formulate a mechanism, determine velocity constants and quantum yields for the phenomenon. The apparatus used here is mainly devised for a study of the effect using multi-wavelength excitation.

Three photosensitive systems were attempted:

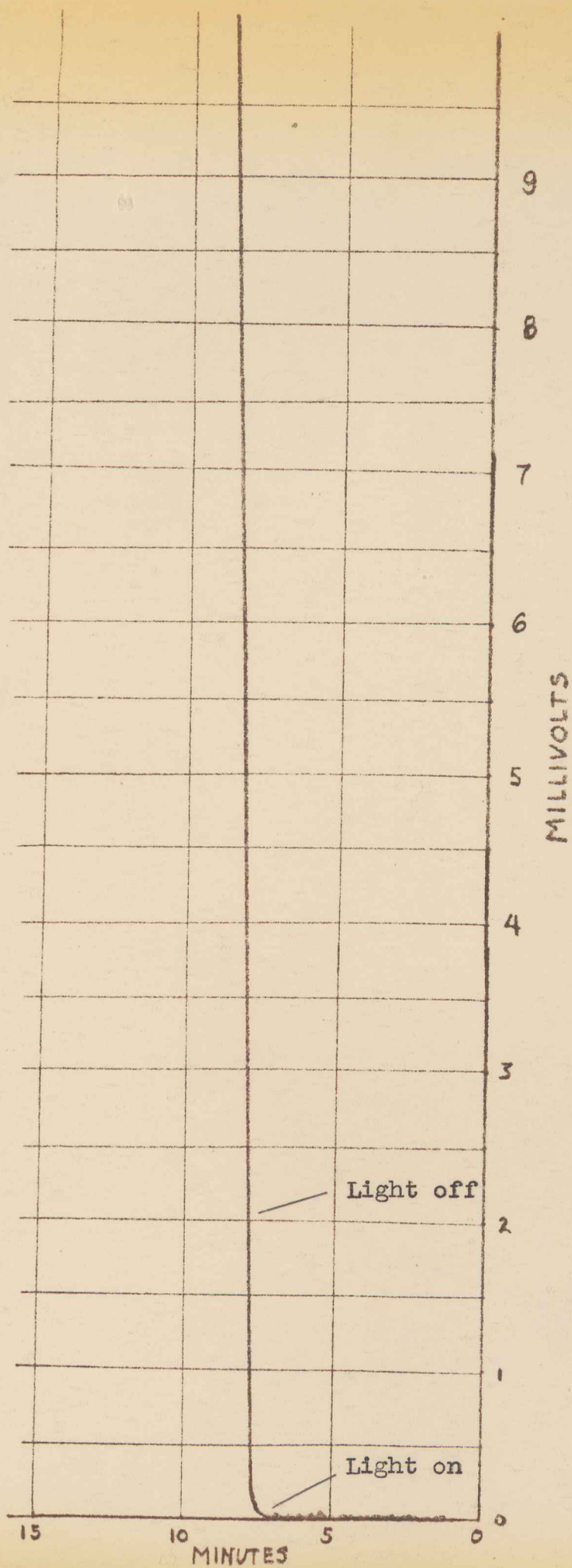
Thionine	5×10^{-5}	moles/l	with	FeSO_4	5×10^{-3}	moles/l	pH 2-2.5
"	"	"	"	CoCl_2	"	"	pH 6.6
"	"	"	"	MnSO_4	"	"	pH 7

Oxygen-free nitrogen gas was bubbled through the solutions in Scheme B and unaltered commercial nitrogen gas was used in Scheme A.

Experimental Results

Curves 1, 2, 3, 4, 8, and 9 were obtained. The ordinate of each curve is in millivolts recorded and not actual millivolts produced by the cell.

Curves 1, 2, 3 were obtained using circuit diagram A and Scheme A for the photosensitive half cell along with unrepurified nitrogen gas. The rest of the curves were recorded using circuit B and Scheme B with nitrogen gas which was made oxygen free.

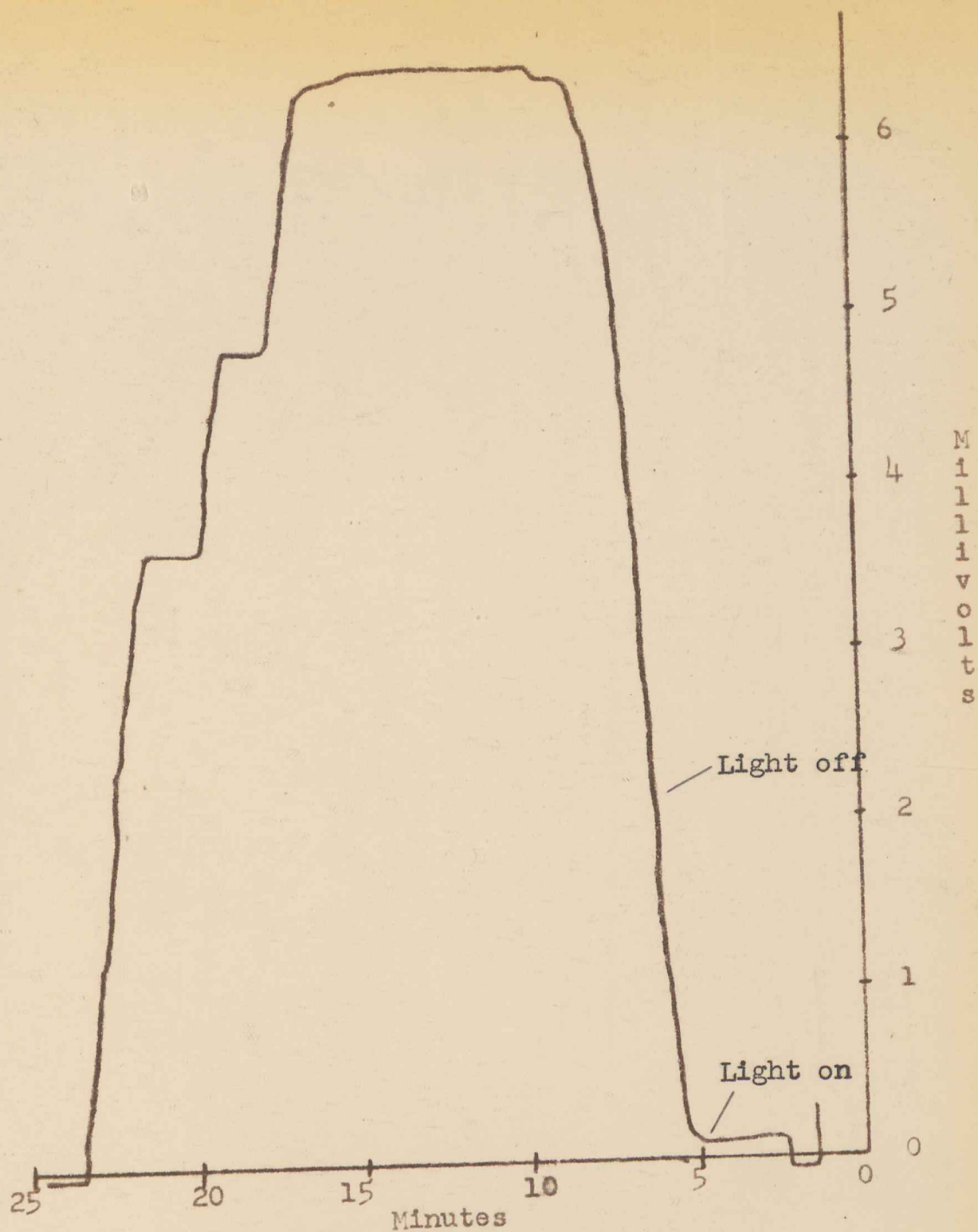


Curve 1.

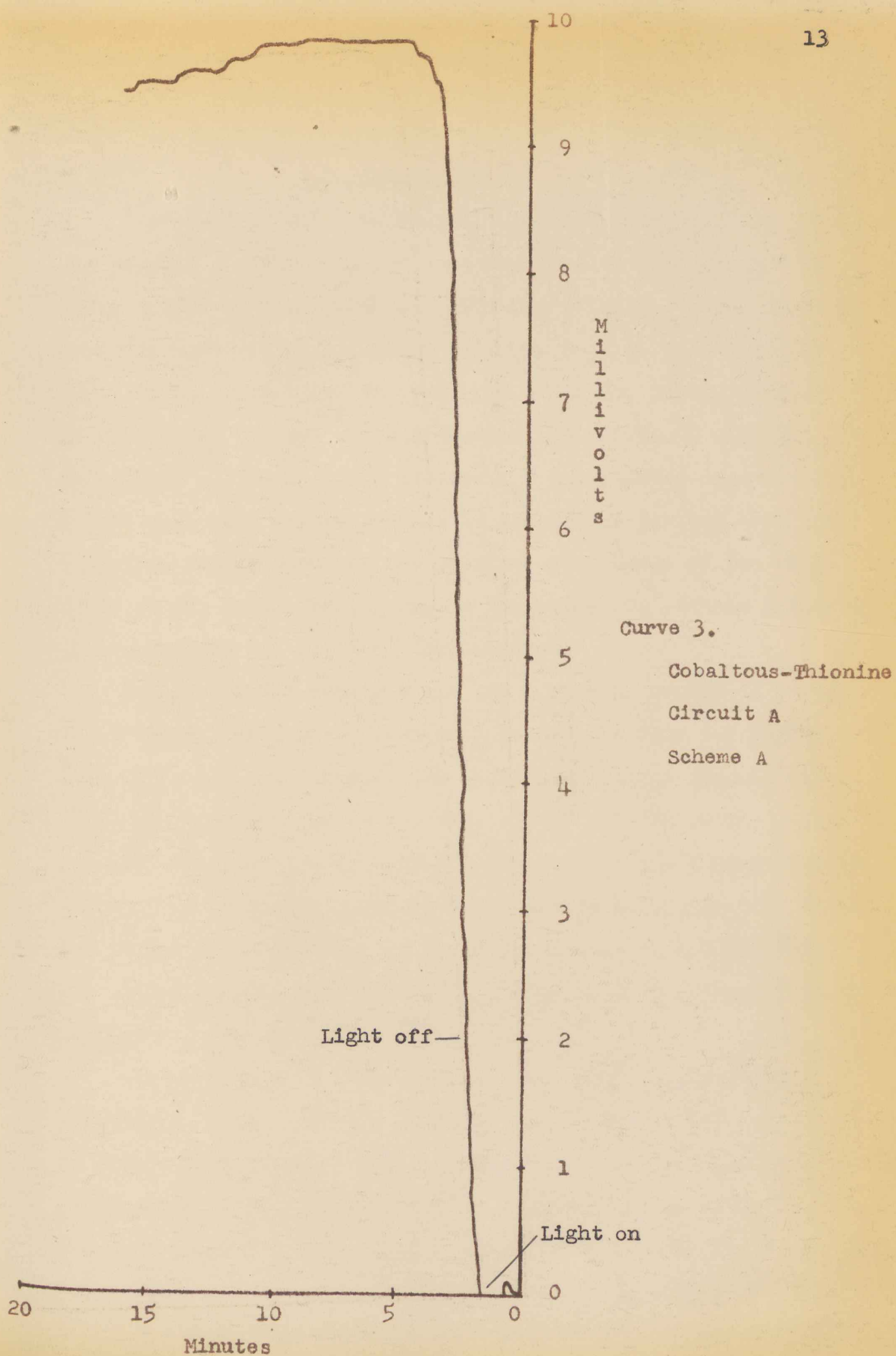
Ferrous-Thionine

Circuit A

Scheme A



Curve 2. Manganous-Thionine
Circuit A
Scheme A



Discussion

Curves 1, 2, and 3 which were obtained incorporating Scheme A and circuit A along with unaltered commercial nitrogen gas at first appear to give good photogalvanic effects. These curves, however, were not reproducible so three main alterations were made on the apparatus. First Scheme B for the photosensitive half-cell was devised which minimized the amount of nitrogen gas collecting on the platinum electrode. Gas bubbles accumulating on the electrode caused changes in its active surface area and thus gave fluctuations in the electromotive force of the cell which showed up as nervousness on the recorder. Scheme B cleared up practically all of these fluctuations.

The commercial nitrogen gas had a certain amount of oxygen gas present. It seemed reasonable to suspect that the oxygen present in the gas oxidized the "ous" ions rather quickly and therefore made our curves invalid. After removal of the oxygen gas from the nitrogen by bubbling the gas through a concentrated solution of potassium pyrogallate no effect (electromotive force) whatsoever was observed. So there was reason to believe that the curves somehow were produced by some other influence than the photogalvanic effect.

The main problem with circuit A was that slight external influences on the variable resistor caused the recorder pointer to become very unsteady and a steady base-line was hard to acquire. After the cell came to equilibrium a base-line was established but soon after this the pointer would drift rapidly for no apparent reason. It might be considered coincidental that when the light was turned on the curve produced was merely the aforesaid

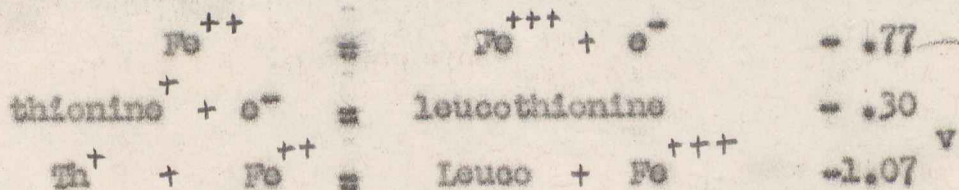
drift. Further evidence to prove these curves invalid is supplied by Rabinowitch who found the average life of the reduced dye molecule in the dark to be only about .5 seconds (6). The curves show that reduced dye molecules must have been present for about 18 minutes with the manganous-thionine solution and for 14 minutes with the cobaltous-thionine system which is highly unlikely. A new Circuit (B) was devised which did not incorporate a bucking potential.

The nitrogen gas now not only played the role of circulating the reduced dye molecules out of the beam of light and onto the electrode but it also swept out of the electrolyte any oxygen that might have dissolved in it from the air.

Photogalvanic effects were now observed with the ferrous-thionine system but werenot found with the other photosensitive systems. The manganous-thionine and cobaltous-thionine systems are less sensitive than the ferrous-thionine system because their inorganic couples are less easily reversible.



When the ferrous-thionine system was exposed to light the dye became reduced as explained in the introduction but it also became bleached. The bleached form is known as leucothionine. The maximum theoretical voltage change produced by the system with concentrations of unit activity is -1.07 volts.



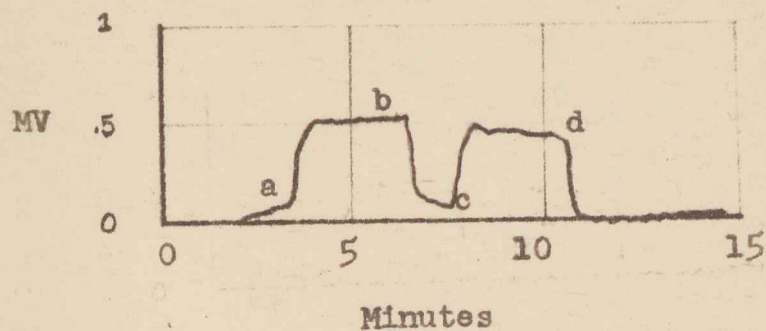
The illuminated half-cell is always negative as compared to the nonilluminated one.

The slowness of the back reaction which allows the reduced dye molecules to traverse the unilluminated distance from the beam of light to the electrode before becoming oxidized by the ferric ion may be attributed to a peculiar relation between ΔF and ΔH of the reaction. That the free energies of each half reaction (to the right) are strongly positive is indicated by their potentials. These are probably exothermic reactions ($-\Delta H$) so the reduced state of thionine has a smaller entropy than its oxidized state. Also the oxidized state of ferrous i.e., ferric has a smaller entropy. All of this obviously favors the back reaction (to the left). The back reaction, however, is endothermic and as such can not proceed with high velocity because in its surroundings there is not enough readily available heat energy (7).

The photosensitive solutions were kept at the proper pH to minimize oxidation by air. Rabinowitch found the maximum sensitivity for the ferrous-thionine system at pH 2-2.5 (curve 5)(8) for his apparatus using $\frac{1}{2}$ intensity of his available light intensity (1000 watt power before filtration). This pH was also used here assuming that our intensity was comparable to his $\frac{1}{2}$ intensity.

Rabinowitch's curve (curve 6)(9) shows maximum $\Delta \epsilon$ at a thionine concentration of 5×10^{-5} moles/l using strong illumination. This concentration was also used in the photosensitive systems here.

The concentration of FeSO_4 (5×10^{-3}) was used in our system as recommended by Rabinowitch (10). He found a maximum sensitivity

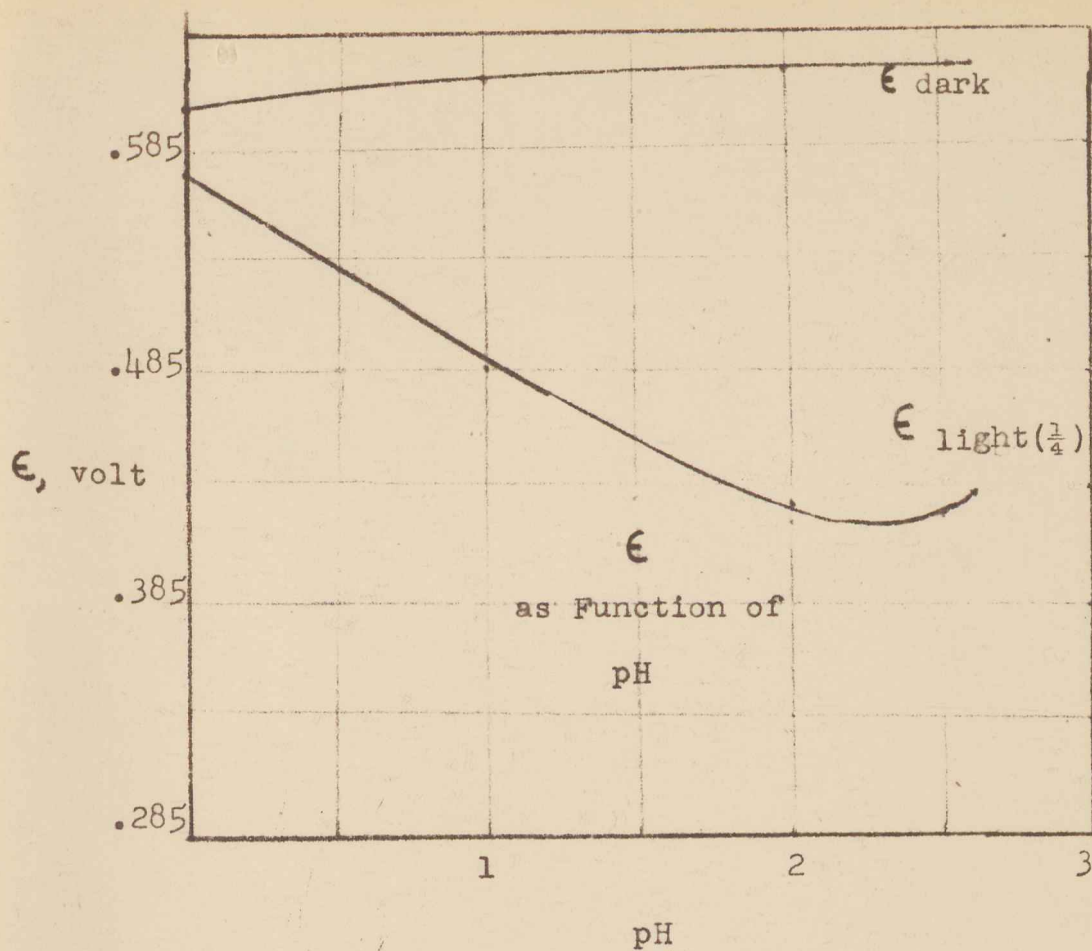


Curve 4. Ferrous-Thionine

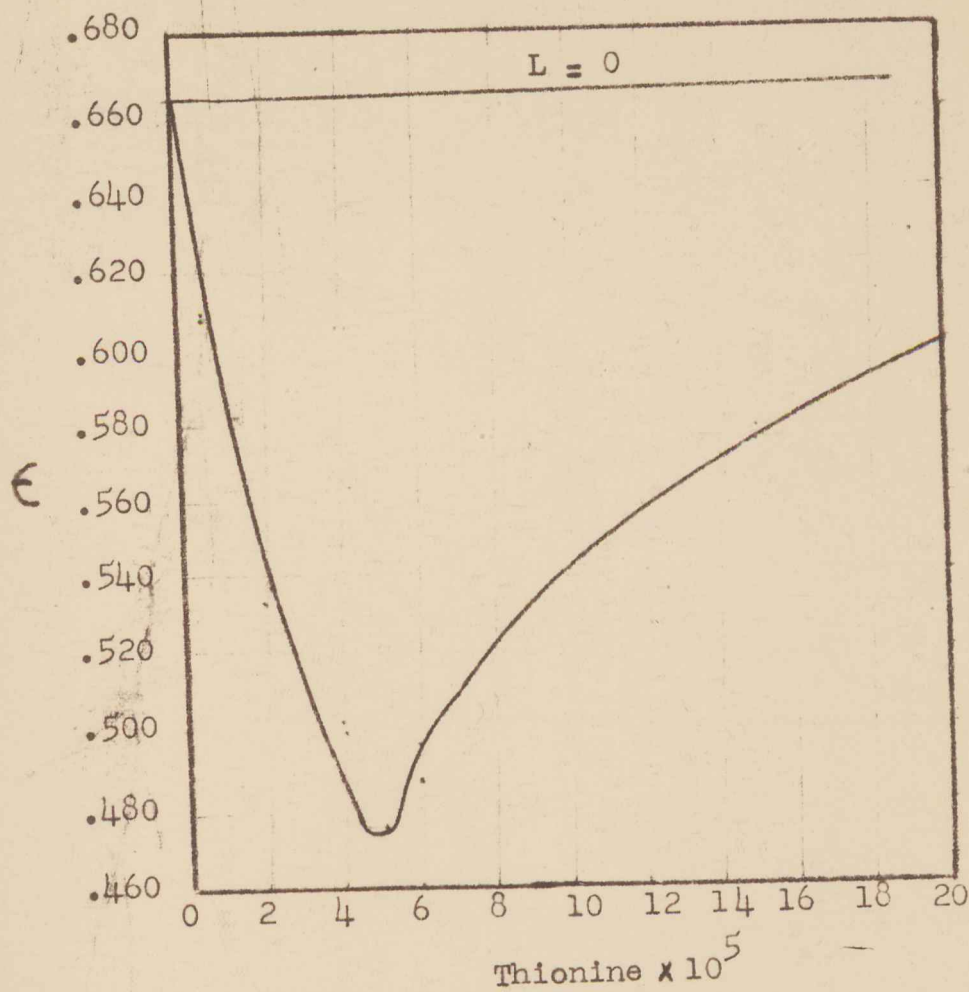
Circuit B

Scheme B

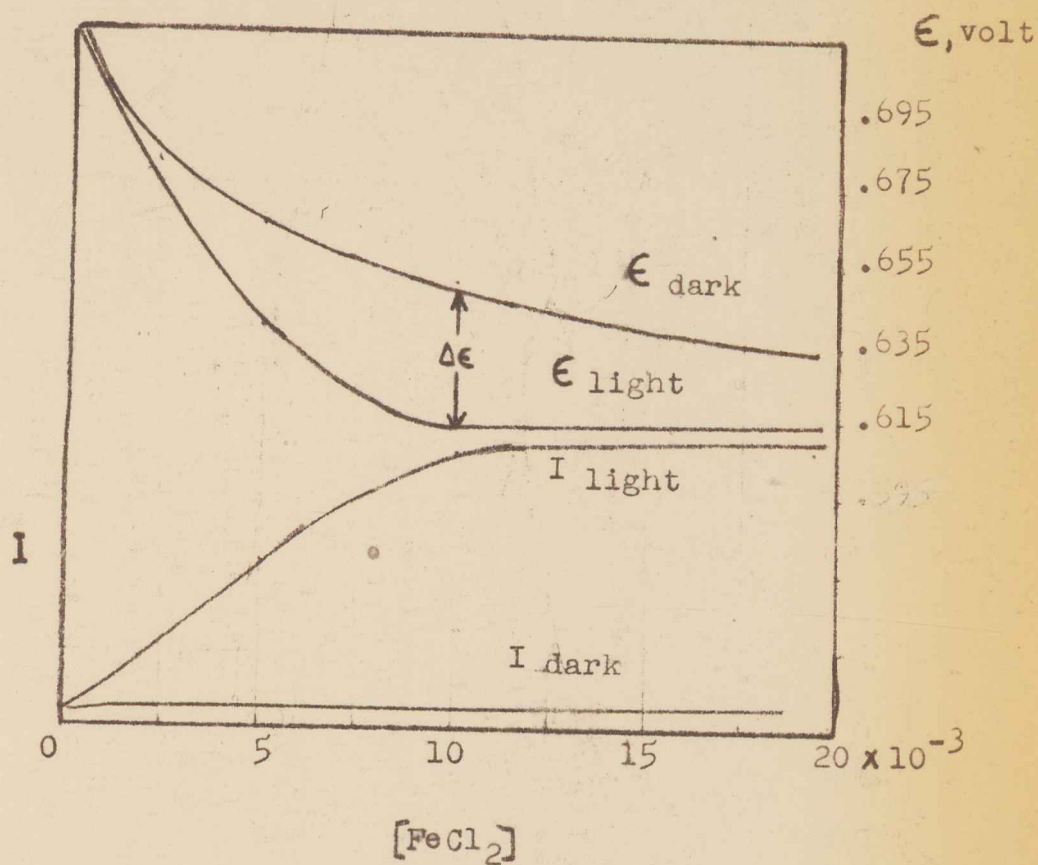
- a Light on
- b Light off
- c Light on
- d Light off



Curve 5. E in relation to pH. $[\text{Fe}^{2+}] = 2 \times 10^{-3}$ mole/l;
 $[\text{Thio}] = 5 \times 10^{-5}$ mole/l; $[\text{Fe}^{3+}] = 2.5 \times 10^{-5}$ mole/l.

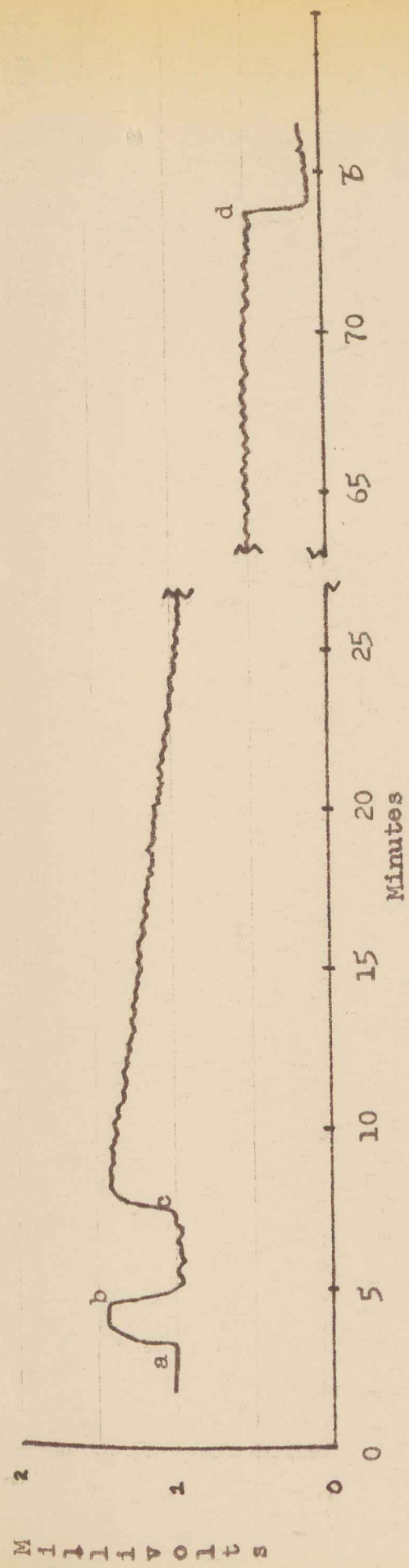


Curve 6. ϵ in relation to [thionine] concentration with strong illumination. pH = 1.7.



Transmission I and
potential E
as functions of $[\text{Fe}^{++}]$

Curve 7. I and E in relation to $[\text{Fe}^{2+}]$. $\text{pH} = 1.7$;
 $[\text{Thio}] = 5 \times 10^{-5}$ mole/l; $[\text{Fe}^{3+}] = 7 \times 10^{-4}$

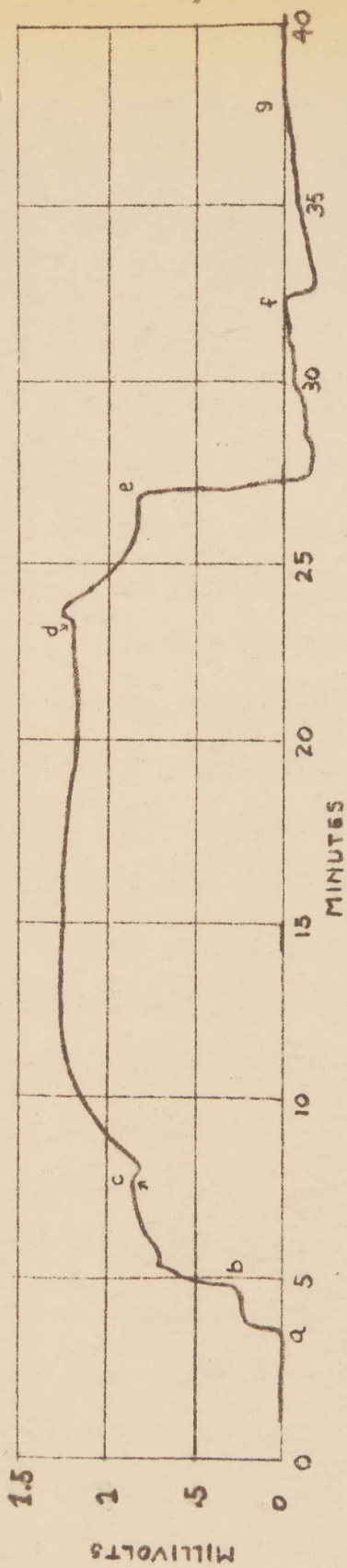


Curve 8. Ferrous - Thionine

Circuit B

Scheme B

- a Light on
- b Light off
- c Light on
- d Light off



CURVE 9-

FERROUS-THIONINE
CIRCUIT B
SCHEME B

a LIGHT ON
b GAS OFF
c LIGHT OFF
d LIGHT ON
e GAS ON
f LIGHT OFF

of a Fe Cl₂-thionine system at pH 1.7 with a ferrous concentration of 1×10^{-2} moles/l. The maximum $\Delta \epsilon$ is shown on curve 7 (11). These values were obtained using two platinum electrodes in the photosensitive cell; one surrounded by illuminated solution and the other in the dark.

Curve 4 shows the photogalvanic effect with the ferrous-thionine system which gave a deflection of .4 mv or by determination a cell output of 20.75 mv. As shown, quick responses were observed when the light was turned on and off.

In curve 8 it can be seen that our cell output was still about 20.75 mv. The photosensitive cell was continuously excited for 66.5 minutes to determine if the output dropped off due to photo-decomposition of the dye. We see, however, that at the end of this time, when the light is turned off, the cell output relaxes by no less than the original 20.75 mv thus indicating that no electromotive force was lost due to dye decomposition. The noticeable overall drift or shifting of the base-line may be explained as being due to the heating effect on the solution through the convection of heat from the source and the absorption of light by the solution.

Reproducible curve 9 was obtained using various alterations on the system and results were obtained which were unpredictable and up to this time are unexplained. At first the light was turned on (a) giving a photogalvanic effect which seemed to be about only one-half as great as previously obtained. This can be explained quite easily as being caused by a slight shifting in the distance between the electrodes causing a different in-

ternal resistance in the cell and or an effect on the photo-sensitive solution due to ageing. The solution used was from the same stock as solutions for the previous determinations but this determination was carried out at a later date and the solution was older. Hence the concentrations might have changed due to slow oxidation of the ferrous ion by air. It should be noted at this time that all solutions were kept under nitrogen but oxygen from the air could have dissolved into them during continual opening and transferring of the electrolyte. About one minute after the system reached equilibrium, the gas was turned off (b). One would expect that due to the decrease in circulation of the reduced dye molecules the electromotive force would drop off accordingly. There was, however, a considerable increase of .6 mv. This increase might be explained as being the result of the elimination of light reflection from the gas bubbles onto the electrode; this illumination of an electrode in solutions would cause a Becquerel Effect apparently of opposite electromotive force to the photogalvanic electromotive force.

The increase in electromotive force might also be attributed to the increase in conductivity between the electrodes which previously had been lower due to slight accumulations of gas on the platinum electrode and the salt bridge.

Now when the light was turned off (c), it was noted that the electromotive force was further increased by .4 mv and a new steady-state or base-line was obtained for the system when the light and gas were both turned off.

At point (d) when the light was again turned on the photogalvanic effect was in the opposite direction by 3.5 mv. Why

at this stage, the photogalvanic effect was in the opposite direction from those previously observed with gas flow can not be explained at this time. When the gas was again turned on at (e) a large deflection occurred back to about the original position and then the photogalvanic potential of .2 mv decreased with the extinction of the light (f). A drift and lower base-line was noticed between (e) and (g) which was probably due to an overall adjustment of the cell due to ion diffusion from the salt bridge but the deflections are the same as originally observed at (a) and (b).

Further experimentation is necessary to explain what happened between points (c) and (e) and why the photogalvanic effect seems to be in the opposite direction when the gas is off to when it is flowing.

If time allowed, trials would have been attempted whereby the effect on the electromotive force of the gas alone would have been determined. The influence of the Becquerel Effect could be determined by varying the amount of light reflection on the electrode. This might indicate whether shielding of the electrode from light reflections is necessary.

Summary

After careful analysis of the apparatus used by Rabinowitch a modified apparatus was constructed. This was further improved when Scheme B and circuit B were incorporated into the apparatus to give steadier base-lines and reproducible curves. The photo-sensitive solutions used by Rabinowitch were studied and used here were those which seemed to be most sensitive.

No photogalvanic effect was observed in the manganous-thionine and the cobaltous-thionine systems but a moderate effect was observed with the ferrous-thionine system.

Curve 9 was obtained with the ferrous-thionine system by making alterations on the system. Further investigations are necessary to fully explain this curve.

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