FOREWORD

This report was prepared by the Chemistry Section of the Engineering Department of Sundstrand Aviation-Denver located at the Engineering and Testing Laboratories, Pacolma, California. The work was carried out under Contract No. AF 33(615)-7011, Project No. 3145, Task No. 60959-11, and under the auspices of the Aeronautical Systems Division with Mr. L. D. Massie as Project Engineer.

The following technical personnel have contributed to the project: Leroy J. Miller, principal investigator and Project Engineer; J. David Margerum, photochemistry and optical systems; Clifford M. Walker, fabrication of special equipment and general assistance; William E. McKeel, Chemistry Section Manager; E. Russ Hardwick, consultant on general aspects; Theodore Kuwana, consultant on electrochemical aspects; Eugene Findl, instrumentation; Warner B. Lee, mathematical analysis, and Etsuo Saito and Elbert C. Sisson, helpful suggestions on general aspects of the project. The report covers the period from March, 1961 to February, 1962.

The author wishes to acknowledge the helpful suggestions and cooperation of the ASD Project Engineer.
ABSTRACT

This report covers a feasibility study of the thionine photogalvanic system for converting solar energy to electrical energy. Theoretical and experimental investigations have been made to determine the maximum voltage and power available from the system. The effects of operating conditions as well as solution composition variables on cell performance have been studied. The low attainable concentration of leucothionine in the photosationary state at present prevents the utilization of the photogalvanic cell as a practical device. Electrode activation and long term dye stability are also important problems. Cell voltages up to 220 mv and power levels up to 1.8 μ watts were obtained. Although the voltage does not represent an improvement over the best previously reported voltage, the power is 1000 times more than the only other reported value. Estimates of the power, weight and cost of a photogalvanic cell have been made on the basis of present knowledge. Recommendations are made for more fundamental investigations to develop a better understanding of this system or similar systems, so that practical devices can be made.

PUBLICATION REVIEW

Publication of this technical documentary report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.
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SECTION I

SUMMARY

Thionine in a slightly acidic solution containing a large excess of ferrous ions is reduced to leucothionine upon absorbing visible light. The colorless leucothionine is spontaneously oxidized by ferric ions, which are the other products of the photochemical reaction, to regenerate the purple dye. Some of the oxidation can be made to proceed via an electrode reaction, leucothionine being oxidized at a platinum electrode in the illuminated solution while ferric ions are reduced at another platinum electrode in a dark portion of the same solution. The thionine photogalvanic cell utilizes this process for converting solar energy to electrical energy. This report covers a study of the feasibility of using the thionine photogalvanic system for power generation. The experimental work was performed between March 6, 1961, and March 16, 1962.

The maximum photogalvanic potential observed during this program was 220 mv. An output of 1.8 μwatts per square centimeter of illuminated surface area was the highest measured power level. The efficiency at this power was not determined, but efficiencies up to 8.44 x 10^{-4}% were determined for other cells. These efficiencies are based on the total energy incident upon the cell. An efficiency of 3 x 10^{-3}% was estimated on the basis of the light absorbed by the solution.

While the 220 mv photogalvanic potential surpassed the 95 mv and 185 mv mentioned in two previous studies of other laboratories, it fell short of the 265 mv reported for a third. The power level of 1.8 μwatts is 1000 times the highest previously observed power level. An efficiency of 3 x 10^{-4}% based on the light absorbed was the only previously reported efficiency backed by experimental details. Voltages as high as 500 mv and efficiencies up to 1% had been claimed, but these claims have thus far not been supported by evidence.

After a thorough study of both literature and experimental results, realistic estimates were made of the maximum voltage, power and efficiency which may be anticipated from optimum cells with the present state-of-the-art. The respective calculated values are 0.383 volt, 8 x 10^{-5} watt/cm, and 0.12% based on the light absorbed. The

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last two figures are based on an illumination intensity of about 1 sun, while the first would probably be achieved only with an intensity of 5 suns or more. (It should be noted that a truly effective method of slowing down the spontaneous back reaction as compared to the electrode reactions would be a means of increasing the power level beyond this calculated optimum value.)

A cell design was suggested, and on the basis of this design and the power estimates, it has been calculated that a practical photogalvanic cell may be expected to deliver 0.07 watt/sq. ft. at a cost of $1300/watt. Because of these disappointing estimates, it is recommended that further work should be long range research without the immediate goal of creating competitive solar energy conversion device.

The experimental portion of the program was mainly directed toward investigating the effects of various electrode configurations and conditions, the nature of the electrode processes, the effects of complexing agents and additives, and the effect of alternately illuminating the electrodes. Six laboratory model cells were fabricated, and three were tested in detail. The tests demonstrated various aspects of decomposition phenomena and the effects of the light intensity, the temperature, the wavelength of the exciting light, the angle of incidence, and the electrode orientation.

The photogalvanic potential was found to decline approximately logarithmically with the distance between the electrode and the illuminated cell window. Rotating the illuminated electrode from a position parallel to the light to a position perpendicular to the light diminished the potential only slightly.

The available power is highly dependent upon the surface area of the illuminated electrode while it is insensitive to changes in the area of the dark electrode except at large illuminated to dark electrode surface area ratios.

Probably the most astonishing observation of the entire program was the fact that the illuminated electrodes seemed to be activated by the adsorption of dye on the electrode surface. This was indicated by a variety of observations. Differences in electrode activation are a suggested explanation for the apparent disagreement between various investigators concerning the photogalvanic potential. Washing the electrodes with a concentrated solution of dye plus a detergent was discovered to be a consistent means of quickly activating the illuminated electrode.
A theory has been advanced to explain the heretofor unexplainable variations in the illuminated electrode potential. The electrolyte contains both the ferric-ferrous and the thionine-leucothionine redox systems. In the dark, they are at equilibrium. However, in the illuminated solution they are not, and the redox potentials of the two systems are different. The potential assumed by the illuminated electrode lies somewhere between the potentials of the two redox systems. It is a mixed potential which is determined by the voltage-current characteristics of both redox systems. Experimental data herein presented support this mixed potential theory. The potential of the illuminated electrode is that at which the anodic and the cathodic components of the current are equal. In strongly bleached solutions the anodic component is almost entirely due to leucothionine and the cathodic component is almost entirely due to ferric ion.

For any given set of solution conditions the potential can be varied by changing the relative ease with which leucothionine and ferric ion can undergo the electrode reaction. The role of the adsorbed layer of dye has thus been explained as a means of favoring the leucothionine electrode reaction over the electrode reaction of ferric ions. The adsorbed thionine either inhibits the reaction of ferric ions or catalyzes the reaction of leucothionine. A plausible rationalization of the leucothionine electrode reaction is that it reacts with the adsorbed thionine to form semithionine free radicals which can then quickly be reduced at the electrode surface. The reaction between thionine and leucothionine is known to occur within the bulk of the solution.

A complete mathematical equation describing the electrode potential as a function of the concentrations of the various components in the photostationary state is provided. However, not only is it unwieldy but it contains a number of constants which as yet can not be evaluated. Some simplifications which can be made for strongly bleached solutions reveal that the potential of the illuminated electrode cannot even theoretically decrease without limit. It has been shown for some solutions that the photogalvanic potential would increase only slightly beyond what was already attained even under illumination of infinite intensity.

Although the actual internal resistance of most of our cells as measured by an impedance bridge was 200 to 800 ohms, the apparent internal resistance when current was drawn was generally on the order of $10^4$ to $10^5$ ohms. The high apparent internal resistance is caused by the very small diffusion limited current of
leucothionine. The most obvious method of magnifying this current is to increase the leucothionine concentration in the photostationary state. In purely aqueous solutions the leucothionine concentration is limited by the solubility of thionine in the starting electrolyte. It had been reported that the photogalvanic potential declined sharply as the thionine concentration was increased beyond $5 \times 10^{-3}$ M. One goal of the program therefore became a means of increasing the thionine concentration in the starting solutions without suffering a great loss in photogalvanic potential.

This task was accomplished. An exploratory investigation of various additives to the electrolyte led to the use of aqueous tetrahydrofuran as the solvent. This change permitted photogalvanic potentials up to 178 mV with thionine concentrations of over $10^{-3}$ M. It was by using these concentrated solutions that the highest power levels were obtained. One such cell was operated for 8 hours at peak power without any notable deterioration in performance.

Thionine solutions containing all of the ingredients necessary for the photogalvanic effect have been prepared with dye concentrations as high as $2 \times 10^{-2}$ M. These most concentrated solutions were prepared by salting in the dye with large quantities of sodium p-toluene sulphonate. These concentrated solutions absorbed at least 99% of solar radiation below 8000 Å in a path length of only 2 mm. Unfortunately the p-toluene sulphonate salt seemed to deactivate the electrode, and the photogalvanic potential was practically zero.

The addition of phosphate and citrate as ferric ion complexing agents produced increases in power of 40% and over 100%, respectively. The improvement varied with the load and probably was specific for the solutions investigated. At present there is no evidence that complexing agents have any other effect than to reduce the activity of the ferric ion.

Alternately illuminating the electrodes is an effective means of reducing power losses caused by concentration polarization. Improvements by as much as a factor of 110 were measured. It must be noted, however, that alternating illumination can do no more than eliminate the slow decrease in power due to accumulation of ferric ions in the illuminated solution and the depletion of ferric ions in the dark solution. It cannot increase the power which is initially drawn from the cell. Since it is a means of combating concentration polarization, its influence is most pronounced for cells which otherwise are subject to serious limitations.
by concentration polarization. For example, it would produce marked improvement in cells with a low initial thionine concentration or cells from which a high current is being drawn.

Three laboratory model cells were constructed with Lucite containers. When it was discovered that the power available from these cells was very low, the problem was attributed to electrode deactivation by substances extracted from the plastic containers. In retrospect it seems likely that electrode activation with a dye-detergent solution might have prevented the deactivation. Three other laboratory model cells were consequently fabricated from glass. An epoxy resin was used where sealing by fusion of the glass was impossible. These cells were tested extensively.

Two of the model cells were designed specifically for use with concentrated thionine solutions in aqueous tetrahydrofuran. The earlier experimental cells operated quite successfully with these solutions, but for reasons not yet understood the solutions failed to yield significant potentials in the model cells. Because of the press of meeting time schedules, the difficulty could not be investigated fully. Therefore, the model cells were tested only with purely aqueous solutions containing thionine at lower concentrations.

The maximum efficiency measured with the model cells was, as mentioned above, $8.44 \times 10^{-4}$% based on the total incident energy.

A study of deterioration in performance during prolonged periods of illumination indicated that cells could in some cases be operated for periods of 1 to 3 days without serious deterioration. Mere loss of dye by decomposition could not account for the deterioration. The decrease in power seemed to be directly caused by changes on the electrode surface, although these in turn may have been due to dye decomposition. The decrease in power due to deterioration is most pronounced at high load resistances. Whereas one previous report suggested that useful cell lifetimes were measured in minutes, this study found that it was at least hours or days. The influence of ultraviolet light was not determined, but it is suspected of causing at least some of the trouble. A better understanding of the problems concerning electrode activation might help greatly in extending the lifetime.
The variation in power with the light intensity was measured for the three model cells, and the power was extrapolated to an illumination intensity of 10 suns.

While the photogalvanic potential increases with decreasing temperatures, the power of the model cells was found to pass through a maximum around 20° to 30°C. The advantage of increased voltage is overcome by the diminished rate of material transfer at the lower temperatures. The low rate of material transfer is evidenced by the high concentration polarization. Temperature cycling, which undoubtedly causes strong connection currents, can multiply the power by a factor of 3 over what it is at any given constant temperature.

The effectiveness of visible light in accomplishing the reduction of thionine is directly proportional to the absorbance of thionine at the same wavelength. Ultraviolet and infrared light are detrimental in their effect, the latter because of its influence on the temperature of the solution.

An electrode orientation which inhibits convection currents greatly increases concentration polarization. This observation plus the observation on the effects of temperature cycling arouses the suspicion that material transfer between the dark and the illuminated solutions is primarily carried out by convection and not by diffusion. This would necessitate forced circulation in the absence of gravity in order to maintain the same output.

Varying the angle of incidence produces the same effect as correspondingly varying the incident light energy without changing the angle of incidence.

A fairly comprehensive review of the literature on the characteristics of thionine and the thionine-iron system is included in this report.

It is recommended that the role and the nature of the electrode surface as well as a means of inhibiting the oxidation of leukothionine in the bulk of the solution be made the subjects of new research.
SECTION 2

INTRODUCTION

An aqueous solution containing the purple dye, thionine, and ferrous and ferric ions is bleached when illuminated with light in the 6000 Å region. The bleaching is the result of the photoinduced reduction of thionine to leuco-thionine by the ferrous ions. The reaction is reversible, the leucothionine being reconverted to thionine by ferric ions when the illumination is discontinued. An inert electrode immersed in the illuminated solution is negative with respect to another inert electrode immersed in a dark portion of the same solution. This system thus presents a method for converting solar energy to electrical energy. Voltages up to 0.5 volts and efficiencies up to 1% had been reported by a previous investigator, although without experimental details. Furthermore, the reported efficiency was not considered to be a limit in any way. However, conflicting results were obtained in another more recent study in which a maximum efficiency of $3 \times 10^{-4}$% was observed. If the efficiency of the photogalvanic cell could be made comparable to that of currently used solar devices, a far more economical system would be possible. The inherent mechanical simplicity of the photogalvanic cell would eliminate much of the complexity required in other types of large area collectors.

Specific items on the research program included studies of the electrode processes, the effect of complexing agents, the effect of varying electrode configurations and conditions, and the effect of alternate illumination of the electrodes. The performance of three laboratory model photogalvanic cells was studied in detail.
SECTION 3
HISTORICAL BACKGROUND

The general historical background of the thionine-iron system is presented in this section. Additional background information which was not previously related to the system will be presented in Section 4 in connection with the experimental results.

3.1 CHARACTERISTICS OF THIONINE AND ITS SOLUTIONS

3.1.1 Structure

Thionine, also known as Lauth's Violet, is the common name for 2,7-diaminophenothiazine which is commercially available in the form of the hydrochloride salt. The structural formula of the cation present in this salt is shown below.

The two-headed arrow indicates that the structures are contributors to a resonance hybrid, and the dotted circles represent the usual resonance of aromatic rings. Only the primary contributors to the ground state of thionine are shown. Other structures which made very much smaller contributions to the ground state are as follows:
Although these may contribute only slightly to the nature of the ground state, their contribution is undoubtedly far greater in the excited states of the thionine cation.

The name "thionine" is used throughout this report to refer to the dye in the form of its various salts or complexes or cationic or neutral forms without distinction. When a distinction is vital to the discussion, the specific form is noted. Whenever the solid material is indicated, "thionine" will refer to the commercially available hydrochloride.

3.1.2 Absorption Spectrum

As is frequently the case for compounds which can be depicted as the sum of many resonance structures at various energy levels, thionine absorbs light strongly in the visible region. To the eye solid thionine and its concentrated aqueous solutions are an intense purple. Very dilute aqueous solutions appear more bluish in color.

The absorption spectrum of an aqueous thionine solution is reproduced in Figure 1. This spectrum was obtained in the Sundstrand Laboratory on a Cary recording spectrophotometer using a 1 M solution with a pH of 2.6.

Since commercial thionine is not pure, the concentration of thionine solutions cannot be calculated from the weight of solid dissolved. The concentration is conveniently determined from the absorbance at 6000 Å of an appropriately diluted aliquot.
Figure 1. The Absorption Spectrum of an Aqueous Solution of Thionine (9.47 x 10^-6 moles/l, pH = 2.0)
There is considerable disagreement about the molar absorptivity of thionine. The spectrum will vary strongly with the conditions under which it is determined, and an exact comparison of the literature results is impossible. Nevertheless, a rough comparison can be made of the results listed in Table I.

The molar absorptivity of $7.12 \times 10^4$ reported by Schlag was the highest measured, and in his concentration measurements this value was rounded off to $7 \times 10^4$. In view of the uncertainty that anyone was able to purify thionine completely, the highest reported value probably should be given preference. Throughout this report the precedent of Schlag will be followed, and all thionine concentrations are based on the assumption that the molar absorptivity at the maximum near 6000 Å is $7.00 \times 10^4$. If this value should prove incorrect in the future, the correct thionine concentration can readily be calculated.

3.1.3 Basicity

Because of the basic properties of thionine, the pH of the solution has to be specified when discussing the spectrum of thionine. Epstein, Karush and Rabinowitch obtained the spectra of the free base and the mono-, di- and trivalent cations, and reported conditions under which these predominated in solution.

The common form of thionine is the monovalent cation (structure 1), which exists in solution in the pH range 2-10. In a strongly basic solutions the free base (structure 3) is found, while in strong acid the divalent cation (structure 4) if formed. The trivalent cation (structure 5) exists only in concentrated sulfuric acid.

![Structure 3](image)

(orange)
<table>
<thead>
<tr>
<th>Thionine Concentration, moles/l ( \times 10^5 )</th>
<th>pH</th>
<th>Wavelength of Max. Absorption, Å</th>
<th>Molar Absorptivity</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 2.5 \times 10^{-5} )</td>
<td>3.5</td>
<td>5970</td>
<td>( 5.29 \times 10^4 )</td>
<td>53, 12</td>
</tr>
<tr>
<td>( 2.5 \times 10^{-6} )</td>
<td>3.5</td>
<td>5970</td>
<td>( 5.43 \times 10^4 )</td>
<td>53</td>
</tr>
<tr>
<td>( 2.5 \times 10^{-7} )</td>
<td>3.5</td>
<td>5970</td>
<td>( 5.76 \times 10^4 )</td>
<td>53</td>
</tr>
<tr>
<td>( 2.5 \times 10^{-5} )</td>
<td>1</td>
<td>5970</td>
<td>( 5.1 \times 10^4 )</td>
<td>12</td>
</tr>
<tr>
<td>( 2.5 \times 10^{-5} )</td>
<td>*</td>
<td>5970</td>
<td>( 5.52 \times 10^4 )</td>
<td>12</td>
</tr>
<tr>
<td>( 10^{-5} )</td>
<td>2</td>
<td>5980</td>
<td>( 7.12 \times 10^4 )</td>
<td>59</td>
</tr>
<tr>
<td>infinite dilution</td>
<td>1</td>
<td>5970</td>
<td>( 6.5 \times 10^4 )</td>
<td>19</td>
</tr>
<tr>
<td>( 1.1 \times 10^{-5} )</td>
<td>1</td>
<td>6020</td>
<td>( 6.5 \times 10^4 )</td>
<td>20</td>
</tr>
</tbody>
</table>

* pH not specified; absorption is simply listed as that being due to the monovalent cation.
The possibility for resonance, which confers the greatest stability, is present only in the mono and divalent cationic species. Free thionine (structure 3) is a very strong base, the pKa of its conjugate acid (structure 4) being about 11.10, 12, 74. The strong basicity of the free thionine may be attributed to the gain in stability achieved by attaching a proton to form the monovalent cation (structure 5).

3.1.4 Dimerization

A second variable which must be specified when describing the spectrum of thionine is the dye concentration. The monovalent thionine cation (structure 1) does not follow Beer's law. This behavior is indicative of a tendency for the dye to dimerize in aqueous solutions. 12, 18, 38, 44, 53

The absorption spectrum of the dimer has a maximum at 5570 Å, and the extent of dimerization may be estimated from the absorptivities at 5570 Å and 5970 Å. The extent of dimerization increases with an increase in the concentration and with a decrease in the temperature. The tendency to dimerize has been detected at concentrations as low as 10^{-6} M. In alcohol-water solutions dimerization is inhibited, and it is completely absent in alcohol. 53 Rabino-witch and Epstein 53 believed that the anion concentration did not affect
the monomer-dimer equilibrium, but Hardwick and Haugen\textsuperscript{18} found that it was dependent on both the nature of the anion and its concentra-
tion. Only the monovalent cation exhibits the tendency to dimerize.\textsuperscript{12}

Dimerization is accompanied not only by changes in the absorp-
tion spectrum but also by quenching of fluorescence and small changes in the oxidation-reduction potential.\textsuperscript{53}

The effect of the presence of various miscellaneous materials on the monomer-dimer equilibrium has been studied. Some of the work was related to the interest in thionine as a biological stain. Many of these substances tend to form colloidal solutions. Thus it has been reported that agar\textsuperscript{44, 45} and sodium silicate\textsuperscript{43} enhance dimerisation and that nucleic acid\textsuperscript{44, 45} and various detergents\textsuperscript{32, 43, 44, 45, 65} in small quantities enhance dimerization and in larger quantities suppress it. Complex formation with other dyes which show a similar tendency toward dimerization has also been observed.\textsuperscript{5, 53}

The dimerization of thionine is important to the investigator of the photogalvanic effect because the dimer may or may not undergo the same photochemical and electrochemical reactions as the monomer. Any comprehensive study of the effects of thionine concentration must cope with the additional variable introduced by dimerization.

3.1.5 Decomposition

When thionine solutions are stored in soft glass bottles, the dye slowly decomposes.\textsuperscript{12, 53} The decomposition is minimized in acid solutions, and acid solutions in Pyrex bottles are reported to be quite stable. It has been suggested that the decomposition may be related to the alkaline nature of the glass, since thionine also decomposes in alkaline solutions.\textsuperscript{12, 43}

3.1.6 Redox Properties

Thionine can be reversibly reduced to leucothionine, a color-
less compound which can exist as the free base or as the mono-, di-, or trivalent cations.\textsuperscript{12}
Because various ionic species of both the oxidized and the reduced forms of the dye are involved, the standard redox potential of the thionine-leucothionine system varies with the pH of the solution.\textsuperscript{10} Over the pH range 1 to 4 the standard potential decreases by 0.090 volt for each increase of one pH unit, and the value can be calculated with the formula \( E = +0.563 - (0.090 \times \text{pH}) \).\textsuperscript{*} Between a pH of 6 and 10, the standard potential decreases by 0.030 volt per pH unit, and between 11 and 13 it again decreases by 0.090 volt per pH unit.

The reduction of thionine for purposes of preparing the leuco-dye is most readily accomplished by hydrogenation with a finely divided palladium\textsuperscript{12} or platinum oxide\textsuperscript{17} catalyst. Leucothionine has also been prepared by reduction of solid thionine with hydrogen sulfide.\textsuperscript{67}

\* The European electrode sign convention will be followed throughout this report. For a detailed explanation of the relationship to the American sign convention see reference 4.
Semithionine is a free radical intermediate in the reduction of thionine to leucothionine. The structure of the monovalent cation of semithionine may be represented as:

\[
\begin{array}{c}
\text{H}_6\text{N}_2\text{S} \quad \text{NH}_4
\end{array}
\]

\[
\begin{array}{c}
\text{H}_6\text{N}_2\text{S} \quad \text{NH}_4
\end{array}
\]

Two semithionine molecules can undergo a reversible disproportionation reaction.

\[
2\text{S} \quad \text{Th} + \text{L}
\]

(The above symbols for semithionine, thionine, and leucothionine will be used throughout this report.) The equilibrium ordinarily lies far to the right due to the great rapidity of the reaction of semithionine with itself.\cite{19} In a solution of thionine and leucothionine in equilibrium in the usual pH range no more than a few tenths of one percent of the dye will be in the form of semithionine. In strong acid ($>10$ N), however, it is more stable, and its absorption bands have been identified.\cite{15, 46}

The property of thionine which is the underlying basis for its use in photogalvanic cells is its greater facility toward reduction when it is in the triplet state than when it is in the ground state. The triplet is formed via the singlet excited state after the molecule absorbs visible light. In this state thionine will react more rapidly with oxidizing agents than does the ground state; that is, light behaves as a catalyst in the reaction. Moreover, the position of equilibrium as well as the rate of reaction is affected. Reactions can occur with the triplet (or the excited singlet) which in the ground state may even be reversed. This is true of the thionine-iron system which will be discussed in detail in Section 3.2.
The photochemical reduction of thionine has been studied with a host of reducing agents. In addition to ferrous ions, the following have been reported: thiosinamid; 4, 5, 19, 24, 48, 70, 72 diethylthiourea; 41, 48, 70, 71, 72 nicotine; 73 ethanol; 7, 36 (with FeCl₃ as a photocatalyst); 7 acetone; 48 stannous chloride 48 ascorbic acid; 44, 47 phenylhydrazine; 35, 47 formaldehyde, glycerides and succinic acid (with ZnO as a photocatalyst); 6 glucose; 46 thiourea; 46 water; 14, 51 the sulfhydryl groups of urease; 66 1,4-diazabicyclo[2.2.2]octane; 42 N', N'-dimethylpipеразине; 42 sulfite ions; 13 hydroquinone; 53 and ethylenediaminetetraacetic acid. 61 Most of these reactions were irreversible and should not be considered for a photogalvanic cell.

Leucothionine is rapidly oxidized to thionine by air; 47 consequently in the presence of air and light thionine may merely serve as a photocatalyst for the oxidation of a substrate by air. 13, 66

3.2 CHARACTERISTICS OF THE THIONINE-IRON SYSTEM

3.2.1 Photobleaching

3.2.1.1 Qualitative Aspects

In 1932 Weber 71 reported that thionine is reduced by ferrous ions when illuminated and that the reaction is reversed in the dark. This behavior is the basis for the thionine-iron photogalvanic system. The overall reaction is as follows:

\[
\text{Th} + 2 \text{Fe}^{II} \xrightarrow{\text{hv}} \text{L} + 2 \text{Fe}^{III}
\]  

(9)

The photochemical reaction is accompanied by bleaching of the solution, since the purple thionine is converted to the colorless leucothionine.

The photobleaching of the thionine-iron system has been investigated intensively by Rabinowitch 51, HardwicK16, Havemann and co-workers, 20, 21, 22, 25-28 Ainsworth 1, 2, Schlag59, and Hatchard and Parker. The last authors have reported what is probably the most thorough study, because they employed flash photolysis and were able to measure the rates of extremely rapid reactions. They were also able to evaluate and utilize the results of the previous investigations.

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There is general agreement on the reactions which might occur. These may be summarized in the following manner:

\[
\begin{align*}
\text{Fe}^{2+} & \xrightarrow{k_1} \text{Fe}^{3+} + \text{h} \nu, \\
\text{Fe}^{3+} & \xrightarrow{k_3} \text{Fe}^{2+}, \\
\text{S} & \xrightarrow{k_5} \text{L}, \\
\text{L} & \xrightarrow{k_6} \text{Th}, \\
\text{S} & \xrightarrow{k_5} \text{L}, \\
\text{L} & \xrightarrow{k_6} \text{Th}. \\
\end{align*}
\]

(10)

Thionine is photochemically reduced by ferrous ions to semithionine. Semithionine may then be either reduced further to leucothionine by more ferrous ion or may be oxidized to thionine by ferric ion. It may also react with another semithionine to disproportionate into thionine and leucothionine. Leucothionine may be used up in two ways - either through oxidation by ferric ion or through a reaction with thionine in the reverse of the disproportionation reaction.

The photostationary state is attained when the rate at which each species is produced is equal to the rate at which it disappears. The extent of bleaching in the photostationary state is increased by increasing the ferrous ion concentration, the acid concentration, and the light intensity, and by decreasing the ferric ion concentration. At low thionine concentrations (<4 \times 10^{-3} M) the reduced dye is proportional to the amount of light absorbed, but at higher concentrations the effectiveness of the absorbed light diminishes. Strong ferric ion complexing agents, which effectively decrease the activity of the ferric ion, also enhance bleaching. Oxygen, of course, quickly oxidizes leucothionine and makes the photochemical reaction irreversible, because then the net result is the oxidation of ferrous ions to ferric ions.

3.2.1.2 Rates of Reactions

The rates at which the various reactions in equation 10 take place determine the composition of the system in the photostationary state. Because the system is quite complex and because some of the reactions are unusually rapid, the various studies mentioned in 3.2.1.1 have frequently arrived at conflicting opinions.
The absorption of light by thionine raises the molecule from the ground state to the singlet excited state. The singlet excited state is extremely short-lived, so that it is conceded no significant photochemical reactions have time to occur. The singlet excited state can return to the ground state with the release of heat or with the emission of light (fluorescence). The return to the ground state can be catalyzed by a collision with ferric or ferrous ions, the energy being released as heat. The useful reaction of the excited singlet, however, is the conversion to the triplet, which has a relatively long lifetime (approximately 20 µ sec)\(^1\). The conversion from the excited singlet to the triplet can be made almost quantitative (at a pH of 1) according to Hardwick\(^16\), but can account for only 40% of the excited singlet (at a pH of 2) according to Schlag\(^59\). This is an important and unresolved difference of opinion, since the latter case 60% of the absorbed energy would immediately be lost.

The triplet can be converted to the ground state with the production of heat, and again the conversion may be catalyzed by ferric or ferrous ions. The lifetime of the triplet is sufficiently long to permit reduction by ferrous ion which is the desired reaction. For the ferric and ferrous ion concentrations generally employed in photogalvanic cells, the triplet is almost completely reduced to semithionine\(^19\).

The manner in which semithionine is reduced to leucothionine has been a subject of controversy. Rabinowitch\(^51\) estimated the redox potentials of the semithionine-leucothionine couple from the equilibrium concentration of semithionine in a thionine-leucothionine mixture\(^46\). On the basis of the redox potentials he stated that semithionine could not be reduced any further by ferrous ion. Accordingly he assumed that leucothionine must arise from a disproportionation reaction involving two semithionine ions and forming thionine and leucothionine. Schlag\(^59\) and Alnsworth\(^1\) concurred in this opinion. Havemann and Pletsch\(^52\) disagreed on the basis that the concentration of semithionine was too small to permit a reaction which is second order in semithionine to occur to any significant extent. The reduction, they claimed, is carried out by the much more abundant ferrous ion in spite of the unfavorable redox potential because the semithionine is still in an excited state. Hardwick\(^16\) found that the disproportionation reaction was not consistent with his interpretation of the kinetics and consequently was led to the conclusion.

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that the reduced form in the photosynthetic state is mostly semi-thionine. Hatchard and Parker\textsuperscript{19}, using the more versatile technique of flash photolysis, were able to show that the disproportionation is so extremely rapid (occurring once for every three kinetic encounters) that it can indeed account for all of the leucothionine formed. They found no evidence for reduction of semithionine by ferrous ion.

Concurrently with the disproportionation, semithionine is rapidly oxidized by ferric ions. The extent of reduction to leuco-thionine is thus sharply limited by high ferric ion concentrations. Low semithionine concentrations, resulting from weak illumination, also limits the extent of conversion to leucothionine. Since the disproportionation rate depends on the square of the semithionine concentration while the ferric oxidation rate depends on the first power of the semithionine concentration, the oxidation becomes the favored means of disposing of semithionine when relatively small quantities are present.\textsuperscript{19}

Because of the rapid reactions which remove semithionine, its concentration is kept small, probably no more than a few percent of the reduced dye in the photosynthetic state. Hatchard and Parker have calculated the photosynthetic state concentrations for typical light intensities and typical ferric ion concentrations.

The oxidation of leucothionine, it is agreed by all investigators, is primarily effected by ferric ions. The alternative mechanism, the oxidation by thionine in the reverse of the disproportionation reaction, is rejected by various investigators for various reasons.

The most important reactions may probably be represented by the equations:

\[
\begin{align*}
&\text{hv, Fe}^{+++} \\
\rightarrow & \text{Fe}^{+++} (\kappa_3)
\end{align*}
\]

\[
\begin{align*}
&\text{Th} \\
\rightarrow & \text{Fe}^{+++} (\kappa_4)
\end{align*}
\]

\[
\begin{align*}
&\text{S} \\
\rightarrow & \text{L} \quad (\kappa_5)
\end{align*}
\]

20

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The circular mechanism involving the formation and the disappearance of leucothionine is permissible only because adherence to the law of microscopic reversibility is not required of photostationary states. According to Hatchard and Parker, \( k_3 = 7.9 \times 10^{14} \text{ mole}^{-1} \text{ sec}^{-1} \), \( k_4 = 2.6 \times 10^2 \text{ mole}^{-1} \text{ sec}^{-1} \), and \( k_5 = 2.4 \times 10^9 \text{ mole}^{-1} \text{ sec}^{-1} \). They have equated \( k_4 \) with the rate constant for the restoration of color, which has been given the following values by other investigators: Rabinowitch, \( 2.5 \times 10^3 \) \text{ mole}^{-1} \text{ sec}^{-1} (\text{pH} = 2)\); Hardwick, \( 4.25 \times 10^2 \) \( (25^\circ, \text{pH} = 1) \); Ainsworth, \( 6.50 \times 10^2 \) \( (20^\circ, \text{pH} = 2) \); Schlag, \( 2.75 \times 10^2 \) \( (22^\circ, \text{pH} = 2) \); Havemann and Reimer, \( 6.50 \times 10^2 \), calculated from first order rate constant at \([\text{Fe}^{+++}] = 10^{-3} \text{ M (pH} = 1.20)\). The rate of formation of semithionine depends on the amount of light absorbed and on the ferrous ion concentration. The quantum yield of reduced dye, i.e., the fraction of the absorbed quanta which lead to thionine reduction was calculated by Rabinowitch to be about 0.25. Hardwick reported values up to 0.75 and stated that it approached unity, the quantum yield for the formation of semithionine being implied, Havemann and Reimer\(^{28}\) claimed that the quantum yield for leucothionine formation approaches 1 at a ferrous ion concentration of 1 mole/l. Schlag, on the other hand, reported that the maximum quantum yield of leucothionine formation could be only 0.2, mainly because he found that only 40% of the singlet excited state underwent conversion to the triplet. Ainsworth calculated a quantum yield of bleaching of about 0.65. Hatchard and Parker made no quantum yield measurements, but their kinetic studies indicated that the quantum yield of leucothionine formation could be no more than half of the quantum yield of semithionine formation, since two semithionine ions were required to make one leucothionine ion.

3.2.1.3 Complex Formation

Havemann and Ainsworth have postulated that the formation of a complex between ferrous ion and thionine is either necessary for or greatly facilitates the photoreduction of thionine. Havemann and Pietsch\(^{20}\) presented the results of a study on the nature of fluorescence quenching by ferrous ions in support of their view. They also isolated a solid product with the formula \(2 \text{ Th} \cdot \text{FeCl}_2 \cdot 2 \text{ HCl}\). The decreased bleaching

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at higher temperatures was explained as a result of greater dis-
sociation of the complex. The accelerating effect of acetone on
the bleaching reaction was also rationalised as an effect on the
dissociation of the complex. The dependence of the rate of
bleaching on the ferrous ion concentration was interpreted in
accordance with the mechanism of complex formation, \(^{26, 28}\)

Ainsworth\(^1, 2\) observed light saturation in the reduction of
thionine by ferrous ions. He interpreted this as evidence for com-
plex formation, since the rate at which the complex is formed could
limit the rate at which the photoreduction could take place.

Ainsworth, Havemann\(^{20}\) and Hardwick\(^{16}\) all noted that the
absorption spectrum of thionine was altered little if at all by the
presence of ferrous ions. Ainsworth cited precedents for invoking
the formation of a complex to explain kinetic data when spectral
evidence was lacking. Hatchard and Parker\(^{19}\) found no necessity
for assuming the presence of a complex in explaining their kinetic
data.

Havemann and Reimer\(^{25}\) also presented kinetic data to support
their contention that leucothionine formed a complex with ferric ion
prior to oxidation. They maintained that the reaction was unimole-
cular, although the rate constant varied with the ferric ion concen-
tration. A first order reaction was observed not only for high ferric ion
concentrations, where a pseudo-first order reaction would be antici-
pated, but also for ferric ion concentrations comparable to the leuco-
thionine concentration. The first order reaction was explained as
involving in the rate determining step a leucothionine complex, the
concentration of which was dependent upon the concentrations of ferric
ion and leucothionine. This evidence is open to question, however,
since a mechanism involving prior reversible complex formation is
kinetically indistinguishable from a second order reaction involving
the free reactants.

3.2.1.4 The Effect of pH

The qualitative effect of pH was noted in Section 3.2.1.1, nam-
eely, that the extent of bleaching in the photostationary state in-
creases with decreasing pH. Havemann and Reimer\(^{27}\) demonstrated

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that the PIF (between 1 and 4) has no effect on the photobleaching reaction. The influence is exerted solely on the superimposed reverse reaction, the oxidation of the reduced dye. The effect on the oxidation is consistent with the fact that lowering the pH decreases the difference between the standard redox potentials of the thionine - leucothionine and the ferric-ferrous redox systems.\textsuperscript{10}

3.2.1.5 The Effect of the Wavelength of the Exciting Light

Few measurements have been made on the effect of the wavelength of the exciting light. Hardwick\textsuperscript{16} reported, however, that the action spectrum was approximately equivalent to the absorption spectrum, except that the shoulder at 5600 A was not detected.

Ichimura and Rabinowitch\textsuperscript{10} reported that colloidal chlorophyll can be used to sensitize the photoreduction of thionine to red light which otherwise was ineffective in their solutions. The light is absorbed only by the chlorophyll although the chlorophyll is not reduced to any measurable extent in the photosynthetic state. This sensitization could be an important means of extending the useful range of the spectrum.

3.2.2 The Photogalvanic Effect

A great deal of attention has been attracted to the photogalvanic effect of the thionine-iron system. It was the subject of investigations by Rabinowitch\textsuperscript{52}, Potter and Thaller\textsuperscript{49}, Silverman\textsuperscript{50, 63} and Anderson\textsuperscript{1}, and has been discussed repeatedly as one means of harnessing solar energy\textsuperscript{54-56}.

Rabinowitch\textsuperscript{51} defined the term "photogalvanic effect" as the influence of light on the electrode potential which is due to a photochemical process in the body of the electrolyte. The absorption of light has been shown (3.2.1) to cause bleaching of thionine-ferrous solutions. These changes are accompanied by a change in the potential of an inert platinum electrode immersed in the solutions. Thus if two platinum electrodes are immersed in the same solution and the solution around one is illuminated, a current can be made to flow through the external circuit connecting the electrodes.
3.2.2.1 The Photogalvanic Potential

The photogalvanic potential is the change in the electrode potential induced by illumination. The electrode potential in the dark is determined by that of the ferric-ferrous redox system. In the illuminated solution the potential is changed because of the change in the potential of the thionine-leucothionine redox system. The relationship between the photogalvanic potential and the potentials of the two electrodes is illustrated below.

\[
\begin{align*}
\text{Dark} & \rightarrow \text{Photogalvanic Potential} \\
\text{Illuminated} & \rightarrow \text{Illuminated Electrode Potential} \\
\text{Dark Electrode Potential} & \rightarrow \text{Standard Hydrogen Reference}
\end{align*}
\]

In his original papers Rabinowitch\textsuperscript{51, 52} reported photogalvanic potentials up to 265 mv. The photogalvanic potential for any given solution is proportional to the extent of bleaching and consequently is proportional to the light intensity. It does not follow, however, that solutions which bleach the most give the highest photogalvanic potentials; in fact, the highest value was observed with a solution which underwent little bleaching.

To demonstrate the effects of the concentrations of various solution components, Rabinowitch pointed out the influence of each variable on both the dark electrode potential and the illuminated elec-
trode potential. Low photogalvanic potentials are sometimes due to low dark potentials.

Increasing the ferrous ion concentration was shown to increase the photogalvanic potential up to a concentration of $1 \times 10^{-2}$ mole/l. Above that concentration the illuminated electrode potential (and the extent of bleaching) remains the same, while the dark potential continues to decrease, thus diminishing the difference.

Lowering the ferric ion concentration, which increases the extent of bleaching, decreases the potential of the illuminated electrode. At the same time it decreases the potential of the dark electrode. An optimum concentration was found to be about $5 \times 10^{-5}$ moles/l. Because the illuminated solution contains more ferric ions than the dark solution, since they are products of the photochemical reaction, the dark electrode potential decreases more rapidly than does the illuminated potential as the initial concentration is further reduced.

The optimum thionine concentration was found to be about $5 \times 10^{-5}$ mole/l. The effect of the thionine concentration is parallel to its effect on the extent of bleaching. The increase in the illuminated electrode potential at higher dye concentrations was first ascribed to participation of thionine in the oxidation of leucothionine. It was subsequently suggested that at high concentrations the dimer dissipates the absorbed energy without undergoing reduction.

The potential of the dark electrode is independent of the pH. For the same extent of bleaching the photogalvanic potential increases with increasing pH, because the standard potential of the thionine-leucothionine couple (and consequently the illuminated electrode potential) decreases. However, the extent of bleaching in the illuminated solution increases with decreasing pH. The counteracting effects result in an optimum pH of about 2-2.5. The optimum pH depends on the light intensity, since the extent of bleaching is a function of light intensity.

Potter and Thaller were able to obtain a maximum photogalvanic potential of only 185 mv and Silverman observed only 95 mv.
These workers used a 750-watt photoflood lamp and a 750-watt projection lamp, respectively, as sources of illumination, whereas Rabinowitch used either a 1000-watt projection lamp or a 20-amp carbon arc. In later communications Rabinowitch claimed that potentials up to 400 mV or 500 mV could be obtained; however, a private communication regarding these reports is recorded in Appendix I.

3.2.2.2 Electrode Mechanisms

It is known of course, that the electrode potential is changed by illumination because of the change in potential of the dye couple. However, no detailed picture of the electrode processes seems to be available in the literature. Rabinowitch recognized that ferric ions in the illuminated solution also have a direct affect on the electrode potential. The ferrous ion concentration seemed to have no direct influence in the presence of reduced dye. Rabinowitch postulated that the rate of electron losses by the electrode was independent of the nature of the electron acceptor in solution. It would appear that this view is not tenable.

Some have assumed that the potential of the illuminated electrode is simply the potential of the dye redox couple. However, this does not seem to be consistent with the data of Rabinowitch. The problem is discussed further in Section 4.3.

3.2.2.3 The Power Available from Thionine Photogalvanic Cells

The only detailed measurements of power from thionine photogalvanic cells recorded in the literature have been made by Potter and Thaller.

Two cells were used in their studies. The one consisted of a flat container with two flat platinum electrodes cemented to a back plate and covered with a layer of an appropriate solution. Only one electrode was illuminated at a time, and alternating illumination was contemplated as a means of combating concentration polarization. The other cell contained a porous glass disc coated on each side with a layer of porous gold to serve as the electrodes.
The highest energy conversion efficiency was observed for the first cell with a solution which contained $3.0 \times 10^{-5}$ mole/l of thionine, $1.0 \times 10^{-2}$ mole/l of ferrous ions, $5.0 \times 10^{-5}$ mole/l of ferric ions, and $3.0 \times 10^{-3}$ mole/l of hydrogen ions. A 750-watt photoflood lamp was the source of illumination. A maximum efficiency of 0.0003% was reported. The maximum power level can be calculated from their data to be $1.8 \times 10^{-7}$ watts/sq cm.

The low power was attributed to a high electrode polarization. The actual internal resistance was about 100 ohms, but the cells were characterized by an apparent internal resistance in the range of $10^4$ to $10^5$ ohms. The dark and the illuminated electrodes were approximately equally polarized.

The authors computed what they claim to be the maximum theoretical efficiency. The power efficiency they assumed to be equal to the photon efficiency, $I_c/N$, times the voltage efficiency, $E_c^2/\epsilon$, where $I_c$ is the short circuit current, $N$ is the number of photons absorbed per second, $E_c^2$ is the open circuit voltage, and $\epsilon$ is the average energy per photon absorbed by thionine in electron volts. The maximum theoretical photon efficiency and voltage efficiency were calculated to be 70% and 8.7%, respectively. Only 50% of this power would be delivered to an external load, they explained, since 1/2 of the power was lost on the internal resistance. The maximum theoretical efficiency was thus purported to be $0.70 \times 0.087 \times 0.50 = 0.03$, or about 3%.

There are a number of errors in this calculation. First, the voltage they observed (0.182 V) was by no means the maximum theoretical voltage. Second, the calculation of the voltage efficiency

$$\frac{E_c^2}{\epsilon} = \frac{0.182 \text{ V}}{2.1 \text{ eV}}$$

would give an answer with the dimensions of coulombs, and not % efficiency. Third, no relationship between the voltage and the energy of the absorbed photons can be expected, since the potential of a redox
couple is dependent upon the concentrations of the reduced and the oxidized forms as well as upon the standard potential. The concentrations are in turn dependent upon the number of photons absorbed per unit volume per unit of time and not simply upon the energy of each photon. Therefore, dividing the voltage by the energy per photon has no significance. Fourth, Potter and Thaller demonstrated that maximum power can be obtained when the load resistance is equal to the apparent internal resistance. Since for their cells the apparent internal resistance was about 100 to 1000 times the actual ohmic resistance of the cell, very little power was lost on the internal resistance. The voltage drop under conditions of maximum power was essentially entirely across the external resistance. Consequently the power delivered to the load is not limited to 50% as they claimed.

By using platinum black electrodes and citric acid instead of hydrochloric acid, Potter and Thaller were able to increase the photogalvanic potential to 245 mv, but the potential developed over a period of 45 minutes. For this solution they calculated that an efficiency of 0.05% could theoretically be obtained. The effect of the citric acid on the extent of bleaching was not discussed. Undoubtedly it tied up the ferric ion in a complex and increased the extent of bleaching. A change in the dark potential must have occurred, also.

Rabinowitch reported that efficiencies of up to a few tenths of one percent$^{56}$ or even one percent$^{54}$ could be achieved. The statements were not supported by experimental details.

3.2.2.4 Decomposition

While no one else seems to have encountered serious trouble with the decomposition of the dye during the photochemical studies, Potter and Thaller$^{49}$ found this to be the major problem of their photogalvanic cells. They prepared their test solutions under nitrogen from air-free stock solutions. The stock solutions deteriorated so rapidly that they never used solutions over 48 hours old.
The original photogalvanic potential could never be duplicated after a current was drawn from the cell. Analysis of the used solution revealed a colorless compound which they believed to be a product of the decomposition of the dye. The decomposition was so rapid that it was not feasible to investigate concentration polarization effects, which would have required about 1/2 hour of operation. Apparently deterioration was quite obvious even after a few minutes of cell operation.

Although it was not explicitly stated, cell deterioration was apparently associated with the electrode reaction. The maximum photogalvanic potential of one cell was not established until after 45 minutes or even an hour of illumination. Yet for another cell deterioration was so rapid when current was drawn that it severely reduced the photogalvanic potential within 3 minutes. The nature of this deterioration is the subject of further discussion in Section 4.

3.2.2.5 Energy Storage Possibilities

Anderson has demonstrated a method of separating the leucothionine from the ferric ions by absorbing the reduced dye in starch and allowing the ferric ion to diffuse out. This represents a means of storing energy, but only for a very short time. Rabinowitch described a way of separating leucothionine from ferric ions by partitioning them between water and ether. The only feasible means presently available for storing energy from photogalvanic cells is to use storage batteries or some similar device in which an auxiliary redox system is utilized.
SECTION 4

EXPERIMENTAL PROGRAM

The experimental program was designed to accomplish the following tasks: (1) to clarify the electrode processes and to obtain a better understanding of why a photogalvanic effect exists; (2) to investigate the efficacy of certain specific measures, namely, to complex the ferric ions, to alter electrode configurations and conditions, and to illuminate the electrodes in an alternating fashion; and (3) to construct and test compact laboratory model cells using the background of information obtained. In practice, however, it was impossible, to keep the program neatly compartmented.

The results are presented in the following order: equipment and materials; electrode configurations and conditions; electrode processes; the effect of complexing agents and additives; the effect of pulsed or alternating illumination, and testing of the laboratory model cells. The presentation on equipment and materials will describe the mechanics by which the data were obtained. The discussion will then turn to the development of the theories which were consistent with the behavior of the photogalvanic cells. It will conclude with a study of practical means of increasing the power and the presentation of a series of measurements on three model cells.

4.1 EQUIPMENT AND MATERIALS

4.1.1 Optical Systems

Most of the early work on this program was carried out with a 1000-watt tungsten filament projection lamp as the light source. It was incorporated in the optical system shown in Figure 2. For certain specific experiments the filter combination was varied or the position of the light was altered so as to change the light from an approximately parallel to a focused beam. Each of these modifications has been designated OS-1-a, OS-1-b, etc., for reference in the remainder of the report.
FIGURE 2. OPTICAL SYSTEM OS-1

Legend:

OS-1-a:

A = spherical mirror
B = 1000-watt tungsten filament projection lamp in forced-air cooled housing
C = 3" diameter quartz lens with 3" focal length, placed so as to illuminate H with approximately parallel light
D = 16.6 cm flowing water filter
E = 9.6 cm saturated ferrous sulfate solution filter
F = shutter with aperture slightly larger than cell window
G = Corning CS-1-59 infrared filter
H = photovoltaic cell

OS-1-b: similar to OS-1-a, but with G removed
OS-1-c: similar to OS-1-a, but with G and E removed
OS-1-d: similar to OS-1-a, but with light concentrated on cell window
OS-1-e: similar to OS-1-b, but with light concentrated on cell window
OS-1-f: similar to OS-1-c, but with light concentrated on cell window
OS-1-g: similar to OS-1-d, but with a 750-watt lamp (1000-watt lamp not available at the time)
Late in the program a Hanovia 1000-watt mercury-xenon compact arc lamp became available. The optical system used with this source is shown in Figure 3 and is designated OS-2-a, etc.

The intensities of illumination in these optical systems have been determined, and in Table 2 they are compared with terrestrial solar intensity. Only the designated spectral range is considered, and the solar intensities shown are those calculated for light passing through the same filter combination. The 5100-6300 Å range is the spectral range believed to be most effective. The light intensities in systems OS-1-a to c are only approximate, since they were measured for only one lamp. The lamp life was about 10 hours.

A description of the intensity measurements and the spectral distributions of the energy is provided in Appendix.

The optical systems used in the study of the electrode processes are described in Section 4.1.4 with the remainder of the apparatus used for that purpose.

4.1.2 Photogalvanic Cells

The photogalvanic cells which were constructed for various specific studies are shown in Figures 4-9. Several modifications of the cell in Figure 4 are indicated. These experimental cells are referred to by number throughout the report (e.g., EC-1-b). All of the electrodes were made of 95.95% pure platinum wire, sheet or mesh unless otherwise indicated.

The cells in Figures 4, 6 and 7 have no provision for deaerating the photogalvanic solution. In spite of this, considerable useful data were obtained with these cells, and EC-1-c produced the most power per unit of illuminated surface area.

EC-4 was somewhat inconvenient in that slight movements in the top joint caused the illuminated electrode to move slightly which in turn made significant differences in the photogalvanic potential if concentrated solutions were used. The provision for the constant temperature bath of EC-4 was never used.
FIGURE 3. OPTICAL SYSTEM OS-2

Legend:

OS-2-b: Approximately parallel light on cell.
A 1000-watt Hanovia mercury-xenon compact arc lamp in forced-air cooled housing
B 3" diameter quartz lens with 3" focal length
C 15 cm water filter
D neutral density or colored filters (optional)
E shutter with aperture slightly larger than cell window
F Corning CS-1-59 infrared filter
G light baffle with aperture slightly larger than cell window
H photogalvanic cell

OS-2-a: similar to OS-2-b, but with G removed and with the light focused on the cell

OS-2-c: similar to OS-2-a, but with Corning filters CS-2-73 and CS-4-70 and Bausch and Lomb interference filter 602 added (see Figure 32 for spectrum)
Table 2
Light Energy through Filters Used for Photogalvanic Cells

<table>
<thead>
<tr>
<th>Light Source</th>
<th>Optical &amp; Filter Combination</th>
<th>Total Energy Transmitted $\text{watts/cm}^2$</th>
<th>Portion of Transmitted Energy in 5100-6300Å Band $\text{watts/cm}^2$</th>
<th>$\text{no. suns}^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000 W Tungsten</td>
<td>OS-1-a</td>
<td>0.023</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>OS-1-b</td>
<td>0.027</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>OS-1-c</td>
<td>0.175</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>1000 W Hg-Xe</td>
<td>OS-2-a</td>
<td>0.100</td>
<td>2.9</td>
<td>0.047</td>
</tr>
<tr>
<td></td>
<td>OS-2-b</td>
<td>0.016</td>
<td>0.7</td>
<td>0.012</td>
</tr>
<tr>
<td></td>
<td>OS-2-c</td>
<td>0.0002$_6$</td>
<td>---</td>
<td>0.0002$_6$</td>
</tr>
<tr>
<td>Solar (on Earth)</td>
<td>OS-2-a</td>
<td>0.035</td>
<td>1.0</td>
<td>0.011</td>
</tr>
</tbody>
</table>

* Refers to the equivalent solar intensity through the same filter combination.
FIGURE 4. PHOTOCALVANIC CELL EC-1

Legend:

EC-1-a:

1. Flat Pyrex glass window, 20 mm in diameter, fastened to end of 18 mm OD Pyrex tubing with Glyptal or Scotchcast 808.

2. Illuminated electrode made of 20 ga platinum wire and consisting of a spiral parallel to window 1 with an insulated lead.

3. Measuring scale marked in millimeters fastened to the outer surface of the cell and located parallel to a long, narrow, viewing window, the remainder of the cell being painted a flat black.

4. Two-way stopcock used in filling cell.

5. Dark electrode made of 20 ga platinum wire.

6, 7. Rubber stoppers with holes for electrodes.
Legend for Figure 4 (continued)

EC-1-b: Electrode 2 replaced by that shown in Figure 5; electrode 5 replaced by a 1 sq inch piece of 52 mesh platinum gauze.

EC-1-c: Electrode 1 replaced by platinum plate electrodes of different sizes perpendicular to window 1 and with uninsulated platinum wire leads; electrode 5 replaced by a 1 sq inch piece of 52 mesh platinum gauze.

EC-1-d: Electrode 2 replaced by a 1 sq cm plate parallel to window 1 with an insulated lead; electrode 5 replaced as specified in text.

EC-1-e: Similar to EC-1-d, but with electrode 5 replaced by a 1 sq inch piece of 52 mesh platinum gauze.
FIGURE 5. ELECTRODE WITH PARALLEL PLATES
FIGURE 6. PHOTOGALVANIC CELL EC-2

Legend:

EC-2-a:

1. Flat Pyrex glass window, 20 mm in diameter, fastened to end of 20 mm Pyrex glass tubing with Glyptal.

2, 6 Rubber stoppers with holes for the electrodes.

3. Illuminated electrode consisting of 11.1 x 11.7 mm platinum plate welded to 20 ga platinum wire lead.

4. Two-way stopper used in filling cell.

5. Dark electrode made of 20 ga platinum wire with 2 cm length in the solution; later replaced by a 1 sq inch piece of 52 mesh platinum gauze.

EC-2-b: Similar to EC-2-a, but with the electrode shown in Figure 5 in place of the illuminated electrode 1.
For electrode materials see Tables 7 and 9.

FIGURE 7. PHOTOGALVANIC CELL EC-3
FIGURE 8. PHOTOCALVANIC CELL EC-4
FIGURE 9. PHOTOGALVANIC CELL EC-5
EC-5 was prepared for use with solutions for which both the dark and the illuminated electrode potentials were of interest. In addition to the electrode potentials, the effect of the composition of the solution on the current can also be studied. Unfortunately this cell was prepared too late in the program and the press of meeting contractual obligations prevented its use. It is presented here, however, because it is felt that such a cell would be of greatest value in any future experimental program.

In addition to the experimental cells, six laboratory model cells were fabricated. The first three of these (MC-1, 2 and 3) were constructed from Lucite and failed to yield significant potentials. The cause of this poor performance is not yet clear, but at the time it was blamed on the extraction of materials from the Lucite containers. As a result, MC-4, 5 and 6 were constructed of glass, and extensive tests were made on these. Drawings and photographs of these cells are provided in Figures 10-25. The epoxy resin Scotchcast 808 was used to seal in the electrodes and to join the various portions of MC-4.

The cell which was an integral part of the apparatus for the study of electrode processes is described in Section 4.1.4.

4.1.3 Electronic Equipment

Measurements of the photogalvanic potential and of the current were made with a Sanborn 150 dual channel recorder and a Keithley Instrument 610A electrometer connected in parallel in the external circuit. The input resistance of the electrometer could be varied between 1 and \(10^{14}\) ohms. The voltage drop across these resistances was measured by both the electrometer and the recorder. Since the resistances in the electrometer were varied only by powers of 10, the current could readily be calculated from the voltage and the electrometer resistance. The input resistance of the recorder was so high that at no time did the removal of the recorder from the circuit affect the electrometer readings. In addition to serving as a check on each other, the two instruments were complementary in that the electrometer was more accurate at low potentials and the recorder provided a permanent record.

Cell resistances were measured with a General Radio Model 1650A impedance bridge.
Leads .032 Dia. Platinum Wire Fused to Gauze

Fill Tube

Front View (Actual Size)

Black Blotter Paper

Side View (Actual Size)

52 Mesh Platinum Gauze

Detailed Cell Construction - Enlarged 4 Times

FIGURE 16. PHOTOG.-LVANIC CELL MC-1
Note: Plexiglass Construction

Figure 12. PHOTOGALVANIC CELL MG-2 (Actual Size)
Plexiglass Construction (Typical)

Front View

Side View

1/2" x 6" 52 Mesh Platinum Gauze Folded (Typical)

opening thru cell dividers

FIGURE 14. PHOTOGALVANIC CELL MG-3 (Actual Size)
Figure 16. Photogalvanic Cell MC-4 for the Study of Alternating Illumination
Figure 18. Top View of Laboratory Model Cell MG-4
Figure 19. LONGITUDINAL CROSS SECTION OF LABORATORY MODEL CELL
MC-5
Figure 20. ILLUMINATED ELECTRODE - FRONT VIEW
(MC-5)
Figure 22. LONGITUDINAL CROSS SECTION OF LABORATORY MODEL CELL MC-6
Figure 23. ILLUMINATED ELECTRODE - FRONT VIEW
(MC-6)

25 mm

Platinum Plates
3/8" wide
about 1 mm apart

Platinum Spacers

20 ga. Platinum Wire Lead
Figure 24. Laboratory Model Cell MC-6
Light intensities were determined with a large surface bolometer (made by R. H. Röhig) and an Eppley thermopile. In the light intensity determinations, voltages were measured with a Keithley Instrument 149 milli-microvoltmeter.

pH measurements were made with a Beckman Model G pH meter using a glass electrode with a saturated calomel electrode reference. Concentrated thionine solutions sometimes deposited dye in the fiber of the calomel electrode and caused drifting. A potassium chloride solution with a capillary connection to the thionine solution was inserted as an additional salt bridge to prevent this.

4.1.4 Apparatus for the Study of Electrode Processes

The study of electrode processes was carried out with the apparatus shown diagrammatically in Figure 26 and in the photographs in Figures 27 and 28. The legend accompanying Figure 26 describes the function of the various parts of this apparatus. In brief, the system provided means for preparing, storing, and dispensing deoxygenated solutions of thionine, leucothionine, ferric sulfate, ferric sulfate, and two dilute sulfuric acid solutions. The solutions could be mixed in known proportions and transferred to either of two electrode compartments. The two compartments were connected by means of a salt bridge which could be employed by turning the V-bore stopcocks open to the bridge. Figure 29 is a close-up showing the relationship of these electrode compartments.

The system was freed from oxygen by evacuating it and flushing it with prepurified nitrogen which was passed over copper turnings at 300°C. Solution transfers were made utilizing gravity as well as pressure differences.

In one electrode compartment (see Figure 30) the solution could be illuminated in one direction with an intense light and at the same time be analyzed by measuring the absorption of a weak beam of light perpendicular to the exciting beam. The electrode was a 20 gauge platinum wire which extended into the solution where the two beams intersected. A saturated calomel electrode was used for reference. The salt bridge from
Figure 26. Diagram of the Apparatus for the Study of Electrode Processes
(See legend on next page)
Legend: For Figures 26-29.

1. Reservoir for denaturation of ferrous sulfate solution.
2. Column packed with iron powder for reduction of ferric impurities in ferrous sulfate solution.
3. Reservoir for purified ferrous sulfate solution.
4. Flask used for preparation of leucothionine by hydrogenation.
5. Fritted glass filter for removing catalyst from leucothionine solution.
6. Reservoir for leucothionine solution.
7. Reservoir for ferric sulfate solution.
8. Reservoir for thionine solution.
9. Reservoir for sulfuric acid solution with a low pH.
10. Reservoir for sulfuric acid solution with a higher pH.
11. Vacuum line.
15. Nitrogen purification tube (heated copper turnings to remove oxygen).
16. Stopcock to be used with that at 14 for regeneration of copper from copper oxide by means of a hydrogen gas stream.
17. Manifold for dispensing solutions (2 stoppered openings for possible use with other solutions).
19. Mixing chamber containing magnetic stirring bar.
20. Stopcock for diverting solutions to either cell.
21. Stopcock for diverting flow to waste reservoir 26 during washing of burette.
22. Illuminated electrode compartment.
23. Dark electrode compartment.
24. Reservoir for potassium chloride solution for salt bridge.
25. Salt bridge (bounded by 3 stopcocks, each of which can divert the flow to the waste reservoir 26).
26. Reservoir for waste.
Figure 7. Apparatus for Study of Tellurium Photocell Anode Processes
Figure 28. Apparatus for Studying Thiourea Photovoltaic Electrode Processes with Illumination System Removed.
Figure 29. Apparatus for Studying Thionine Photogalvanic Electrode Processes. Close-up of Electrode Compartments.
FIGURE 30. THE ILLUMINATED ELECTRODE COMPARTMENT
from the reference electrode was in contact with the test solution by means of an asbestos fiber. A stopcock in the salt bridge was kept closed at all times when the pressure in the system was not atmospheric pressure. This was necessary to prevent disturbance in the calomel electrode. A pressure equalizing tube equalized the pressures above the test solution and above contiguous salt solution in the bridge. This was required in order to prevent a vacuum in the electrode compartment from drawing the potassium chloride solution out of the bridge through the asbestos fiber.

The drawing in Figure 30 and the photograph in Figure 29 show the illuminated electrode compartment before constant temper- ature coils were added. The compartment was first painted black to reduce light reflections. A coil of $\frac{1}{8}$" copper tubing was then wrapped around it. Copper wire was used to wrap both the compart- ment and the tubing in order to enhance heat flow between the coil and the solution. A second coil of $\frac{3}{16}$" copper tubing was added, and the whole was wrapped with more copper wire and covered with asbestos, leaving only the windows exposed. The temperature of a thionine solution as measured by a thermometer in the normal elec- trode position could be controlled to within 0.2°C by controlling the temperature of the water in the coils. The extremes of temperature variation were observed before illumination was begun and after about 1/2 hour of illumination. Since the temperature of the solution was not determined while actual electrical measurements were being taken, it seemed reasonable to widen the limits of reliability to $\pm 0.3°C$.

The optical systems which were used to effect the reduction of thionine and to measure the thionine concentration in the photostation- ary state are diagramed in Figure 31. The spectrum of the filter combination which was used to obtain approximately monochromatic light in the analytical system is given in Figure 32. The light ab- sorption was approximately linear with the absorbance at the 6000 Å absorbance peak, as is shown in Figure 33. Figure 34 presents the calibration curve used in determining the thionine concentrations in the illuminated cell compartment. This curve corrected at once for the use of non-monochromatic light, for the unmeasured path length through the solution, and for the variation in the molar absorption
FIGURE 31. OPTICAL SYSTEMS USED IN THE STUDY OF ELECTRODE PROCESSES
Legend: (Figure 31)

A  illuminated cell compartment with platinum wire electrode in path of analyzing light beam
B-G  analytical optical system
G-M  excitation optical system
B  2 watt tungsten concentrated arc lamp
C  variable neutral density filter
D  convex lens surrounded by light baffle (5/8" diameter, 1-1/2" focal length)
E  light filters: Bausch and Lomb interference filter 602-46-22, Corning Glass filters #273 and #470
F  30 cm collimating tube
G  phototube
H  10 cm collimating tube with attached shutter and light baffle
I  neutral density filter (optional)
J  9.8 cm saturated ferrous sulfate solution filter
K  10.6 cm flowing water filter
L  light baffle
M  3" diameter quartz lens with 3" focal length
N  1000-watt tungsten filament projection lamp backed up by spherical mirror and contained in a forced-air cooled housing
Figure 32. Spectrum of Filter Combination for Spectral Analysis of Thionine
Figure 33. Calibration Curve for Thionine Absorbance Measurements on the Optical Bench using the Interference Filter Combination.
Figure 34. Thionine Concentration in the Illuminated Cell Compartment as a Function of the Measured Absorbance
coefficient with concentration. Very little scattered light from the projection lamp reached the phototube, and that which did could be corrected for by an appropriate adjustment of the zero level response. The response of the phototube was translated directly into absorbance and percent transmission by a DC photovoltaic (Model No. 501 M, Photovolt Corporation).

The intensity of the exciting light was varied by inserting neutral density filters in the light path. The percentages of light transmitted by these filters were measured for the 5000-6500 Å region of the spectrum where thionine absorbs most strongly. The percent transmission at 5850 Å was taken as a measure of light intensity. This wavelength is the center of the absorption band of thionine at an absorbance 1/2 of that of the absorption peak. The absorbance of the filters over the entire 5000-6500 Å range did not vary by more than ± 3% of the absorbance at 5850 Å with but one exception. The exception was the filter with an absorbance of 0.075 (84.1% transmission), which varied by ± 7% of the absorbance at 5850 Å.

A drawing of the dark electrode compartment is given as Figure 35. No provision for illumination or temperature control was required.

4.1.5 Solutions

Thionine solutions were prepared from commercial thionine without purification and were filtered before use. The concentration was determined spectrophotometrically assuming a molar absorptivity of 7,00 x 10^4 for the absorption maximum at 6000 Å. 59

Ferrous sulfate solutions were prepared by dissolving a weighed amount of the analytical reagent grade in very dilute sulfuric acid (pH of about 2).

Concentrated ferric sulfate solutions were standardized against potassium dichromate. 34 Allquots were diluted to prepare solutions of the required concentrations.
Figure 35. DARK ELECTRODE COMPARTMENT
Stock organic solvents were used without purification except for tetrahydrofuran. Commercial tetrahydrofuran was treated with an aqueous solution of ferrous sulfate and sodium hydrogen sulfate to remove peroxides, dried first over sodium hydroxide pellets and then over anhydrous calcium sulfate, and distilled in the presence of a few ferrous sulfate crystals. The purified solvent was stored in the dark.

The solutions used in the vacuum rack (Figures 27-29) had to be analyzed after their preparation and de-aeration. The ferrous sulfate solution in flask 1 (Figure 27) was slowly passed through the tube 2 loosely packed with iron powder to reduce ferric impurities. The purified solution was stored in flask 3. A sample was withdrawn for iron analysis and pH determination. The sample was passed into the dark electrode compartment 23 and pipetted out. The solution storage flasks were closed to the atmosphere at all times, and the system was evacuated and thoroughly flushed with nitrogen before measuring out samples.

Leucothionine was prepared by hydrogenating an aqueous solution of thionine in flask 4 in the presence of Adams' catalyst. The flask was then connected to the vacuum system, and the connecting lines were evacuated and repeatedly flushed with nitrogen. The leucothionine solution was filtered through the fritted glass disc 5 and stored in flask 6. Analytical samples were withdrawn in the manner described above and oxidized with air for spectrophotometric analysis.

The first 50 ml always turned blue on passing through the fritted disc and had to be drained from flask 6. Whenever the leucothionine was exposed to light for about a day, the solution developed a light blue color. The solution was consequently protected from light by painting flasks 4 and 6 black and covering the connecting lines with aluminum foil. Even so, the leucothionine was slowly oxidized during long periods of storage, probably by small oxygen leaks into the system.

The ferric solution in flask 7, the thionine solution in flask 8, and the dilute acid solutions in flasks 9 and 10 were purged with prepurified nitrogen for two hours and then were degassed under vacuum for 3 hours. The latter three solutions were analyzed in the usual manner.
but the ferric solution was too dilute for volumetric analysis. Suitable aliquots of the ferric solution (containing from $3 \times 10^{-6}$ to $1 \times 10^{-5}$ equivalents of iron) were mixed with 10 ml of 3 M hydrochloric acid and 10 ml of 5 M ammonium thiocyanate and diluted to 100 ml. The absorption of the solution at the maximum of 4840 Å was followed for several minutes. The absorption was extrapolated back to zero time, the time at which the thiocyanate was added. The value of a blank determination was subtracted, and the concentration was taken from a plot of absorption versus concentration made by treating a series of standard solutions in the same manner.

4.2 ELECTRODE CONFIGURATIONS AND CONDITIONS

4.2.1 Electrode Orientation and Surface Area Effects

The first set of experiments was designed to determine the relationship between the potential and the distance separating the illuminated electrode from the illuminated surface of the solution. Optical system OS-1-d and cell EC-1-a (shown in Figure 7) were used. The position of the illuminated electrode (2) was adjusted by sliding it in and out of the stopper (7).

Solution I-2-1 was used in this and a number of other experiments. Its composition was as follows:

- Thionine: $4 \times 10^{-5}$ M
- FeSO$_4$: $1 \times 10^{-2}$ M
- Fe$_2$(SO$_4$)$_3$: unknown quantity introduced as an impurity in the FeSO$_4$ or formed by subsequent oxidation
- pH: $\sim 2.5$

Careful control of the composition was not considered necessary at the time because the experiments in which this solution was used were designed to study electrode parameters only. Although no special provision was made to eliminate oxygen, other than to keep the flask stoppered, and although it was exposed to room lighting for much of the time, the solution yielded approximately the same photogalvanic potential.

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over a period of 3 months. The stability of the solution was consider-
ably greater than one would expect from the report of Potter and Thaller, who found it necessary to prepare fresh electrolyte under nitrogen, from stock solutions no more than 48 hours old.

Because of tendency for the photogalvanic potential to change for any given electrode position while measurements were being made, a simple routine was finally adopted. The potential obtained with the electrode against the window was used to follow cell changes. Each measurement at any other position was preceded and followed by measure-
ments with the electrode against the window. The potential was then divided by the average of the preceding and following potentials to give an "adjusted" potential for that position. This treatment put all measure-
ments on the same basis.

A typical set of data is given in Table 3. Figure 36 is a plot of the summarized data from 53 measurements. This plot, as well as plots of other data, indicated that the potential decreased logarithmically with the distance between the electrode and the window.

Since according to Beer's law the light intensity decreases loga-
ithmically with its path through an absorbing solution, one might antici-
pate that the electrode potential is approximately linear with the light intensity. As will be seen in Section 4.1.2.3, this is not the case. Furthermore, this line of reasoning ignores the bleaching of the solution. The logarithmic relationship is consequently an approximate result of all factors (light absorption, bleaching, relationship between bleaching and light intensity and between potential and bleaching). It should be used only as a rule of thumb which may vary somewhat from one solution to another.

A second set of experiments was designed to determine the effect on the photogalvanic potential of orienting the illuminated electrode either parallel or perpendicular to the light beam. The cell used in these experi-
ments was EC-2-a, the solution was I-2-1, and the optical system was OS-1-d. The illuminated electrode was rotated, and the potential was determined for positions with each side and each edge facing the window. The center of the electrode was kept in approximately the same spot regardless of orientation.
<table>
<thead>
<tr>
<th>Distance from Window, mm</th>
<th>Potential, mv</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dark</td>
<td>Illuminated</td>
</tr>
<tr>
<td>0</td>
<td>-14</td>
<td>+76</td>
</tr>
<tr>
<td>22.5</td>
<td>-14</td>
<td>-7</td>
</tr>
<tr>
<td>0</td>
<td>-14</td>
<td>+74</td>
</tr>
<tr>
<td>7.5</td>
<td>-15</td>
<td>+36</td>
</tr>
<tr>
<td>0</td>
<td>-15</td>
<td>+74</td>
</tr>
<tr>
<td>17.5</td>
<td>-15</td>
<td>-3</td>
</tr>
<tr>
<td>0</td>
<td>-15</td>
<td>+71</td>
</tr>
<tr>
<td>2.5</td>
<td>-15</td>
<td>+54</td>
</tr>
<tr>
<td>0</td>
<td>-6</td>
<td>+78</td>
</tr>
<tr>
<td>12.5</td>
<td>-15</td>
<td>+9</td>
</tr>
<tr>
<td>0</td>
<td>-10</td>
<td>+75</td>
</tr>
</tbody>
</table>
FIGURE 36

The Relationship between the Photogalvanic Potential and the Distance Separating the Illuminated Electrode from the Illuminated Surface of the Solution
A decrease in potential was anticipated for the perpendicular orientation. The plate (1.11 x 1.17 cm) was in contact with a dark solution on the side facing its own shadow, and this was expected to behave like a short circuit. The electrons could simply pass through the electrode to the dark solution and would not need to pass through the external circuit. Nevertheless, after taking more than 100 measurements, no significant difference could be detected between the parallel and the perpendicular positions. Even when appreciable current was drawn from the cell no differences were evident. The dark electrode was made of a one inch square of 52 mesh platinum gauze to increase the dark electrode surface to more than twice that of the illuminated electrode, but this, too, had no effect.

A more severe test of orientation effects was made by employing an electrode with four parallel plates (EC-2-b; Figures 5 and 6). In the perpendicular orientation 3 1/2 plates were at least partially shielded from the light. When the plates were parallel to the light the photogalvanic potentials averaged 80% higher than those of the perpendicular orientations. This was the expected result, but the perpendicular arrangement did not diminish the photogalvanic potential as much as had been anticipated.

The third set of experiments was planned to investigate the effects on voltage and current incurred by placing parallel plates on the illuminated electrode in close proximity to one another. Thus it was anticipated that moving the plates close to one another would tend to deplete the surrounding solution of the reactive species more quickly than when the plates were far apart.

Cell EC-1-b, Solution I-2-1, and OS-1-g were used in making these measurements. The illuminated electrode was withdrawn from the cell between measurements and the plates were readjusted to a new position each time. The manipulation was found to have no effect on the photogalvanic potential.

The data for this study are recorded in Table 4. It can be seen that a spacing of 1 mm or more had no effect on the power level. Pressing the plates together, however, although this was done only loosely,
TABLE 4
Effect of Distance between Parallel Plates of Illuminated Electrodes on Photogalvanic Potential

<table>
<thead>
<tr>
<th>Distance between Plates, mm</th>
<th>Photogalvanic Potential, ( \text{mv, and Current, amp} \times 10^7 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>8/3</td>
<td>46.5</td>
</tr>
<tr>
<td>4/3</td>
<td>44</td>
</tr>
<tr>
<td>8/3</td>
<td>42.5</td>
</tr>
<tr>
<td>4/3</td>
<td>42</td>
</tr>
<tr>
<td>8/3</td>
<td>43</td>
</tr>
<tr>
<td>5/3</td>
<td>42</td>
</tr>
<tr>
<td>8/3</td>
<td>40</td>
</tr>
<tr>
<td>pressed together</td>
<td>27</td>
</tr>
<tr>
<td>8/3</td>
<td>42</td>
</tr>
<tr>
<td>pressed together</td>
<td>26.5</td>
</tr>
<tr>
<td>8/3</td>
<td>42</td>
</tr>
</tbody>
</table>

* The overall distance between the first and fourth plates divided by the three spaces between the plates. The middle plates were spaced as evenly as possible in between.

** With a load resistance of 10^4 ohms.
decreased the output to almost that of a single plate (2.35 μa, 23.5 mv). Similar results were obtained with 3 plates and 2 plates, although the voltage and the current each decreased proportionately for the separated plates.

The effect of the number of plates in the illuminated electrode on the power is shown in Figure 37. It was apparent that the power was highly dependent upon the surface area of the illuminated electrode. The implications are discussed in Section 4.4.1.

The effect was demonstrated further by comparing the power obtainable from a cell with 1 cm² plate electrode parallel to the illuminated surface with that obtainable by using 8 plates (in an electrode similar to that in Figure 5) perpendicular to the illuminated surface. All other variables were kept constant. The illuminated surface over the 8 plates was about 0.8 times that over the single plate, but the 8 plates produced over 20 times the power of the single plate.

A similar study was made on the effect of the dark electrode surface area using cell EC-1-d, Solution I-2-1, and optical system OS-1-d. The dark electrode consisted of five parallel platinum plates in a wire holder, its surface area being varied by removing the plates one by one. The smaller surface areas were provided by replacing this with a 20 gauge platinum wire electrode. The surface of this electrode was varied by exposing various lengths of wire to the solution.

The results have been expressed in terms of apparent internal resistance, a quantity also determined by Potter and Thaller to describe their cells. The quantity can be calculated by means of the following equations:

\[ V_t = \frac{E R_{ext}}{R_{ext} + R_{int}} \]  \hspace{1cm} (12)

or \[ R_{int} = \frac{R_{ext} (E - V_t)}{V_t} \]  \hspace{1cm} (13)
Figure 37. THE EFFECT OF THE ILLUMINATED ELECTRODE SURFACE AREA ON THE POWER (EC-1-b, I-2-1, OS-1-g)
where \( V_t \) = terminal voltage, or the voltage drop across the resistance in the external circuit

\[ E = \text{reaction potential} \]

\[ R_{ext} = \text{resistance in the external circuit} \]

\[ R_{int} = \text{apparent internal resistance} \]

When \( R_{ext} \) is very much larger than \( R_{int} \), \( E \) equals \( V_t \). The measurements which are required for the calculation are, therefore, the terminal voltages both with a huge external resistance and with an external resistance approximately equal to the apparent internal resistance. It must be pointed out that the apparent internal resistance of the cell can be much greater than the actual ohmic resistance as measured by a high frequency impedance bridge.

The data from this study are recorded in Table 5 and are plotted in Figure 38. The apparent internal resistance increased for a given electrode area while the series of measurements was being taken (note measurements 1 and 12). In spite of this the results are sufficiently clear to demonstrate that the power of the cell is relatively insensitive to the surface area of the dark electrode until it is approximately equal to or smaller than the area of the illuminated electrode.

4.2.2 Electrode Activation

Probably the most fascinating observations made in this program were those concerning electrode activation. Numerous incidental observations were made while carrying out experiments which were primarily concerned with other objectives. Nevertheless, this subject remains the most mysterious factor governing the performance of the photovoltaic cells.

No mention was made in the literature of the necessity for any electrode activation procedure. In the first experiments performed on this project the electrodes were activated accidentally without any activation step being evident. It seems likely that activation was also overlooked in previous investigations.
<table>
<thead>
<tr>
<th>Chronological Order of Measurement</th>
<th>Dark Electrode Surface Areas, cm²</th>
<th>$R_{int} \times 10^{-4}$, ohms</th>
</tr>
</thead>
<tbody>
<tr>
<td>1, 12</td>
<td>13.14</td>
<td>4.2, 6.1</td>
</tr>
<tr>
<td>2</td>
<td>10.63</td>
<td>4.7</td>
</tr>
<tr>
<td>3</td>
<td>7.98</td>
<td>4.5</td>
</tr>
<tr>
<td>4</td>
<td>5.71</td>
<td>4.7</td>
</tr>
<tr>
<td>5</td>
<td>1.42</td>
<td>5.3</td>
</tr>
<tr>
<td>6</td>
<td>1.45</td>
<td>5.5</td>
</tr>
<tr>
<td>11</td>
<td>0.89</td>
<td>6.3</td>
</tr>
<tr>
<td>7</td>
<td>0.51</td>
<td>6.0</td>
</tr>
<tr>
<td>8</td>
<td>0.25</td>
<td>8.2</td>
</tr>
<tr>
<td>9</td>
<td>0.10</td>
<td>14</td>
</tr>
<tr>
<td>10</td>
<td>0.05</td>
<td>31</td>
</tr>
</tbody>
</table>

* Illuminated electrode was a platinum plate oriented perpendicular to the light so that a surface area of 1 cm² was illuminated.
Figure 38. THE DEPENDENCE OF APPARENT INTERNAL RESISTANCE ON THE DARK ELECTRODE SURFACE AREA (SURFACE AREA OF ILLUMINATED ELECTRODE = 2.9 cm², 1/2 OF WHICH WAS ILLUMINATED)
The extreme importance of electrode activation first became apparent in an experiment which was intended to be a study of electrode configurations. Two electrodes of different shapes and sizes were fashioned out of the same piece of 99.95% pure platinum plate. They were not treated in any way before testing them as the illuminated electrode in EC-1-c. Exceptionally low photogalvanic potentials were obtained (4 and 6 mv; see Table 6). After remaining in the closed cell for 24 hours, electrode B exhibited a photogalvanic potential of 21 mv while electrode A, when placed in the same solution, still yielded only a few millivolts. Upon placing A in the cell for a prolonged period of time, it, too, gave higher photogalvanic potentials. Some of these changes undoubtedly took place in the electrolyte, but further perusal of Table 6 will reveal that wide discrepancies in the photogalvanic effect were found for the same electrolyte by simply changing electrodes, and that the electrode which most recently was in prolonged contact with the solution was favored. The electrolyte clearly activated the electrode surface for enhancement of the photogalvanic effect.

Alternative methods of electrode activation were studied in another series of experiments. Five identical pairs of platinum electrodes were cut from the same sheet. Each was given a different treatment as shown in Table 7. The electrodes were then checked in EC-1 using OS-1-2, each with fresh portions of the same stock electrolyte solution (I-2-1). The results again indicated that the electrolyte itself did an excellent job of electrode activation.

Electrode pair 2, after the methanolic potassium hydroxide-dilute aqua regia treatment, was platinized and tested again. The result, as indicated in Table 7, was completely disappointing. The experiment was repeated later with a nitrogen-purged solution, but it yielded only 1 mv.

At the close of the series of experiments described in Table 6, a new series was undertaken with electrode B as shown in Table 8. The same solution (I-2-1) was used throughout this series with occasional replenishment from the stock solution. The changes occurring in the bulk of the solution must have been small, but the photogalvanic potential was quite dependent upon the treatment given the electrode.
<table>
<thead>
<tr>
<th>Time, hr</th>
<th>Time in Cell, hr</th>
<th>Photogalvanic Potential, mv</th>
<th>Time, hr</th>
<th>Time in Cell, hr</th>
<th>Photogalvanic Potential, mv</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>11</td>
<td>15</td>
<td>15</td>
<td>20</td>
</tr>
<tr>
<td>21</td>
<td>21</td>
<td>25</td>
<td>24</td>
<td>24</td>
<td>21</td>
</tr>
<tr>
<td>24</td>
<td>0</td>
<td>3</td>
<td>24</td>
<td>24</td>
<td>21</td>
</tr>
<tr>
<td>24</td>
<td>24</td>
<td>21</td>
<td>26</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>46</td>
<td>22</td>
<td>22</td>
<td>67</td>
<td>43</td>
<td>45</td>
</tr>
<tr>
<td>67</td>
<td>24</td>
<td>42</td>
<td>355</td>
<td>312</td>
<td>177</td>
</tr>
<tr>
<td>355</td>
<td>43</td>
<td>10</td>
<td>355</td>
<td>312</td>
<td>143</td>
</tr>
</tbody>
</table>
TABLE 7
Miscellaneous Experiments on Electrode Activation

<table>
<thead>
<tr>
<th>Electrode Pair No.</th>
<th>Treatment</th>
<th>Photogalvonic Potential, mv</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Washed with distilled water and wiped with Kimwipe</td>
<td>7</td>
</tr>
<tr>
<td>2</td>
<td>Dipped in turn in 10% methanolic solution of KOH, distilled water, warm &quot;dilute&quot; aqua regia (1:16 HNO₃:HCl:H₂O), and more distilled water, the cycle being repeated four times, the final dip in the acid lasting 2 min.ᵃ</td>
<td>13</td>
</tr>
<tr>
<td>3</td>
<td>18 hr. in concentrated HClᵇ</td>
<td>60</td>
</tr>
<tr>
<td>4</td>
<td>18 hr. in 1:3 nitric acid</td>
<td>43</td>
</tr>
<tr>
<td>5</td>
<td>18 hr. in stock electrolyte solutionᶜ</td>
<td>89</td>
</tr>
<tr>
<td>2</td>
<td>Platinized cathodically using a 2% solution of chloroplatinic acid in N HCl and a current density of 0.2 amp/cm² for 15 min.</td>
<td>0</td>
</tr>
</tbody>
</table>

ᵃ) Reference 9.
ᵇ) Reference 49.
ᶜ) The illuminated electrode had been used previously in photogalvanic cells, but at no time was in contact with anything but the electrolyte or a dilute sulfuric acid solution of equal strength.
TABLE 8
Miscellaneous Experiments on Electrode Activation

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Treatment</th>
<th>Photogalvanic Potential, mv</th>
</tr>
</thead>
<tbody>
<tr>
<td>380</td>
<td>(Last result from Table 6)</td>
<td>143</td>
</tr>
<tr>
<td>381</td>
<td>Cathodic reduction</td>
<td>8</td>
</tr>
<tr>
<td>382</td>
<td>Anodic oxidation</td>
<td>4</td>
</tr>
<tr>
<td>383</td>
<td>Dipped in acetone solution of thionine, dried, washed</td>
<td>20</td>
</tr>
<tr>
<td>384</td>
<td>Treatment repeated</td>
<td>29</td>
</tr>
<tr>
<td>385</td>
<td>Treatment repeated</td>
<td>44</td>
</tr>
<tr>
<td>386</td>
<td>Soaked in acetone solution of thionine, washed</td>
<td>46</td>
</tr>
<tr>
<td>387</td>
<td>Dipping, drying, washing treatment repeated</td>
<td>56</td>
</tr>
<tr>
<td>388</td>
<td>Treatment repeated</td>
<td>59</td>
</tr>
<tr>
<td>389</td>
<td>Treatment repeated</td>
<td>68</td>
</tr>
<tr>
<td>390</td>
<td>Electrode thoroughly washed and dried</td>
<td>58</td>
</tr>
<tr>
<td>391</td>
<td>Anodic oxidation</td>
<td>17</td>
</tr>
<tr>
<td>392</td>
<td>Dipped in methanol solution of thionine, dried, washed</td>
<td>35</td>
</tr>
<tr>
<td>393</td>
<td>Treatment repeated</td>
<td>44</td>
</tr>
<tr>
<td>394</td>
<td>Soaked 20 min. in methanol solution of thionine, washed</td>
<td>50</td>
</tr>
<tr>
<td>395</td>
<td>Washed with dilute sulfuric electrolysis solution</td>
<td>54</td>
</tr>
<tr>
<td>396</td>
<td>Anodic oxidation for 10 sec</td>
<td>12</td>
</tr>
<tr>
<td>397</td>
<td>No treatment, 1 min later</td>
<td>14</td>
</tr>
<tr>
<td>Run No.</td>
<td>Treatment</td>
<td>Photogalvanic Potential, mv</td>
</tr>
<tr>
<td>---------</td>
<td>------------------------------------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>398</td>
<td>No treatment, 3 3/4 min later</td>
<td>22</td>
</tr>
<tr>
<td>399</td>
<td>Cathode reduction for 1 min</td>
<td>6</td>
</tr>
<tr>
<td>400</td>
<td>No treatment, 3 1/2 min later</td>
<td>7</td>
</tr>
<tr>
<td>401</td>
<td>No treatment, 2 min later</td>
<td>8</td>
</tr>
<tr>
<td>402</td>
<td>Soaked in methanol overnight</td>
<td>8</td>
</tr>
</tbody>
</table>
It was found that a platinum electrode could be deactivated by cathodically reducing or anodically oxidizing the electrode with a strong current using a dilute sulfuric acid solution for the electrolyte (Runs 381-2, 391, 396, 399). In each case the cell was short circuited after electrode oxidation or reduction until the dark potential due to the reduced or oxidized electrode surface decayed to a small value. The passage of a heavy current through the electrode would destroy any thionine on its surface. (A similar electrolysis of a thionine solution causes an irreversible bleaching of thionine in the bulk of the solution.) A partial reactivation could be accomplished by treating the electrode with a solution of thionine in acetone or methanol, drying, and then washing with water until it appeared to be clean (Runs 383-389, 392-394). Excessive washing tended to deactivate the electrode (Run 390). The organic solvent itself had no beneficial effect (Run 402). These and other similar results indicated that thionine must be adsorbed on the electrode surface to activate the electrode. It seems likely that the adsorption of dye is the activation process which occurs within the electrolyte.

An activated electrode was illuminated in a cell which contained only 10^{-2} M ferrous sulfate with a trace of ferric ions. The adsorbed layer of thionine, if it was indeed present, was unable to produce any photogalvanic effect. The contact with ferrous ions did not increase the activity of the electrode when it was returned to a thionine solution.

The importance of proper electrode activation was shown in several experiments while studying the electrode processes (Section 4, 3; see Test 26, Table 13). A photogalvanic potential of 35 mV was recorded one day; three days later when illuminated under the same conditions the same cell yielded a photogalvanic potential of 82 mV. Since the concentration of thionine in the photostationary state remained the same, the increased photogalvanic potential could not have resulted from changes in the solution but must have been caused by changes on the electrode surface.

The electrode was then removed from the solution for 30 seconds and replaced to see if slight contamination by air had any effect. This was done twice, and it had no effect. The electrode was then dipped in concentrated sulfuric acid for 15 seconds followed by washing with water. When the electrode was replaced in the solution and illuminated as before
the photogalvanic effect was completely eliminated. Even after 3
days a photogalvanic potential of only 8 mv was observed. The elec-
trode was then washed with dilute nitric acid and with water and
replaced. Within a few minutes a photogalvanic potential of 50 mv
was obtained. A similar experiment was carried out with another
solution, and although the sulfuric acid wash did not completely
eliminate the photogalvanic effect, the results were qualitatively
the same.

The sulfuric acid was expected merely to remove the adsorbed
dye, because it removes thionine from stained glassware. Apparently
it had other effects, since it prevented the reactivation of the electrode.
Oxidation of the electrode surface might be suspected, but certainly
the dilute nitric acid wash should have had a similar effect. However,
the nature of the electrode surface obviously exerts a remarkable
influence on the open circuit photogalvanic potential.

The problem of electrode activation arose during the testing of
the laboratory model cells (Section 4.6). Immersing the electrodes
in a thionine solution to activate them gave irregular results. Visual
observation of the behavior of aqueous solutions on platinum surfaces
led to the suspicion that the surface was not being wetted properly. It
was found that the electrodes could be activated within a few minutes
by washing them with a thionine solution containing a surface active
agent. Such a solution could be prepared by stirring 2 g. of thionine
and 10 g. of dodecyl sodium sulfate into a liter of water. The dye does
not dissolve completely, but the solution can be used without filtering.
The effects of such a treatment are discussed in Section 4.6 for specific
cells and solutions.

The implications of these observations on electrode activation
are discussed in connection with the electrode processes in Section
4.3.1.

4.2.3 Electrode Materials

Four pairs of electrodes of identical surface areas were pre-
pared from platinum, tantalum, nickel and monei sheets and soaked
overnight in dilute sulfuric acid solution with a pH of 2.5. The nickel
electrodes were attached to some extent by the acid. Each pair was

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tested in EC-3 with separate portions of stock solution of 1-2-1 and with the optical system OS-1-d. The photogalvanic potentials are given in Table 9. It is evident that the platinum was far superior to the other metals.

The experiments were carried out without an awareness of the problem of electrode activation. Electrode materials should be the subject of further investigation.

**TABLE 9**

<table>
<thead>
<tr>
<th>Electrode Material</th>
<th>Photogalvanic Potential, mv</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platinum</td>
<td>111</td>
</tr>
<tr>
<td>Tantalum</td>
<td>10</td>
</tr>
<tr>
<td>Nickel</td>
<td>2</td>
</tr>
<tr>
<td>Monel</td>
<td>2</td>
</tr>
</tbody>
</table>

4.2.4 General Aspects of Cell Performance

Several aspects of photogalvanic cell performance became apparent during the experiments on electrode configurations and conditions. The first of these was that open circuit photogalvanic potentials were generally less than 200 mv. The maximum voltage which was observed was 220 mv, using cell EC-1-b, solution 1-2-1 and optical system OS-1-d. While this was somewhat lower than the maximum of 265 mv reported by Rabinowitch,52 it was higher than 185 mv obtained by Potter and Thaller49 and the 95 mv reported by Silverman.61

The second general observation was that the apparent internal resistance calculated by equation 12 or 13, was generally on the order of $10^4$ to $10^6$ ohms. The actual resistance of the same cells was about
usually 0.05 cm. The value of \( t \) undoubtedly approaches 0 for our solutions since most of the current is carried by the hydrogen, sulfate, and ferrous ions in solution, and \( n \) can be assumed to be 2. Thus, \( i_1 = 3 \times 10^{-2} \text{ A} \), and if \( a = 4 \times 10^{-5} \text{ mole/l}, i_1 = 1 \times 10^{-6} \text{ amp/cm}^2 \).

This value for the limiting current with a photogalvanic potential of 0.2 volt would make the apparent internal resistance

\[
R_{\text{app}} = \frac{2}{1 \times 10^{-6}} = 2 \times 10^{-5} \text{ ohms.}
\]

The calculation does not take into account the fact that some of the oxidized product may be photochemically reduced and be available for another reaction at the electrode before it leaves the diffusion layer; nor does it consider the competing reaction with ferric ions in solution. Nevertheless, the result is close enough to the observed polarization to lend credence to the view that the current is limited by the concentration of leucothionine and its rate of diffusion to the electrode.

4.3 ELECTRODE PROCESSES

A considerable effort was made to understand the electrode processes with the goal of providing a means for predicting the photogalvanic potential obtainable from a given cell. A theory which is consistent with the behavior of photogalvanic cells is being proposed. Although the development of the theory proceeded simultaneously with the acquisition of supporting data, the theory is presented here first in some detail. Much of the theory resulted from reasoning based on literature sources.

4.3.1 Theoretical Analysis

The solution in the thionine photogalvanic cell contains the components of two redox systems:

\[
\text{Leucothionine} \rightarrow \text{Thionine} + 2e^- \quad (15)
\]

\[
\text{Fe}^{++} \rightarrow \text{Fe}^{+++} + e^- \quad (16)
\]
200 to 800 ohms. The high apparent internal resistance obviously was almost entirely due to polarization. This fact was recognized by Potter and Thaller, but they failed to explain the cause of polarization.

Since the available power was far more dependent upon the area of the illuminated electrode than it was on the area of the dark electrode, the polarization was occurring primarily at the illuminated electrode. The conclusion must be that the species which supplies electrons to the illuminated electrode tends to be in short supply near the electrode surface. The power is therefore limited by the small amount of leucothionine reaching the electrode.

The rate of the electrode reaction of any species in solution is limited by the rate of diffusion to the electrode (assuming that more stringent limitations are not imposed). The diffusion limited current density, \( i_1 \), is given by

\[
    i_1 = \frac{D n F a}{(1 - t) \delta}
\]

(14)

Applying this equation to the case of the illuminated electrode in the thionine-iron system,

- \( D \) = diffusion coefficient for leucothionine
- \( n \) = number of electrons transferred per reacting species
- \( F \) = the value of the Faraday
- \( a \) = activity of leucothionine
- \( t \) = transport number of leucothionine
- \( \delta \) = thickness of the diffusion layer adjacent to the electrode in which the concentration gradient of the electrolyte occurs.

Vetter and Bardeleben found that \( D \) for methylene blue (which is \( N_2 N_2' N_4 N_4'-tetramethylthionine \)) was \( 7.6 \times 10^{-6} \text{ cm}^2/\text{sec} \), and we can use this value for thionine. Potter states that for unstirred solutions \( \delta \) is

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In that portion of the solution which is illuminated the two systems are not at equilibrium. The solution approaches a steady state upon continued illumination in which the concentrations of the solution components remain constant; however, this is a photosationary state and not a thermodynamic equilibrium. The components continuously react in such a manner as to strive to achieve equilibrium, but as long as the solution is illuminated the photochemical reaction prevents equilibrium from being attained.

The potential of an electrode in contact with two redox systems which are not at equilibrium is a mixed potential. The potential of the illuminated electrode therefore should be governed by the principles affecting any mixed potential. The discussion below follows the presentations by Delahay,

Even when no current is flowing through the external circuit of the cell, i.e., at open circuit conditions, a current is still flowing through the illuminated electrode. This current consists of anodic and cathodic components which are equal in magnitude and opposite in sign.

Each individual redox system produces a current \( i \) given by the equation

\[
\frac{1}{i} = \frac{1}{i_c} + \frac{1}{i_a}
\]  \hspace{1cm} (17)

where

\[
i_c = \text{cathodic component of the current}
\]

\[
i_a = \text{anodic component of the current}
\]

The cathodic and anodic components are defined by equations 18 and 19.

\[
i_c = n\frac{\mathcal{F}}{A} C_0 k'_c, \quad n \exp \left( \frac{-\mathcal{F}n}{RT} E \right)
\]  \hspace{1cm} (18)

\[
i_a = -n\frac{\mathcal{F}}{A} C_0 k'_a, \quad n \exp \left( \frac{1 - \alpha_0}{RT} \cdot \frac{\mathcal{F}}{RT} E \right)
\]  \hspace{1cm} (19)
where:

\[ n = \text{number of electrons transferred in the redox equation} \]

\[ \mathcal{F} = \text{the Faraday} \]

\[ A = \text{area of the electrode} \]

\[ C_0 = \text{concentration of the oxidised form} \]

\[ C_r = \text{concentration of the reduced form} \]

\[ k_{f,h}^* = \text{(forward, heterolytic) rate constant for the reaction of the oxidised form at the electrode when } E = 0 \]

\[ k_{b,h}^* = \text{(backward, heterolytic) rate constant for the reaction of the reduced form at the electrode when } E = 0 \]

\[ \alpha = \text{transfer coefficient} \]

\[ R = \text{gas constant} \]

\[ T = \text{absolute temperature} \]

\[ E = \text{electrode potential} \]

\[ \alpha E = \text{fraction of the potential favoring the cathodic reaction} \]

\[ (1-\alpha) E = \text{fraction of the potential favoring the anodic reaction} \]

Since there are two redox systems in contact with the electrode, there are two cathodic components and two anodic components of the current. Their equality in magnitude is given by equation 20 for the specific case of the thionine cell. Since the components are opposite in sign, the sign of the anodic components has been changed in the equation.
In this equation \( n \) is 1, \( n' \) is 2, and \( n'' \) may be either 1 or 2, depending upon the number of electrons involved in the rate determining step of the electrode reactions of thionine and leucothionine. The constants \( \alpha \) and \( \alpha' \), have no relationship to each other. In place of the constants \( k_{f,b} \) and \( k_{b,f} \), the constants \( k_1 \), \( k_2 \), \( k_3 \) and \( k_4 \) have been used, each applying to a different electrode reaction. Substituting in equation 20 for \( n \) and \( n' \) and dividing through by \( \mathcal{J} A \) gives equation 21.

\[
\begin{align*}
    n A k_1 \left[ Fe^{++} \right] \exp \left( \frac{-\alpha A}{RT} \right) + n' A k_2 \left[ Th \right] \\
    \exp \left( \frac{-\alpha' n'' A}{RT} \right) \\
    + n'' A k_4 \left[ L_{r} \right] \exp \left( \frac{\left(1 - \alpha'\right) n'' A}{RT} \right) \\
    + \frac{n A k_3 \left[ Fe^{++} \right]}{RT} \exp \left( \frac{\left(1 - \alpha'\right) n'' A}{RT} \right) \\
\end{align*}
\]

(20)

Equation 21 may be considered to be an exact though unwieldy equation describing the relationship between the electrode potential and the concentrations of the active components at a given pH.

Delahay\textsuperscript{11b} has shown that for a single redox system the effect of either the anodic or the cathodic component of the current can be neglected when the potential differs from the equilibrium potential \( E_0 \) by 0.12 volt. That is,

\[
i = i_a \text{ when } \left( E - E_0 \right) > 0.12 \text{ volt}\]

(22)
\[ i = i_c \quad \text{when} \quad \frac{(E E - E)}{n} > 0.12 \text{volt} \quad \text{(23)} \]

In terms of the redox systems at the illuminated electrode,

\[ i_{\text{TH-L}} \equiv i_{a_{\text{TH-L}}} \quad \text{when} \quad (E - E_{\text{TH-L}}) > 0.12 \text{volt} \]

(of 0.06 volt if \( n'' = 2 \)) \quad \text{(24)}

\[ i_{(\text{Fe}^{3+} - \text{Fe}^{2+})} \equiv i_{(\text{Fe}^{3+} - \text{Fe}^{2+})} \quad \text{when} \quad (E_{(\text{Fe}^{3+} - \text{Fe}^{2+})} - E) > 0.12 \text{volt} \quad \text{(25)} \]

where the subscripts identify the currents and voltages as being those of a particular redox system and \( E \) is the potential of the illuminated electrode. While either one or the other of these conditions is usually met, the two are generally not met at the same time. However, as a first approximation these simplifications can be adopted. They lead to the following equations by simplifying equation 21.

\[ k_1 \left[ \text{Fe}^{3+} \right] \exp \left( \frac{-\alpha \mathcal{A}}{RT} E \right) = 2k_4 \left[ L \right] \exp \left( \frac{\left(1 - \alpha \right) n'' \mathcal{A}}{RT} E \right) \quad \text{(26)} \]

\[ \frac{\left[ \text{Fe}^{3+} \right]}{[L]} = \frac{2k_4}{k_1} \exp \left( \frac{(1 - \alpha) n'' \mathcal{A}}{RT} E + \frac{\alpha \mathcal{A}}{RT} E \right) \quad \text{(27)} \]

\[ \log \frac{\left[ \text{Fe}^{3+} \right]}{[L]} = \frac{(n'' - \alpha n'' + \alpha)}{2.3RT} E + \log \frac{2k_4}{k_1} \quad \text{(28)} \]

As long as equation 28 is adequate, a plot of \( \log \frac{[\text{Fe}^{3+}]}{[L]} \) versus \( E \) should define a straight line with a slope \( \left( n'' - \alpha + n'' + \alpha \right) \frac{\mathcal{A}}{2.3RT} \) and a \( y \) intercept equal to \( \log \frac{2k_4}{k_1} \).
It is interesting to note that Rabinowitch\textsuperscript{52} reported a linear relationship between $E$ and $\log \left[ \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} \right]$ (where his quantity $\Delta$ equals $[L]$) for strongly bleached thionine solutions. He used this observation to support a different line of reasoning, but it is consistent with equation 28 as well.

Rabinowitch recorded data from a sample experiment in Table II of reference 51. These data can be used to calculate the potential of each redox system in the photochemical state for comparison with the illuminated electrode potential. The calculations are based on the assumption that the reduced thionine is almost exclusively leucothionine. The results are shown in Table 10. It may be noted that for the last five determinations in the table the illuminated electrode potential, $E_I$, is more than 0.12 volts greater than the equilibrium potential of the thionine-leucothionine system, and that it also is more than 0.12 volt less than the equilibrium potential of the ferrous-ferric couple. The simplifying assumptions made in equations 26-28 should be valid for these points. The cathodic component of the current was essentially entirely due to ferric ions, and the anodic component was almost completely due to leucothionine. Thus, equation 28 may explain in part the linear relationship between $E_I$ and $\log \left( \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} \right)$ found by Rabinowitch.\textsuperscript{52}

Consider the last set of measurements in Table 10. The electrode potential is 163 mv removed from the equilibrium potential of the ferrous-ferric couple and only 132 mv greater than the potential of the leucothionine-thionine couple. The electrode potential, therefore, would appear to favor the reaction by ferric ions. Moreover, the concentration of ferric ions is about 15 times as great as the concentration of leucothionine. True, leucothionine need react only half as rapidly to carry the same current as the ferric ions since it yields two electrons per molecule. However, the current carried by both species must be equal, and it would appear that the ease with which leucothionine undergoes the electrode reaction is comparable to the reactivity of ferric ions.

The reactivity of a substance at the electrode may be described in terms of its exchange current, i.e., the current that flows through an
TABLE 10
Photogalvanic Data from Rabinowitch* and Calculated
Redox Potentials from the Photostationary State

<table>
<thead>
<tr>
<th>Concentration, ** moles/lxL</th>
<th>[L]</th>
<th>[Fe++]</th>
<th>(E_{(\text{Th-L})})</th>
<th>(E_{(\text{Fe}^{+++}-\text{Fe}^{++})})</th>
<th>(E_{1\text{ (obs.)}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20</td>
<td>33</td>
<td></td>
<td>+0.454</td>
<td>+0.704</td>
<td>+0.679</td>
</tr>
<tr>
<td>0.60</td>
<td>34</td>
<td></td>
<td>0.439</td>
<td>0.705</td>
<td>0.643</td>
</tr>
<tr>
<td>0.80</td>
<td>35</td>
<td></td>
<td>0.435</td>
<td>0.706</td>
<td>0.637</td>
</tr>
<tr>
<td>2.15</td>
<td>37</td>
<td></td>
<td>0.418</td>
<td>0.707</td>
<td>0.570</td>
</tr>
<tr>
<td>2.35</td>
<td>38</td>
<td></td>
<td>0.416</td>
<td>0.707</td>
<td>0.556</td>
</tr>
<tr>
<td>2.45</td>
<td>38</td>
<td></td>
<td>0.416</td>
<td>0.707</td>
<td>0.555</td>
</tr>
<tr>
<td>2.55</td>
<td>38</td>
<td></td>
<td>0.415</td>
<td>0.707</td>
<td>0.554</td>
</tr>
<tr>
<td>2.65</td>
<td>39</td>
<td></td>
<td>0.414</td>
<td>0.709</td>
<td>0.546</td>
</tr>
</tbody>
</table>

* Reference 51. For \([\text{Fe}]\), \([\text{Fe}^{++}]\), and \([\text{H}^{+}]\), see Table II in the paper cited.

** Designated as \(\Delta\) by Rabinowitch.
electrode in contact with the electrolyte when the external circuit is open. The exchange current of the ferrous-ferric system is very high (≈0.1 amp cm⁻²) while that of organic systems is usually quite low (≈10⁻⁹ to 10⁻⁸ amp cm⁻²). Consequently, it is somewhat surprising to find that the electrode potential is so close to the equilibrium potential of the thionine-leucothionine system. If the ferric ions would react at the electrode much more rapidly than the leucothionine, the electrode potential would be quite close to the equilibrium potential of the ferric-ferrous system.

An explanation is thus at hand for the observation that the adsorption of thionine on the electrode is a necessary activation process. The adsorption of dye on the electrode surface either enhances the rate of reaction of leucothionine or suppresses the rate of reaction of ferric ions. Adsorption of a surface active agent on the electrode is known to hinder the reaction of some ions at the electrode. This interference takes the form of increased activation polarization resistance. The layer of dye covering the electrode may present an energy barrier toward the reaction of ferric ions.

The leucothionine must be able to react at the electrode in spite of (or perhaps because of) this layer of adsorbed dye. A plausible explanation of how this can occur is available from our knowledge of reactions in the bulk of the solution. Leucothionine is known to react with thionine in the reverse of the semithionine disproportionation reaction.

\[ L + Th \xrightarrow{2 S} \]

(29)

In the bulk of the solution, it is true, this equilibrium lies far to the left. However, the semithionine free radicals which would be formed by reaction of leucothionine with adsorbed thionine could lose their odd electrons exceedingly rapidly to the electrode. This would remove the semithionine ions converting them to thionine ions, and reaction 29 would proceed from left to right because of the rapid removal of semithionine. The adsorbed layer of thionine might, therefore, present a greater barrier to the electrode reaction of ferric ions than it does to the electrode reaction of leucothionine. In fact, the adsorbed layer may even catalyze the electrode reaction of leucothionine.
According to this mechanism, inactive or deactitivated electrodes simply do not have a well-formed layer of adsorbed dye. The reaction of ferric ions is thus not retarded, nor is the reactivity of leucothionine enhanced. Consequently ferric ions in the vicinity of the illuminated electrode can react far more rapidly than the leucothionine, and the electrode potential lies close to that of the ferric-ferrous system. It is conceivable that under some conditions the reaction of ferric ions may be favored so much that the illuminated electrode may be positive with respect to the dark electrode. This is possible because the ferric-ferrous potential in the illuminated solution is greater than the dark potential. A reversal in polarity of the two electrodes has actually been observed, as will be noted in Sections 4.4 and 4.6.

The case for the role of dye adsorption is not conclusively proven, but the evidence is entirely consistent with the mechanism described above.

4.3.2 Experimental Results

It was the objective of the experimental work on electrode processes to obtain data which would provide a test for theories of the electrode processes in photogalvanic cells. Some of the hypotheses which were considered were not supported by the data and are not presented in this report. The data which are discussed below are intended, first, to show that the electrode potential is not determined by the thionine-leucothionine couple alone, and second, to demonstrate that the electrode potential is a function of the current available from both redox systems as is characteristic for half-cells with a mixed potential. Some additional observations are made concerning the effects of temperature, light intensity, and ferrous ion concentrations.

The data were obtained with the use of the apparatus described in Section 4.1.4.

4.3.2.1 Calculation of Redox Potentials

In order to prove that the illuminated electrode potential is not the potential of either redox system alone, the potentials of the two redox systems must be available for comparison. If the composition
of the solution in the photostationary state and the standard potentials are known, the redox potentials of the two systems can be calculated. It was necessary to demonstrate, however, that the redox potentials could be calculated with confidence, and to do this the potentials of thionine-leucothionine and ferric-ferrous half-cells were measured and compared with the calculated values.

The concentrations of the various components in the test solutions were calculated from the concentrations of the stock solutions and the quantities of each used. Since the standard potential of the thionine-leucothionine redox system is pH dependent, the pH had to be calculated in the same manner.

The potential of the thionine-leucothionine half-cells could be calculated with the formula

\[ E = 0.563 - 0.090\, \text{pH} + 0.0591 \log \left( \frac{[T]}{[L]} \right) \]  \hspace{1cm} (30)

The applicability of this equation, of course, has been adequately substantiated by Clark, Cohen and Gibbs. The results obtained in the present work are shown in Table 11. The most probable source of error is the estimation of the pH, on which the standard potential is dependent. The accuracy is not of the highest order, but it is quite sufficient for estimating the potentials in the photostationary state. It may be noted that the presence of ferrous sulfate in the solution had no effect on the electrode potential.

The standard potential of the ferric-ferrous system is strongly dependent on the presence of complexing agents in the solution. In the test solutions a relatively high concentration of sulfate ions was present, and the standard potential was found to be quite different from that of the hydrated ions. Sulfate ions complex with ferric ions more strongly than with ferrous ions, consequently the formal standard potential is lowered.

In Table 12 are listed the potentials of a number of ferric-ferrous half-cells and the formal standard potentials calculated from these results. The formal standard potential was quite independent of the concentrations

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TABLE II
A Comparison of Calculated and Observed Potentials for the Thionine-Leucothionine System

<table>
<thead>
<tr>
<th>Concentration (moles/l)</th>
<th>Potential, volts</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Th]</td>
<td>[L]</td>
</tr>
<tr>
<td>7.96x10^{-5}</td>
<td>6.79x10^{-6}</td>
</tr>
<tr>
<td>7.67x10^{-6}</td>
<td>8.38x10^{-5}</td>
</tr>
<tr>
<td>2.88x10^{-5}</td>
<td>5.17x10^{-5}</td>
</tr>
<tr>
<td>------------</td>
<td>------------</td>
</tr>
<tr>
<td>4.64x10^{-2}</td>
<td>1.05x10^{-5}</td>
</tr>
<tr>
<td>1.64x10^{-2}</td>
<td>2.07x10^{-5}</td>
</tr>
<tr>
<td>3.73x10^{-2}</td>
<td>4.20x10^{-5}</td>
</tr>
<tr>
<td>9.78x10^{-3}</td>
<td>9.92x10^{-6}</td>
</tr>
<tr>
<td>1.10x10^{-2}</td>
<td>1.09x10^{-5}</td>
</tr>
<tr>
<td>1.67x10^{-2}</td>
<td>2.02x10^{-5}</td>
</tr>
</tbody>
</table>
of sulfate ion, thionine, chloride ion, and hydrogen ion over the concentration ranges used. A formal standard potential of +0.665 volt was adopted.

4.3.2.2 Experimental Data in Support of the Mixed Potential Theory

The compositions of the solutions discussed in this section are given in Table 13. Only representative data are herein presented.

The measurements consisted of determining the electrode potential with reference to a saturated calomel electrode and the absorption of the thionine solution in the photosynthetic state at various light intensities. From this information the concentrations of the various components and the potentials of the thionine-leucothionine and the ferric-ferrous redox systems were calculated and tabulated as shown for one such solution in Table 14. This table is intended to show the differences between the illuminated electrode potential and the calculated potentials of the thionine-leucothionine and the ferric-ferrous redox systems.

The potential of the dye redox system was calculated on the assumption that the reduced form was entirely leucothionine. If appreciable amounts of the reduced dye consisted of semithionine, the potential might have been somewhat lower, since the potential of the thionine-semithionine couple is lower than that of the thionine-leucothionine couple. 51

The calculated values were based on a value of +0.665 volt for the formal standard potential of the ferric-ferrous system. The slight discrepancies between the measured and the calculated values for the dark potential could lead to confusion when comparing electrode potentials with calculated potentials of the two redox systems. It did not seem desirable to change the method of calculation for each solution; consequently the measured values for the electrode potential were "corrected" by the difference between the measured and calculated values for the dark potential (see Table 14). These "corrected" values for the electrode potentials are used in the following discussions.
<table>
<thead>
<tr>
<th>Test No</th>
<th>Temperature, °C</th>
<th>pH</th>
<th>Dark Concentrations (mMoles/liter)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>[Ti]</td>
</tr>
<tr>
<td>22</td>
<td>ambient</td>
<td>2.75</td>
<td>1.55 x 10^-5</td>
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<td>23</td>
<td>ambient</td>
<td>2.90</td>
<td>1.34 x 10^-5</td>
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<tr>
<td>26</td>
<td>ca 24</td>
<td>2.66</td>
<td>7.84 x 10^-6</td>
</tr>
<tr>
<td>30</td>
<td>18.0</td>
<td>2.70</td>
<td>1.55 x 10^-5</td>
</tr>
<tr>
<td>31</td>
<td>29.7</td>
<td>2.70</td>
<td>1.55 x 10^-5</td>
</tr>
<tr>
<td>32</td>
<td>25.0</td>
<td>2.70</td>
<td>1.55 x 10^-5</td>
</tr>
<tr>
<td>34</td>
<td>25.0</td>
<td>2.74</td>
<td>1.55 x 10^-5</td>
</tr>
<tr>
<td>35</td>
<td>25.0</td>
<td>2.67</td>
<td>1.54 x 10^-5</td>
</tr>
<tr>
<td>36</td>
<td>25.0</td>
<td>2.77</td>
<td>1.55 x 10^-5</td>
</tr>
<tr>
<td>38</td>
<td>25.0</td>
<td>1.10</td>
<td>1.64 x 10^-6</td>
</tr>
<tr>
<td>40</td>
<td>25.0</td>
<td>2.86</td>
<td>3.15 x 10^-6</td>
</tr>
</tbody>
</table>

* These concentrations are those calculated from the concentration of the stock solution and the quantity measured into the test solution.
<table>
<thead>
<tr>
<th>Light Intensity (%) of Exciting Light</th>
<th>Table of Data on Light Intensities, Photostationary State Concentrations, and Potentials (Test 32)</th>
<th>Light</th>
<th>Photostationary State Concentrations (moles/liter) x 10^5</th>
<th>E\text{th, obs.} V</th>
<th>E\text{th, corr.} V</th>
<th>E(Tb-L) V</th>
<th>E(Fe+++Fe+++) V</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.47 --- 26.4</td>
<td>0.568</td>
<td>0.563</td>
<td>0.563</td>
<td>0.563</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.41</td>
<td>1.47 --- 26.4</td>
<td>0.568</td>
<td>0.563</td>
<td>0.563</td>
<td>0.563</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.06</td>
<td>1.47 --- 26.4</td>
<td>0.568</td>
<td>0.563</td>
<td>0.563</td>
<td>0.563</td>
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<td></td>
</tr>
<tr>
<td>6.14</td>
<td>1.46 0.01 26.4</td>
<td>0.566</td>
<td>0.561</td>
<td>0.383</td>
<td>0.563</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9.64</td>
<td>1.42 0.05 26.5</td>
<td>0.562</td>
<td>0.557</td>
<td>0.362</td>
<td>0.563</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12.2</td>
<td>1.45 0.02 26.4</td>
<td>0.562</td>
<td>0.557</td>
<td>0.374</td>
<td>0.563</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16.8</td>
<td>1.42 0.05 26.5</td>
<td>0.559</td>
<td>0.554</td>
<td>0.362</td>
<td>0.563</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19.5</td>
<td>1.40 0.07 26.5</td>
<td>0.555</td>
<td>0.550</td>
<td>0.357</td>
<td>0.563</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25.5</td>
<td>1.42 0.05 26.5</td>
<td>0.543</td>
<td>0.538</td>
<td>0.362</td>
<td>0.563</td>
<td></td>
<td></td>
</tr>
<tr>
<td>34.9</td>
<td>1.29 0.18 26.8</td>
<td>0.530</td>
<td>0.525</td>
<td>0.344</td>
<td>0.563</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40.0</td>
<td>1.19 0.28 27.0</td>
<td>0.516</td>
<td>0.511</td>
<td>0.338</td>
<td>0.564</td>
<td></td>
<td></td>
</tr>
<tr>
<td>52.5</td>
<td>1.09 0.38 27.2</td>
<td>0.496</td>
<td>0.491</td>
<td>0.333</td>
<td>0.564</td>
<td></td>
<td></td>
</tr>
<tr>
<td>61.7</td>
<td>0.95 0.52 27.4</td>
<td>0.481</td>
<td>0.476</td>
<td>0.327</td>
<td>0.564</td>
<td></td>
<td></td>
</tr>
<tr>
<td>84.1</td>
<td>0.77 0.70 27.8</td>
<td>0.460</td>
<td>0.455</td>
<td>0.320</td>
<td>0.564</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100.0</td>
<td>0.673 0.80 28.0</td>
<td>0.444</td>
<td>0.439</td>
<td>0.317</td>
<td>0.565</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
A similar source of confusion could be the discrepancies between the two values for the thionine concentration. One value was determined by measuring the concentration of the stock solution and the extent of dilution in making up the test solution. A second value, which did not always agree exactly with the first, was obtained by measuring the absorption of the test solution in the cell. The second determination was used in plotting the graphs which follow. Since the thionine concentration in the photostationary state was determined in the same manner (by directly measuring the absorption of the test solution), this undoubtedly gave more reliable values for the leucothionine concentration, which was determined by difference.

In studying the proflavine-ascorbic acid photogalvanic system, Silverman found that the potential of the illuminated electrode was linear with the log of the ratio of the concentrations of the oxidized and the reduced forms of the dye. (The slopes of the straight line plots varied, however, in conflict with the assumption that the electrode potential was that of the dye system alone.) Figure 39 shows a similar treatment of the data from Test 21. Obviously there is no simple linear relationship in the case of the thionine-iron photogalvanic cell, and the electrode potential is not that of the dye reduct system alone.

Figures 40 and 41 are plots of the electrode potential against the thionine concentration in the photostationary state. The calculated reduct potentials of the two reduct systems are also shown for comparison. First of all, it is again perfectly clear that the electrode potential is not determined by either system alone, but that it is some intermediate value. Second, the electrode potential decreases much more slowly at first than does the potential of the thionine-leucothionine system as the thionine is reduced. The initial slow decrease is more obvious in Figure 40 than in Figure 41 (and is completely obscured in Figure 51). As further bleaching occurs, the electrode potential decreases more rapidly, than slowly once again (Figure 41).

This behavior is qualitatively characteristic of a solution having two reduct systems which are not at equilibrium. Although the potential of the thionine-leucothionine system decreases rapidly as the leucothionine content is at first increased, the current which is available is still very small because of the low leucothionine concentration. The
Figure 39. The Relationship between the Electrode Potential and the Log of the Ratio of the Concentrations of Thionine and Leucothionine (Test 23)
Figure 40. Variation of the Potential with the Extent of Bleaching (Test 18)
Figure 41. Variation of the Potential with the Extent of Bleaching (Test 34)
potential of the electrode is established so that the cathodic current component (mainly due to ferric ions) is equal to the anodic component (mainly due to leucothionine). The potential at which these current components are equal lies very close to the potential of the ferric-ferrous system. As more leucothionine is formed, the potential at which the two components of the current are equal rapidly increases. When most of the thionine is reduced to leucothionine, further reduction will result in further decreases in the potential of the thionine-leucothionine system, but the available current will not increase significantly. While the potential of the thionine-leucothionine system can theoretically decrease without limit, the current is limited by the limiting value for the leucothionine concentration. Since the electrode potential is controlled by the current, it will reach a limiting value, also.

Figure 42 is a similar plot but includes values obtained at three temperatures. Obviously the potential of the electrode was dependent upon the extent of bleaching but was otherwise essentially independent of temperature.

Figure 43 is a plot of the potential against the absorbance for Test 22. Some of the points are photostationary state values, and some are measurements made while the back reaction was taking place following the removal of illumination. The photogalvanic effect at a given absorbance was slightly higher for the solution in the photostationary state. An extrapolation of the curves in Figure 43 to an absorbance of 0, i.e., to where the thionine is all converted to leucothionine, predicts a maximum photogalvanic potential of about 0,180 volt for this cell regardless of illumination intensity. This would be the limit only for a solution with the composition of the test solution in contact with an electrode of the same activity.

The extrapolation is justified by equation 29. When bleaching is almost complete the electrode potential is approximately linear with the log of the ratio of the concentrations of ferric ion and leucothionine. The relationship is shown graphically in Figures 44 and 45. A short extrapolation to the maximum value of log \[ \frac{[C]_{+++}}{[C]_{+}} \] reveals what the maximum photogalvanic potential would be with light of infinite

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Figure 42. Variation of the Potential with the Extent of Bleaching (Tests 30, 31 and 32)
Figure 43. The Electrode Potential as a Function of the Absorbance (Test 22)
Figure 44. The Photogalvanic Potential as a Function of the Log of the Ratio of the Concentrations of Ferric Ion and Leucothionine (Test 22)
Figure 45. The Photogalvanic Potential as a Function of the Log of the Ratio of the Concentrations of Ferric Ion and Leucothionine (Test 23)
intensity. Since the current is also a function of the concentration of leucothionine, the power of a photogalvanic cell containing such a solution would be increased very little by using a light of infinite intensity. Equation 25 predicts that a finite limit exists for any given solution (assuming that the electrode reaction of ferric ion is never completely eliminated), and that this limit can be determined from a plot such as those in Figures 44 and 45. The limiting photopotential is obtained when the leucothionine concentration is equal to the thionine concentration of the dark solution.

4.3.2.3 The Effect of Light Intensity

The effect of light intensity on both the extent of bleaching and the electrode potential is given in Figures 46 and 47. In general these curves are S-shaped, especially for the more concentrated solutions. A small initial effect is followed by a much more rapid increase in bleaching which in turn is followed by a slower change with light intensity. The small initial effect is probably due to light absorption by the thionine in front of the electrode. After this thionine is bleached, the effect of the increased light becomes more pronounced in the region of the electrode. With a dilute thionine solution (Figure 46) even a weak light will have a strong effect on the extent of bleaching and it is assumed that this would be true for all solutions if measurements were made in the region directly next to the window.

The changes in potential with light intensity roughly follow the changes in the extent of bleaching. That this is not an exact correlation is revealed, of course, in plots such as Figures 40 and 42.

The analytical light beam was found to affect the electrode potential in Test 34 (Figure 47). Without this light the potential was 2 mv higher, indicating that some bleaching resulted from this week illumination. This was not true for most solutions. Consequently the dark concentration for Test 34 could not be determined directly. The curve in Figure 47 is extrapolated to the value calculated from the concentration of the stock solution ($1.55 \times 10^{-5} \text{M}$).

In Figures 48 and 49 the effect of light intensity is shown for several temperatures. Bleaching is more complete at lower temperatures because temperature affects the rate of oxidation of leuco-
Figure 47. Variation of the Extent of Bleaching and the Electrode Potential with the Light Intensity (Test 34)
Figure 48. Variation of the Extent of Bleaching with Light Intensity (Tests 30, 31, and 32)
Figure 49. Variation of the Electrode Potential with the Light Intensity (Tests 30, 31 and 32)
thionine more than it does the reduction of thionine. According to Figure 42, this is the only significant influence of temperature on the electrode potential.

4.3.2.4 The Effect of the Ferrous Ion Concentration

Rabinowitch reported that around $10^{-2}$ moles/l of ferrous ions the extent of bleaching reaches a constant value. The reasons for this result did not seem perfectly clear, and conflicting results have now been obtained. Figure 50 describes the effect of light intensity on bleaching for three solutions in which only the ferrous ion concentration was varied. (The pH varied slightly but in such a manner as to give an effect opposite to that observed.) Obviously increasing the ferrous ion concentration above $10^{-2} M$ resulted in an increase in the extent of bleaching. This result is in agreement with the report of Havemann and Reimer.

Rabinowitch also reported that ferrous ions did not affect the potential of the illuminated electrode directly but only indirectly by affecting the extent of bleaching. The present results as summarized in Figure 51 are again in conflict with this view. For the same extent of bleaching (i.e., the same thionine concentration), the electrode potentials in general decreased with increasing ferrous ion concentrations. Ferrous ions are, therefore, effective electron donors even in the presence of leucothionine.

It is interesting to see in Figure 51 that Tests 35 and 36 exhibited parallel behavior while Test 32 was somewhat erratic by comparison. Test 35 and 36 were performed on one day, while Test 32 was carried out at a separate time. A possible explanation is that by some means, e.g., by excessive washing, the activity of the electrode was changed between the two sets of measurements.

4.3.2.5 The Potential of an Illuminated Thionine Solution

In the photogalvanic cell thionine is reduced by ferrous ions when the solution is illuminated, while leucothionine is oxidized by ferric ions in the dark. This basic fact indicates that there is a change in the potential of the thionine-leucothionine couple when the solution is
Figure 50. Variation of the Extent of Bleaching with the Light Intensity and the Effect of Ferrous Ion Concentration (Tests 32, 35 and 36)
Figure 51. Variation of the Electrode Potential with the Extent of Bleaching and the Effect of Ferrous Ion Concentration (Tests 32, 35 and 36).
illuminated. An experiment was performed to determine if the change in potential of a thionine solution can be detected when no ferrous ions are present.

There is some controversy about the necessity of forming a thionine-ferrous ion complex before reduction can be effected by light (see Section 3.2.1.2). If complex formation is not required, illuminated thionine could perhaps be reduced by ferrous ions equally as well in an electrode reaction as by a reaction between the ions in the same solution. A thionine solution could be placed in one cell compartment and a ferrous solution in the other, the two compartments being connected by a salt bridge. Illumination of the thionine could then cause its reduction by ferrous ion via an electrode reaction, and, when the thionine would be completely reduced, the external circuit could be broken to prevent the back reaction. The result would be a charged storage battery from which power could be drawn at any time, simply by closing the circuit.

To test this concept, a $4.3 \times 10^{-5}$M thionine solution was put in one electrode compartment, a ferrous solution was put in the other, and the two were connected by a salt bridge. The potential of the cell was measured both in the dark and with the thionine solution illuminated. The change in potential upon illumination was very small, a drop of 5 mv occurring at first, followed by a return within 2 minutes to the original potential. It was concluded that the electrode potential of a thionine solution is changed very little by the absorption of light. Complex formation may be a prerequisite for reduction, or, what is more probable, the population of thionine molecules in the excited state is too small to have any significant effect upon the electrode potential. At any rate, a storage battery of the type described does not appear to be feasible.

Similar experiments were reported by Silverman, who concluded that the small effects which were observed were due to thermal rather than photochemical changes.
4.4 EFFECTS OF COMPLEXING AGENTS AND ADDITIVES

4.4.1 Theoretical Study

The addition of ferric ion complexing agents and other additives to the electrolyte has been considered as a means of achieving some of the following desirable effects:

a. Increased Photogalvanic Potential

An increased photogalvanic potential can be attained by increasing the difference between the potentials of the two redox systems as long as the extent of bleaching is not affected. It is unlikely, however, that the extent of bleaching would not be affected. The addition of ferric ion complexing agents stronger than sulfate ions may be expected to decrease the dark potential and thus to decrease the photogalvanic potential for the same extent of bleaching. Complete elimination of complexing, on the other hand, would increase the dark potential and thereby increase the photogalvanic potential if bleaching is not suppressed.

b. Increased Current

In Section 4.2.4 it was pointed out that the current is limited by the concentration of leucothionine in the photostationary state. The addition of reagents which strongly complex the ferric ion generally increases the extent of bleaching by decreasing the rate of the back reaction. The resulting increase in leucothionine concentration in the photostationary state will increase the current. Complexing the ferric ion therefore becomes a way of producing more current for a given light intensity.

Additives can aid in increasing the current in another way. The leucothionine concentration, regardless of light intensity, is limited by the dark concentration of thionine. The concentration of thionine is in turn limited by its low solubility in the presence of ferrous sulfate and sulfuric acid in the required concentrations. The dye is salted out of solution by inorganic salts or acids.

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To illustrate this "salting out" effect, a solution was prepared with sufficient ingredients to make it $2.9 \times 10^{-3}$ M in thionine, $2.0 \times 10^{-2}$ M in ferrous ion, and $1.6 \times 10^{-4}$ M in ferric ion, and the pH was adjusted to 2.3. The thionine (or any compound it may have formed with the iron salts) which precipitated was removed by filtration. The concentration of thionine in the solution was thus reduced to $8.3 \times 10^{-5}$ moles/l.

The solubility of thionine in a practical electrolyte solution, therefore, may be considerably different from the solubility in the solvent alone. The addition of the organic materials to the electrolyte was expected to permit higher thionine concentrations and thereby make possible higher leucoatinnine concentrations in the photostationary state.

Additives could serve to increase the leucoatinnine concentration in still another way. Rabinowitch demonstrated that the extent of bleaching is inversely proportional to the thionine concentration at high concentrations in aqueous solutions. The decrease in the extent of bleaching is accompanied by a decrease in the photogalvanic potential. It has been suggested that the dimeric form is responsible for this decrease, the dimer probably being better able to dissipate the excitation energy as vibrational energy, thus preventing the reaction with ferrous ions. The addition of an organic solvent seemed to be an appropriate way of suppressing dimerization, since it has been noted that the addition of alcohol to an aqueous thionine solution sharply lowers the dimer concentration.

As was mentioned in Section 3.2.1, Havemann and Pleisch found that the addition of acetone to the thionine-iron system both accelerated the bleaching reaction and made bleaching more complete in the photostationary state. Their explanation of the result, however, was that the organic solvent enhanced complex formation between thionine and ferrous ions, and that it was actually the complex which was reduced. Whatever the explanation, the greater ease of bleaching is the desired result.
Since dimerization is dependent upon the nature and the concentration of the anion, another method of preventing dimerization would be to introduce an appropriate anion. By analogy to the results of Levinson, Simpson and Curtis, it seems likely that the dimerization of the ion pair, ion pair information being favored in concentrated solutions.

![Chemical Structure](image)

The cation in this ion pair is largely represented by the two equivalent resonance structures shown as in (32) (see Section 3.1.1.).

![Resonance Structures](image)

In one structure the positive charge resides on one amino nitrogen atom, while in the other it is located on the other amino nitrogen. The hybrid can be represented by the structure shown in (31), with partial positive charges on each nitrogen. In the ion pair the anion can be associated with only one of these; consequently, the equivalence of the resonance structures (32) is destroyed, and some of the stabilizing influence is lost. The dimer of (31), on the other hand, retains this equivalent resonance as shown by structure (33).

![Resonance Structures](image)

In (33) an anion is in close proximity to each partial positive charge. In addition to the better resonance stabilization and the closer
association of positive and negative charges, the electronic interaction of the two thionine cations may be a stronger mutual solvating force than the solvation by the solvent.

If this viewpoint is correct, a bulky organic anion might sterically hinder dimerization. An anion with partial negative charge at two centers equally as far apart as the amino nitrogens on the thionine cation would seem to be especially desirable. This would permit simultaneous association of the negative charge with both centers of positive charge without dimerization.

c. Improved Electrode Activation

It is conceivable that the activation of the illuminated electrode might be improved by including appropriate additives in the electrolyte. Such an additive should inhibit the electrode reaction of ferric ions.

Since the electrode activation can be affected by treating the electrodes with a thionine solution containing a detergent, it seems reasonable that a detergent in the electrolyte itself might improve the electrode activation. Complexing agents which form a bulky complex with ferric ion might sterically hinder the electrode reaction, and ferric complexes with a high negative charge should be electrostatically repelled by the negatively charged illuminated electrode. While these complexing agents would not affect the absorbed layer on the electrode surface, they might serve to enhance its influence.

4.4.2 The Effect of Additives

A number of common water-soluble organic compounds were tested in an exploratory manner to see what types of additives might have a beneficial effect. The primary basis for the selection of the various additives was their solubility in water and their availability. It was recognized at the time that perhaps not all of the organic additives would be completely inert,7 but this was ignored in the initial exploratory work. The solutions were prepared with stock solvents and were tested in EC-1-e with OS-1-d. Table 15 describes the results.
### TABLE 15

The Effects of Some Organic Additives on Cell Performance

<table>
<thead>
<tr>
<th>Additive</th>
<th>10% By Volume</th>
<th>40% By Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Photogalvanic Potential, mv</td>
<td>Photogalvanic Power Level** watts x 10^3</td>
</tr>
<tr>
<td>Acetone</td>
<td>128</td>
<td>8.4</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>147</td>
<td>7.8</td>
</tr>
<tr>
<td>Dimethylformamide</td>
<td>93</td>
<td>2.6</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>140</td>
<td>11</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>144</td>
<td>12</td>
</tr>
<tr>
<td>Ethanol (95%)</td>
<td>125</td>
<td>7.3</td>
</tr>
<tr>
<td>Dioxane</td>
<td>28</td>
<td>1.0</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>151</td>
<td>34</td>
</tr>
<tr>
<td>Dextrose</td>
<td>155</td>
<td>9.0</td>
</tr>
<tr>
<td>None</td>
<td>149</td>
<td>6.8</td>
</tr>
</tbody>
</table>

* Solutions were $5 \times 10^{-4} \text{ M}$ in thionine and $1 \times 10^{-2} \text{ M}$ in ferrous ion. Ferric ions were added only as an impurity in the ferrous salt or by subsequent oxidation. The pH of all solutions was adjusted to $2.5 \pm 0.1$ except for the 10% acetone and the 10% acetic acid solutions, which had a pH of 2.6. Dextrose solution contained 10 g of the additive.

** Load resistance = $10^4$ ohms.
The most promising additives were tetrahydrofuran and acetic acid. Since acetic acid affects the pH of the solution, tetrahydrofuran was chosen for further study.

Tetrahydrofuran is a water soluble cyclic ether (as is dioxane, which was a poor additive). This led to the testing of other water soluble ethers as shown in Table 16. The results were compared with those using tetrahydrofuran, and, while all seemed to be beneficial, tetrahydrofuran still seemed to be the most promising.

Since tetrahydrofuran forms peroxides when exposed to air and light, the commercial solvent generally contains hydroquinone as an oxidation inhibitor. The tetrahydrofuran used in the experiments listed in Table 16 was purified by shaking it with an aqueous solution of ferrous sulfate and sodium hydrogen sulfate, drying over sodium hydroxide and over anhydrous calcium sulfate, and distilling.

The results in Table 16 indicate that the 20% tetrahydrofuran solution was best. In subsequent tests it was found that dys sometimes precipitated from 20% tetrahydrofuran solutions while 40% would keep it dissolved.

Rabinowitch discovered that the photogalvanic potential dropped steadily as the thionine concentration increased beyond $5 \times 10^{-5} M$ in aqueous solutions. When he raised the concentration to $2 \times 10^{-5} M$, the potential dropped to 69 mv. Voltages as high as 178 mv have now been obtained at concentrations over $10^{-3} M$; consequently, voltages need not decrease with increasing concentrations if the proper solution environment exists.

In section 4.4.1 the addition of bulky organic anions was suggested as a means of preventing thionine dimerization. The addition of p-toluene sulfonates was tested for this purpose, but it was found that the addition of a small amount of p-toluene sulfonic acid to concentrated solutions salted out the dye.

The addition of large amounts of p-toluene sulfonic acid or sodium p-toluenesulfonate, however, "salted in" the thionine and made it more soluble. By incorporating both p-toluenesulfonate salts and tetrahydrofuran, relatively high concentrations of dye can be achieved in solutions which contain all the other necessary ingredients. For example, the following solution was prepared:

\[ \text{[Solution]} \]
<table>
<thead>
<tr>
<th>Solvent</th>
<th>Open Circuit Photogalvanic Potential, mv</th>
<th>Attained Power Level, µwatts</th>
</tr>
</thead>
<tbody>
<tr>
<td>40% triethylene glycol **</td>
<td>132</td>
<td>0.34</td>
</tr>
<tr>
<td>40% 2-(2-ethoxyethoxy)ethanol **</td>
<td>135</td>
<td>0.32</td>
</tr>
<tr>
<td>40% 1,2-bis-(2-methoxyethoxy)ethane **</td>
<td>138</td>
<td>0.44</td>
</tr>
<tr>
<td>40% 2-(2-ethoxyethoxy)ethyl acetate **</td>
<td>143</td>
<td>0.56</td>
</tr>
<tr>
<td>20% tetrahydrofuran</td>
<td>168</td>
<td>1.21</td>
</tr>
<tr>
<td>40% tetrahydrofuran</td>
<td>139</td>
<td>0.90</td>
</tr>
<tr>
<td>60% tetrahydrofuran</td>
<td>118</td>
<td>0.44</td>
</tr>
</tbody>
</table>

* Thionine = 1.16 x 10^{-3} M  
Fe^{++} = 1.00 x 10^{-2} M  
Fe^{+++} = 7.94 x 10^{-6} M  
pH = 2.5  

** Matheson Coleman and Bell technical or practical grade.
Contrails

sodium p-toluenesulfonate: 25 g/100 ml
thionine: 1.99 x 10^-2 M
ferrous p-toluenesulfonate: 5.80 x 10^-2 M
p-toluenesulfonic acid: to give a pH of 2.0
tetrahydrofuran: 45 ± 5 ml/100 ml
ferric ions: traces due to oxidation of Fe++

The solution was tested in cell EC-4 with system OS-1-a, but the photopotential was essentially zero.

A similar solution was prepared with p-toluenesulfonic acid instead of the sodium salt. The composition was as follows:

p-toluenesulfonic acid: 50 g/100 ml
thionine: 1.08 x 10^-2 M
ferrous p-toluenesulfonate: 1.11 x 10^-2 M
tetrahydrofuran: 20 ml/100 ml
ferric ions: traces due to oxidation of Fe++
pH: ~0

When tested in EC-4, the solution produced a photogalvanic potential which was opposite in polarity to all those previously found. The effect was small, being only 18 mv when the cell was held next to the lamp; but the fact that the illuminated electrode can be positive is certainly noteworthy.

The very low pH was probably responsible for the reversal of polarity for two reasons. First, at that pH the potential of the thionine-teucothionine system did not differ greatly from the potential of the dark electrode, while the potential of the ferric-ferrous system was not affected by the pH. Second, the electrode was deactivated by the p-toluene sulfonic acid. This was demonstrated by the fact that when the cell was subsequently used with a
normal electrolyte, the photogalvanic potential was very much smaller than it had been before with the same solution. The deactivating influence of the acid may be compared with the similar effect of sulfuric acid described in Section 4.2.2. Electrode deactivation has been assumed to be any process which either accelerates the electrode reaction of ferric ions or retards the electrode reaction of leucothionine. The presence of \( \mu \)-toluenesulfonic acid therefore favored the reaction of ferric ions. As a consequence the electrode potential which was established in the illuminated solution lay close to the potential of the ferric-ferrous system. Since the ferric-ferrous system has a more positive potential in the illuminated solution than in the dark solution, the illuminated electrode potential was more positive, too. This explanation is pure speculation, but the results can be satisfactorily rationalized with the postulated electrode mechanism.

4.4.3 The Effect of Ferric Ion Complexing Agents

The effect of adding phosphate and citrate salts in order to complex the ferric ion was investigated. The data are recorded in Table 17.

The experiments were carried out in cell EC-4 with optical system OS-1-a. Each solution was purged of oxygen by bubbling argon through it for 10 minutes. Further purging had little or no effect upon the photogalvanic potential.

A pH of 2 was required in order to prevent ferrous phosphate from precipitating from the more concentrated phosphate solutions. A tendency for the dye to precipitate slowly from 20% tetrahydrofuran solutions led to the use of 40% tetrahydrofuran.

As the phosphate concentration was increased, the photogalvanic potential first increased, then decreased. The diminished photogalvanic potential at higher concentrations was partly compensated for by a diminished apparent internal resistance. An optimum concentration was found to be about \( 5 \times 10^{-3} \) moles/l. A maximum improvement in power of 40% was obtained.

The addition of citrate led to an increased photogalvanic potential and a decreased apparent internal resistance. An optimum concentration was not established. However, thionine was bleached.

137
<table>
<thead>
<tr>
<th>Completing agent concentration, mol/L</th>
<th>10^{-4} ohms</th>
<th>Load Resistance 10^{-3} ohms</th>
<th>Voltage, Power, Rint, Pint</th>
<th>Apparent Rint, Pint, ohms x 10^{-3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>62</td>
<td>0.38</td>
<td>3.1</td>
<td>17</td>
</tr>
<tr>
<td>none</td>
<td>66</td>
<td>0.44</td>
<td>3.6</td>
<td>17</td>
</tr>
<tr>
<td>none</td>
<td>69</td>
<td>0.48</td>
<td>3.6</td>
<td>18</td>
</tr>
<tr>
<td>none</td>
<td>90</td>
<td>0.48</td>
<td>3.5</td>
<td>18</td>
</tr>
<tr>
<td>none</td>
<td>93</td>
<td>0.48</td>
<td>4.2</td>
<td>18</td>
</tr>
<tr>
<td>1.02 x 10^{-3}</td>
<td>64</td>
<td>0.41</td>
<td>3.9</td>
<td>16</td>
</tr>
<tr>
<td>1.02 x 10^{-3}</td>
<td>65</td>
<td>0.42</td>
<td>4.0</td>
<td>14</td>
</tr>
<tr>
<td>1.02 x 10^{-3}</td>
<td>72</td>
<td>0.52</td>
<td>4.3</td>
<td>14</td>
</tr>
<tr>
<td>1.02 x 10^{-3}</td>
<td>96</td>
<td>0.92</td>
<td>2.7</td>
<td>31</td>
</tr>
<tr>
<td>1.02 x 10^{-3}</td>
<td>122</td>
<td>0.96</td>
<td>2.9</td>
<td>31</td>
</tr>
</tbody>
</table>

*TABLE 17: Effect of Completing Agents on Cell Performance*
TABLE 17 (Continued)

Effect of Complexing Agents on Cell Performance

* \[ [\text{Th}] = 1.02 \times 10^{-3} \text{ M} \]
   \[ [\text{Fe}^{2+}] = 1.01 \times 10^{-2} \text{ M} \]
   \[ [\text{Fe}^{3+}] = 5.02 \times 10^{-5} \text{ M} \]
   \[ \text{pH} = 2.0 \]
   \[ [\text{Tetrahydrofuran}] = 40\% \text{ by volume} \]
in the dark by ferrous ion in a solution containing 20% tetra-
hydrofuran and 0.1 mole/l of citrate. Obviously, the influence
must be reversed at sufficiently high citrate concentra-
tions. The best solution investigated yielded twice as much power as a
similar solution without a complexing agent.

While the data indicate what the overall effect of the
complexing agent is, this is probably the sum of several individual
effects. First, the effective concentration of ferric ions is
reduced, which decreases the potential of the dark electrode and
thus tends to lower the photogalvanic potential. Second, because
the ferric ion concentration is reduced, the back reaction between
leucothionine and ferric ions becomes slower, the photosationary
state concentration of leucothionine is increased, and thus the
photogalvanic potential and the current are both increased. Third,
the phosphate and citrate complexes with ferric ion may react more
rapidly or more slowly at the illuminated electrode than does the
sulfate complex, thus providing an unpredictable effect on the
photogalvanic potential. No attempt was made to separate these
effects. A cell such as EC-5, which was not available at the time,
should be used for studies on the effects of complexing agents.
The inclusion of a reference electrode would permit the determina-
tion of each electrode potential, and the effect of lowering the
dark potential would be apparent.

4.4.4 Miscellaneous Observations on Cells Containing Additives

During the study of the effects of additives a cell was prepared
which yielded 1.80 Nwatts with an illuminated electrode area of 1 sq
cm. This was the best performance that was observed. The cell was
EC-1-0 and the optical system was OS-1-4. The solution had the
following composition:

- thionine: $1.16 \times 10^{-3}$ M
- ferrous ion: $1.00 \times 10^{-4}$ M
- ferric ion: $7.94 \times 10^{-5}$ M
- phosphate: $1.00 \times 10^{-5}$ M
- tetrahydrofuran: 45% by volume
- pH: 2.4
illumination interval to increase the voltage and the current passing in the opposite direction in the next illumination interval. Therefore the most advantageous effects might be anticipated when the most current is being drawn.

Since several seconds of illumination were required before the illuminated electrode reached its maximum potential, very short illumination periods actually decreased the output of the cell. The output increased rapidly at first as the illumination period was increased. The interval length passed through an optimum, and slowly the output of the cell decreased as the illumination interval was increased. The optimum interval is not clearly evident on all of the graphs, but Figure 55 indicates that it increased as the load resistance was increased. This behavior would be expected, since increasing the resistance until the circuit is essentially open would increase the optimum interval to infinity; that is, at open circuit conditions when no concentration polarization occurs, it is impossible to increase the power by alternating illumination.

The optimum performances are summarised in Table 19. The power was increased by a factor of as much as 130. As discussed above, the factor by which the power was increased became larger as the load resistance became smaller.

The maximum power level with constant illumination was achieved with solution II-75-1, containing $4 \times 10^{-4}$ moles of thionine per liter. Maximum power using alternating illumination was observed for II-75-5, however, which had only $4 \times 10^{-5}$ moles of thionine per liter. Thus alternating illumination was far more effective in the more dilute solution. A perusal of Tables 18 and 19 will reveal that this was generally true. Concentration polarization at the illuminated electrode can be decreased by increasing the concentration of leucothionine in the photostationary state, which is in turn limited by the initial concentration of thionine. Since concentration polarization is already reduced in the more concentrated solutions, the additional improvement afforded by alternating illumination is not as great as that of the dilute solutions.
The phosphate ion concentration was so low that it probably had no effect.

The power level attained by Potter and Thaller was not stated explicitly, but a maximum of $1.8 \times 10^{-9}$ watts/sq cm can be calculated from their data. The power level was therefore increased by a factor of 1000 over that of Potter and Thaller.

In the course of these experiments one cell was operated in two periods for a total of over 8 hours at power levels ranging from 0.81 to 0.98 $\mu$ watts. The cell was EC-1-e, the optical system was OS-1-d, and the solution had the following concentrations:

- thionine: $2.89 \times 10^{-3}$M
- ferrous ion: $1.00 \times 10^{-2}$M
- ferric ion: $7.94 \times 10^{-5}$M
- tetrahydrofuran: 40% by volume
- pH: 2.5

An open circuit photogalvanic potential of 172 mv was obtained with this cell. After 8 hours of operation the power level was still 0.88 $\mu$ watts.

One of the advantages of using relatively high concentrations of thionine in the photogalvanic cell is the extended absorption range of these solutions, as may be seen from the spectrum in Figure 52. It indicates that solutions greater than about $1.6 \times 10^{-3}$M with 2 mm path lengths would have absorbances greater than 2 for almost all wavelengths below 8000Å. In fact, such solutions apparently would have strong absorption up to at least 10,000Å in the near infrared. One of the objectives of this program was to determine the actual upper and lower wavelengths of photogalvanic activity. It seems likely that thionine is active over the entire visible spectrum in these concentrated solutions.

4.5 THE EFFECT OF PULSED OR ALTERNATING ILLUMINATION

The effect of pulsed or alternating illumination was investigated with cell MC-4 using optical system OS-1-b. The solution for this study are described in Table 18.
Figure 52. Spectrum of a Concentrated Solution of Thionine (1.0 x 10^{-3} M, 0.1 cm path length)
### TABLE 18
The Composition of the Test Solutions
Used in the Study of Alternating Illumination

<table>
<thead>
<tr>
<th>Designation</th>
<th>Concentration, moles/l.</th>
<th>Volume % Tetrahydro-furan</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Thionine</td>
<td>FeSO₄</td>
</tr>
<tr>
<td>II-75-1</td>
<td>4.07x10⁻⁴</td>
<td>1.01x10⁻²</td>
</tr>
<tr>
<td>II-75-4</td>
<td>4.07x10⁻⁵</td>
<td>1.00x10⁻¹</td>
</tr>
<tr>
<td>II-75-5</td>
<td>4.07x10⁻⁵</td>
<td>1.00x10⁻²</td>
</tr>
<tr>
<td>II-75-6</td>
<td>1.97x10⁻³</td>
<td>9.74x10⁻²</td>
</tr>
</tbody>
</table>
The solenoid-operated shutter is shown in Figure 15 with the cell MC-3. The solenoid was activated by closing a microswitch which in turn was controlled by a rotating cam. The speed of rotation of the cam, and consequently the illumination interval, was adjusted with a powerstat.

Electrodes 1 and 3 of MC-4 were illuminated simultaneously while electrodes 2 and 4 were kept dark, and vice versa. Some leakage of light around the shutter to the dark electrodes was unavoidable.

The cell performance at constant illumination was determined by permitting maximum polarization to occur at low resistances, then increasing the resistance and waiting until a constant voltage was observed. This procedure required 20–30 minutes each time, and the average set of alternating illumination measurements required 15–30 minutes. Consequently there might be some doubt that the cell characteristics remained exactly the same throughout this period. However, checks on cell performance at constant illumination before and after the alternating illumination experiment indicated that only small changes occurred if the solution was first thoroughly de-aerated.

The areas under the voltage curves recorded during alternating illumination were measured with a compensating polar planimeter for several consecutive illumination intervals of constant interval length. The average voltage was calculated as follows:

\[
\text{Area (sq mm)} \times \frac{\text{No. of mv/mm}}{\text{Time (sec)}} \times \frac{\text{No. of mm/sec}}{\text{average voltage (mv)}} = 34
\]

This voltage was compared with the average of the voltages observed when each pair of electrodes was illuminated constantly.

The results for four typical experiments are shown graphically in Figures 53–56. The effect of alternating illumination varied with the composition of the solution, the load resistance, and the illumination interval. The improvement was greatest with the lower load resistances when the most current was drawn. The higher the current is, the greater is the concentration polarization. Alternately illuminating the electrodes takes advantage of the concentration polarization incurred during one
Figure 53. The Effect of Alternating Illumination on Cell Performance

(MC-4 with Solution II-75-1)
Figure 54. The Effect of Alternating Illumination on Cell Performance
(MC-4 with Solution II-75-6)
Figure 55. The Effect of Alternating Illumination on Cell Performance
(MC-4 with Solution II-75-4)
Figure 56. The Effect of Alternating Illumination on Cell Performance
(MC-4 with Solution II-75-5)
illumination interval to increase the voltage and the current passing in the opposite direction in the next illumination interval. Therefore the most advantageous effects might be anticipated when the most current is being drawn.

Since several seconds of illumination were required before the illuminated electrode reached its maximum potential, very short illumination periods actually decreased the output of the cell. The output increased rapidly at first as the illumination period was increased. The interval length passed through an optimum, and slowly the output of the cell decreased as the illumination interval was increased. The optimum interval is not clearly evident on all of the graphs, but Figure 55 indicates that it increased as the load resistance was increased. This behavior would be expected, since increasing the resistance until the circuit is essentially open would increase the optimum interval to infinity; that is at open circuit conditions when no concentration polarization occurs, it is impossible to increase the power by alternating illumination.

The optimum performances are summarized in Table 19. The power was increased by a factor of as much as 130. As discussed above, the factor by which the power was increased became larger as the load resistance became smaller.

The maximum power level with constant illumination was achieved with solution II-75-1, containing $4 \times 10^{-4}$ moles of thionine per liter. Maximum power using alternating illumination was observed for II-75-5, however, which had only $4 \times 10^{-5}$ moles of thionine per liter. Thus alternating illumination was far more effective in the more dilute solution. A perusal of Tables 18 and 19 will reveal that this was generally true. Concentration polarization at the illuminated electrode can be decreased by increasing the concentration of leucothionine in the photostationary state, which in turn limited by the initial concentration of thionine. Since concentration polarization is already reduced in the more concentrated solutions, the additional improvement afforded by alternating illumination is not as great as that of the dilute solutions.
<table>
<thead>
<tr>
<th>Solution</th>
<th>Figure</th>
<th>Load Resistance, ohms</th>
<th>Power Level, μ watts</th>
<th>Power Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Constant Illumination</td>
<td>Alternating Illumination</td>
<td></td>
</tr>
<tr>
<td>II-75-1</td>
<td>10</td>
<td>$10^3$</td>
<td>0.29</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$10^2$</td>
<td>0.076</td>
<td>1.0</td>
</tr>
<tr>
<td>II-75-6</td>
<td>11</td>
<td>$10^3$</td>
<td>0.025</td>
<td>0.088</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$10^2$</td>
<td>0.026</td>
<td>0.15</td>
</tr>
<tr>
<td>II-75-4</td>
<td>12</td>
<td>$10^4$</td>
<td>0.014</td>
<td>0.029</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$10^3$</td>
<td>0.036</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$10^2$</td>
<td>0.01</td>
<td>0.28</td>
</tr>
<tr>
<td>II-75-5</td>
<td>13</td>
<td>$10^4$</td>
<td>0.041</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$10^3$</td>
<td>0.030</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$10^2$</td>
<td>0.005</td>
<td>0.64</td>
</tr>
</tbody>
</table>
4.6 TESTING OF THE LABORATORY CELLS

The model cells MC-1, MC-2, and MC-3 were constructed with Lucite (Plexiglass) containers. The potentials obtained from these cells were quite low. For example, immediately upon illuminating MC-1 containing a dilute, aqueous electrolyte, a potential of about 120 mv was observed. However, this potential dropped off to a few millivolts within a matter of minutes. At the time of the experiment, this behavior was attributed to electrode deactivation by some substance extracted from the Lucite. In view of our very sketchy knowledge at that time about the problem of electrode activation, it seems that the utility of these cells should be re-examined.

Cells MC-4, MC-5, and MC-6 were tested in detail. MC-4 was designed for the investigation of alternating illumination discussed in Section 4.5. This electrodes made of platinum gauze were placed close to the window because the cell was intended for use with a fairly concentrated thionine solution. In a concentrated solution significant bleaching occurs only to a depth of a few millimeters. MC-5 was designed for the same type of electrolyte, while MC-6 was designed to be most efficient with a dilute solution. In a dilute thionine solution the dye is bleached to a greater depth than in a concentrated solution. MC-6 had a wide illuminated electrode extending farther into the solution so as to be in contact with more of the reduced dye and to utilize more of the incident light.

Table 20 provides the composition of all the solutions used in testing the model cells.

4.6.1 Cell Deterioration and Decomposition Phenomena

The problem of cell deterioration during use was basic to the investigation of other cell characteristics; consequently the results of this study are discussed first.

The output of each cell (MC-4, 5, and 6) was followed during prolonged periods of illumination at various load resistances. The performances are shown in Figures 57-66; however, these figures by themselves may be misleading, and they should not be consulted
<table>
<thead>
<tr>
<th>Solution Designation</th>
<th>Concentration, moles/liter</th>
<th>pH</th>
<th>%THF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Th</td>
<td>Fe²⁺</td>
<td>Fe³⁺</td>
</tr>
<tr>
<td>II-75-4</td>
<td>4.07 x 10⁻⁵</td>
<td>1.00 x 10⁻¹</td>
<td>3.01 x 10⁻⁵</td>
</tr>
<tr>
<td>II-75-6</td>
<td>1.97 x 10⁻³</td>
<td>9.74 x 10⁻²</td>
<td>2.92 x 10⁻⁵</td>
</tr>
<tr>
<td>II-77-2</td>
<td>4.07 x 10⁻⁵</td>
<td>1.01 x 10⁻²</td>
<td>1.00 x 10⁻⁵</td>
</tr>
<tr>
<td>II-77-4</td>
<td>4.07 x 10⁻⁵</td>
<td>1.00 x 10⁻²</td>
<td>1.00 x 10⁻⁵</td>
</tr>
<tr>
<td>II-77-6</td>
<td>4.07 x 10⁻⁵</td>
<td>1.00 x 10⁻²</td>
<td>1.00 x 10⁻⁵</td>
</tr>
<tr>
<td>II-77-8</td>
<td>4.07 x 10⁻⁵</td>
<td>1.00 x 10⁻²</td>
<td>1.00 x 10⁻⁵</td>
</tr>
<tr>
<td>II-79-2</td>
<td>4.07 x 10⁻⁵</td>
<td>1.01 x 10⁻²</td>
<td>4.02 x 10⁻⁶</td>
</tr>
<tr>
<td>II-81-4</td>
<td>1.02 x 10⁻³</td>
<td>1.00 x 10⁻²</td>
<td>5.02 x 10⁻⁵</td>
</tr>
<tr>
<td>II-82-1</td>
<td>1.02 x 10⁻³</td>
<td>1.00 x 10⁻²</td>
<td>5.02 x 10⁻⁵</td>
</tr>
<tr>
<td>II-83-1</td>
<td>1.02 x 10⁻³</td>
<td>1.00 x 10⁻²</td>
<td>5.02 x 10⁻⁵</td>
</tr>
<tr>
<td>II-83-2</td>
<td>6.10 x 10⁻⁴</td>
<td>1.00 x 10⁻²</td>
<td>5.02 x 10⁻⁵</td>
</tr>
<tr>
<td>II-83-3</td>
<td>6.10 x 10⁻⁴</td>
<td>1.00 x 10⁻²</td>
<td>5.02 x 10⁻⁵</td>
</tr>
<tr>
<td>II-83-4</td>
<td>6.10 x 10⁻⁴</td>
<td>1.00 x 10⁻²</td>
<td>5.02 x 10⁻⁵</td>
</tr>
<tr>
<td>II-83-5</td>
<td>6.10 x 10⁻⁴</td>
<td>1.00 x 10⁻²</td>
<td>5.02 x 10⁻⁵</td>
</tr>
<tr>
<td>II-83-6</td>
<td>6.10 x 10⁻⁴</td>
<td>1.00 x 10⁻²</td>
<td>1.00 x 10⁻⁴</td>
</tr>
<tr>
<td>II-83-7</td>
<td>6.10 x 10⁻⁴</td>
<td>1.00 x 10⁻²</td>
<td>2.08 x 10⁻⁵</td>
</tr>
<tr>
<td>II-84-2</td>
<td>4.07 x 10⁻⁵</td>
<td>1.00 x 10⁻²</td>
<td>5.02 x 10⁻⁵</td>
</tr>
<tr>
<td>II-84-5</td>
<td>4.07 x 10⁻⁵</td>
<td>1.00 x 10⁻²</td>
<td>5.02 x 10⁻⁵</td>
</tr>
<tr>
<td>II-85-1</td>
<td>4.07 x 10⁻⁵</td>
<td>1.00 x 10⁻²</td>
<td>5.02 x 10⁻⁵</td>
</tr>
<tr>
<td>II-85-4</td>
<td>4.07 x 10⁻⁵</td>
<td>1.00 x 10⁻²</td>
<td>1.00 x 10⁻⁵</td>
</tr>
</tbody>
</table>
Figure 58. Cell Performance During Prolonged Illumination
(MC-6 with Solution II-77-4; OS-2-b; Load Resistance = 10^3 ohms)
Figure 59. Cell Performance During Prolonged Illumination

(MC-6 with Solution II-77-6; OS-2-b with Corning Filter CS-3-73; Load Resistance = 10^3 ohms)
Figure 60. Cell Performance During Prolonged Illumination

(MC-6 with Solution II-77-8; OS-2-b with Corning Filter CS-3-73; Load Resistance = $10^3$ ohms)
Figure 62. Cell Performance During Prolonged Illumination
(MC-5 with Solution II-79-2; OS-2-b; Load Resistance = 10^8 ohms)
Figure 63. Cell Performance During Prolonged Illumination
(MC-5 with Solution II-81-4; OS-2-a; Load Resistance = \(10^3\) ohms)
Fig. 64. Cell Performance During Prolonged Illumination

(MC-5 with Solutions II-81-4 and II-82-1; OS-2-a; Load Resistance = 10^4 ohms)
Figure 65. Cell Performance During Prolonged Illumination
(MC-4 with Solution II-84-5; OS-2-a; Load Resistance = 10^4 ohms)
Figure 66. Cell Performance During Prolonged Illumination
(MC=4 with Solution II-84-5; OS-2-a; Load Resistance = 10^3 ohms)
without following the explanation in the text. The figures describe experiments for each cell in the chronological order in which they were performed. The results of these tests provided further information about the importance of electrode activation.

MC-6 was tested first at a load resistance of $10^6$ ohms with the results shown in Figure 57. The open circuit potential at the start of the test was 74 mv. The terminal voltage was recorded during a period of 7 hours of illumination with OS-2-b. The voltage decreased rapidly at first due to concentration polarization, then increased to a maximum in a little less than 2 hours. At this point the power was 0.44 $\mu$watt. After 2 hours of illumination the output decreased rapidly, so that after 7 hours the power level was only 0.0030 $\mu$watt, or less than 0.7% of the maximum.

When the same cell was illuminated 3 days later, the open circuit photogalvanic potential was only 35 mv. With an external load resistance of $10^6$ ohms the voltage decreased within 1 hour to the value which was recorded as the final voltage 3 days earlier. Apparently the deterioration was irreversible.

The total current was calculated from the area under the curve in Figure 57 to be $8.50 \times 10^{-2}$ coulomb. This was equivalent to about 1.8 electrons per molecule of thionine present in the cell.

A spectrophotometric analysis of the electrolyte after the experiment revealed that only 20% of the dye had been destroyed. It was quite surprising to find that decomposition of no more than 20% could cause such a drastic reduction in power.

The cell was next tested with a similar solution at a load resistance of $10^3$ ohms. Open circuit voltage at the start of the experiment was 85 mv. Figure 58 describes the voltage and the current produced during 35 hours of illumination. Only 14% of the dye decomposed during this test.

At this load resistance the output of the cell (after concentration polarization had reached a maximum) was about 0.22 $\mu$watt. After 35 hours of illumination the power level was 0.016 $\mu$watt, or about 7% of the earlier power level. A total of 1.12 coulombs, or about 23 electrons per molecule of thionine, were taken from the cell during this time. Obviously the extent of deterioration was not simply a function of the current drawn from the cell.
Testing of MC-6 continued with fresh solutions and yielded the results shown in Figures 59 and 60. Figure 59 indicates that the power level of the cell dropped within 15 minutes to less than that at the end of the previous run. This power level was maintained throughout the 16 hour run. At the beginning of the run shown in Figure 60 the open circuit potential was only 37 mv, and the power dropped within 30 minutes to about the same level as was maintained in the previous run.

The above results revealed that cell deterioration was not rectified completely by replacing the solution with a similar fresh solution. The conclusion is that cell deterioration is primarily due to a change in the condition of the electrode surface, and that this condition persists even after the solution is replaced.

At this point in the testing program the method of activating the electrode with a detergent-dye solution was discovered (see Section 4.2.2). The cell performance was again followed at 10$^4$ ohms, this time for a period of 23 hours (see Figure 60). The open circuit potential at the beginning was raised to 127 mv because of the electrode treatment, and this time the output diminished far more slowly than it did in the original test presented in Figure 57.

MC-5 was tested first with a dilute aqueous solution. Since the cell was designed to be used with a concentrated solution, it had high apparent internal resistance with a dilute solution. The performance is shown in Figure 62 at a load resistance of 10$^5$ ohms.

The great disappointment of the model cells was that they did not work well with concentrated solutions in aqueous tetrahydrofuran. Figures 63 and 64 describe the performance of MC-5 in three such solutions. The open circuit voltages at the start of these tests were 97, 66, and 19 mv, respectively. The electrode was activated with a dodecyl sodium sulfate-thionine solution prior to each run. Apparently the activation procedure was not effective for tetrahydrofuran solutions. The cause of the very poor performance of the tetrahydrofuran solutions was not determined. In Table II are listed the open circuit voltages of MC-5 with other tetrahydrofuran solutions with various component concentrations, and all of these solutions were unsuccessful. Because of the necessity of fulfilling the demands of the contract within a limited time, the use of the concentrated thionine solutions in aqueous tetrahydrofuran had to be abandoned for this testing program. While earlier experiments
<table>
<thead>
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<th>Solution Designation</th>
<th>Photogalvanic Potential, mV</th>
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</thead>
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<tr>
<td>II-83-1</td>
<td>8</td>
</tr>
<tr>
<td>II-83-2</td>
<td>23</td>
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<tr>
<td>II-83-3</td>
<td>12</td>
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<td>II-83-4</td>
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<td>27</td>
</tr>
<tr>
<td>II-83-7</td>
<td>38</td>
</tr>
</tbody>
</table>
had indicated that such solutions were capable of markedly increasing the power (see Section 4.4), they simply could not be made to work properly in the model cells within the allotted time.

Not only did the tetrabromoforman solutions fail to yield the anticipated open circuit voltages, but, as Figure 64 demonstrates, after several hours of illumination they even produced photogalvanic potentials which were reversed in polarity. That is, the illuminated electrode became more positive upon illumination. No explanation of this unusual behavior can be given at this time. As was stated in Section 4.4.4, EC-1-e exhibited normal behavior when illuminated for 10 hours with a similar solution.

MC-4 also had to be tested with dilute solutions instead of the concentrated solutions for which it was intended. Figures 65 and 66 provide the results of these tests. (In testing the effects of prolonged illumination, light intensity, and temperature on MC-4 the center two electrodes were illuminated continuously while the outer electrodes were kept dark.)

The run described in Figure 66 permitted further conclusions concerning the nature of the cell deterioration. The open circuit potential at the beginning of the experiment was 130 mv. After 24 hours and 50 minutes this value declined to 69 mv, after 63 hours it was 24 mv, and at the end of the test it was 23 mv. While the open circuit potential had diminished considerably, the difference between the power at the beginning and at the end of the run with a load of $10^3$ ohms was hardly significant. The power obtained with high load resistances will decrease more rapidly than the power obtained at relatively low-load resistances even with the same solution.

After the completion of the experiment described in Figure 66, the test solution was put into MC-5. The electrode of MC-5 had been freshly activated. With fresh solutions this cell ordinarily gave a photogalvanic potential of about 120 mv. With the used portion of II-84-5 a photogalvanic potential of 91 mv was produced at first, although the potential decreased rather rapidly to about 70 mv. It must be concluded that the cell deterioration is not directly caused by decomposition of the dye, since a 'spent' solution will work far better with a freshly activated electrode.
The effect of ultraviolet light was not thoroughly investigated. An ultraviolet filter (CS-3-73) was inserted in the light beam in the tests described in Figures 59 and 60, but when these tests produced poor results (for other reasons, as has been discussed), the filter was eliminated. It seems likely that the dye decomposition was caused at least partially by the ultraviolet light, and if the cell deterioration was indirectly due to dye decomposition, an ultraviolet filter might have extended the useful cell life significantly.

In summary the most important observations are:

1. Cell performance is decreased tremendously by a relatively small amount of dye decomposition.
2. Cell deterioration is not erased simply by replacing the solution with a fresh portion.
3. The used solution produces much higher voltages when tested in a cell with a freshly activated electrode.
4. The decrease in power is most pronounced at high load resistances.
5. Concentrated thionine solutions in aqueous tetrahydrofuran did not perform as well as was expected.

The rationalization for these observations and some general conclusions are:

1. Cell deterioration is caused by electrode poisoning which is probably a result of dye decomposition, but the deterioration is not directly due to the photochemical destruction and loss of the dye.
2. During prolonged illumination the voltage-current characteristics of the two redox systems at the illuminated electrode surface are changed in such a way that the open circuit electrode potential is considerably decreased but that the current available at an electrode potential close to the dark potential is not as greatly diminished.
Electrode activation is somehow different for solutions containing tetrahydrofuran.

A better understanding of electrode activation and the effects of ultraviolet light might lead to ways of eliminating cell deterioration.

The problem of cell deterioration is not nearly as severe as indicated by Potter and Thaller. 49

4.6.2 The Effects of the Intensity of Illumination

The effects of the intensity of illumination were studied with system OS-1-a, in which the cell was illuminated with an intensity of 2.9 suns in the 3300-9500 Å range and 4.3 suns over the limited but more effective range of 5100-6300 Å. The intensity in "suns" is based on a comparison with the solar radiation which would pass through the same filter combination.

Figures 67-75 present the experimental results. It was difficult to obtain satisfactory data because one had to continue illumination long enough to allow concentration polarisation to reach a maximum, and yet the experiments had to be completed before cell deterioration (Section 4.6.1) had seriously altered the cell characteristics.

The potential of MC-6 at various light intensities and various loads is shown by Figure 67. Figures 68 and 69 are plots of the power against the light intensity in terrestrial suns. The output levels off at high light intensities in agreement with the results in Section 4.3.2.3. Extrapolation of the curves to an intensity of 10 suns suggests that the power would be about 2.8 µwatts at that intensity. While the test solution was quite suitable for the intensities actually used, other solutions (e.g., solutions with a higher pH22) would probably be more effective at 10 suns.

Figure 70 gives the efficiency at various light intensities for two load resistances. The efficiency was calculated on the basis of the incident energy and not on the basis of the light actually absorbed by the dye in the illuminated solution. The latter method of calculating efficiencies is generally used, but since there is no hope of recovering the rejected light for further use it seemed more meaningful to ignore the unabsorbed light.

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Figure 67. The Variation of Potential with Light Intensity (MC-6 with Solution II-79-2)
Figure 68. The Effect of Light Intensity on Power (MC-6 with Solution II-79-2)
Figure 69. The Effect of Light Intensity on Power (MC-6 with Solution II-79-2)
Figure 70. The Effect of Light Intensity on the Efficiency
(MG-6 with Solution II-7-2).

Light intensity, sun at earth's surface (3300-9500 A).

10^3 ohms

10^4 ohms

Efficiency, % × 10^4

0 1 2 3 4 5

0 1 2 3 4 5 6 7 8 9 10

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Figure 71. The Variation of Potential with Light Intensity (MC-4 with Solution II-85-I)
Figure 72. The Effect of Light Intensity on Power (MC-4 with Solution II-85-1)
Figure 73. The Effect of Light Intensity on Power (MC-4 with Solution II-85-1)
Figure 74. The Effect of Light Intensity on the Efficiency (MC-4 with Solution II-85-1)
Figure 75. The Effect of Light Intensity on Power (MC-5 with Solution II-84-2)
It was found (Section 4.6.4) that about 60% of the incident energy was ineffective and that some of this was even detrimental. Of the 40% which was useful it is estimated that only about 70% was absorbed (assuming that the solution was 75% bleached in the photo-stationary state). Thus about 26% of the light was absorbed, and the estimated efficiency on this basis was about $3 \times 10^{-3}$, 10 times the efficiency reported by Potter and Thaller\textsuperscript{49} and 1/30 of the efficiency estimated by Rabinowitz.

The efficiency passes through a maximum as the light intensity is increased, and the maximum moves toward higher intensities as the current being drawn is increased. At high current densities the amount of bleaching at the electrode surface may be considerably less than that in the bulk of the solution. The solution at the electrode surface is thus better able to utilize more intense light. As the current density increases and the extent of bleaching at the electrode surface decreases, the utilization of higher intensities is enhanced and the maximum efficiency is shifted toward higher illumination levels.

The discussion of the behavior of MC-5 is borne out by the results with MC-4 shown in Figures 71 to 74. The data obtained with MC-5 were so scattered that a reliable extrapolation of the power level to 10 sans was almost impossible (see Figure 75). The scatter was probably caused by cell deterioration plus errors in judging concentration polarization to be complete before this was actually true.

4.6.3 The Effect of Temperature

The effect of temperature was measured with OS-2-b by placing the cells in a wooden box and passing air at the desired temperature through the box. The air entered at the rear of the box and passed by the cell window through the opening provided for the light beam. The temperature was measured by a thermometer placed directly beneath the cell window.

Figures 76-78 demonstrate the effects of temperature on the photogalvanic potential and on the power level after concentration polarization had reached a maximum. The open circuit potential increased with decreasing temperature (see also Figure 49), but the power level passed through a maximum in the vicinity of 20-30°C.

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Figure 76. The Effect of Temperature on the Photogalvanic Potential and the Power Level (MC-6 with Solution II-79-2)
Figure 77. The Effect of Temperature on the Photogalvanic Potential and the Power Level (MC-5 with Solution II-85-1)
Figure 78. THE EFFECT OF TEMPERATURE ON THE PHOTOCALVANIC POTENTIAL AND THE POWER LEVEL (MC-4 with Solution II-85-3)
The effect on the temperature is therefore the sum of at least two competing effects. The first effect is that on the potential. The second effect is that on the rate of material transfer. Since the electrochemical process constantly increases the ferric ion concentration at the illuminated electrode and decreases it at the dark electrode, ferric ions must be transferred by diffusion or convection in the opposite direction. As the temperature decreases, the rates of diffusion and convection also decrease, and concentration polarization becomes more pronounced. Consequently, the power level is decided by a balance of the two factors.

The data at $50^\circ$ in Figure 78 was obtained one day before the remainder of the data on MC-4. The lack of agreement is an indication of the difficulty experienced in general in obtaining coherent data. It is also an indication of the degree of involvement of the poorly understood electrode activation processes.

While Figures 76-78 show the relationship between the power and temperature, these are valid only if the temperature is held constant for a long period of time. Temperature cycling, i.e., periods of warming closely followed by periods of cooling, can increase the power tremendously. This was demonstrated with MC-6 and solution II-79-2. Figure 76 reveals that when the temperature was held constant the power was never more than 0.37 $\mu$watts. Temperature cycling between $5^\circ$ and $27^\circ$ raised the power level to between 0.66 and 1.37 $\mu$watts, where it was kept for a period of almost 3 hours. The improvement must have been the result of convection currents induced by the temperature changes.

4.6.4 The Effect of the Wavelength of the Exciting Light

The effect of varying the wavelength of the exciting light was investigated for cells MC-4 and MC-6 with OS-1-c. The photogalvanic potential had a tendency to drop during the tests. Inserting an additional infrared filter (CS-1-69) helped to maintain a more nearly constant potential. Obviously infrared light will diminish the photogalvanic potential, which is not surprising, since any heating of the solution has this effect.
The tests were carried out by noting the effect of various light filters placed in the light beam on the cell response. Corning filters CS 2-56 to CS 2-64, CS 2-73, and CS 3-66 to CS 3-75 were used. These filters have sharp cut-off points and strongly absorb all radiation of shorter wavelengths. The wavelength at which 37% of the light is transmitted is designated the "cut" by Corning; this wavelength will be used in discussing the effect of the filters.

In solution II-75-4 in MC-4 the wavelength of the cut-offs were approximately 6390 Å on the long wavelength side of the maximum and 5280 Å on the short wavelength side. When filters with a cut of these wavelengths were inserted the photogalvanic potential of the cell under open circuit conditions was within about 1% of the minimum and the maximum responses, respectively. The effect of wavelength was qualitatively independent of the load resistance.

With solution II-75-6, a considerably more concentrated solution, the short wavelength cut-off was about 4930 Å and the long wavelength cut-off lay between 6390 and 6570 Å. The response to a wider region of the spectrum may be attributed to the higher thionine concentration. As the concentration is increased the absorption at both longer and shorter wavelengths becomes significant. Enhanced absorption at these wavelengths produces an apparent shift in the arbitrary "cut-off". In highly concentrated solutions the cut-off limits should be spread so that visible light of any wavelength is utilized.

A more detailed approach was taken in studying the response of MC-6 to wavelength changes using solution II-77-2. The effect of the colored filters was then measured, and the percentage of exciting light transmitted was taken from the curve. These values are plotted in Figure 79 against the cut of the filters (circled dots in Figure 79). From a smooth curve through these points the ratio of the increment of exciting light to the increment of the wavelength was calculated and plotted against the average wavelength (points in squares). The resulting curve is a rough version of the action spectrum. Its similarity to the thionine absorption curve (dotted curve) is apparent. The thionine absorption curve is a plot of absorbance versus wavelength, however, and only a qualitative resemblance should be expected. Furthermore, this treatment assumes that the light intensity was approximately the same at all wavelengths throughout the effective spectral range.
The wavelength dependence of MC-5 with solution II-85-1 was measured with optical system OS-2-a. A plot of the percentage of the exciting light transmitted versus the cut of the filter is presented in Figure 80. The greatest response was obtained between 5410 and 5550 Å and between 5720 and 5820 Å. This response was not due to any special sensitivity of thionine but to the intensity of the light from the mercury lines in these spectral regions. The cut-offs were approximately 5400 and 6400 Å between which 40% of the energy lies. The short wavelength cut-off was determined more accurately with a neutral density filter which transmitted 19.5% of the light placed in the light beam. At the lower light intensity the cell was more sensitive to small intensity changes. A very weak response was detected down to at least 4660 Å.

The filters with cuts at 5410 Å and below are shown in Figure 80 as having transmitted all of the exciting light. The photogalvanic potential of the cell was actually greater than without any filter at all. Apparently the ultraviolet light which these filters remove lowers the cell responses. The effect is possibly due to the re-oxidation of leucothionine upon absorption of the ultraviolet light. This influence reinforces the suspicion that ultraviolet light may be involved in cell deterioration.

Optical system OS-2-c was employed for testing the cells with approximately monochromatic light. Unfortunately the light intensity was so low that the photogalvanic potentials were extremely small. The results, which are presented in Table 22, are simply what one would expect with very weak illumination.

Table 22

<table>
<thead>
<tr>
<th>Load Resistance, ohms</th>
<th>Voltage, mv</th>
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<tr>
<td></td>
<td>MC-4, II-85-1</td>
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<tr>
<td>Open circuit</td>
<td>12.6</td>
</tr>
<tr>
<td>$10^5$</td>
<td>6.6</td>
</tr>
<tr>
<td>$10^4$</td>
<td>3.1</td>
</tr>
<tr>
<td>$10^3$</td>
<td>--</td>
</tr>
</tbody>
</table>
Figure 80. Relationship Between Cell Response and Wavelength of Light (MC-5 with Solution II-85-1)
4.6.5 Electrode Orientation and Spacing Effects

It was not practical to construct model cells with movable electrodes so that electrode orientation and spacing effects could be studied in detail; however, these effects were examined in Section 4.2.1 with various experimental cells.

One new influence of electrode orientation was displayed by MC-6. At the beginning of the test recorded in Figure 61 the plates of the illuminated electrode were in a horizontal position, and severe concentration polarization was observed. Rotating the cell 90° so that the electrodes were vertical reduced polarization and increased the power.

Visual observation of an illuminated and partially bleached thionine solution revealed that convection currents rose upward past the window. When the plates were placed horizontally they undoubtedly hindered these currents. This hinderance decreased the rate of material transfer through the solution and accentuated concentration polarization effects. Convection is apparently more effective than diffusion as a means of material transfer in these cells. In light of this result MC-5 would appear to have a particularly inappropriate illuminated electrode.

The relatively low open circuit photogalvanic potentials (about 120 to 140 mv) of MC-5 and MC-6 were probably due to light leakage to the dark electrode. Higher photogalvanic potentials (about 170 mv) were obtained with MC-4, in which the dark electrodes were better shielded.

4.6.6 The Effect of Varying the Angle of Incidence

The effect of varying the angle of incidence on the photogalvanic potential is shown in Figures 81-83. Optical system OS-1-b was employed for these experiments. Each cell was mounted on a rotatable platform in such a fashion that the cell could be pivoted about a point underneath the center of the illuminated cell window or windows. MC-4 was tested only with continuous illumination of one pair of windows. MC-6 was mounted so that the plates were in a horizontal position parallel to the platform which was being rotated.
Figure 81. EFFECT OF VARYING THE ANGLE OF INCIDENCE
(MC-4 with Solution II-75-6)
Figure 83. EFFECT OF VARYING THE ANGLE OF INCIDENCE
(MC-6 with Solution II-77-2)
The photogalvanic potential for each position is expressed as a percentage of the maximum, which, of course, was achieved when the angle of the incidence was 90°. Theoretically the light energy falling upon the window should vary with the cosine of the angle that the light beam forms with the normal. The dotted curves in Figures 81-83 denote the theoretical changes in the incident light energy.

The potential changes followed the energy changes rather closely for MC-4 and MC-6. A perfect parallel should not be expected, since the electrode potential is not exactly linear with light intensity (Section 4.3.2.2). This fact is particularly evident for MC-5. Apparently bleaching was almost complete with the light received at an angle of 60°, and the more intense illumination received at 75° and 90° had no effect on the photogalvanic potential. Nevertheless, the general conformity of the potential curves with the incident energy curves indicates that the effect of varying the angle of incidence is almost the same as decreasing the incident light energy by the same amount without changing the angle of incidence.
SECTION 5

CONCLUSIONS AND RECOMMENDATIONS
FOR FUTURE DEVELOPMENT

5.1 GENERAL DISCUSSION OF CONCLUSIONS

This section contains a general discussion of the feasibility of thionine photogalvanic power generation system. The evaluation is divided into five areas: the voltage, the current and the power, the efficiency, the rate of cell deterioration, and the efficacy of certain specific measures. Each is discussed in terms of what may probably ultimately be attained.

5.1.1 The Voltage

The maximum photogalvanic potential observed during this study was 220 mv, but Rabinowitch has evidence for potentials up to 265 mv. His reports of 400 and 500 mv must at present, at least, be disregarded for lack of supporting data. In this section we will attempt to make a reasonable estimate of what the maximum voltage might be.

The electrode mechanism presented in Section 4.3 allows for photogalvanic potentials approaching, but never quite achieving, the difference between the dark potential (determined by the ferric-ferrous redox system) and the potential of the thionine-leucothionine system in the photostationary state.

The limiting photogalvanic potential for a practical photogalvanic cell would probably be attained in a solution with a pH of 3. This estimate is largely based on the experience of Rabinowitch who obtained a maximum potential at a pH of about 2.7. Because of the pH of 3 an illumination of about 5 suns intensity would probably be required to bleach the solution sufficiently to take advantage of the large difference in the potentials of the ferric-ferrous and the thionine-leucothionine redox systems.
The potential of the dark electrode would depend on the relative amounts of ferric and ferrous ions that could be introduced without completely preventing bleaching. Rabinowitch\textsuperscript{52} used a solution which was \(2.5 \times 10^{-5}\) M in ferric ion and \(2 \times 10^{-3}\) M in ferrous ion in order to obtain his maximum photogalvanic potential. In the same paper he stated that for other solutions a maximum photogalvanic potential was obtained with ferrous ion concentrations of \(1 \times 10^{-2}\). In order to achieve a maximum rate of bleaching (which is indeed necessary because of the rapidity of the back reaction at this pH\textsuperscript{27}), a minimum ferrous ion concentration would probably be \(1 \times 10^{-2}\) M. The back reaction is strongly dependent on the ferric ion concentration. In fact, Hatchard and Parker\textsuperscript{19} state that the quantum yield of leucothionine formation tends to zero at high ferric ion concentrations, especially if the light intensity is low. A concentration of \(5 \times 10^{-4}\) M is considered to be the maximum ferric ion concentration that could be tolerated under the conditions described. Assume that no ferric ion complexing agents other than water are present. In this investigation sulfate and chloride ions were always present; in the hypothetical case perchlorate salts would have to be used to eliminate complexing, and we will assume that this would not significantly decrease the extent of bleaching (see Section 4.4.1). For the sake of simplicity a temperature of 25°C will be considered. The dark potential of such a system would be 0.694 volt.

The extent of bleaching in such a system would probably be quite small even at intensities of 5 to 10 suns. At a pH of 2.7 Rabinowitch\textsuperscript{52} found practically no bleaching, and his illumination level was probably about 3 suns. We will assume that the thionine concentration is about \(1 \times 10^{-4}\) M and will estimate 20% bleaching for the hypothetical case. The potential of the thionine-leucothionine couple in the photo- stationary state would consequently be 0.311 volt.

The maximum photogalvanic potential for such a system would therefore be about 0.383 volt. In our opinion this would probably be a maximum attainable potential under optimum conditions at reasonable illumination levels, the reports to the contrary notwithstanding. Under anything less than optimum conditions the photogalvanic potential would be much smaller. Moreover, according to the proposed electrode mech-
anism the illuminated electrode potential could never achieve the potential of the thionine system completely, and the photogalvanic potential would be lowered to a corresponding extent.

In our systems where sulfate salts were used the formal standard potential of the ferric-ferrrous system was about +0.665 volt (Section 4, 3, 2, 1). In such a system the potential of the dark electrode would be decreased by 0.186 volt and the maximum photogalvanic potential would decline by a corresponding amount to 0.277 volt. It is easy to understand why the present effort could not match the reported 0.500 volt.

5.1.2 The Current and Power

The power of photogalvanic cells is seriously restricted by the minute currents which can be drawn. The current is in turn limited by the rate at which leucothionine can reach the electrode surface, as was noted in Section 4, 2, 4. The maximum power level obtained in this work was $1.8 \times 10^{-5}$ watts/cm$^2$.

The leucothionine concentration in the hypothetical cell was estimated to be $2 \times 10^{-5}$ M. From equation 14 one may calculate that the diffusion limited current would be $6 \times 10^{-7}$ amp. It would follow that the maximum power which could be delivered to a load would be $1/2 \times 0.383 \times 6 \times 10^{-7} = 1.15 \times 10^{-7}$ watts per square centimeter of electrode surface area. The electrode surface area might be made 20 times the illuminated surface area by making an illuminated electrode of 1 cm wide platinum plates spaced 1 mm apart (similar to that shown in Figure 23). The maximum power with such a electrode would be multiplied by 20 to give $2.3 \times 10^{-6}$ watts per square centimeter of illuminated surface area.

The objection may be raised that all of the solution is already within the diffusion layer if the electrode plates are only 1 mm apart. This is a valid objection, and to compensate for the fact that leucothionine is produced within the diffusion layer we may presume that the effective thickness of the diffusion layer has been diminished. An effective thickness of 5% of its normal thickness seems to be a generous estimate. The power might therefore be as high as $4.6 \times 10^{-5}$ watt/cm$^2$. 

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A thionine concentration of $2 \times 10^{-2}$ moles/liter has been achieved, and such a solution would absorb all of the visible light within a solution thickness of 2 mm (see Section 4.4). While we are assuming a solution thickness of only 0.5 mm, we can still accept the simplification that virtually all of the visible spectrum is absorbed.

For an intensity of 1 sun, $2.04 \times 10^{17}$ quanta are available per square centimeter per second. Based on considerations of all of the investigations discussed in Section 3.2.1, a quantum yield for leucothionine formation of no more than 0.3 would be expected. It follows that $6 \times 10^{16}$ molecules of leucothionine may be produced each second behind each square centimeter of illuminated surface area. Since we have assumed that all of this light is absorbed within a 0.5 mm layer of electrolyte, the rate of formation of leucothionine would be

$$\frac{6 \times 10^{16} \text{ molecules/sec cm}^2}{6 \times 10^{23} \text{ molecules/mole} \times 5 \times 10^{-5} \text{ liter/cm}^2} = 2 \times 10^{-3} \text{ moles/liter sec}$$

The concentration of leucothionine in the photostationary state is that which would be established when the rate of oxidation of leucothionine is equal to its rate of formation. At a ferric ion concentration of $3 \times 10^{-3}$ M the rate constant $k$ for the velocity $v$ of leucothionine oxidation at a pH of 1 is 160; at a pH of 2, which would most probably be the minimum pH used because of its effect on the photogalvanic potential, this would very likely be doubled, since this was approximately the effect found by Havenmann and Reimer. Thus for a leucothionine concentration of $L$ and a ferric ion concentration of $2 L$

$$v = 320 \times 2 \quad L^2 = 2 \times 10^{-3}$$

$$L = 1.8 \times 10^{-3} \text{ moles/liter}$$

This is the photostationary state concentration of leucothionine in the bulk of the solution, and to a first approximation this is not affected appreciably by the electrode reactions. A limiting current may be calculated from equation 14, assuming an effective diffusion...
One may pursue another course and sacrifice somewhat in potential while gaining in current. Inspection of equation 14 reveals that the diffusion limited current can be increased by accelerating the diffusion of leucotinone, by minimizing the thickness of the diffusion layer, or by increasing the concentration of leucotinone.

The rate of diffusion may be enhanced by raising the temperature, but this approach is unacceptable because of its influence on the voltage. It may also be improved by lowering the viscosity of the solvent, but this would not enlarge the current to the degree desired. The thickness of the diffusion layer may be diminished by stirring the solution. A gain in the current by a factor of 50 might thus be realized; however, the power required to stir the solution would have to be subtracted from the power output of the cell.

Consequently one is left with only the variable of concentration as a means of multiplying the power to the desired extent, at least without introducing a power-consuming device. To increase the leucotinone concentration in the photostationary state the original thionine concentration must be increased beyond that generally used by other investigators. The experimental approach outlined in Section 4.4 was designed to accomplish this task, and it succeeded in producing the highest power level that was measured. Nevertheless, the power still fell short of that of other solar energy conversion devices by a factor of 5000 or more. One may therefore inquire what the ultimate advantage of raising the thionine concentration might be.

A second hypothetical cell will now be considered, but it will be designed for maximum power instead of maximum voltage. A concentrated thionine solution will be used. For the dilute solutions in the case above, we introduced an electrode surface area 10 times the illuminated surface area. For concentrated solutions of thionine, however, the effective radiation would not penetrate to a depth of more than about one millimeter; consequently it would be virtually impossible to have an electrode surface area much greater than the illuminated surface area. For the sake of simplicity we will assume that the illuminated electrode is a flat plate perpendicular to the light beam and 0.5 mm away from the window.
layer thickness of 0.025 mm to allow for leucothionine within the diffusion layer. The value for the limiting current thereby derived is $1.1 \times 10^{-3}$ amp/cm².

The photogalvanic potential of such a concentrated solution with a pH of 2 would be considerably less than the 0.383 volt estimated in 1.1. The dark electrode potential may again be estimated to be +0.694 mv. The potential of the thionine-leucothionine redox system in the stationary state at a pH of 2 can be calculated to be +0.412 volt, using the above concentrations of thionine and leucothionine. The maximum photogalvanic potential would then be 0.282 volt. This maximum would actually never be attained. (This statement is supported by consideration of the electrode processes and of all past experience.) A maximum of 0.280 volt will be assumed.

The apparent internal resistance is given by the voltage divided by the limiting current.

$$R_{app} = \frac{0.280}{1.1 \times 10^{-3}} = 2.5 \times 10^{2} \text{ohms.}$$

Since the maximum power is delivered when the external load equals the internal resistance, and since the potential drop across the load is then 1/2 the open circuit potential, the maximum power would be

$$\frac{(0.140)^2}{2.5 \times 10^{2}} = 8 \times 10^{-5} \text{watt/cm}^2.$$

This calculated value is considered to be the best realistic estimate of what may logically be anticipated without making some radical innovations. It is some 40 times greater than our best observed value of $1.8 \times 10^{-6}$ watt/cm².

The rapidity of the spontaneous back reaction limits the concentration of leucothionine, which in turn limits the power that can be obtained. If the rate of the back reaction were decreased by a factor of
100 (perhaps by use of perchlorate solutions), the leucotinoline concentration would be increased by a factor of 10, and the maximum power would be in the order of 1 milliwatt/cm².

While the work on this project was in progress, an estimate of the ultimate feasibility of the thionine photovoltaic cell was carried out at the request of the ASID project engineer. At that time the factors that would limit the power level were not as clearly defined (by theory or by experiment) as they are now. Therefore the earlier estimate of the ultimate power level was considerably greater than that presented in this report.

In conclusion it may be stated that one is forced to agree with Zaromb, Lasser and Kalhammer that "the problems of diffusion-limited current with low photochemical product concentrations and recombination with higher concentrations is likely to be encountered in most photovoltaic systems".

5.1.3 Efficiency

The efficiency of energy conversion assuming a power level of 8 x 10⁻⁵ watts/cm² under an illumination intensity of one sun (outside the earth's atmosphere) would be as follows:

\[
\frac{8 \times 10^{-5} \text{ watt/cm}^2 \text{ (output)}}{1.4 \times 10^{-1} \text{ watt/cm}^2 \text{ (solar)}} \times 100 = 0.66\% \text{ efficiency based on total radiation}
\]

\[
\frac{8 \times 10^{-5} \text{ watt/cm}^2 \text{ (output)} \times 100}{6.9 \times 10^{-2} \text{ watt/cm}^2 \text{ (solar)}} = 0.12\% \text{ efficiency based on absorbed light}
\]

A higher efficiency based on the absorbed light could undoubtedly be obtained with a dilute electrolyte, but this would also yield very little power. The maximum efficiency measured in this study was 0.000844% based on the total incident energy in the 3300-9500 Å range. The efficiency based on the absorbed light was estimated to be 0.003%.
5.1.4 The Rate of Cell Deterioration

The rate of cell deterioration, which Potter and Thaller considered to be the most serious drawback of the thionine photo-galvanic cell, is not nearly as troublesome as was reported. The useful cell life is definitely measured in hours or days, and not in minutes. The unusually short lifetime found by Potter and Thaller was probably the result of inadequate electrode activation.

Since the deterioration is connected with changes on the electrode surface, a fuller understanding of the nature of the surface effects might well enable one to extend the lifetime of the cells. The influence of ultraviolet light is not yet clear, and its rejection may prevent cell deterioration.

5.1.5 The Efficacy of Certain Specific Measures

A number of specific methods of improving cell performance were studied in detail under this program. These measures included the adjustment of electrode geometry, the addition of complexing agents and additives, and the use of alternating illumination. Conclusions on the effectiveness of each will be summarised in this section.

The best orientation of the illuminated electrode depends on the solution employed. For a dilute solution one can use an electrode with a large surface area to good advantage. For a concentrated solution the light is absorbed within such a short distance of the window that a simple flat plate parallel to the window will suffice. The cell which yielded maximum power had such an electrode. A solid plate parallel to the window is apt to hinder or prevent material transfer by diffusion and convection, however. A fine mesh wire gauze would provide an equally large surface area without preventing free diffusion and convection through the electrode. If the illuminated electrode has some dark surfaces some of the power is lost, but the loss is relatively small.

The effects of adding ferric ion complexing agents could not be thoroughly explored within this program. To the best of our knowledge the effects can be entirely explained by the resulting decreases in the activity of the ferric ions. Further research might reveal other effects, as discussed in Section 4.4.1.
Other additives were studied primarily for the purpose of permitting the use of concentrated thionine solutions (10^4 M) without sacrificing voltage. This objective was met. Potentials up to 172 mv have been obtained at a thionine concentration of 2.9 x 10^-3 M. Solutions have been prepared with concentrations up to 2.0 x 10^-2 M, but these more concentrated solutions failed to exhibit a photogalvanic effect. It is felt that with further work cells can be made operable at these higher concentrations. A thionine concentration of 2 x 10^-2 M was assumed for the hypothetical optimum cell in Section 5.1.2. The preparation of more concentrated solutions would serve no useful purpose, since 2 x 10^-2 M solutions already absorb essentially all of the visible light within a very short path length.

Alternating illumination was demonstrated to be capable of increasing the power by as much as 130 times. However, it must be understood the alternating illumination is merely a means of minimizing the effects of concentration polarization. When current is drawn from a cell the power decreases steadily until a steady state value is finally achieved—sometimes only after an hour or more of operation. This decrease is due to the build-up of the ferric ion concentration in the illuminated solution and the reduction of the ferric ion concentration in the dark solution. Alternating illumination simply eliminates the loss in power due to this process. It does not affect the initial power level in any way.

Because it combats concentration polarization, alternating illumination is a most effective measure in cells in which this places a serious limitation of the power. For example, dilute thionine solutions are more subject to concentration polarization than are concentrated solutions. It follows that alternating offers a greater improvement to dilute dye solutions. Similarly it would evoke the greatest response in cells which are operating at low temperatures or at high current densities, or which have long distances between the electrodes, or (probably) which have extremely low ferric ion concentrations. The cell which is most seriously hampered by concentration polarization should respond in the most pronounced manner to alternating illumination. It is impossible to specify what specific characteristics this cell would have.
The hypothetical optimum cell in Section 5.1.2 assumes that high photostationary state concentrations of both leucothionine and ferric ion would be maintained. If we further assume that a short path length separates the dark and the illuminated electrode, we may conclude that concentration polarization would not be a serious problem. Consequently concentration polarization was not even considered in calculating the probable maximum power level. If concentration polarization is a problem, alternating illumination would serve to minimize it; but it could in no way boost the power above the level already calculated.

5.2 AN OPTIMUM PHOTOVOLTAIC CELL

Section 5.1.2 presents a realistic appraisal of what the optimum performance of a thionine photovoltaic power generation system would be. This section describes the probable physical appearance of such a device and presents cost and weight estimates.

The cell would probably consist of a flat plastic container enclosing the two electrodes and an opaque porous partition. The container could be made of 1/16" Lucite (and it is assumed that Lucite can yet be used) with an interior thickness of 2 mm or less. An infrared reflecting coating would be on the surface receiving the illumination, and the plastic would contain an ultraviolet light absorbing material. Occasional ridges on the inside surface of the window would keep the illuminated electrode from pressing too tightly against the window. The electrodes would consist of a fine mesh platinum-plated titanium gauze, which would behave essentially the same as a plate electrode except that it would not restrict material transfer back and forth through the electrode. The opaque partition separating them would be a black, acid-resistant fabric.

The weight of the cell would be as follows per square foot of illuminated area:

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Window and backing</td>
<td>0.75 lb</td>
</tr>
<tr>
<td>Spacers</td>
<td>0.01 lb</td>
</tr>
<tr>
<td>Solution</td>
<td>0.41 lb</td>
</tr>
<tr>
<td>Electrodes</td>
<td>0.32 lb</td>
</tr>
</tbody>
</table>

1.49 lb/sq ft

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The cost of the materials and the labor has been estimated to be as follows for each square foot:

<table>
<thead>
<tr>
<th>Material</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thionine</td>
<td>$.65</td>
</tr>
<tr>
<td>Iron sulfates</td>
<td>.50</td>
</tr>
<tr>
<td>Lucite container and spacers</td>
<td>2.75</td>
</tr>
<tr>
<td>Electrodes</td>
<td>70.00</td>
</tr>
<tr>
<td>Additives (tetrahydrofuran, etc.)</td>
<td>1.00</td>
</tr>
<tr>
<td>Assembly (mass production basis)</td>
<td>20.00</td>
</tr>
<tr>
<td></td>
<td>$94.90/sq ft</td>
</tr>
</tbody>
</table>

The power of such a cell was estimated in 5.1.2 to be \(8 \times 10^{-5}\) watt/cm\(^2\), or about 0.07 watt/ft\(^2\). The photogalvanic cell would, therefore, probably produce 0.05 watt/lb at a cost of $1300/watt.

5.3 RECOMMENDATIONS FOR FUTURE WORK

The estimated power to weight and cost to power ratios do not encourage further development of the thionine photogalvanic cell if it is undertaken for the purpose of manufacturing a competitive solar energy conversion device within a short period of time. The long-range development of photogalvanic devices in general — and the thionine-iron system may be chosen as a representative example — should be continued, however.

While many interesting details soon arouse the curiosity of the worker in this field, two broad areas of general interest present themselves. The first of these subjects is the influence of electrode surface conditions. The second is a means of slowing down the spontaneous return to equilibrium conditions in the bulk of the solution so that the power producing electrode reactions would be able to compete more effectively.

The intriguing requirement that dye be adsorbed on the electrode surface was rationalized in connection with the discussion of the electrode processes in Section 4.3.1. Experiments should be carried out to test
this hypothesis and the exact role of the surface layer should be
defined. The effects of platinum oxide or finely divided platinum
on the surface should be assessed. A chronopotentiometric inves-
tigation of the electrode processes should be performed.

It appears that the electrode surfaces behave as catalysts for
the spontaneous back reaction. Ideally the illuminated electrode should
selectively catalyze only the oxidation of leucothionine, while the dark
electrode should catalyze the reduction of ferric ion. The catalytic
role of the electrodes should become a field of continued effort.

The spontaneous oxidation of leucothionine in the bulk of the
solution becomes so rapid at high leucothionine concentrations that
either one must be satisfied with the small currents at low concentra-
tions or he must be willing to sacrifice most of the absorbed energy to
the back reaction. Some fundamental research on means of suppressing
the back reaction is required. The influence of the electrical charge
on the two reacting species -- leucothionine and ferric ions or whatever
complexes they may appear in -- and the influence of the solvent might
be made the starting points for such a study.

Photogalvanic systems may yet become an important means of
harnessing solar energy, but a greater store of fundamental knowledge
must first be secured.
REFERENCES

REFERENCES (Cont'd)


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REFERENCES (Cont'd)


37. Kuwana, T., Private communication.


REFERENCES (Cont'd)

REFERENCES (Cont'd)


REFERENCES (Cont'd)


73. Weil, L., and Maber, J.; Arch. Biochem., 29, 241 (1950); C. A., 45, 4563g (1951).


APPENDIX

MEASUREMENT OF LIGHT INTENSITY

A bolometer was used to measure the intensity of the filtered light from the 1000 watt projection lamp and from the 1000 watt Hg-Xe arc. Various filters were used, primarily to reject ultraviolet and infrared radiation from the photogalvanic cell. The bolometer was a Röhig large surface Kuribau-type, which can integrate directly a beam of light up to 10 cm² in cross-sectional area. Figure A shows a schematic diagram of the circuit used to control and to read the bolometer. It was operated at an applied voltage (sensitivity) of 5.0 volts. Reproducibility of response was checked with the 1 K calibrating shunt resistor, (which gave a 26 mv reading) that simulated the exposure of the bolometer to light. The zero-adjust of the bolometer control was used to null the milli-microvoltmeter with the bolometer exposed only to background light; then the deflection from zero measured the intensity of the light beam with the shutter open.

An Epply Thermopile was used to calibrate the bolometer. The response of each detector was measured directly behind a fixed shutter (2.92 x 17.1 mm) with a uniform beam of approximately parallel visible radiation from the Hg-Xe arc. This data is shown in Figures B and C. Neutral density filters further reduced the filtered light to the percent indicated. Although the Epply thermopile is calibrated only in the 2 to 4 microvolt range, it gave a linear response up to 90 microvolts and the straight line in Figure B was used to calculate the intensity of the light through the slit:

\[
\text{Thermopile reading at } 5\% \text{ T} = 67 \mu V
\]

\[
\text{Thermopile calib. (2.92 mm) } = \frac{\frac{2.92}{3.0}}{0.052} = 0.050_6 \mu V/\mu \text{ watt/cm}^2
\]

\[
\text{Intensity (thru slit) at } 5\% \text{ T} = \frac{67}{0.050_6} = 1320 \mu \text{ watts/cm}^2
\]

\[
\text{Intensity at } 100\% \text{ T} = 1320 \times 20 = 2.6 \times 10^4 \mu \text{ watts/cm}^2 = 0.026 \text{ watts/cm}^2
\]
Figure A. SCHEMATIC OF BOLOMETER READ-OUT AND CONTROL CIRCUIT
Figure A. THERMOPILE READINGS AND LINEARITY CHECK
Figure C. BOLOMETER CALIBRATION AND LINEARITY CHECK
The response of the bolometer behind this same slit is shown in Figure C. It gave a linear response over the entire range, although there was too much noise to take accurate readings below 10% transmission.

Bolometer reading at 100% T = 2.0 mV/0.5 cm² = 4.0 mV/cm²

Bolometer calibration = 0.026 watts/cm² = 6.5 x 10⁻³ watts/mv
4.0 mV/cm²

= 6.5 m Watts/mV or 6.5 watts/V

The bolometer also gave a linear response up to 15 mV with the same light beam through a larger aperture of 2.18 cm diameter, as is shown in Figure C. The ratio of response of the aperture to the slit was 15 mV/2 mV, which is identical with the ratio of their cross sectional areas: 3.75 cm²/0.5 cm².

The light intensities measured with the bolometer for the various optical systems and filter combinations are shown in Table 2. The measured intensities are compared with the calculated solar intensities through the same IR-UV rejecting filter combination used with the Hg-Xe arc. This consisted of 15 cm path length of water in a quartz cell and a Corning CS 1-59 glass filter. The transmission curve is shown in Figure D. The 5100-6300 Å portion of the energy from the arc and from sunlight that was transmitted through the filter was calculated using the energy distribution plots shown in Figures E and G. These were calculated from the relative distribution of the light source and the fraction of light transmitted by the filter shown in Figure D. A Hanovia bulletin gives the distribution of the Mercury-Xenon Compact Arc. The NRL Report #1005 by D. Friedman was used for the solar energy distribution data.
Figure D. TRANSMISSION CURVE FOR FILTER COMBINATION USED FOR HG-KE ARC
Figure E. RELATIVE ENERGY DISTRIBUTION OF FILTERED LIGHT FROM HG-XE ARC
Figure F. RELATIVE QUANTUM DISTRIBUTION OF FILTERED LIGHT FROM Hg-Xe ARC
Figure G. RELATIVE SOLAR ENERGY DISTRIBUTION THROUGH FILTER USED FOR HG-XE ARC