STUDIES ON THE PHOTOVOLTAIC EFFECT

WITH METALS AND FLUORESCENT SOLUTIONS

By

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ABSTRACT

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The primary object of these studies was to develop a sensitive method of detecting the presence and estimating the concentration of a fluorescing substance in solution. This was attempted by combining two separate photo-electric phenomena to produce a larger photo-effect than either one alone; these two distinct photo-electric phenomena were considered as being primordially due to (1) the light-sensitive electrode and (2) the fluorescent solution. In the former, the electrode was a metal which was covered with a light-sensitive layer, a semi-conductor, by means of heating in air or immersion in certain solutions. Existing theories on the photo-electric property of semi-conductors have been discussed. The use of a glass membrane in the form of the conventional glass electrode, which was the dark electrode, and the complete paraffining of the light-sensitive electrode except where it was irradiated produced fairly large photopotentials from the incident light but very poor photopotentials from the fluorescent light of a solution. A sensitive vacuum-tube electrometer was used to

measure the photopotentials. This part of the research with metals was therefore abandoned and full attention given to the fluorescent solution.

The research on fluorescent solutions, here called the "fluoro-photovoltaic effect" because the potential was at first thought to be produced only in the presence of a fluorescing molecule but was later found to be produced by non-fluorescing compounds as well, has yielded very promising results. The irradiated electrode was simply a point of an inert metal such as platinum; the dark electrode was a piece of platinum foil. The vacuum-tube electrometer above was also used here to measure these fluoro-photopotentials. Fluorescing substances which displayed fluorescence throughout the solution (volume fluorescence) produced a fluoro-photopotential which was always positive and proportional to the concentration within a certain optimum range; fluorescing substances which were sufficiently concentrated to produce fluorescence only at the surface where the incident light first approached the solution (surface fluorescence) yielded constant fluoro-photopotentials which were independent of the concentration. The range of concentration in which the point could best operate was much greater than the "trace" concentrations which the eye and external photocell can readily detect. This fluoro-photovoltaic method, therefore, is supplementary to the visual and photometric methods of estimating concentrations of fluorescent substances in solution.

Other variables which had an effect on the fluoro-

photopotential were temperature, size of probe-point, intensity of the incident light, stirring, and the dielectric constant of the solvent.

The theory, introduced here to explain this fluoro-photovoltaic effect, proposed that the fluoro-photo-active molecule must have a low electron-density group such as a carbonyl to which photo-electrons can move from an electron source such as a benzene ring or the solvent, which subsequently forms the positive fluoro-photopotential.

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WITH METALS AND FLUORESCENT SOLUTIONS

GENERAL INTRODUCTION

The primary object of these studies is to develop a
sensitive method of detecting the presence and estimating the
concentration of a fluorescing substance in solution. This
is accomplished at present by measuring the fluorescent light
with a photocell or by visual comparison with standards. How-
ever, it was thought that the peculiar photovoltaic property
of the fluorescing molecule in solution could be utilized for
its quantitative estimation and, therefore, these studies were
undertaken with the secondary purpose of studying this fluores-
cent photovoltaic effect or, more briefly, the "fluoro-photo-
voltaic effect".

Zworykin and Wilson (73) divide all photo-electric effects
into three classes as follows:

I- The Photo-emissive Effect, where an actual liberation
of electrons as photo-electrons takes place. Examples
of this class are the vacuum and gas-filled alkali-
metal photo-electric cells.

II- The Photoconductive Effect, where a change in the
ohmic resistance of matter results on irradiation.
Examples of this class are selenium; sulfides of lead,
antimony, bismuth, molybdenum, silver, and combina-
tions of these; oxides of copper and silver; alloy of
selenium and tellurium; and thallium oxysulfide (Tha-
lofide cell). Photocells which operate on this effect
are sometimes called "light-sensitive resistors" (56).
The new "thermistors" or thermal resistors (2, 49)
which have a negative resistance-temperature coeffici-
ent seem to have some relationship to the light-sen-
sitive resistors of this class.

III- The Photovoltaic Effect, where a chemical or physical reaction results in producing an electromotive force. It is in this class where all of these studies have been concentrated.

Hughes and DuBridge (28) divide the photovoltaic effect, Class III above, further into four groups as follows:

1- Cells in which the electrodes are oxides, sulfides, or halides of certain metals and in which the electrolyte is a solution of an acid or an inorganic salt.

2- Cells in which pure metal electrodes dip in a fluorescing solution, here called the "fluoro-photovoltaic" cell.

3- Cells in which the electrodes are pure metals dipping in inorganic electrolytes; photo-ionization differences are probably detected.

4- Cells consisting of two metals with a partial conductor such as selenium between them; this indicates a relationship to the photoconductive effect mentioned above and this relationship will be mentioned again below.

In this division of the photovoltaic effect, the first three groups deal with solutions and the fourth embraces the so-called dry photovoltaic cells which are now used in many industrial devices. Only two out of the four groups have been studied here, i.e. groups 1 and 2. The purpose of studying the photovoltaic effect of these two groups, (1) metals and their compounds and (2) fluorescent solutions, is to determine whether a combination of these two groups would give a greater photovoltaic effect than either of the effects of the two groups alone. In other words, by forming an electrode which is sensitive to the fluorescent light of the solution, its immersion in the fluorescing volume might give still a greater photovoltaic effect due to the presence of the excited fluorescing molecule.

This research has been divided into two parts according

to the above-mentioned two groups. Part I is entitled "Studies on the Photovoltaic Effect with Metals" and Part II, "Studies on the Photovoltaic Effect with Fluorescent Solutions". Part I has been extensively studied by many workers and several theories have already been propounded to explain the photovoltaic effect of this part; on the other hand, Part II, the studies with fluorescent solutions, has not had much development. Although this present work has produced poor semi-conductor light-sensitive electrodes for detecting the weak fluorescent light, the most promising results were obtained with the fluorescent solutions of Part II. However, since the studies with the metal-oxide system have uncovered interesting phenomena which may lead to a better understanding of their behavior on irradiating with light, they have been included in this paper.

The photovoltaic effect was originally studied by Becquerel (3) with solutions of electrolytes, later by others with non-electrolytes (30, 39, 53), and finally with solid semi-conductors as mentioned in group 4, page 2. Semi- or partial-conductors are roughly those having an electrical resistance not greater than 10^{10} ohms per centimeter cube; those substances having a greater value are classified as insulators although temperature variation affects this demarcation value considerably. Much theory has been developed by the physicist on the semi-conductor (40, 71). Practically all of the studies in this research have been made with solutions in order that the primary object, the development

of a sensitive method of detecting and estimating the concentration of a fluorescent substance in solution, could be fulfilled.

Sommer (56) points out that "... the photovoltaic cell commands a greater variety of terms than any other photo-electric device; for example, dry-disc cell, rectifier cell, blocking-layer cell, boundary-layer cell, insulating-layer cell, barrier-layer cell, sandwich cell, photo-e.m.f. cell, self-generating cell, sperrschicht-cell ...". He also states that since all of these named cells do not contain any liquid medium, they should not be called "photovoltaic cells" but photo-e.m.f. cells"; those cells which do contain a liquid medium usually as an electrolyte should be classified as "photovoltaic" or "photolytic" and not "photo-electrolytic". In this paper, the term "photovoltaic cell" is applied to all the cells studied which produce a photopotential, and since nearly all of the cells studied here contain a liquid medium, Sommer's suggestion has been followed.

PART I

STUDIES ON THE PHOTOVOLTAIC EFFECT WITH METALS

CHAPTER I

INTRODUCTION

As indicated above, the studies of this part have been made with photovoltaic cells that contain sensitized electrodes covered usually with a semi-conducting oxide layer and immersed in a liquid medium which may or may not be an electrolyte. The liquid medium seems to act as a contact or connecting agent to the seat of photo-electric activity which is in the semi-conducting layer on the surface of the irradiated electrode. The electrolytic photovoltaic cells described in this part of the research may be considered as a revival of the obsolete "wet" cells such as the Rayfoto (11, 73), Arcturus Photolytic (73), and Ruben (73) cells, which were rapidly replaced by the "dry" photo-e.m.f. cell type of group 4, page 2; commercial examples of this dry photo-e.m.f. cell type are the Weston Photronic Cell (68), the German Tungsram Cell (30), the General Electric "Blocking-Layer" Cell (38), and the Westinghouse Photox Cell (67).

The former "wet" commercial photovoltaic cells mentioned above usually contained cuprous oxide on copper as the light-sensitive electrode and metallic lead or cuprous oxide on copper as the dark electrode; a solution of lead nitrate, copper sulfate, or some other salt, or their gels, or a moist

rock-salt crystal were the means of connecting the dark and irradiated electrodes.

In most of the above "dry" photo-e.m.f. cells, the light-sensitive layer is selenium which is spread over a sheet of iron. Selenium when irradiated produces a negative charge on the electrode or contact which is nearest the light as shown after exhaustive studies by Adams and Day (1) in 1876. The irradiated surface, therefore, assumes a negative polarity or is "photonegative"; the dark iron base electrode is consequently "photopositive". The sensitivity of these electrodes is sufficient to detect the fluorescent light from 0.0001 mg. of sodium fluorescein per ml. of solution (33). The polarity of the irradiated electrode is of theoretical significance and much discussion will be given on this below.

The obsolete form of wet cell has been recalled here not for the purpose of developing a more efficient photovoltaic cell but to determine if any effect with the liquid medium as a fluorescent solution could be obtained which would have some analytical significance according to the primary object of this research.

CHAPTER II

HISTORICAL BACKGROUND

Becquerel (3) is considered the discoverer of the photo-
voltaic effect in 1839. His photovoltaic cell was of the
groups 1 and 3 types described on page 2; it consisted essen-
tially of two similar metallic electrodes such as silver,
each covered with silver chloride to enhance the photo-effect
over that obtained with the plain uncovered electrodes in an
inorganic electrolyte. When these electrodes were placed in
a dilute inorganic acid such as sulfuric and only one of the
two electrodes irradiated with light from an arc, a potential
difference or photopotential was obtained. Goldmann (18) in
1908 and Goldmann and Brodsky (19) in 1914 studied this
effect, often called the Becquerel effect, and concluded that
the phenomenon was primarily photo-electric in nature and that
any photochemical action on the electrolyte or electrode was
a secondary effect as a result of the photo-electronic current
produced by the light. Their method of experimentation was
unique at that time in that a potentiometric circuit was
utilized to balance the photopotential generated by the photo-
voltaic cell. The change in current with applied voltage at
constant light intensity using white light was derived which
is similar to that obtained with alkali-metal photo-emissive
cells. This curve, shown in Fig. 1, page 8, indicates the
photo-electric property of the light-sensitive electrode.
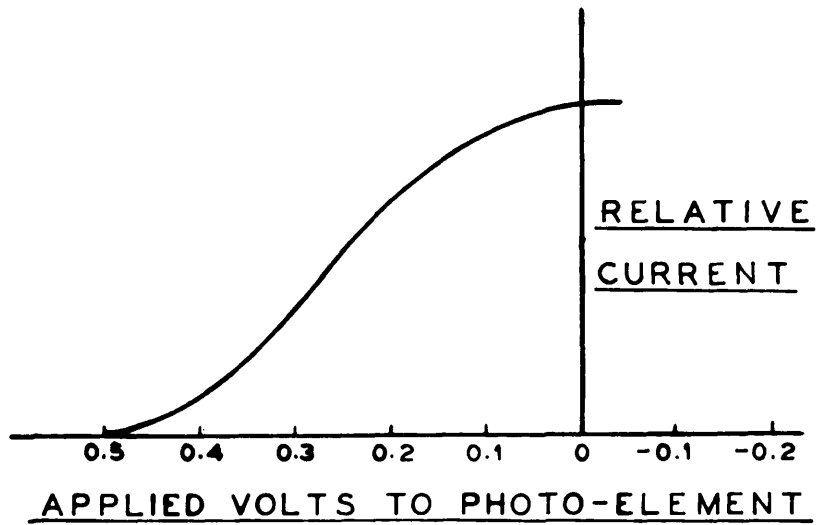
Fig. 1 - Current-voltage characteristic of a photovoltaic
        cell (intensity and wave-length of light constant)
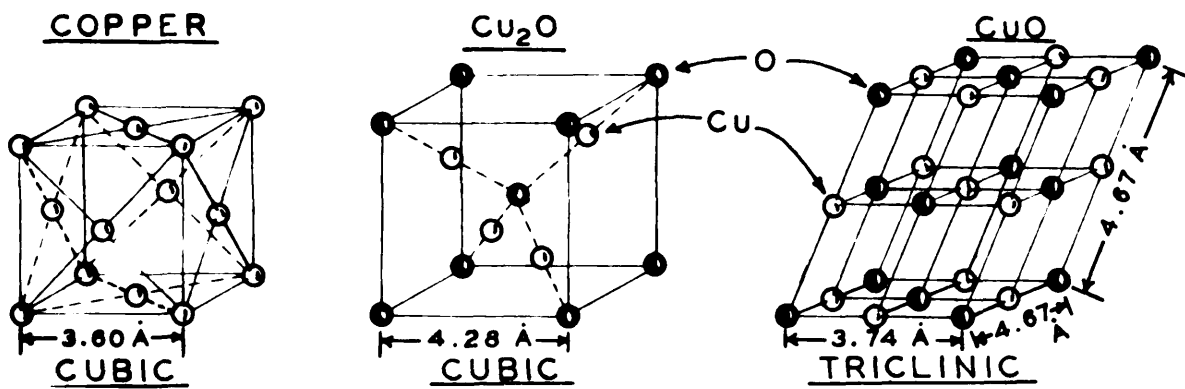
Fig. 2 - Crystal structures of copper and its oxides

Later, in 1925, van Dyok[V] (63) using monochromatic light veri-
fied these experiments and also maintained the photo-electric
explanation. However, many workers, according to Hughes and
DuBridge (23) and Lange (30), did not consider the photo-
electric effect as primary; instead, a purely photochemical
explanation was adhered to because of certain peculiar results
with cuprous oxide and silver halide surfaces.

In 1878, Sabine (53) constructed a photovoltaic cell
utilizing selenium as the semi-conducting photo-sensitive
electrode and distilled water as the "electrolyte". Later
in 1893, Minchin (39) ingeniously used with the selenium semi-
conductor, acetone, methyl alcohol, and oenanthol (heptylic
aldehyde) separately in order to obtain more favorable and
stable results. Although the use of organic liquids was not
continued after Minchin's work, it indicates that the seat of
photo-activity is not in the liquid medium but in the photo-
electrically-excited selenium. This action in the neighbor-
hood of the liquid-electrode interface is similar to the old
explanation given by Davy who assumed that the location of
the electromotive force produced in an electrolytic cell is
at the junction between metal and solution and not at the
junction of the dissimilar metals of the circuit as assumed
by Volta (53). The use of organic solvents in the above

[V]Misspelled as "Dijok" by Hughes and DuBridge (28) and
others in the literature.

manner of Minchin and also to dissolve fluorescent substances
has been attempted in this research and is described in Part
II of this paper.

CHAPTER III

EXISTING THEORIES OF THE

PHOTO-ACTIVITY OF SEMI-CONDUCTORS

In order to explain the phenomena obtained with photo-
voltaic cells which produce a current on irradiation with
light, existing theories based on Lange's discussion of copper
(30) will be reviewed.

An electric current may be carried by electrons in metals
as conductors of the first class or by ions in solutions as
conductors of the second class or by both electrons and ions
simultaneously as in certain crystals. It will be shown later
in the experimental section of this part how the current,
primarily due to photo-electrons being liberated by irradia-
tion of the light-sensitive electrode, has been practically
eliminated so that only electronic "pressures" or "concentra-
tions" can be measured as true photopotentials.

The Concept of Lattice Distortion Points. If one main-
tains a single copper crystal at 1000°C in the presence of
sufficient oxygen, a single crystal of cuprous oxide will
eventually result. During the chemical transition, the elec-
trical resistance of the crystal will increase until, theoret-
ically, a non-conductor will result when the crystal is of
pure cuprous oxide. However, in the actual case, definite
and constant values of thermal and electrical conductivities
among many samples are not obtainable even though chemical
tests show complete oxidation to cuprous oxide. To explain

this peculiarity, the concept of lattice distortion points has been introduced. Englehard (10, 30) calculated from experimental evidence that a single distortion point among a thousand molecules or unlike-ion pairs in the crystal is capable of producing good photo-activity.

Lange (30), quoting previous workers, especially Wagner (66), mentions three types of distortion points in the cuprous oxide crystal lattice; these are as follows:

1- The Substitution Type. An oxygen ion replaces a cuprous ion in the cuprous oxide crystal lattice. This type has not been utilized to any extent for explaining photo-activity by means of distortion points. Fig. 2, page 8, shows the various crystal structures of copper, cuprous oxide, and cupric oxide. It does not seem likely that an oxygen ion can actually replace a cuprous ion in the cuprous oxide crystal; instead, any oxygen entering the cuprous oxide structure would form the cupric oxide crystal lattice.

2- The Interstitial or Inter-Lattice Type. Excess neutral copper atoms are among fully occupied cuprous oxide lattice positions. This is represented in Fig. 3, page 13, and causes "excess conduction", to be discussed further below.

3- The Vacant-Place Type. Cuprous ions are missing in the cuprous oxide crystal, represented in Fig. 4, page 13. This type of distortion point causes "deficiency conduction" also to be explained further below.

Regardless of the type of distortion point or center in the crystal, the presence of oxygen, sulfur, or other suitable electronegative elements loosens the electrons of the electropositive metal. On irradiating, the electron which has been loosened by the presence of these electronegative elements may escape. This escaping electron may be a primary or secondary valence one, depending on the metal or its state of valence at
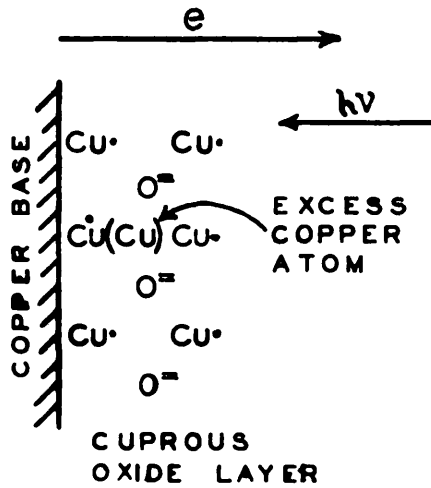
Fig. 3 - Interstitial type
lattice distortion
point causing excess
conduction
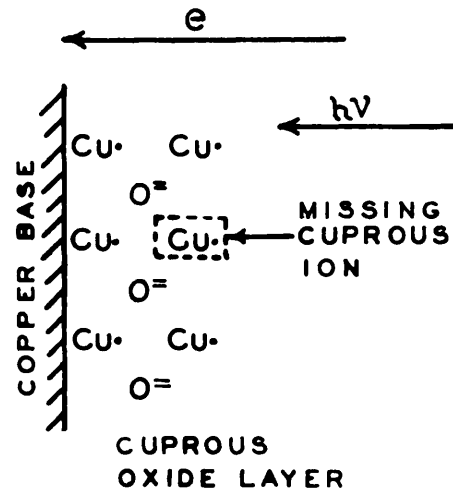
Fig. 4 - Vacant-place type
lattice distortion
point causing
deficiency conduc-
tion
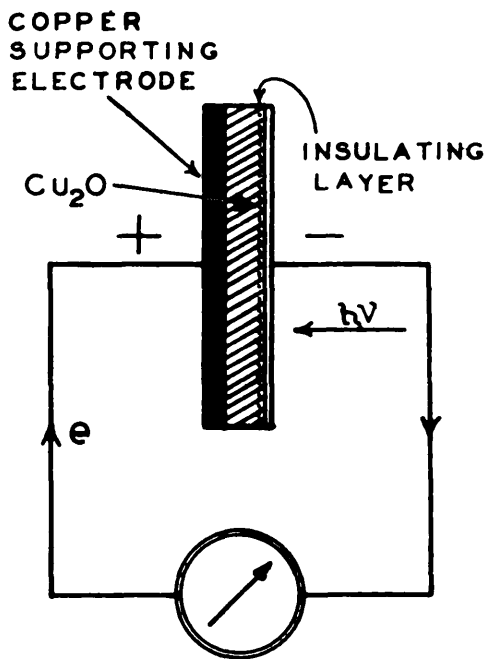
Fig. 5 - Frontwall cell with
photopositive suppor-
ting electrode
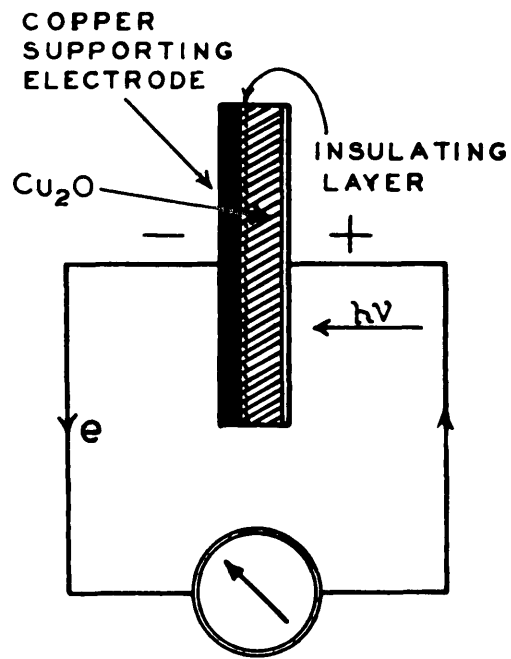
Fig. 6 - Backwall cell with
photonegative suppor-
ting electrode

the distortion point and the wave-length of the light. Only
the metal — as copper, whether it be atomically trapped in a
cuprous oxide lattice (excess conduction) or as a cuprous ion
surrounded by oxygen that belonged to another cuprous ion
which is now missing (deficiency conduction) — can cause a
distortion point. The cuprous ion deficiency conduction is
believed to result in "backwall" photo-elements where the
photo-active layer is behind the cuprous oxide thickness at
the cuprous oxide-copper junction, giving a photonegative
effect to the copper base electrode. The trapped neutral
copper atoms in excess conduction are thought to form "front-
wall" cells in which the photo-activity takes place just where
the light penetrates the front translucent metallic electrode
and strikes the cuprous oxide layer immediately underneath,
causing a photopositive effect with respect to the rear copper
base metal supporting electrode. These effects are illustrated
in Figs. 5 and 6, page 13.

The deficiency conduction of the vacant-place type and
the excess conduction of the interstitial type of distortion
points were studied and differentiated by Schottky and Waibel
(30, 55) by means of the Hall effect (44, 58). They found
that in air below 400°C, excess conduction or the interstitial
type of Fig. 3 is stable but that above 500°C, copper ions
are missing and an excess of oxygen is present to cause defi-
ciency conduction or the vacant-place type of Fig. 4.

It may be well here to stress the fact that the above
discussion is based on dry electrodes which have a translucent

electrode over it. The previous studies on the crystal of cuprous oxide have not been made with solutions or any other liquid medium. However, the above discussion has been given here because a correlation exists between the studies with the dry cuprous oxide crystal and the wet Becquerel photovoltaic cell as studied in this part of the research. Lange also stresses this same relationship as follows (30):

"The same fundamental photo-electric process underlies the Becquerel effect (the wet photovoltaic cell), the crystal photo-effect (3), and the barrier-layer effect (the dry photo-e.m.f. cell). We group these three phenomena, differing only outwardly, together as 'semi-conductor photo-effects' and designate the various photocells depending thereon as 'photo-elements', so as to emphasize thus their characteristic property of acting as spontaneous sources of current."

The spectral sensitivities of the "frontwall" and "backwall" photo-e.m.f. cells are not discussed fully here except to point out that each has its own definite maximum sensitivity wave-length, probably due to the two different types of distortion centers. These two different types are concerned with the copper atom in one case and the cuprous ion in the other; the two different maxima for each case may be due to the following two separate oxidation reactions:

$$Cu^0 + E_1 \xrightleftharpoons{h\nu_1} Cu^+ + \text{ electron (frontwall excess conduction)}$$

$$Cu^+ + E_2 \xrightleftharpoons{h\nu_2} Cu^{++} + \text{ electron (backwall deficiency conduction)}$$
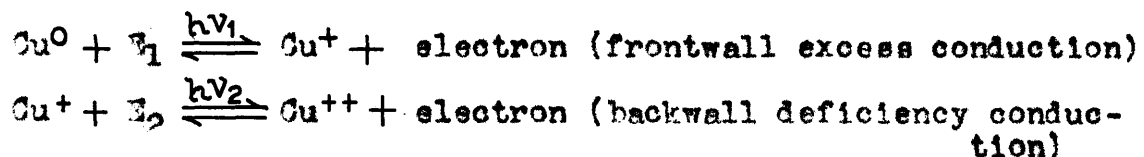
where E_1 and E_2 are different energies of ionization, obtainable from the incident light. Lange (30) showed that the wave-length maximum of the backwall cell is not dependent on the red color of the cuprous oxide layer through which the light

must penetrate in order to reach the photo-active interface between the rear copper base and the cuprous oxide, as stated by Hughes and DuBridge (23). Instead, the two above reactions may be involved to give the separate wave-length maximum in each case. Table I summarizes the above discussion.

<div align="center">

TABLE I

COMPARISON OF FRONTWALL
AND BACKWALL CELLS

</div>

Photo-e.m.f. cell	Frontwall cell	Backwall cell
Photo-effect	Photopositive	Photonegative
Type of conduction	Excess	Deficiency
Type of distortion lattice	Interstitial	Vacant-place
State of copper at distortion point	Neutral copper atom	Cuprous ion
Photo-reaction resulting	$Cu^{\circ} + h\nu_1 \longrightarrow Cu^+ + e$	$Cu^+ + h\nu_2 \longrightarrow Cu^{++} + e$

Much work has been done on the spectral sensitivity of light sensitized layers on common metals, such as copper, silver and gold (7), cadmium, zinc and silver (4), etc. Many of the workers on this phase of the photovoltaic problem adhere strongly to a photochemical explanation and photochemical theories have been advanced by van Dyck (63), by Garrison (13), by Vanselow and Sheppard (64), and by others (28). The electrons liberated by the photochemical process, according to these workers, do not necessarily obey laws of photo-electric emission.

Lange (30) apparently is the first worker to differentiate distinctly between the frontwall and backwall photo-e.m.f.

cells. The importance of both is indicated by Sommer (56)
who recommends separate symbols for each type as shown in Fig.
7, page 13.

A recent discussion on distortion points not only in
thermistor material but in semi-conductors in general has been
made by Becker, Green, and Pearson (?); the following is quoted
from their paper:

"Some impurities are much more effective in increasing
the conductivity (of semi-conductors) than others. One hun-
dred parts per million of some impurities may increase the
conductivity of pure silicon at room temperature by a factor
of 10^7. Other impurities may be present in 100,000 parts
per million and have a small effect on the conductivity.
Two samples may contain the same concentration of an impurity
and still differ greatly in their low temperature conduc-
tivity. If the impurity is in solid solution, that is,
atomically dispersed, the (current) effect is great; if the
impurity is segregated in atomically large particles, the
effect is small. Since heat treatments affect the disper-
sion of impurities in solids, the conductivity of semi-con-
ductors frequently may be altered radically by heat treat-
ment. Some other semi-conductors are not affected greatly
by heat treatment."

"The impurity need not be a foreign element; in the case
of oxides or sulfides, it can be an excess or a deficiency
of oxygen or sulfur from the exact stoichiometric relation.
This excess can be brought about by heat treatment. ...
For a number of samples of cuprous oxide, heat-treated in
such a way as to result in varying amounts of excess oxygen
....the greater the amount of excess oxygen, the greater is
the conductivity in the low temperature range. At high
temperatures, all samples (of the same compound) have about
the same conductivity."

"Semi-conductors can be classified on the basis of the
carriers of the current into ionic, electronic, and mixed
conductors. Chlorides such as NaCl and some sulfides are
ionic semi-conductors; other sulfides and a few oxides, such
as uranium oxide, are mixed semi-conductors; electronic semi-
conductors include most oxides (fortunately) such as Mn_2O_3,
Fe_2O_3, NiO, carbides such as silicon carbide, and elements
such as boron, silicon, germanium, and tellurium. In ionic
and mixed conductors, ions are transported through the solid.
This changes the density of carriers in various regions, and
thus changes the conductivity. Because this is undesirable,
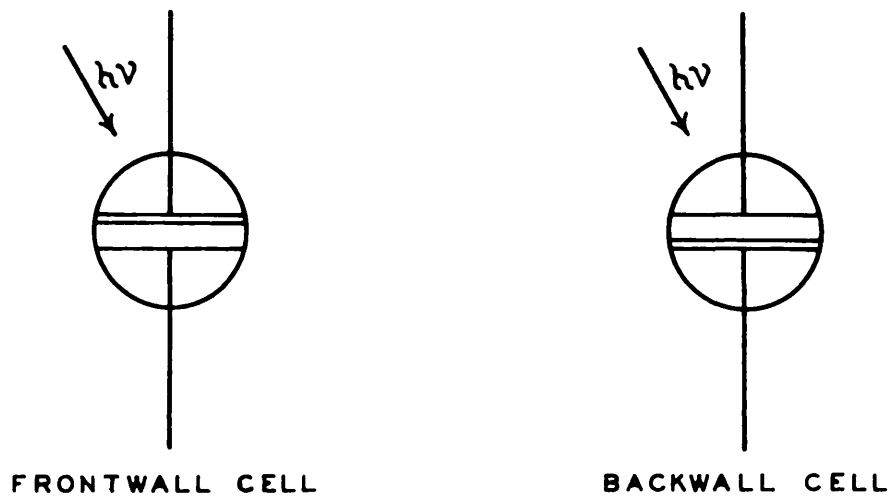
Fig. 7 - Symbols for photo-e.m.f. cells
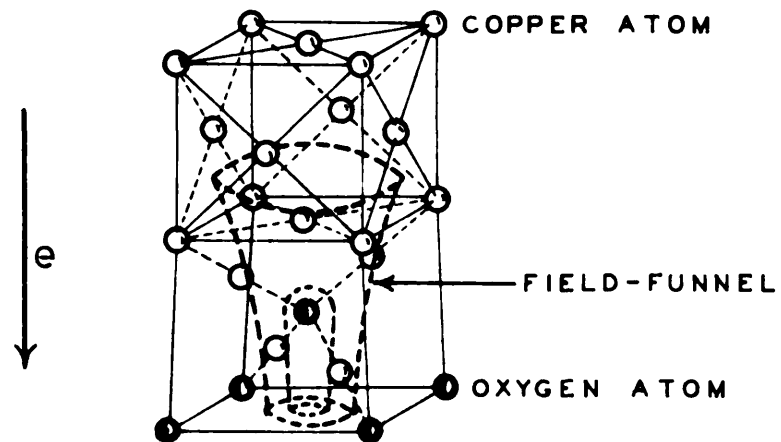
Fig. 8 - Location of the field-funnel in a copper-cuprous oxide mixed crystal

they rarely are used in making thermistors (or dry photo-e.m.f. cells)."

Electronic semi-conductors are therefore of primary importance not only as thermistor material but for light-sensitive semi-conductors. Further theory given by the above authors is not necessary here except to quote their summary:

"1- N-type (where negative electrons are the current carriers as determined by the Hall effect) oxides, such as ZnO, when heated in a neutral or slightly reducing atmosphere become good conductors, presumably because they contain excess zinc which can donate electrons. If they then are heated in atmospheres which are increasingly more oxidizing, their conductivity decreases until eventually they are intrinsic semi-conductors or insulators.

2- P-type (where positive 'holes' appear to be the current carriers as ascertained by measurement of the sign of the Hall effect) oxides, such as NiO, when heated in strongly oxidizing atmospheres are good conductors. Very likely they contain (atomic) oxygen in excess of the stoichiometric reaction and this oxygen (as atoms) accepts additional electrons. When these are heated in less oxidizing or neutral atmospheres they become poorer conductors, semi-conductors, or insulators.

3- When a P-type oxide is sintered with another P-type oxide, the conductivity increases; similarly for two N-type oxides. But when a P-type is added to an N-type the conductivity decreases.

4- If a metal forms several oxides, the one in which the metal exerts its highest valence is N-type, while the one in which it exerts its lowest valence will be P-type (31)."

Pearson (44) quotes the following:

"By impurities we mean added foreign atoms, physical defects in the lattice, or differences from stoichiometric composition... .

When a metal point is placed against an impurity semi-conductor, the combination has a non-linear current versus voltage characteristic and acts as a rectifier. For a P-type sample the current is large when the semi-conductor is made positive and the metal point is negative, but is small when these polarities are reversed. For an N-type sample the sign of the effect is reversed so that the current is large when the semi-conductor is negative."

Pearson also combines electrical resistivity, photo-effect, Hall effect, thermo-effect, rectification, and thermictor effect of semi-conductors into one based on the impurity or distortion point concept.

The Barrier-Layer Theory. Schottky (30, 54) found that when cuprous oxide is formed on copper at high temperatures (ca. 1000°C) in the air, a resistance ratio of 1 to 100 or more is obtained at room temperature between the electronic resistance from copper to cuprous oxide versus the electronic resistance from cuprous oxide to copper with high voltage; in other words, electrons travel more readily from copper to cuprous oxide at high applied voltages. At low voltages, the resistances were approximately the same for either direction. Now in the frontwall photo-e.m.f. cell, the electrons pass readily from the copper to the cuprous oxide and are practically blocked in the reverse direction, as in the above oxide-copper system. But in the backwall photo-e.m.f. cell as prepared above by Schottky, the photo-electrons pass readily in the opposite direction to that of the above conduction electrons with high voltage; the photo-electrons here pass readily from oxide to metal to give a photonegative electrode. Schottky assumed that in the backwall metal-oxide interface, only the edges of the cubic cuprous oxide crystals are imbedded in the copper base to give a "resistance sieve" which he termed the "barrier-layer". This backwall barrier layer supposedly has a high resistance or insulating layer to photo-electrons going in one direction, from metal to oxide, and this layer

prevents internal short-circuiting so that an external current can be generated.

Teichmann (30, 60) extended this barrier-layer contact-point idea by introducing his famous "field-funnel" concept; he proposed an analogy that more molecules of a gas can be caused to flow through the top of a funnel than initially through its stem. Similarly, the mixed crystal of copper and cuprous oxide form a field-funnel; the copper atom acts as its wide mouth allowing electrons to flow through it readily since it is a metal; the stem of this field-funnel is the cuprous oxide crystal, the negative electric fields of the oxygen ions in the mixed crystals retarding electron movement through it. The field-funnel idea is depicted in Fig. 8, page 13.

The barrier-layer theory and its field-funnel extension does not explain the seat of photo-activity and the dependence of the photopotential on light intensity. The theory attempts to explain the behavior of electric currents or the flow of electrons through the copper-cuprous oxide layer but does not provide for the production of photopotentials when no current is allowed to flow, nor does it explain in a satisfactory manner the backwall effect where electrons pass readily from oxide to copper to give a photonegative supporting copper electrode. This theory was therefore superseded by the following Insulating-Layer Theory.

The Insulating-Layer Theory. This theory is apparently due to Lange (30) and is based on the work of Rother and Fohmke

(50). From the studies with large separate crystals of cup-
rous oxide and with crystalline layers of cuprous oxide on
copper, Lange showed that the semi-conducting photoproperties
of these large crystals (the crystal photo-effect) and the
crystalline layers on the copper surface (the Becquerel and
barrier-layer photo-effects) are the same. The blocking layer
and its inherent high resistance are not necessary for photo-
activity. This fact attempts to explain the anomaly mentioned
above that photo-electrons in the backwall cell flow readily
in the opposite direction to conduction electrons that flow
during rectification, to be discussed further below.

When a copper surface is heated at $1000^\circ C$, oxygen from
the air diffuses into the surface to form cuprous oxide; the
amount of neutral copper atoms remaining of course depends on
the distance below the original copper surface. At $1000^\circ C$ the
equilibrium is favored toward cuprous oxide as follows:

$$2Cu_2O + O_2 \xrightleftharpoons[\rightarrow]{1000\,^\circ C} 4CuO \qquad .$$
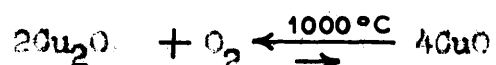
This results in a backwall cell whose photo-active layer
contains monovalent cuprous ions and whose supporting electrode
according to Lange is photonegative. This is represented in
Fig. 6, page 13, where the translucent electrode may be a
thin metal or a solution. The insulating layer which results
from this treatment is zone 3 in Fig. 9, page 23, presumably
composed of pure cuprous oxide in which the electrical conduc-
tivity is lowest. Zone 4 of this figure is composed of cup-
rous oxide with many lattice distortion points and possessing
deficiency conduction or vacant-place type of distortion point
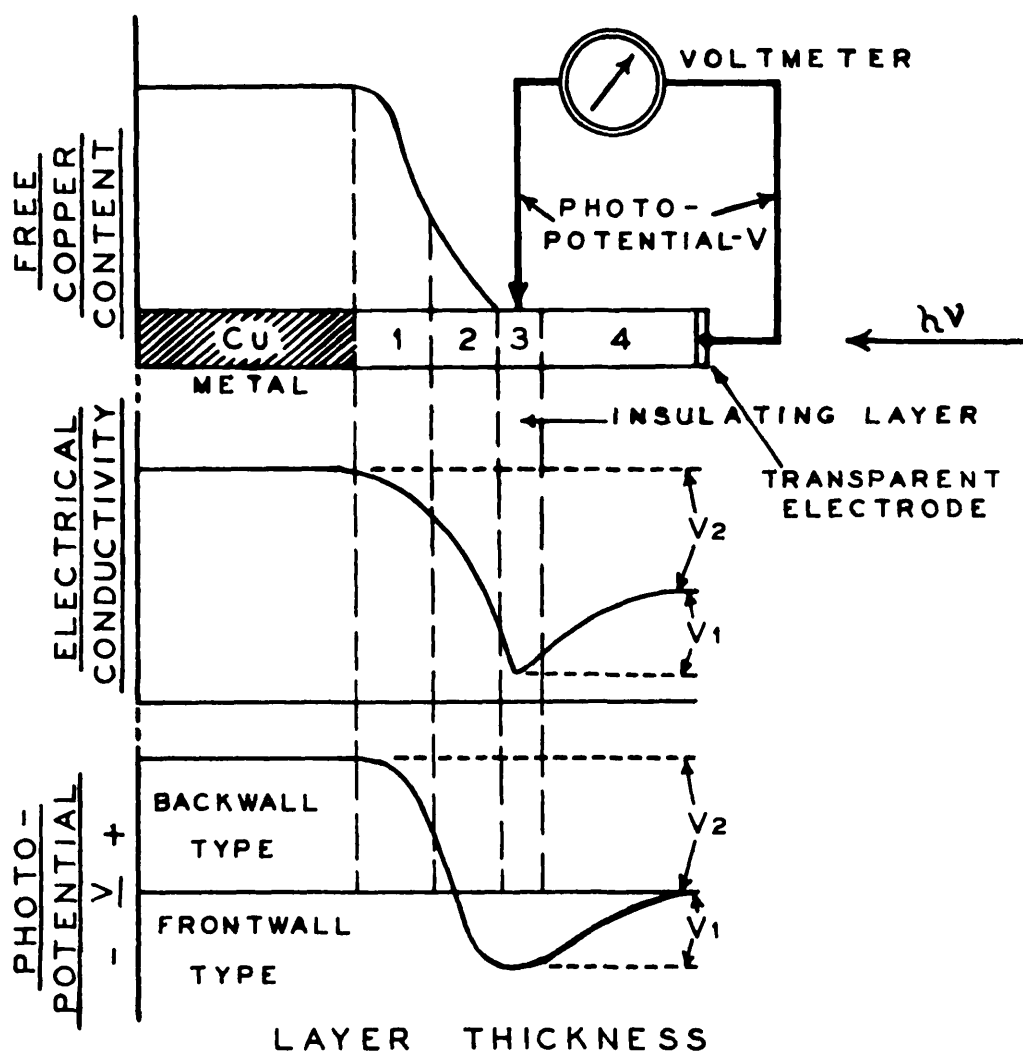
Zone 1 - Cuprous oxide layer rich in copper particles

Zone 2 - Cuprous oxide layer poor in copper particles

Zone 3 - Least contaminated cuprous oxide layer acting as a
semi-conducting barrier layer having the lowest
electrical conductivity due to a few embedded
lattice distortion points

Zone 4 - Cuprous oxide layer rich in oxygen atoms as distor-
tion points

Fig. 9 - Dependence of the content of free copper, electrical
conductivity, and photopotential on the layer thick-
ness in the thermal oxidation of copper

as given in Table I, page 16; this would give a photonegative supporting electrode according to Lange. However, in this research, a photopositive electrode was found with copper electrodes prepared in the bunsen flame. Garrison (13) states that an initial chemical treatment of copper to form cuprous oxide over it gave a photopositive electrode while subsequent chemical treatment produced a photonegative electrode. This will be discussed further below.

If the partial reduction of the surface of a layer of cuprous oxide on the supporting copper is performed by quenching the cuprous oxide at $1000^{\circ}C$ in mineral oil, formaldehyde, or other reducing agent, or by a glow discharge, a frontwall electrode results because neutral copper atoms are now present in zone 4, Fig. 9. The copper atoms freshly formed in this frontwall electrode, which contains an interstitial type of distortion center to cause excess conduction, should result in a photopositive supporting electrode as in Fig. 3 and Fig. 5, page 13.

The blocking-layer theory explained the current phenomena of the oxide-copper system but neglected the production of the photopotential on open circuit. The insulating-layer theory, on the other hand, elucidates the open-circuit photopotential by assuming that the light-sensitive electrode is a photo-electron concentration cell and that the insulating layer separates two different photo-electron concentrations or forms a photo-electron/electron system so that the potential difference between them can be measured, analogous to pH measurements

with the glass electrode. The external current is a result
of this difference in electron concentration which diminishes
as the cell deteriorates. The two electron concentrations
are assumed to be brought about by the insulating layer, zone
3 of Fig. 9, having a lesser number (N_1) of photo-electrons
produced by the light due to a much less number of distortion
centers than that contained in zone 4, which contains a larger
number (N_2) of photo-electrons on irradiation. The resulting
photopotential can be treated as a Maxwell-Boltzmann distribu-
tion and put into the form of the Nernst equation for the
ionic concentrations of two solutions, as follows:

$$E = (u-v/u+v) \cdot RT/nF \cdot \ln N_1/N_2$$

where u and v are the ionic mobilities of the anion and cation
respectively. Since the mobilities of the electron u and
positive cuprous ion v (assuming a mixed conductor as mentioned
on page 17) are involved here, and since the mobility of the
electron is so much greater in crystals than that of the ion,
the above equation becomes:

$$E = (RT/F) \cdot \ln N_1/N_2$$

Garrison (13) and Vanselow and Sheppard (64) utilize the
difference in electron and ion mobilities in crystalline silver
bromide to explain an effect called here the "transient photo-
inductive effect", to be described and discussed below.
Englehard (10, 30), mentioned above on page 12, from experi-
mental work calculated by means of this equation an open cir-
cuit maximum theoretical photopotential of 183 millivolts
which is a much lower value than Garrison's (13) 300 millivolt

experimental maximum or the 370 millivolt value obtained experimentally in this research. The larger photopotential may be due to two factors: (1) Englehard calculated the potential difference between zones 3 and 4 of Fig. 9 as illustrated by the voltmeter and V_1; a much higher theoretical value would probably be obtained between the base copper metal and zone 4, illustrated in the figure by V_2 in order to explain the higher opposite-polarity values obtained in this research. And (2), the glass membrane used in this work has a higher resistance than the insulating layer of zone 3 thereby allowing a greater photopotential to be built up across it in the photovoltaic cell. The use of the glass membrane to separate two different electron "concentrations" is similar to that of the insulating layer of zone 3 of Fig. 9, and recent research (23) has shown that this artificial glass barrier-layer may prove advantageous in certain dry rectifiers, some using "blue" conductive titanium dioxide. Some promising results have been obtained with varnish on selenium (22, 23) and thin rice paper sandwiched in a magnesium/iron oxide rectifier (32). The use of the glass membrane in the photovoltaic cells studied in this research will be discussed further below.

Thus, in the irradiated crystal of cuprous oxide, regardless of the crystal size, a certain concentration of photo-electrons exists within it which, when electrically compared to the electron concentration of another conductor or semiconductor that touches the crystal or is separated from it by an insulating membrane, produces a photopotential which may be used to provide an external current. In this research, this photopotential is measured by a vacuum-tube electrometer.

CHAPTER IV

THE PRESENT MODE OF EXPERIMENTATION

<u>Introduction</u>. In a photochemical change or reaction,
irradiation with light of certain wave-lengths has caused the
irradiated substances to change its chemical as well as its
physical properties. The loss or gain of electrons by irradia-
tion with light, which may be considered as the primary effect
obeying photo-electric laws, causes the chemical change which
may be considered as the secondary photochemical effect. If
some means can be introduced whereby the electrons can not
leave the substance permanently but can return when the light
is removed, the substance can remain stable indefinitely and
can then be utilized to give a consistent and reproducable
photo-electric or photovoltaic effect. Prevention of the
permanent loss of electrons can be done by not allowing a
current to flow from the cell or locally in the photo-element.
In this part of the research, the method used to study the
photovoltaic effect of metals and their oxides and to reduce
current flow is to introduce a glass membrane and to paraffin
the light-sensitive electrode except where it is irradiated.
A difference of potential, the photopotential, is allowed to
form across the glass membrane and this photopotential is
measured by means of a vacuum-tube electrometer, similar to
the conventional glass-electrode pH assembly.

<u>The Photovoltaic Cell</u>. The photovoltaic cell system used
in this research is shown in detail in Fig. 10, page 28. The

TO POTENTIOMETER

TO ELECTROMETER
TUBE

COPPER BASE

CUPROUS OXIDE LAYER

PARAFFIN COATING

UNPARAFFINED AREA

IRIS
DIAPHRAGM

CUBICAL
OPTICAL -
GLASS CELL
5 X 5 X 5 CM.

LIGHT BEAM

LIGHT
SOURCE

CORNING 015
GLASS MEMBRANE

PLATINUM -
0.1 N - HCl -
QUINHYDRONE
HALF - CELL

DISTILLED WATER,
ELECTROLYTE OR
FLUORESCENT
SOLUTION

◄——— 25 CM. ———►
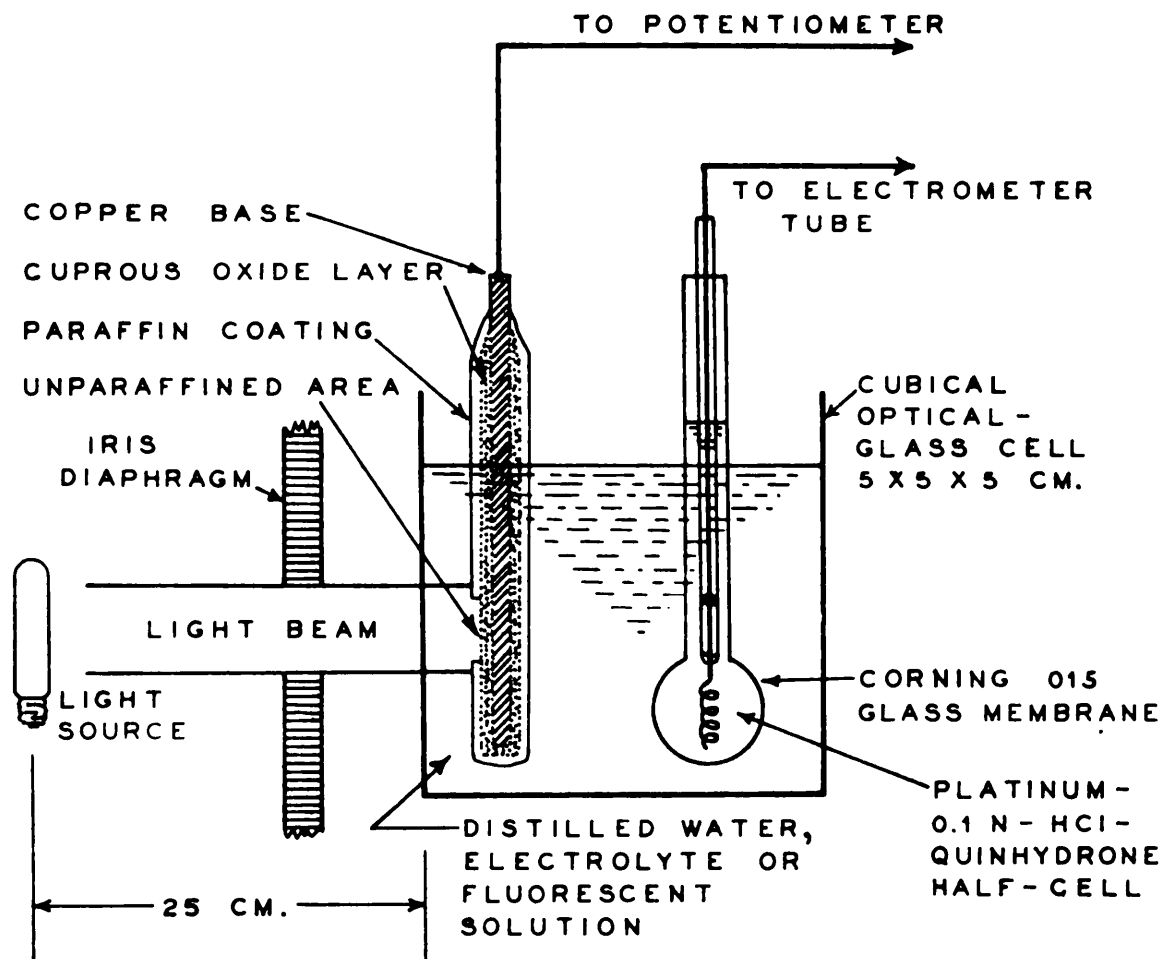
Fig. 10 - The photovoltaic cell (layer thicknesses on the
copper photo-element have been greatly exaggerated)

inside of the glass membrane shell or electrode, which is the
dark or unirradiated electrode, usually contains the conven-
tional 0.1 N HCl-quinhydrone half-cell for electrical stability.
In the early experiments of this research, a bare platinum
wire was placed inside the glass electrode together with the
same solution as on the outside but this caused erratic results.
Changing to the internal 0.1 N HCl-quinhydrone system caused
the electrometer to be more stable. The necessity of the
glass membrane was roughly indicated by the reduction of electro-
meter drift when compared to a metal electrode or calomel half-
cell.

The surface of the irradiated electrode was paraffined
wherever it was immersed in the liquid, except for a small
area usually a square 1 cm. on an edge which was left unparaf-
finxed so as to be completely irradiated by the light. Garri-
son (13) also paraffined his electrodes, apparently the first
to do so, on the dark side only. This procedure of paraffin-
ing aided in giving the maximum photopotential because if the
electrode, which was only partly irradiated, were completely
unparaffined, current might flow locally between the dark and
irradiated areas of the electrode via the semi-conducting layer,
electrolyte, or base metal. This local current was to a large
extent reduced by the insulating property of the paraffin and
thus most of the electrons affected by the light could have
the effect of building up a potential difference across the
glass membrane as shown in Fig 10. The necessity of the paraf-
fin coating was simply shown by the following experiment:

A cuprous oxide layer was formed on a 1 by 3 inch strip of 0.003 inch thick electrolytic sheet copper (used throughout this research) by heating in a bunsen flame. Irradiating the cuprous oxide layer with a cylindrical light beam 1 cm. in diameter gave an average photopositive value of 8 units on the galvanometer scale. After coating with paraffin except for a square area of 1 cm. on an edge and using the same light beam, an average photopotential of 62 positive units was obtained - an increase of approximately 8-fold !

The Electrometer Circuit. Fig. 11, page 31, shows the complete electrical circuit of the apparatus used in this part of the research. The electrometer circuit is an improved d.c. voltmeter developed by DuBridge and Brown (9) and has also been used with photovoltaic cells by Clark and Garrett (7) and others (41). Although Muller, Garman, and Droz (41) point out that this circuit has a high input resistance and therefore is not suitable for barrier-layer cells due to their low resistance, the glass membrane increases the resistance of the photovoltaic cell in this research so as to be suitable for this circuit; distilled water and the organic solvents for the fluorescent substances in Part II also render this circuit suitable. The electrometer section was mounted in a closed metal box as a shield which also contained a 500 ml. beaker half-filled with anhydrous lump calcium chloride as a dehydrant. The control-grid lead emerged from the metal box through a large molded and lathe-turned sulfur insulator. The calibration curve of this vacuum-tube electrometer is shown in Fig. 12, page 32, which indicates a maximum sensitivity of 1.1 x 10^{-5} volt per mm. division with a slight deviation at the higher galvanometer readings.
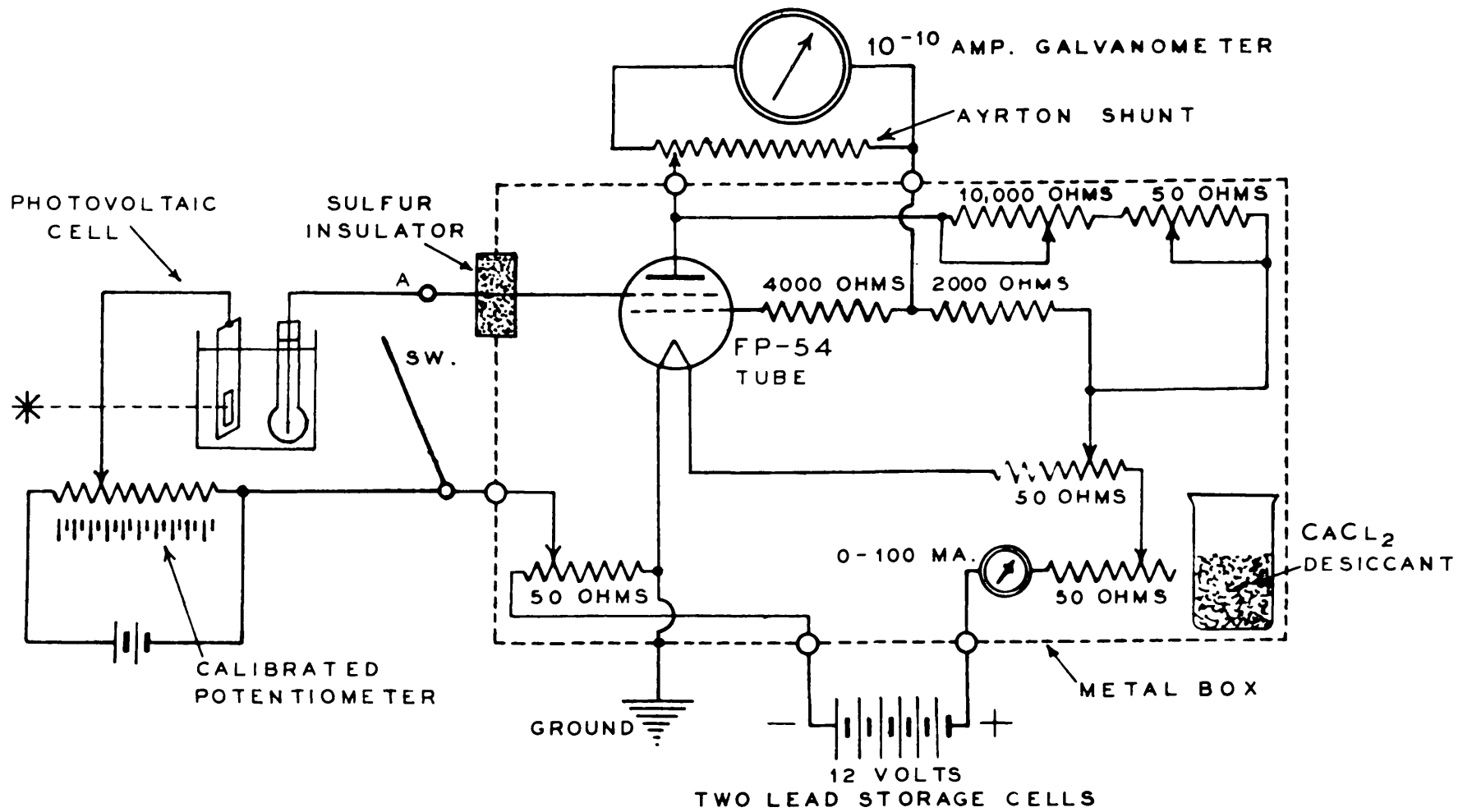
FIG. 11 — THE ELECTROMETER CIRCUIT WITH PHOTOVOLTAIC CELL AND CALIBRATED POTENTIOMETER
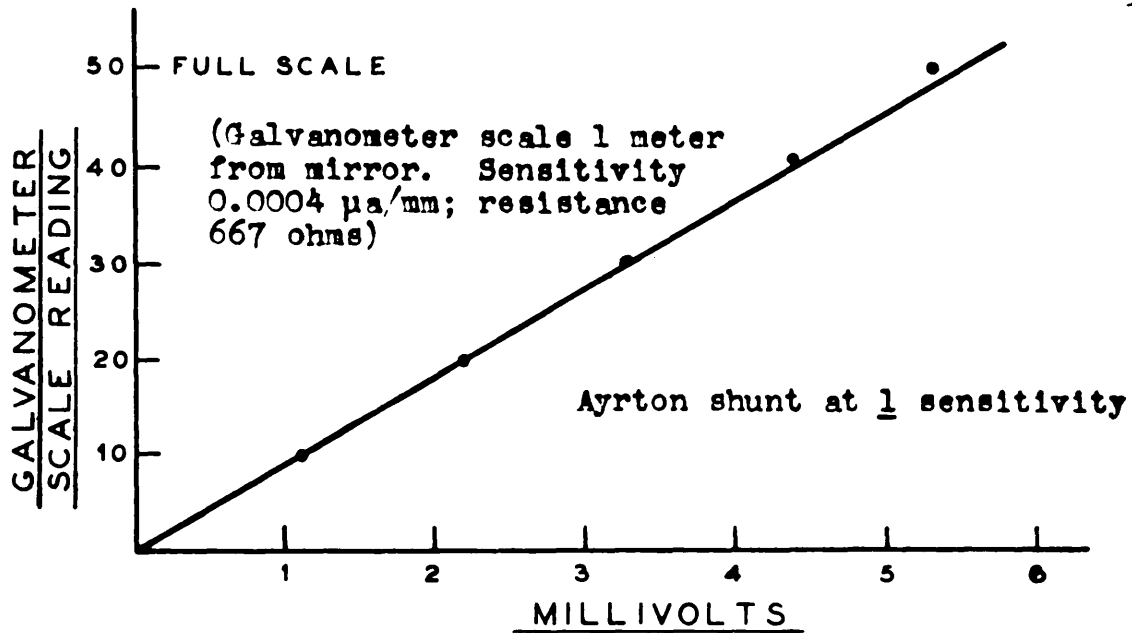
Fig. 12 - Calibration of electrometer
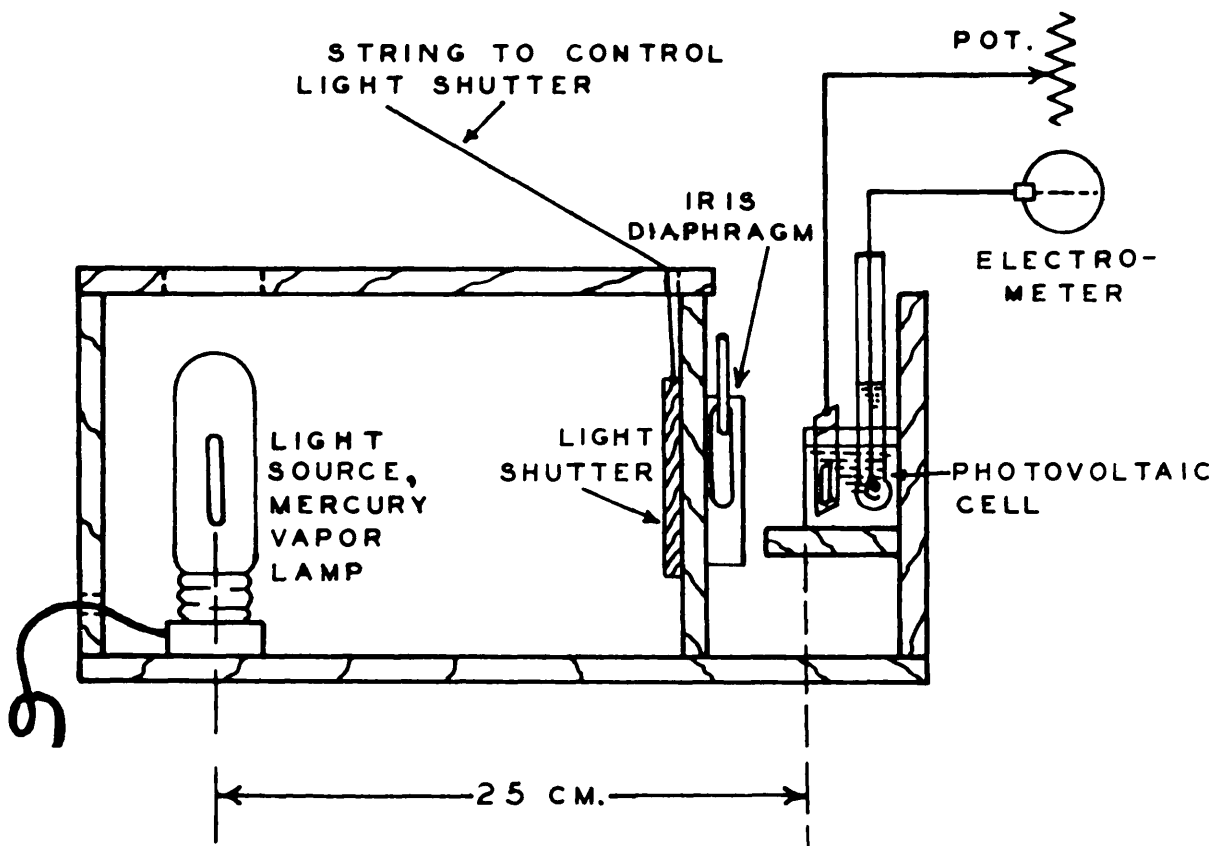
Fig. 13 - Irradiation system

The Light-Source and Other Parameters. The light-source used throughout this research was the General Electric 100 watt Type H-4 clear-glass mercury vapor lamp (14) fixed at a distance of 25cm. from the cubical optical cell, as indicated in Figs. 10 and 13. This lamp was energized by a special auxiliary transformer which was connected to the a.c. mains. No effort was made for obtaining a constant light free from variations because these studies were made qualitatively at first in order to determine if a photo-element could be prepared sensitive to fluorescent light. Reference (14) and Blooher and Garrett (4) give the relative spectral content of the light from this lamp. Also, no glass filters were used because the longer wave-lengths of light which could retard photo-electric emission in the light-sensitive layer or quench the fluorescence of the substances studied in Part II are not present to any detrimental degree as compared with the shorter fluorescence-exciting wave-lengths of light which are present in the mercury arc. Ultra-violet glass filters were used only when it was necessary to see the fluorescence with the eye. The work described in Part II with fluorescent solutions also shows that filters were not needed for the electrical measurements and, in fact, they usually diminished the fluoro-photo-potential to a low value as compared with no filters. Voltage regulation for the light source for the work of Part II was therefore not necessary.

The light source and photovoltaic cell system were mounted in a box similar to that described by Levin (33) and shown in Fig. 13, page 32.

CHAPTER V

THE PHOTOVOLTAIC BEHAVIOR OF COPPER

Freshly cleaned copper in distilled water displayed no
photo-activity; if allowed to remain in the distilled water
for a few hours, a slight photonegative effect resulted due
to some chemical activity. A strip of electrolytic sheet
copper 1 by 3 inches and 0.008 inch thick (this thickness
used throughout this work) was cleaned and polished with steel
wool, carefully wiped to remove any adhering iron, and heated
in a bunsen flame at a glowing temperature of approximately
$800^\circ C$ for about 1 minute. After allowing to cool to room
temperature, the loose black cupric oxide was blown or light-
ly wiped away exposing the tenacious red cuprous oxide layer
underneath. This red layer was coated with paraffin except
for a square area of 1 cm. on an edge and the electrode was
immersed in distilled water; a photopositive value of 20 milli-
volts was thus obtained. When the copper was heated so as to
prevent glowing and allowed to blacken to the cupric oxide
color, a photopositive value of 250 millivolts was obtained
in distilled water. The photopositive values indicate that
photo-electrons are moving from the supporting copper elect-
rode into the oxide and toward the liquid medium and light.
Although Lange (30) indicates that copper which he prepared by
heating in air yielded a photonegative effect as a dry photo-
element, those prepared similarly in this research and by Gold-
mann and Brodsky (19) yielded a photopositive effect.

When distilled water was used as the liquid medium with the cuprous oxide photo-element, a higher positive photopotential was obtained than when a salt solution was used.

When freshly cleaned copper strips were placed in distilled water and irradiated for an hour, a varicolored layer of cuprous oxide appeared which yielded a negative photopotential of approximately 3 millivolts, an effect opposite to that obtained by heating copper in air. Immersion of freshly cleaned copper strips for 4 days in 0.1 N KCl yielded a photosensitive surface whose average negative photopotential was 150 millivolts after the sensitive surface was carefully washed with distilled water, dried in the air, and paraffined except for a square cm., using distilled water as the liquid medium with the glass electrode as in Fig. 10, page 28. 0.1 N KCl as the liquid medium of the photovoltaic cell yielded a much lower photopotential of approximately 40 millivolts negative with a peculiar transient photo-inductive effect to be described below. Solutions of several other substances were tested for forming a photosensitive surface on copper; these solutions were tested by immersing copper strips in them at hour intervals and overnight and irradiating them; these solutions were of hydrogen peroxide, nitric acid, nitric acid-hydrogen peroxide mixture, cupric chloride[V], cupric nitrate, cupric sulfate,

[V]Garrison (13) used slightly soluble cuprous chloride solutions followed by a slow hydrolysis in water to form cuprous oxide layers. By varying the time of treatment, thin layers were photopositive as obtained with the flame in air and thick layers were found photonegative contrary to Goldmann and Brolsky (19) who concluded from their photo-electric theory that cuprous oxide layers in any thickness were always

ammonium perchlorate, and ammonium persulfate. Of these substances, cupric nitrate formed the most photosensitive layer on the surface of the immersed strip of copper; an overnight immersion in 0.1 M aqueous cupric nitrate solution yielded a _negative_ photopotential of 370 millivolts, the highest photopotential, regardless of polarity, obtained in this part of the research on metals. Longer immersions reduced the photopotential due to thicker precipitating layers. However, reconsidering the primary object of this research, this remarkable photosensitive surface proved to be not at all sensitive to the fluorescent light of such substances as sodium fluorescein dissolved in water when the flat-photo-element was placed parallel to the light beam so as to be illumined only by the weak fluorescent light and not by the stronger light from the mercury arc.

Since the above sensitizing method appeared simple and somewhat promising, it was studied further. An attempt to prepare photosensitive surfaces by electrolysis with the intended copper photo-element as anode and with solutions of various salts at different pH values as the electrolyte did not produce photosensitive surfaces. Also, an attempt to form a light-sensitive electrode by the electrophoretic deposition of cuprous oxide, suspended in water, on copper and platinum did not prove successful, though the suspended particle possessed a negative charge.

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photopositive when prepared in a flame in air. This type of discrepancy is the basis of the present argument between the photochemical and photo-electric adherents.

The effect of the variation of the light-exposed cuprous oxide area on the photopotential using distilled water and the glass electrode as in Fig. 10, page 28, with no filters was studied and is summarized in Table II; this not only shows the importance of the paraffin coating but also points out another fact of theoretical significance to be discussed in Chapter VII.

TABLE II

VARIATION OF PHOTOPOTENTIAL
WITH EXPOSED IRRADIATED AREA

Treatment of prepared electrode	Area irradiated and unparaffined	Average positive photopotential in millivolts
Not paraffined	2 cm. diameter irradiated	17
	1 cm. diameter irradiated	10
	0.5 cm. dia. irradiated	3
Paraffined	4 sq. cm.	60
	1 sq. cm.	83
	0.25 sq. cm.	105
	0.01 sq. cm.	60

When an area of 1 sq. cm. on copper strips 3 by 4 cm., which have remained exposed to the air for a year, was freshly cleaned with steel wool, wiped with a clean cloth to remove adhering iron, and immersed in a 0.1 N potassium chloride solution containing phenolphthalein (to be designated as the KCl-phenolphthalein solution), the solution turned red in the dark at the freshly cleaned surface. The same effect was also obtained when a similar but completely cleaned copper strip was heated in a colorless bunsen flame to form cuprous oxide overall, and a small area cleaned and polished so as to form

a copper area of about 1 sq. cm.; the red test also appeared at this freshly cleaned copper area. This action reveals that an electrolysis of the water is taking place in the dark at the cleaned copper surface which acts as a cathode. The phenolphthalein becomes red at this surface due to the hydroxyl ion which is left behind when the hydrogen ion is discharged by an electron according to the following probable reactions:

$$Cu^{\circ} \longrightarrow Cu^+ + electron$$

$$2H_2O + 2 \; electrons \longrightarrow 2OH^- + H_2$$

$$or \; 2 \; H^+ + 2 \; electrons \longrightarrow H_2$$

$$Cu^+ + Cl^- \longrightarrow CuCl\downarrow$$
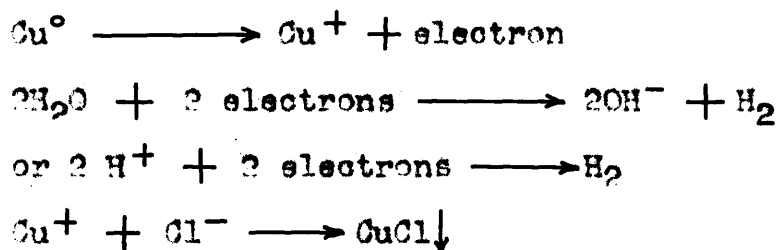
The copper is oxidized to the cuprous ion which reacts with the chloride ion present to form insoluble cuprous chloride on the surface of the cleaned copper area; a chemical test disclosed the chloride. If no chloride ion had been present, insoluble cuprous or cupric hydroxide would probably have been formed just as in the immersion of clean copper in aqueous cupric nitrate as described on page 35.

When the partially-cleaned copper strips immersed in the KCl-phenolphthalein solution were irradiated by means of the mercury-vapor lamp, a definite reverse effect was obtained, the red phenolphthalein color appeared at the cuprous oxide surface. In fact, it was possible to adjust the intensity of the light by varying the distance between test-tube and lamp so that no red test was obtained from either the cleaned copper or cuprous oxide surface; this delicate point of balance has theoretical significance and may be determined precisely by

means of a sensitive galvanometer placed between two separate electrodes in the same KCl solution, no phenolphthalein being required; one electrode is covered with cuprous oxide and the other is cleaned copper, both properly insulated with paraffin and facing the variable light intensity. The light must be of the proper wave-length to eject photo-electrons from cuprous oxide so that the red phenolphthalein color can occur in the solution at this surface according to the following probable reactions:

$$Cu^+ \xrightarrow{h\nu} Cu^{++} + electron$$

$$2H_2O + 2 \; electrons \longrightarrow 2OH^- + H_2$$

$$or \; 2H^+ + 2 \; electrons \longrightarrow H_2$$

$$Cu^{++} + 2OH^- \longrightarrow Cu(OH)_2 \downarrow$$
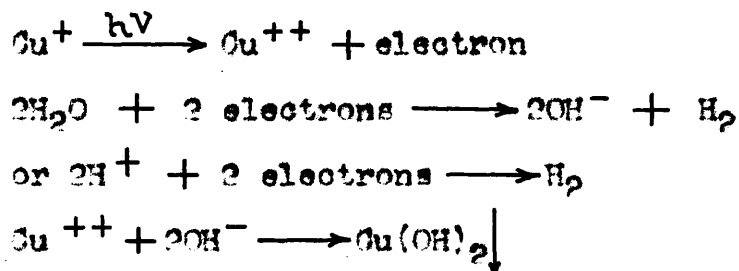
Cupric hydroxide being insoluble unlike cupric chloride precipitates on the cuprous oxide surface. From the above, it might appear that a standard of light intensity could be set up at the balance point in the copper-cuprous-cupric system, but whether this system _per se_ is suitable as a light standard or whether the thickness of the cuprous oxide layer determines the critical light intensity must be considered. It seems that the thickness of the cuprous oxide layer would be a controlling factor if photo-electrons were ejected from the photo-positive metal-oxide interface but no further tests were made to verify this. A discussion will be given in Chapter VII. "Photobalancing" studies were not made with copper photo-elements prepared in cupric nitrate solution as described above, since this would have taken the research too far amiss from the primary object.

One other effect has been obtained in this work with copper. This effect, here called the "transient photo-inductive effect" and mentioned on page 35, has been noticed by many workers working with other metals besides copper. Its explanation has been given by others (4, 13, 28, 63, 64) as one which occurs within the light-sensitive layer. This transient photo-inductive effect was obtained when a photopositive cuprous oxide-covered electrode prepared in the flame was immersed in a dilute KCl solution as described on page 35; immediately on irradiation, the photopotential first assumed a negative value and then a larger positive value. This is illustrated in Fig. 14, page 41. Distilled water did not yield this transient effect but other salts besides potassium chloride did, indicating that the effect is due to the nature of the liquid medium and not to the cuprous oxide layer.

Other metals studied for photo-activity were iron, zinc, magnesium, and tin, and the results of these studies are briefly described in the following chapter.

Fig. 14 - The transient photo-inductive effect

DISTILLED WATER

GLASS
MEMBRANE

LIGHT
BEAM

LOW RESISTANCE
CALOMEL HALF-CELL

FLUORESCENT SOLUTION

PARAFFINED LIGHT-SENSITIVE
ELECTRODE PARALLEL TO LIGHT BEAM
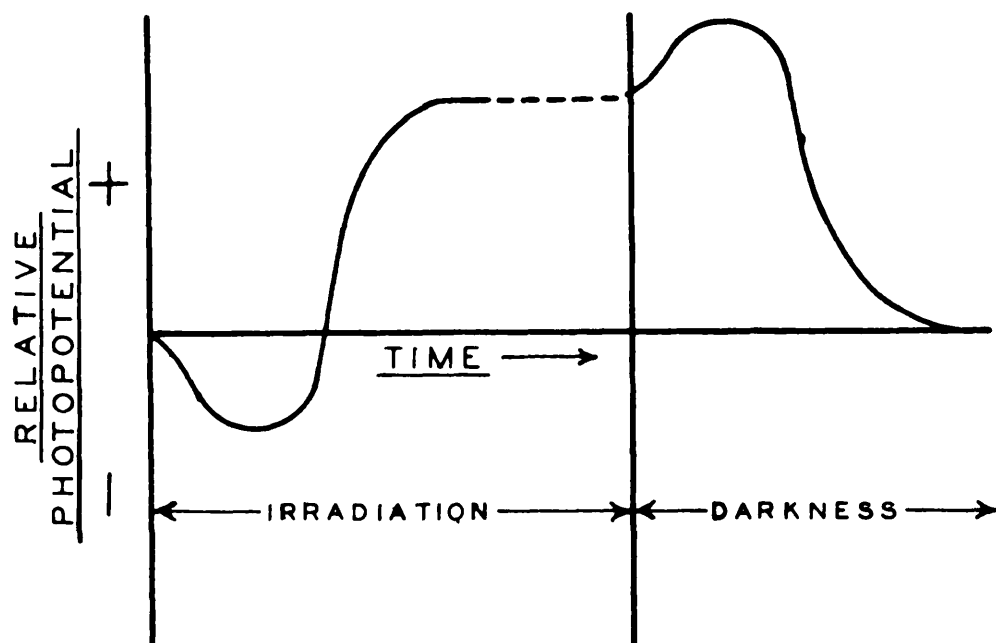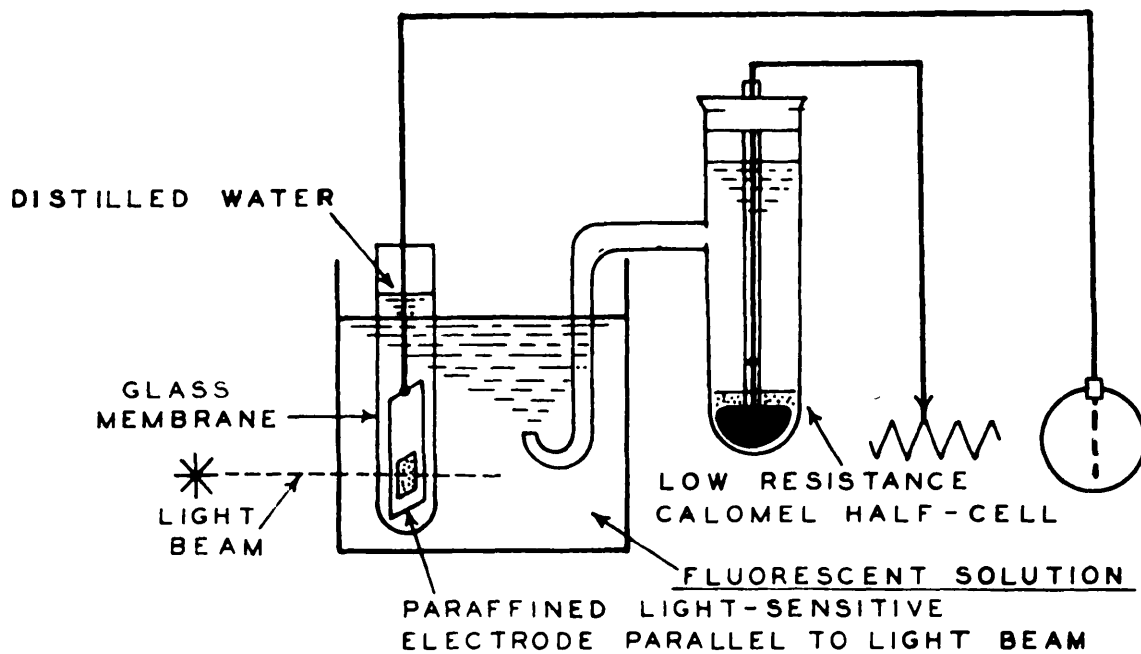
Fig. 15 - "Inverted" photovoltaic cell

CHAPTER VI

THE PHOTO-ACTIVITY OF VARIOUS METALS

Iron. This metal was studied because it has two oxides.
The bare metal had no photo-activity when studied in distilled
water as in Fig. 10, page 28. When allowed to remain in the
distilled water, the metal slowly became photonegative as with
copper, and the iron surface showed the brownish tinge of rust.
When a clean iron strip was covered with paraffin on both
sides except for an area of 1 sq. cm. on both sides, immersed
in distilled water, and one side irradiated, the irradiated
side became attacked and the water quickly became yellow-
colored; no chemical action appeared on the dark side except
for the formation of hydrogen bubbles. This indicates that
the electronic flow in the metal is away from the light. The
very rapid development of the yellow color of the liquid is
due to the formation of colloidal ferric hydroxide which,
since it forms a positive colloid, is repelled away from the
positive irradiated surface perhaps as soon as formed.

With similar iron electrodes immersed in 0.1 N KCl, an
opposite effect to the above resulted on irradiation, no
chemical action occuring this time on the irradiated surface
but on the dark side. The solution here also developed the
yellow color quickly. The electronic flow in the metal is
towards the light in this case, and this was verified with
phenolphthalein turning red only at the irradiated bare sur-
face. However, these surfaces displayed only small photopoten-
tials.

Iron strips which had been heated in air to form black ferrous oxide yielded a poor photo-effect. Also, a clean iron strip immersed in ferric chloride solution displayed only a slight photopositive effect in distilled water, loose black ferrous oxide having apparently been formed during the immersion in the ferric chloride solution; immersion in ferric nitrate solution formed loose ferric oxide which also showed a very slight photopositive effect when tested in distilled water.

The effect of ions in reversing the direction of electronic flow in the metal during irradiation also points to the nature of the liquid medium as the cause of the transient photo-inductive effect, as mentioned on page 40.

Since iron and its water-insoluble oxides did not indicate any significant sensitivity to light photopotentiometrically, they were not studied further in this research. However, it may be interesting to point out here the photochemical reduction of ferric ion to ferrous ion as in the blue-printing process which utilizes potassium ferricyanide to form insoluble Prussian blue. It is known (12) that ferric salts of strong acids as sulfuric and hydrochloric are not reduced by light while ferric salts of weak acids, usually organic acids such as oxalic, citric, and lactic, in solution are reduced to ferrous salts. This blue-print reaction has not been used as an actinometer as, for example, a solution of uranyl sulfate or mercuric chloride (15) together with oxalic acid to measure the intensity of light, carbon monoxide and dioxide being

liberated and their combined volumes quantitatively measured as an index of the light intensity. Similarly, in the blue-print reaction, when the photo-electron is liberated within the dry organic salt, the organic light-sensitive radical may be oxidized to a gaseous or inert product and the ferric ion now low in the e.m.f. series captures the loosened photo-electron. This discussion has been included here to indicate that in order that the ferric-organic radical bond be light-sensitive, it must be less electrovalent than in the inorganic ferric oxide type of bond.

Zinc. Zinc metal was found to be not photopotentially active. Zinc oxide on zinc taken from stock showed a small photonegative effect in distilled water of about 10 millivolts. Since the zinc oxide had a very high electrical resistance, a cleaned zinc electrode was used instead of the glass electrode of Fig. 10, page 29. In the KCl-phenolphthalein solution, zinc behaved like copper and iron, the electrons in the metal flowing towards the light and the red test showing at the irradiated surface, indicating the initial formation of a photopositive electrode. No further studies were made with zinc due to its small photopotentials.

Tin. Tin metal yielded indefinite results when freshly cleaned and when allowed to remain in distilled water for several hours. Some photo-activity was noted by paraffining the tin except for a small area on both sides, immersing in the KCl-phenolphthalein solution, and irradiating for 6 hours; the irradiated side appeared unattacked but definite signs of

chemical attack appeared on the dark side. This indicates the electron flow in the metal to be toward the light tending to render the metal photopositive. The effect was slight and could not be verified by photopotential measurement. Since tin displayed such slight results, it was not studied further.

Magnesium. Magnesium showed no photo-activity due to its chemical activity in water. However, using a piece of magnesium ribbon about 20 cm. long, completely paraffined except for two 0.04 sq. cm. areas about 10 cm. apart, and coiled so as to obtain an irradiated and a dark area, it was dipped into the irradiated KCl-phenolphthalein solution; the irradiated area formed hydrogen bubbles sooner than the dark area during the first few moments of immersion indicating that light does seem to have some effect in causing electrons in the metal to flow toward it, just as in the cases of the above metals. The photo-activity was found to be very small for magnesium and therefore was not studied further.

The experimental work outlined in this chapter may be summarized as follows: (1) all the metals studied here displayed no photo-activity when freshly cleaned, (2) electrons in the metal flowed towards the light on irradiation in salt solution thereby yielding a photopositive electrode, and (3) electrons in the metal on irradiation may tend to flow away from the light in distilled water.

CHAPTER VII

A THEORETICAL DISCUSSION OF THE PHOTOVOLTAIC EFFECT

WITH METALS AND THEIR COMPOUNDS

This chapter, which concludes the work of this first part
with metals, summarizes and discusses the results of the
actual work of the previous chapters and also mentions other
related research. An attempt has been made here to clarify
discrepancies which have been indicated in the previous pages.

The first apparent discrepancy, mentioned on page 24, is
that photo-elements prepared according to the literature by
heating copper in a flame in order to produce a cuprous oxide
semi-conducting layer were photonegative as indicated in Fig.
6, page 13, whereas those prepared similarly in this research
were photopositive. The main difference between the dry con-
ventional photo-e.m.f. cell and the wet photovoltaic cell used
in this research is the high resistance of the glass electrode
or distilled water or solution of the photovoltaic cell; the
internal electrical resistance between the two electrodes of
the dry photo-e.m.f. cell is much smaller than that of the
photovoltaic cell used here. That there should actually be a
change of polarity in the copper photo-element due to the
photovoltaic cell resistance would be difficult to understand,
although the presence of ions which markedly lower the
resistance of the liquid medium produced a smaller photoposi-
tive potential than with distilled water and also caused the
negative transient photo-inductive dip. From an electronic

consideration, a photonegative electrode simply indicates
that photo-electrons are flowing towards the base metal under
the influence of light, while conversely for photopositive
electrodes photo-electrons are going away from the base metal.
The photopositive copper electrodes obtained in this research
also indicate that electrons are moving away from the base
metal towards the liquid and this was verified by the KCl-
phenolphthalein solution on page 38. The photopositive copper
electrodes of this research seem to reveal that an excess of
oxygen atoms is present on the surface of the oxide facing the
liquid as a result of the heating in air, thus causing photo-
electrons in the semi-conducting layer to move towards these
excess oxygen atoms and away from the base metal according to
the theory on page 19 and Fig. 9, page 23. In fact, when a
copper strip was heated carefully to form a tenacious black
layer of cupric oxide, a larger positive photopotential was
obtained in salt solution than with a red cuprous oxide layer;
this result may be explained by assuming that a greater excess
of entrapped atomic oxygen is present in the black N-type
cupric oxide layer which may contain cuprous oxide than in the
red perhaps P-type cuprous oxide layer, considering paragraph
4, page 19.

With the photonegative copper elements prepared by immer-
sion in cupric nitrate solution, a layer of crystalline cupric
hydroxide instead of cuprous oxide is present over the copper
base metal. A large excess of oxygen atoms is not present in
this cupric hydroxide layer so that photo-electrons released

within this N-type semi-conducting layer can move freely towards the base metal rendering it photonegative. It is probable that an excess of cuprous ions is present in this cupric hydroxide layer due to incomplete oxidation to the cupric ion by the nitrate ion. Iron may behave similarly as indicated on page 43. The excess of cuprous ions may form the distortion centers within the cupric hydroxide semi-conducting layer. The surface of the washed and dried photosensitive cupric hydroxide layer appeared opalescent and nacreous to the eye, and at certain angles to incident white light polarized the light, indicating an orientation of crystal faces. Garrison (13) stated, as in the footnote of page 35, that copper strips immersed for the first time in a solution of cuprous chloride and afterwards hydrolyzed to form red cuprous oxide were first photopositive and subsequent treatments formed photonegative electrodes. The first immersion may have occluded or adsorbed excess atomic oxygen from the solution sufficiently to form the photopositive electrode, while further immersion produced cuprous oxide crystals which could move the adsorbed atomic oxygen layer further away from the base metal during formation and trap copper atoms to produce an N-type semi-conductor whose photo-electrons could then influence the base metal negatively by contact. Thus, it appears that an N-type semi-conductor as cupric oxide can form a photopositive electrode by possessing cuprous oxide and oxygen atoms at or near the liquid-oxide interface, while cupric hydroxide, also an N-type semi-conductor prepared

chemically here, forms a photonegative electrode by containing
excess cuprous ions. Cuprous oxide crystals form a photoposi-
tive electrode with excess oxygen atoms at the liquid-oxide
interface, perhaps as in the substitution type of page 12,
and a photonegative electrode with excess copper atoms as
intimated by Lange (30), page 14.

From the previous chapter, when an irradiated metal was
first immersed in an electrolyte, electrons appeared to go
towards the light; the dark side therefore became chemically
attacked and the metal should be photopositive. This initial
action may be due to the Hallwachs photo-electric effect (46,
53). As time proceeds, the positive photopotential of the
electrode may either become more pronounced or may change to
being photonegative as it did for copper because a slight
amount of cuprous oxide which may be formed by local action
on the irradiated side of the metal is now a semi-conductor
with excess copper atoms. This effect was shown with the KCl-
phenolphthalein solution mentioned on page 38.

Another apparent discrepancy is that frontwall and back-
wall cells are a result of the two separate copper-oxidation
reactions given on page 15 and that each has its own respective
optimum excitation wave-length as mentioned on page 15. Yet
from a consideration of the above paragraphs, these two sepa-
rate wave-lengths may be required by (1) photo-electrons
released by the presence of the excess oxygen atoms trapped at
or near the surface of the air-heated photopositive electrode
and (2) photo-electrons within the semi-conducting cuprous

oxide layer released as in the crystal photo-effect mentioned on page 15 due to the excess copper atoms. The work described on pages 37 and 38 with the KCl-phenolphthalein solution indicates that the oxidation of cuprous ion to the cupric form took place as a secondary reaction only during irradiation and not in darkness where the copper metal was electrochemically oxidized to the cuprous form by the salt solution. The reduction of the surface of a cuprous oxide layer by methods indicated on page 24 with the intention of reversing the photopotential may not only have reduced cuprous ions to copper atoms but may also have removed or reduced excess oxygen atoms to yield a photonegative electrode as if it were prepared by immersion. It appears that a longer wave-length of light is required to release the internal electrons in the semi-conductor layer which always produces a photonegative effect just as heat is required to decolorize alkali-halide salts after they are bombarded with electrons; these wave-lengths are longer than those which produce a maximum positive photopotential on electrodes where an excess of oxygen atoms is present on the surface due to the heating in air. The red color of the cuprous oxide does not seem to determine this longer optimum wave-length as pointed out by Lange (30), page 15. Also, according to Lange's theory, cupric hydroxide should not produce a photo-effect since the copper is already in its highest valent state, yet the theory on page 19 implies that a metal in the highest valent form could produce a photo-voltaic effect or at least act as a semi-conductor. The fact

that a cuprous oxide photo-element deteriorates to cupric oxide as the photo-element is irradiated indicates that oxygen atoms may have been originally present to react with the cuprous oxide and that the resulting cupric oxide is much less photo-active than cuprous oxide. It appears, therefore, that as long as there are excess cuprous ions or even copper atoms in cupric oxide or hydroxide, a good photopotential can be obtained as indicated on pages 36 and 47. It is also probable that the light must penetrate through the outer layer of cupric hydroxide to reach cuprous ions close to the supporting copper base; photo-electrons given up by the cuprous ions and its environment render the mother copper base negative. In any event, copper atoms or cuprous ions as distortion centers do seem to be required for photo-activity in agreement with Lange's theory, and therefore to produce a photopotential, an oxidation of copper or cuprous ion must occur. With different metals and non-metals, photo-oxidation or even photo-reduction may occur depending on their different valence states and their position in the e.m.f. series.

As for rectification, Teichmann's field-funnel theory (30, 60), page 21, seems sufficient for it appears that a very careful oxidation of the copper to cuprous oxide with the aid of a protecting film of cupric oxide which can easily be removed after cooling (CuO is triclinic unlike Cu and Cu_2O, Figs. 2 and 3) must be performed in order that conduction electrons can flow from copper to oxide regardless of the thickness of the oxide layer; the thicker the layer, the higher the resis-

tance as well as the breakdown potential of the rectifier.
Oxygen atoms which can form distortion centers in these recti-
fying systems are probably not as abundant as in the above
roughly-heated photopositive elements; these atoms may also
be highly oriented due to the very careful manner of prepara-
tion which is required for them.

Returning to Table II, page 37, the decrease in the posi-
tive photopotential with decrease in irradiated area for the
air-heated cuprous oxide surfaces which were not paraffined
indicates that photo-electrons are at the liquid-oxide inter-
face and that a short-circuiting effect between the irradiated
and dark areas of the same electrode can exist within the
oxide layer. By paraffin coating, much larger photopotentials
were obtained which increased as the unwaxed irradiated area
was decreased. This increase in the positive photopotential
with decrease in unwaxed irradiated area occurred until a
critical area was reached below which the photopotential began
to decrease, as indicated in Table II. This effect seems to
indicate that as the irradiated area is decreased by paraffin,
less electrons can move randomly within the cuprous oxide
layer but more electrons can approach the liquid-oxide inter-
face, or the ratio of the number of internal to surface elec-
trons decreases with a decrease in area to yield a larger
photopotential down to a critical area. However, with photo-
negative surfaces prepared by immersing clean copper strips in
an aqueous solution of 0.1 M cupric nitrate, the negative
photopotential only decreased as the irradiated unwaxed area

decreased unlike the above result with the photopositive elec-
trode. This indicates that for the photonegative electrode,
the photopotential is being produced at the oxide-metal inter-
face and not at the liquid-oxide interface, thereby producing
the negative potential. It therefore appears from Table II
that photo-elements prepared by heating the copper strip in a
bunsen flame are photopositive, contrary to the literature,
because photo-electrons are present at or near the liquid-
oxide interface as indicated in Fig. 9, page 23; photo-elements
prepared chemically by immersion are photonegative due to the
photo-electrons being present at the oxide-metal interface.

The number of electrons which become photo-electrons in
a semi-conductor is very small as compared to the total number
of electrons which are available as photo-electrons. As indi-
cated on pages 12 and 25, Englehard (10, 30) calculated that
the number of trapped copper atoms capable of liberating an
electron for a certain sample of cuprous oxide heated in a
vacuum was 0.1×10^{17} per cc. while for cuprous oxide heated
in oxygen, 230×10^{17} per cc. Using the ratio of these in the
equation on page 25, he obtained 183 millivolts at $18^\circ C$ as the
open circuit voltage. Similarly in thermionic emission (34,
47), it has been calculated that at about $3000^\circ C$ only one
electron out of every 100,000 has enough energy to escape from
tungsten metal and it is therefore apparent that practically
no effect is made on the concentration of electrons in the
metal. In fact, tungsten metal would require a theoretical
temperature of about $53,000^\circ C$ to remove all of its electrons

and the metal would be transparent if it were possible to exist as a metal without its "free electron gas" at that temperature (15). Thus, in photo-semi-conducting elements a similar phenomenon exists. A cuprous oxide rectifier lasts indefinitely due to electrons alone being affected while a copper sulfide rectifier which may contain copper ions in both valent forms eventually degenerates because of ionic migration. A cuprous oxide photo-element in a photovoltaic cell eventually deteriorates on account of secondary chemical effects. It may be theoretically possible to construct a cuprous oxide photo-element which will last indefinitely, as some dry selenium-on-iron photo-e.m.f. cells do, if electrons can be motivated without secondary chemical and ionic effects.

During the experimental work, pure red cuprous oxide was heated in a glass tube which was sealed to prevent oxidation by oxygen of the air. While hot, the cuprous oxide assumed a black cupric oxide color but when cold its color was again red; this action was reversible. When a copper strip was heated in a flame in order to form cuprous and cupric oxide upon it, and powdered soft glass was sprinkled upon these hot oxides allowing the molten glass to dissolve some of these oxides, as the resulting fused thin glass layer cooled, the oxide surface gradually changed from the cupric oxide black color to the red cuprous oxide color. Gradual heating and cooling of this strip caused the slow reversible changes in color between black when hot and red when cold. Oxygen of the air was excluded by the glass layer. Red ferric oxide when fused into soft glass became reversibly black when hot and red when cold. These results indicate a correlation in crystalline

compounds between photo and thermal phenomena, which is strikingly shown by the following experiment:

When the above glass-covered oxide-copper strip which displayed the color changes with temperature variations was paraffined and studied as in Fig. 10, page 28, a surprising positive photopotential of 25 millivolts was obtained in distilled water.

This copper photo-element deteriorated and gradually darkened on continued irradiation indicating irreversible chemical changes in the semi-conducting layer. From these observations, it appears that a light-sensitive semi-conductor may produce its photopotential not only by its contained distortion centers but also by an electronic shift caused by the light in the ionic units of the semi-conductor crystal plasma.

The final attempt to detect fluorescent light by means of these sensitized photopositive and photonegative electrodes did not prove successful. The very last attempt was made by "inverting" the photovoltaic cell of Fig. 10, page 28, into that shown in Fig. 15, page 41; this change would have eliminated the possible interference of salts in the electrolyte on the light-sensitive electrode, but very little sensitivity to fluorescent light was obtained by this device. This part of the research with metals was therefore abandoned and the study of the fluoro-photovoltaic effect entered upon.

PART II

STUDIES ON THE PHOTOVOLTAIC EFFECT

WITH FLUORESCENT SOLUTIONS

CHAPTER VIII

INTRODUCTION

The primary object here was to develop a sensitive method
of detecting the presence and estimating the concentration of
a fluorescing substance in solution utilizing the "fluoro-
photovoltaic effect". This object was accomplished with more
concentrated solutions but not with the "trace" concentrations
used by White (69, 70). This may indicate a disadvantage of
the fluoro-photovoltaic method but further studies and more
experience with this "fluoro-photopotential" method may yield
a very precise and sensitive means of quantitatively determin-
ing the concentration of a fluorescent or related substance in
solution, perhaps as a supplement to the photo-electric cell
which is suitable for the weaker concentrations.

It was mentioned in Part I that this work has produced
poor light-sensitive semi-conductor electrodes for detecting
weak fluorescent light but that the most promising results
have been obtained with the "fluoro-photovoltaic" effect of
fluorescent solutions. Very little has been done by others
using this principle as compared to the use of light-sensitive
semi-conductors which have had great popularity especially
among physicists. Also, little theoretical consideration has
formerly been given to the "fluoro-photovoltaic" cell whose

internal photopotential is produced solely by the fluorescent solution. For this reason, the theory developed in this part on the "fluoro-photovoltaic" effect has been proposed with the hope that it will be favorably accepted as a new principle of molecular behavior under the influence of light.

The terms "fluoro-photovoltaic" and "fluoro-photopotential" are applied here not only to fluorescent organic substances which produce a photopotential in solution but also to non-fluorescent organic substances in solution. Perhaps a better term that would embrace the photovoltaic effects caused by fluorescent and non-fluorescent organic substances in solution would be "organo-photovoltaic" or "organo-photopotential" since this photo-effect is caused primarily by the organic solute and not by the electrode as in the previous part. Nevertheless, even though this research indicates that certain non-fluorescent organic compounds can produce a photopotential as well as certain fluorescent organic compounds, the prefix "fluoro-" has been maintained. The effect in the case of inorganic substances would be indicated as "inorgano-photo-voltaic".

CHAPTER IX

HISTORICAL BACKGROUND

Becquerel (3) in 1839 discovered the photovoltaic effect.
Rigollot (48) in 1897 discovered the fluoro-photovoltaic effect
in which pure metal electrodes dip in a fluorescent solution
and only one of the electrodes is irradiated with light.
Minchin (39) in 1893 used pure organic liquids in a photo-
voltaic cell. Nichols and Merritt (43) in 1904 thought that
the fluoro-photovoltaic effect was a photoconductive one such
as with selenium where the resistance changes on exposure to
light. Hodge (27) showed that a potential difference is formed
between electrode and fluorescent solution. Goldmann (18) in
1908 introduced semi-transparent platinum films fused to the
optical cell wall as electrodes so that a fraction of the
light could penetrate through and cause the solution immediate-
ly next to the electrode to fluoresce; he studied the fluoro-
photovoltaic cell with a potentiometric circuit just as with
the photovoltaic cell mentioned on page 7. Thompson (61) in
1915 using rhodamine B in ethyl alcohol studied the effect of
different metallic electrodes and their oxides and concluded
that only certain metals could give good current output.
Grumbach (20) in 1923 noticed an effect similar to the tran-
sient photo-inductive effect described on page 40; Murdock
(42) in 1921 studied a similar effect with rhodamine B in
alcohol and found that stirring lowered the current. Rule
(51) in 1926 found opposing results with eosin and fluorescein.

Ghosh (16) in 1929 theorized that light excited the fluores-
cent substance in solution to an unstable molecule which
reacted further with another unstable molecule to form a
third molecule; this does seem to be a secondary process
since White[▽] found that in many cases precipitation eventual-
ly occurs in fluorescent solutions on prolonged standing.
Ghosh stated that the fluoro-photopotential was produced from
the Maxwell-Boltzmann distribution of stable and unstable
molecules similar to the theory on page 25. Russell (52) in
1928 concluded that the fluoro-photopotential was not propor-
tional to the light intensity, as Goldmann (18) in 1908 had
done, and even showed that blue light had a lesser effect
than yellow light; the cause of this apparent discrepancy will
be explained by this work which upholds Goldmann's photo-
electric explanation. Finally in 1930, Lowry (36) showed
that the photopotential of the fluoro-photovoltaic effect is
proportional to the concentration of rhodamine B in ethyl
alcohol; his electrodes were also of semi-transparent platinum
through which only part of the incident light could pass. A
very brief historical summary of the effect with "fluorescent
electrolytes" is given by Hughes and DuBridge (28).

Since Lowry's work, little more was done on this fluoro-
photovoltaic effect. Zworykin and Wilson (73) summarize the
fluoro-photovoltaic effect very briefly in a short paragraph
entitled "Sensitive electrolytes" in their chapter on photo-
voltaic cells as follows:

[▽]Private communication

"It had been observed by various investigators that
certain fluorescent electrolytes apparently changed their
conductivity when illuminated, but Goldmann (18) and
others proved later that the change in current was
actually due to an extra electromotive force generated
in the liquid very close to one of the electrodes. The
effect at best is small and at present remains only of
academic interest. The effect is doubtless due to the
liberation of electrons from molecules of the fluorescent
compound."

CHAPTER X

THE DEVELOPMENT OF THE PRESENT FLUORO-PHOTOVOLTAIC CELL

AND THE FLUORO-PHOTOPOTENTIAL METHOD

Zworykin and Wilson (73), as quoted above, state that the electromotive force generated in a light-sensitive fluorescent solution very close to one of the electrodes (the irradiated electrode) is "doubtless due to the liberation of electrons from molecules of the fluorescent compound". Also, pure metals dipping in certain inorganic electrolytes yield a small photopotential when irradiated, as indicated in group 5, page 2, probably due to a slight ionization difference caused by the light. In order for a potential to form on the irradiated electrode, there must exist an excess of a charge of one polarity in the solution next to this electrode. From a prior consideration, it would seem that if the dissolved fluorescent substance does ionize by dissociation or electron-loss during irradiation, it should have no effect in producing a potential on the irradiated electrode because the number of opposite charges would be equal. However, since a potential is actually obtained, an excess of charge of one polarity does exist.

van't Hoff (65) showed that molecules or ions in solution can be treated as molecules of a gas whose volume is the same as the volume of that solution, behaving kinetically like a perfect gas. Similarly, since an excess of charge does exist in the irradiated solution around the electrode, this excess charge in the irradiated solution can be considered as a space charge in a vacuum or space, or as an "electrified atmosphere".

Lemmonier in 1752 discovered that the atmosphere is usually in an electrified condition (62)[V]. Gilbert (17) describes Lord Kelvin's "water-dropper" for measuring the electrification of the atmosphere and also gives a theoretical explanation as follows:

"A collector is placed at the point whose potential is desired. The collector is insulated and connected to one terminal of an electrometer. The other terminal is earthed. To bring the collector to the potential of its surroundings different devices are used such as a pointed wire, a flame, an ionizing (radioactive) salt, or Lord Kelvin's water-dropper. The last consists of an insulated jar of water with a tube extending to the point at which the potential is desired. The tube is nearly closed so that the water must fall in separate drops. The water is connected by a wire to one side of an electrometer. The other side is earthed. If the region around the end of the tube in Fig. 16 (page 63) has a space charge of positive electricity a negative charge is induced on the end of the tube. This charge is carried away by the electrified drops of water until the tube, and the connected apparatus, comes to the potential of the surrounding air. Then no further induction will take place and the electrometer will register the potential of the air at the end of the tube."

[V]It is interesting to quote here from Silvanus Thompson's (62) "Elementary Lessons in Electricity and Magnetism" (London, 1393): "The older observers were content to affix to an electroscope (with gold leaves or pith balls) an insulated pointed rod stretching out into the air above the ground, or to fly a kite, or (as Becquerel did) to shoot into the air an arrow communicating with an electroscope by a fine wire, which was removed before it fell. Gay-Lussac and Biot lowered a wire from a balloon, and found a difference of potential between the upper and lower strata of the air. None of these methods is quite satisfactory, for they do not indicate the potential at any one point. To bring the tip of a rod to the same potential as the surrounding air, it is necessary that material particles should be discharged from that point for a short time, each particle as it breaks away carrying with it a positive or negative charge until the potentials are equalised between the rod and air at that point. Volta did this by means of a small flame at the end of an exploring rod. Sir W. Thomson (Lord Kelvin) has employed a "water-dropper", an insulated cistern provided with a nozzle protruding into the air, from which drops issue to equalise the potentials; in winter he uses a small roll of smouldering touch-paper (paper impregnated with KNO_3 as a fuse). Dell-
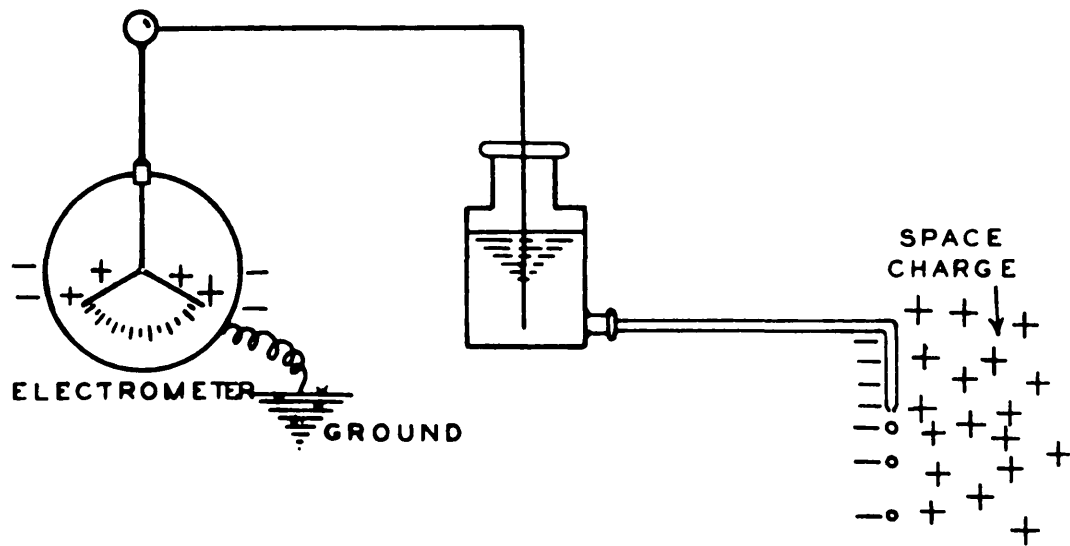
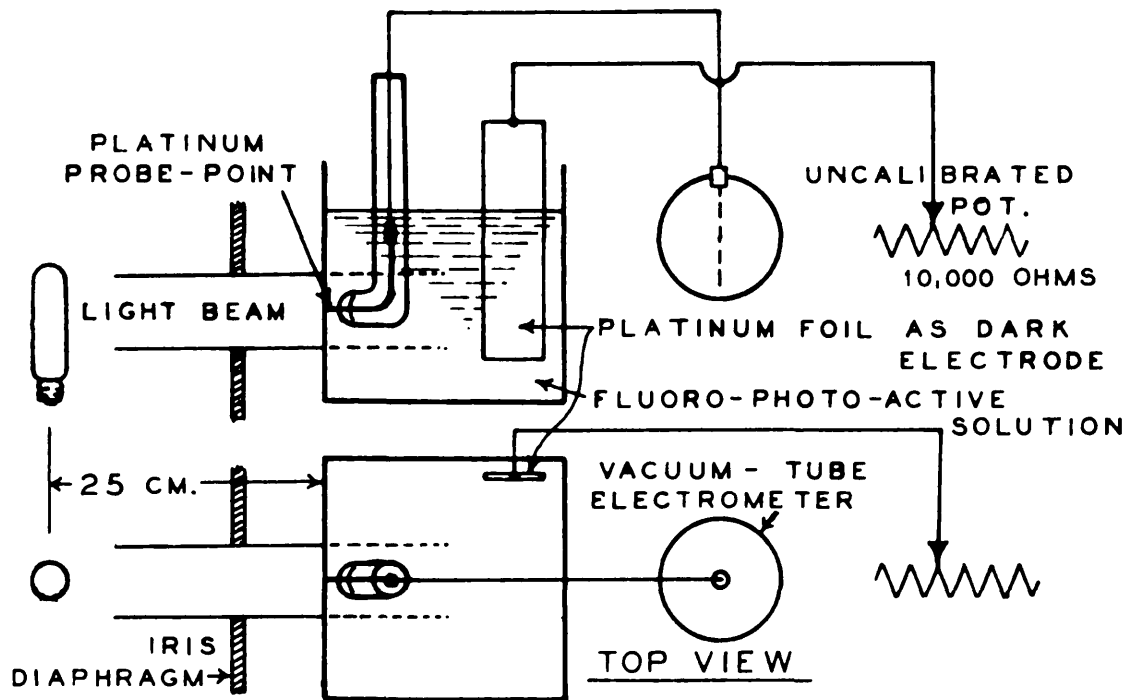Fig. 16 - Kelvin's "water-dropper"

Fig. 17 - The fluoro-photovoltaic cell

It is of course obvious that of the above "collectors",
the only practical one for these studies is the pointed wire.
For this reason, a platinum wire, of R. & S. No. 24 gauge (0.5
mm. diameter), soldered to a copper wire lead was fused in the
end of a piece of 6 mm. soft glass tubing and cut away so as
to leave a small exposed length of approximately 1.5 mm. This
"point" can also be considered as an electrostatic probe such
as used to plot equipotential lines in an electrolytic cell
(26). The point-probe was supported in the fluoro-photovoltaic
cell usually against the center of the irradiated flat side of
the cubical glass cell to give the maximum photopotential, as
shown in Fig. 17, page 63. It was connected to the grid of
the electrometer tube at point $\underline{A}$ indicated in Fig. 11, page
31. All fluoro-photopotentials produced by the probe-point
in these studies were positive.

A piece of clean platinum foil 2 x 6 cm. and 5 mils thick
partly immersed to 5 cm. was used as the dark electrode in
place of the glass electrode of Part I; no artificial insulating
layer was required here as with the semi-conductors of Part I.
The high input resistance of the electrometer is sufficient to
"match" the resistances of the solutions studied in this fluoro-
photovoltaic cell, as indicated on page 30. The platinum foil
dark electrode was connected to a 10,000 ohm uncalibrated

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mann adopted another method, exposing a sphere to induction
by the air, and then insulating it, and bringing it within
doors to examine its charge. Peltier adopted the kindred
expedient of ... charging the electrometer by induction with
electricity of opposite sign to that of the air."

potentiometer which took the place of the calibrated one as shown in Fig. 11, page 31. This dark electrode was mounted so as to be out of the light path as shown in Fig. 17.

No actual voltage readings were taken, the 10,000 ohm uncalibrated potentiometer being set to give no deflection on the electrometer-galvanometer when the complete fluoro-photo-voltaic cell was in darkness. The small potentials occurring in the dark between the point and plane electrodes may be due to their asymmetry, difference in the strains in the metal of the two electrodes, presence of iridium in the platinum wire, etc. Readings of the galvanometer were then taken in galvano-meter scale units after the galvanometer deflection became constant during irradiation of the point electrode. One gal-vanometer scale unit is 1 cm. or 10 mm. divisions of deflec-tion on the galvanometer scale which had been marked at the factory to read thus. The galvanometer scale units may after-wards be converted to millivolts by multiplying by the factor 0.11, the number of millivolts per galvanometer scale unit derived from the sensitivity of the electrometer as given on page 30. The Ayrton shunt was of course used for the large values of fluoro-photopotentials in order to bring the galvano-meter indicator-line within the linear range of its scale.

The light system and the fixed distance of 25 cm. from cell to lamp was the same as used in Part I, shown in Figs. 10 and 13. The cubical cells were also the same as in Part I, being cubes of 5 cm. on an edge to hold 100 ml. of solution. Rough comparisons were made between the affixed mercury lamp and a 150 watt incandescent lamp 20 cm. from the cell, with

and without glass filters; the following table is a typical result with a 0.5 mg/ml solution of fluorescein acid in ethyl alcohol:

TABLE III

RELATIVE EFFECTS OF VARIOUS LIGHT
EXCITATIONS ON THE FLUORO-PHOTOPOTENTIAL

Light excitation	Galvanometer scale units
Mercury lamp, no filters	710
Mercury lamp with Corning No. 5340 (u.v.) filter	45
150 watt lamp, no filters	155

This table indicates, as mentioned above on page 33, that the mercury lamp without filters has practically no quenching wave-lengths, at least as far as the fluoro-photopotential is concerned, and no filters have therefore been used in these studies.

Several advantages of the point-probe may be briefly given as follows: (1) practically all of the light from the lamp can be utilized in fluorescence excitation as compared with the previous semi-transparent platinum film electrodes which allowed part of the light to pass through, (2) the dia-meter of the light beam has little effect on the fluoro-photo-potential, (3) the simplicity and ruggedness of the probe-point and the possibility of interchanging it among various glass cells for comparative studies, and (4) small volumes of solutions can be studied. A further discussion on the theory of the probe-point and the fluoro-photo-active organic mole-cule will be made in Chapter XIII. The two chapters now following describe the experimental work of this part of the research.

CHAPTER XI

THE EFFECT OF VARYING CONDITIONS

ON THE FLUORO-PHOTOPOTENTIAL

In order to obtain the maximum fluoro-photopotential for
a given concentration of fluoro-photo-active substance, the
effects of varying conditions on the fluoro-photopotential
have been studied in order to determine the optimum conditions.
These studies are described below.

The Intensity of the Incident Light. The greater the
intensity of the light striking the fluoro-photovoltaic cell,
the greater is the produced fluoro-photopotential, contrary
to Russell (52) mentioned on page 59. This was determined by
moving the mercury lamp towards and away from the fluoro-
photovoltaic cell. The fixed distance of 25 cm. between lamp
and cell was used because very little heat approached the
fluoro-photovoltaic cell by radiation at this distance. Lenses
were not used in the optical axis.

The Wave-Length of the Incident Light. The effect of
wave-length of incident light on the fluoro-photopotential
was indicated on page 66 and in Table III. Also, it was
mentioned on page 59 that Russell (52) found that blue light
had a lesser effect than yellow light, contrary to photo-
electric phenomena. This discrepancy may be due to the color
or absorption spectrum of the fluorescent solution that he
used, which may absorb the higher wave-lengths of incident
light that could otherwise produce fluorescence. This light-

absorption effect is indicated more definitely in the next chapter with fluorescent solutions. Actual spectral studies were not made; it is probable that a certain optimum wavelength exists for each fluoro-photo-active substance in solution to yield a maximum fluoro-photopotential. The fluoro-photopotential has no relationship to fluorescence as shown below.

The Cross-Section of the Light Beam. The light beam striking the fluoro-photovoltaic cell was controlled in circular cross-section by the iris diaphragm depicted in Fig. 17, page 63. The increase in cross-section did have a small but definite effect of increasing the fluoro-photopotential as shown in Table IV.

TABLE IV

EFFECT OF INCIDENT LIGHT BEAM CROSS-SECTION
(LIGHT INTENSITY CONSTANT) ON THE FLUORO-
PHOTOPOTENTIAL USING A 2% BENZOIN SOLUTION
IN ETHYL ALCOHOL

Diameter of iris diaphragm opening in cm.	Relative fluoro-photopotential in galvanometer units
0.5	300
1	320
2	350
3	370

This effect has some theoretical significance especially for the space-charge concept described on page 62.

The Size of the Probe-Point. The effect of the size of the probe-point on the fluoro-photopotential was studied by starting with a 4.5 mm. exposed length of the B. & S. No. 24 gauge platinum wire. The exposed wire was cut into shorter

lengths after determining the fluoro-photopotential for each remaining length. Fig. 18, page 70, shows the effect of the size of the point on the fluoro-photopotential. This effect of course has much theoretical significance for the probe and indicates that a length of about 1.5 mm. gives the maximum fluoro-photopotential. This can be easily seen from the fact that a large point in a fluorescing volume which possesses a marked fluorescence gradient can not yield the maximum potential at a given point in the fluorescing solution; a very small point, on the other hand, builds up its charge very slowly and can not be influenced by all the photo-active molecules around it, as indicated by the 0.5 mm. exposed length in Fig. 18. The 1.5 mm. probe-point has therefore been used throughout these studies.

The Position of the Probe-Point in the Solution. This effect is perhaps the most striking in illustrating the electro-static nature of the fluorescing solution. If the concentration of a given fluorescent substance in solution could be made sufficiently high, the solution displayed "surface fluorescence" (25), fluorescence which existed only at the interface between the solution and the glass wall where the light beam first approached the solution; here, at this sur-face, the fluorescence could only be seen with the eye in a direction parallel with the incident light and of course per-pendicularly to that surface. When the probe-point was placed so as to touch the glass wall as in Fig. 17, page 63, a definite and sometimes very large fluoro-photopotential for certain fluorescent substances was obtained; but when the point was
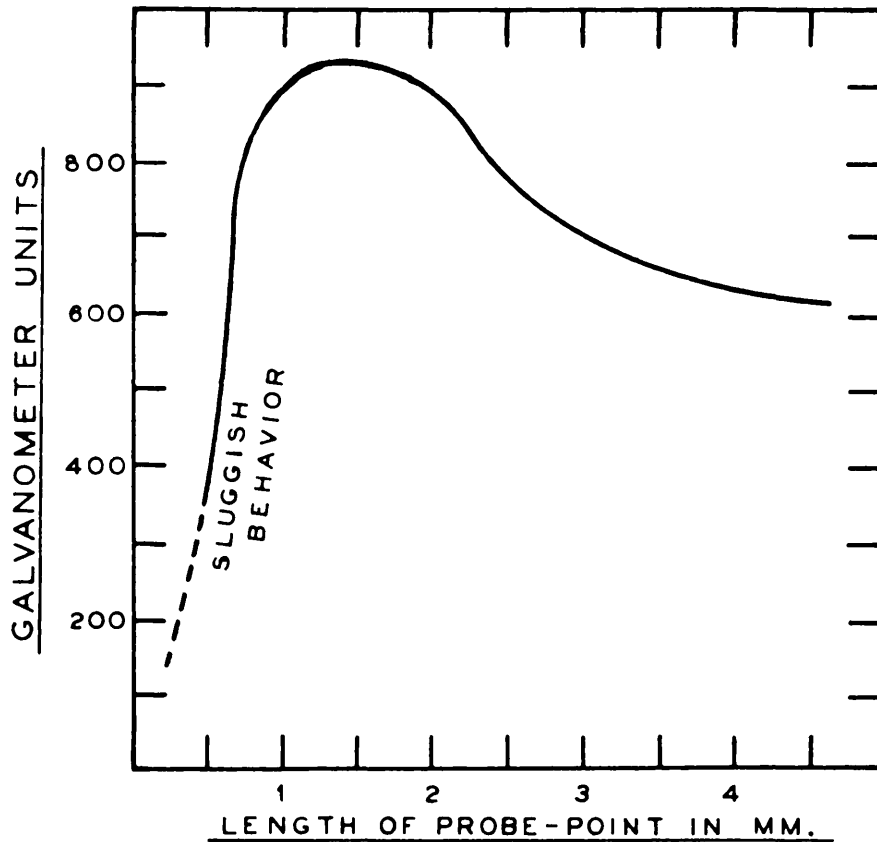
Fig. 18 - Relative effect of size of probe-point on the
fluoro-photopotential using a P. & S. No. 24
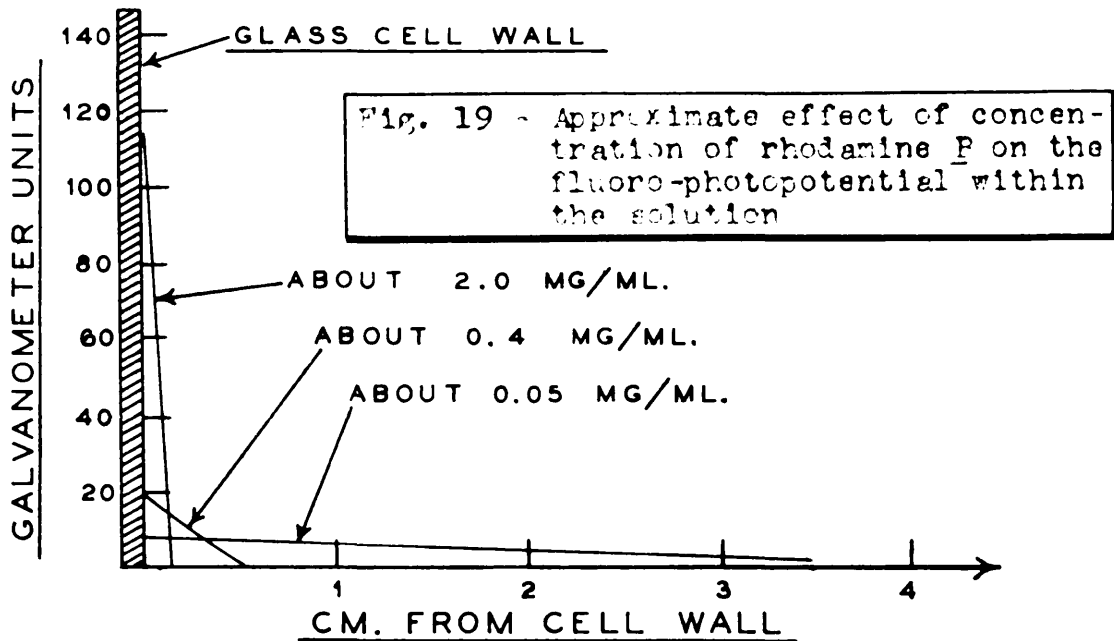gauge Pt wire and 1% benzoin in absolute
ethyl alcohol

Fig. 19 - Approximate effect of concen-
tration of rhodamine P on the
fluoro-photopotential within
the solution

placed about 1 mm. away from the glass wall and fluorescing plane, no fluoro-photopotential was obtained. Also, with the probe-point at the fluorescing plane, the fluoro-photopotential was found to be independent of the concentration of the fluorescing substance as long as surface fluorescence was displayed, to be further described in the next chapter (see Fig. 22). This is reminiscent of the contact potential between dissimilar metals and this phenomenon may also have some bearing on the theory of metals since the surface-fluorescing plane may display specular reflection (25).

On the gradual dilution of the above concentrated fluorescent solution, the fluorescence spread out from the solution-glass interface plane into the volume of the solution; during the first processes of dilution, the fluorescence gradient appeared marked but continued dilution caused the fluorescence to become not only more uniform throughout the volume of the cell but also weaker in most cases where the fluorescent substance rendered little color to the solution^V. This type of fluorescence is called "volume fluorescence" (25) and is of course easily discernible by the eye perpendicularly to the light beam. The position of the probe-point in the fluorescing volume with respect to the initially irradiated wall of the glass cell influenced the fluoro-photopotential; this result is illustrated in Fig. 19 for various concentrations of

^{V}Rhodamine B which formed an intense red solution increased its fluoro-photopotential to a small degree when passing from surface to volume fluorescence, as indicated in Fig. 22.

rhodamine B in absolute ethyl alcohol. However, in the actual fluoro-photopotential method, the probe-point always touched the glass wall to give the maximum fluoro-photopotential for a given solution, as shown in Fig. 17, page 63.

The Effect of Stirring. As indicated on page 58, stirring the fluoro-photo-active solution of the fluoro-photovoltaic cell diminished the fluoro-photopotential due to "equalization effects". The mean life of a fluorescing molecule, about 10^{-9} second (25, 45, 72), is of course too small to allow a fluorescing molecule to approach the dark electrode during rapid stirring. It is probably the orientation of the molecules of the polar solvent which is affected by stirring. Stirring was therefore not done during fluoro-photopotential measurements.

The Effect of Temperature. Using a 100 ml. pyrex beaker instead of the cubical glass cell which was cemented together, the effect of temperature variation on the fluoro-photopotential was noted with a slowly cooling 1% benzoin solution in absolute ethyl alcohol. The cylindrical shape of the beaker, as compared with the flat irradiated wall of the cubical glass cell cube, of course had little effect on the fluoro-photopotential because the probe-point could easily be mounted to touch the cylindrical surface and face the incident light directly. Fig. 20, page 73, shows that the higher the temperature, the smaller the fluoro-photopotential, a fact easily understandable from a kinetic equalization standpoint as mentioned in the above paragraph on stirring. Perrin (45) showed that the higher the temperature, the lower the degree of
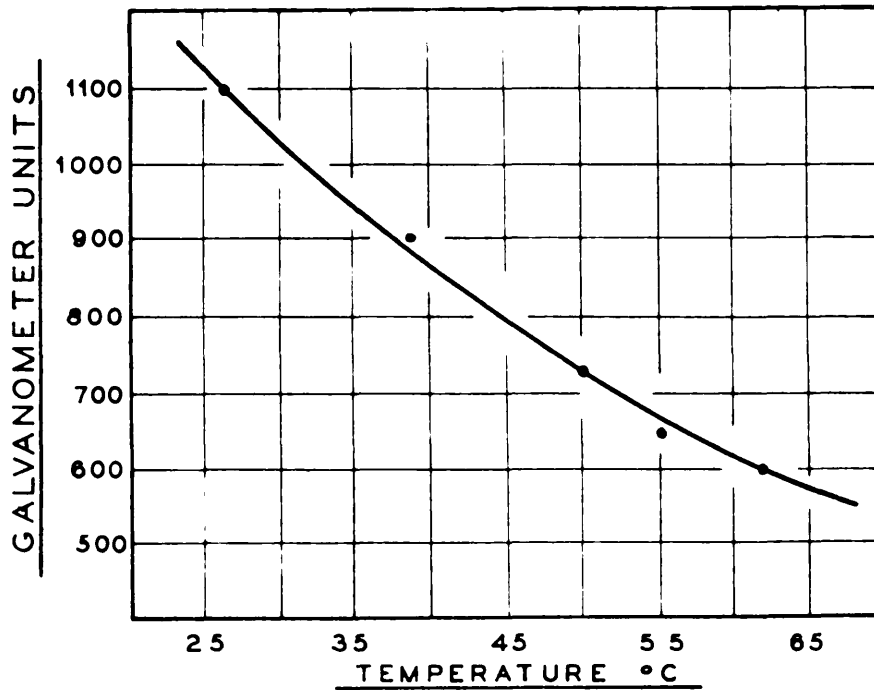
Fig. 20 - Effect of temperature on the fluoro-photo-
potential using a 1% benzoin solution in
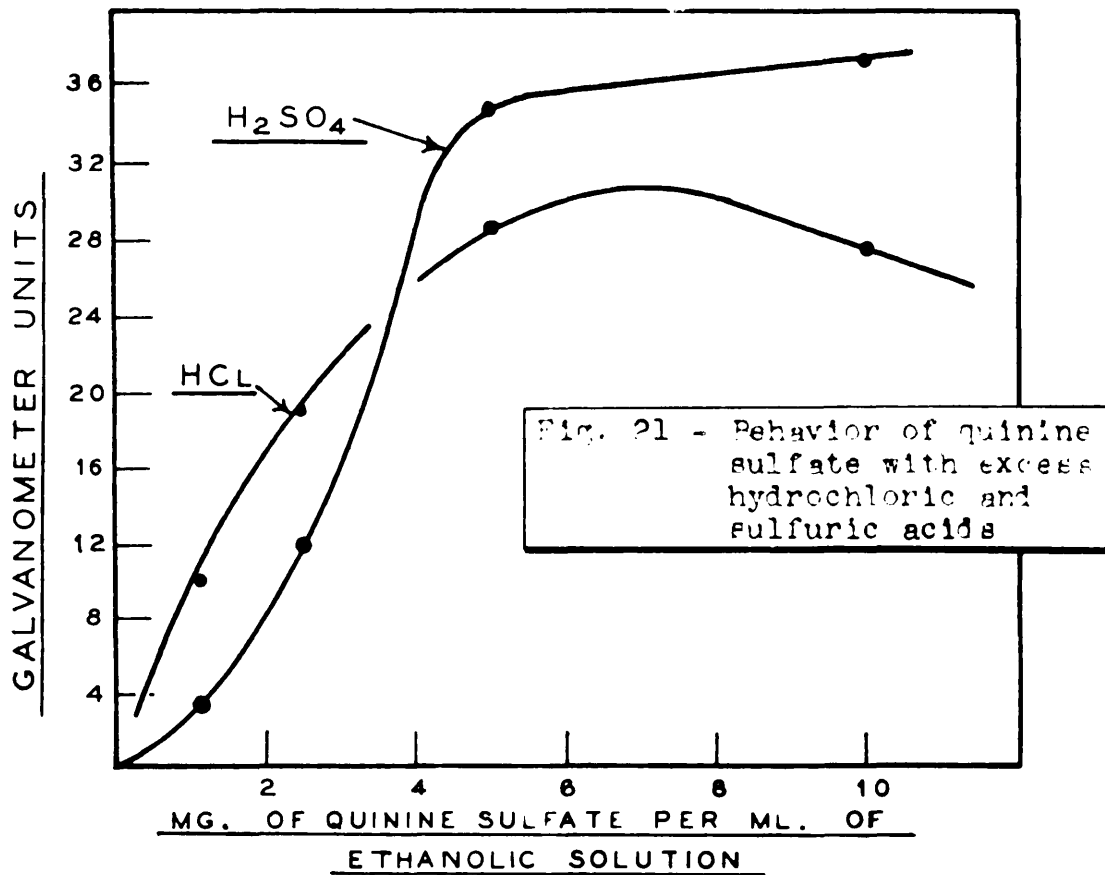absolute ethyl alcohol

Fig. 21 - Behavior of quinine
sulfate with excess
hydrochloric and
sulfuric acids

fluorescence polarization and intensity. This same relation is well known in visual fluorescence measurements.

The Nature of the Solvent. The dielectric constant of the solvent for the fluoro-photo-active substance is probably a very important factor in determining the magnitude of the fluoro-photopotential. The variation in the dielectric constant on the fluoro-photopotential was studied with water-methanol and methanol-benzene mixtures using eosin at a concentration of 1 mg. per ml. of solution for each test. Since there is no definite relationship between the mole fraction of two miscible liquids and the resulting dielectric constant, this method of study was qualitative but sufficiently indicative to show that water caused a poor or no fluoro-photopotential and that methanol (or ethanol in other studies) yields good fluoro-photopotentials. Table V summarizes the results of the studies on the effect of the dielectric constant of the solvent on the fluoro-photopotential and also on the emitted fluorescence as measured by a fluorescence photometer such as the Lumetron.

TABLE V

EFFECT OF THE DIELECTRIC CONSTANT ON THE FLUORO-PHOTOPOTENTIAL AND FLUORESCENCE USING A FIXED CONCENTRATION OF 1 MG. OF EOSIN PER ML. OF SOLUTION

Solvent (parts by volume)	Dielectric constant	Fluoro-photo-potential in galvanometer units	Relative fluorescence, determined by Lumetron
Water	81	0	1
$1H_2O:1CH_3OH$		5	
Methanol	31	15	2.6
$3CH_3OH:1C_6H_6$		13	
$1CH_3OH:1C_6H_6$		36	2.3
$1CH_3OH:3C_6H_6$		129	2.0
Benzene	2.3	eosin insol.	

The last column of Table V points out the effect of the dielectric constant on the intensity of fluorescent light. Although the intensity of fluorescence decreased slightly from methanol to the $1CH_3OH:3C_6H_6$ mixture, the fluoro-photopotential increased to a much greater extent indicating that even if the fluoro-photopotential were related to fluorescence, they would not necessarily by proportional to each other, a fact to be discussed further below. The fact that the fluorescence increases from water to methanol or other solvents having a low dielectric constant is well known for many fluorescent substances; for example, benzoin is not fluorescent in water but is fluorescent in ethyl alcohol.

According to the classical theory of electrostatics (17, 58), when a charged point which has a certain number of tubes of electric flux per unit area r cm. away from the point, or has a flux density D, is placed in a dielectric medium such as the solvent which has a dielectric constant of k, an electric field intensity E will result r cm. away, according to the following relationship:

$$D = k \cdot E \text{ , or } \quad E = D/k \qquad .$$

In the fluoro-photopotential method, it is probably the electric field intensity E at the probe-point r cm. away from the fluoro-photo-active (apparently charged) molecule which affects the probe-point. This indicates the seemingly important effect of the dielectric constant of the solvent on the fluoro-photopotential and also on the fluorescence.

Sodium fluorescein at a concentration of 0.1 mg/ml yielded

practically no fluoro-photopotential regardless of the solvent, its dielectric constant, and the bright emitted fluorescence. Also, the fluorescence intensity of sodium fluorescein determined with the Lumetron fluorescence photometer decreased with a decrease in dielectric constant, unlike eosin (as found by Rule, page 59) and the majority of fluorescent substances, as the dielectric constant decreased from that of water through methanol and towards benzene. This contrary effect of sodium fluorescein when compared with eosin, both being sodium salts of dye substances, is probably due to the peculiar structure of the fluorescein ion which is discussed further in Chapter XIII. After adding a few drops of aqueous sulfuric acid to form the fluorescein acid molecule from the sodium fluorescein in methanol, large fluoro-photopotentials resulted. A titration procedure could probably be worked out from this behavior. Bowen (5) points out that a change in the molecular species (molecule⟷ion) takes place with change in pH. In short, the fluorescein acid molecule being weakly ionized produced the large fluoro-photopotential while the fluorescein ion yielded practically no fluoro-photopotential.

The resistivity of the solvent, since it must usually contain an unionized fluoro-photo-active solute, can not be extremely large or it will be unsuitable as a liquid medium in the fluoro-photovoltaic cell; the vacuum-tube electrometer can not be balanced properly to give a steady and definite reading. This is the only disadvantage of the vacuum-tube type of electrometer but it is not serious since the majority of solvents

are suitable for this fluoro-photopotential method and have a resistivity from 10^6 to 10^{10} ohms per cc., such as ethyl alcohol, methyl alcohol, water, etc., all being polar solvents. Unfortunately, common non-polar solvents such as benzene, hexane, and carbon tetrachloride, have their resistivities at approximately 10^{19} ohms per cc. which is too large for the proper functioning of the vacuum-tube electrometer although their resistivities can be determined by means of a vacuum-tube bridge (37). This fact, that the common non-polar solvents have a much higher resistivity than the majority of solvents which are polar, presented some difficulty in the experimental work here but results to be described in Chapter XIII allow a suitable theoretical explanation.

The presence of ions lowered the fluoro-photopotential. For example, the addition of alcoholic solutions of potassium chloride, aluminum chloride, ammonium iodide, zinc chloride, lithium chloride, sodium hydroxide, and potassium acetate to alcoholic solutions of 1% benzoin decreased the fluoro-photopotentials. The last two inorganic substances produced a peculiar effect probably due to their alkaline nature; this effect, called the "transient fluoro-photo-inductive effect" here, is discussed further in Chapter XII.

The Effect of Fluorescence Intensity. It has already been indicated that for a given fluorescent substance and solvent, the fluoro-photopotential was proportional to the concentration and degree of fluorescence only where volume fluorescence exists. However, with different solvents the fluoro-photo-

potential is not apparently related to the degree of fluorescence for a given substance at a fixed concentration. Also, different fluorescent substances at similar concentrations in the same solvent, having different degrees of fluorescence, do not have the fluoro-photopotential proportional to the fluorescence intensity. This points to the very important fact that it is primarily the molecular structure of the given fluoro-photo-active substance which determines the magnitude of the fluoro-photopotential that it will produce in a certain solvent; this fact will be utilized in explaining the nature of the fluoro-photo-active organic molecule in solution and its production of the fluoro-photopotential in Chapter XIII.

CHAPTER XII

THE FLUORO-PHOTOVOLTAIC BEHAVIOR

OF FLUORESCENT SUBSTANCES IN SOLUTION

This chapter primarily describes the effect of the concentration of various fluorescent and other fluoro-photoactive substances on the fluoro-photopotential. Other effects are also included which have theoretical significance in explaining the nature of the fluorescing molecule and the mechanism of the production of the fluoro-photopotential.

The fluoro-photovoltaic cell in all of these studies was composed of the fluorescent or fluoro-photo-active solution, irradiated probe-point of 1.5 mm., and platinum foil dark electrode as shown in Fig. 17, page 63. No filters were used and the mercury lamp light source was fixed at 25 cm. from the glass cell as mentioned on page 67. No fluoro-photopotentials were obtainable with the pure solvents used here regardless of the wave-length of irradiating light.

The Behavior of Rhodamine B in Absolute Ethyl Alcohol. This was the first solution to be studied because of its apparently great popularity among workers studying the fluoro-photovoltaic effect. Since the rhodamine B contained much foreign salt as inert and insoluble material, the concentration of the rhodamine in ethanol was determined by evaporating to dryness a known volume of the supernatant liquid and weighing the residue. Table VI, page 80, and Fig. 22, page 81, indicate the variation of fluoro-photopotential in galvanometer units

TABLE VI

EFFECT OF CONCENTRATION OF VARIOUS SUBSTANCES IN ABSOLUTE ETHYL ALCOHOL ON THE FLUORO-PHOTOPOTENTIAL AT ROOM TEMPERATURE AND WITH 1.5 MM. PROBE-POINT AT CELL WALL

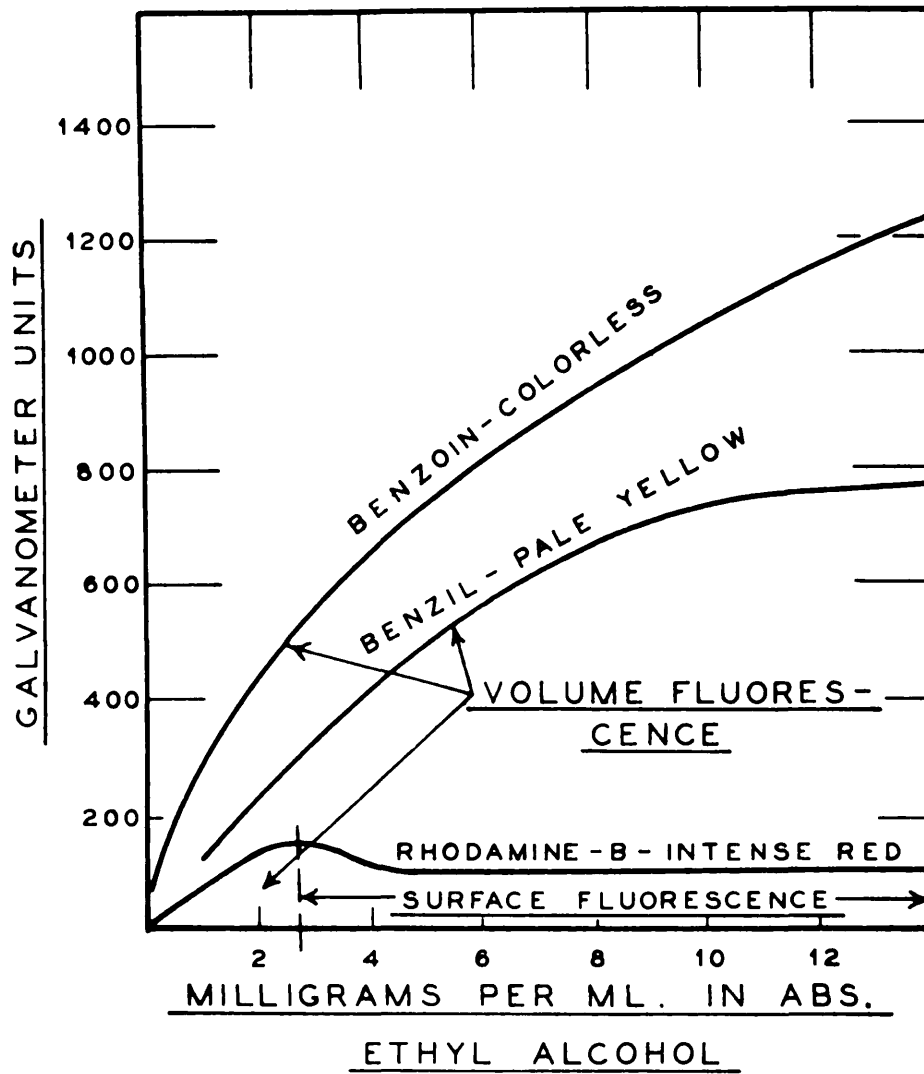| Concentration in mg. per ml.	Average fluoro-photo-potential in galvano-meter units
Benzoin	
16 (sat.)	1300
(The probe-point 1 mm. away from the cell wall yielded 300 units; 3 mm. away, 150 units sluggishly. This indicates a volume type of fluorescence which in this case was faint to the eye. See Table VIII.)	
10	1070
8	950
4	700
2	460
1	330
0.50	220
0.25	85
0.10	60
Benzil	
10	710
(The probe-point 1 mm. away from the cell wall yielded 400 units; 2 mm. away, 100 units. This indicates a volume type of fluorescence which also in this case was faint to the eye. See Table VIII.)	
5	500
2.5	240
1.25	160
Rhodamine B	
14	100
(The probe-point 1 mm. away from the cell wall yielded no fluoro-photopotential. This indicates surface fluorescence. See Table VIII.)	
10	100
7	100
3.5	147
1.75	140
(Slight volume fluorescence appeared. See Fig. 19, page 70.)	
0.375	80
0.44	25 (sluggish)
0.22	6 (sluggish)

Fig. 22 - Comparison of the fluoro-photopotential vs.
concentration characteristics of benzoin,
benzil, and rhodamine B plotted from
Table VI

with concentration of rhodamine B. The maximum "hump" in the curve is due to the intense red color having a greater tendency to absorb the ultra-violet light as the concentration is increased.

When the concentration of rhodamine B was sufficiently high to produce surface fluorescence and the probe-point was placed at the glass cell wall where the surface fluorescence existed, the maximum fluoro-photopotential was obtained which was used to derive Table VI and the curve of Fig. 22. However, when the probe-point was placed about 1 mm. away from this surface, no fluoro-photopotential was obtained as indicated in Fig. 19, page 70. This indicates that the probe followed the eye somewhat in detecting fluorescence. When the concentration was sufficiently low to give volume fluorescence, which the eye could see when an ultra-violet filter was placed in the light path, the probe yielded a fluoro-photopotential throughout the solution but of a magnitude depending on how far the probe was from the cell wall which first received the light.

Stirring the fluorescing solution in the fluoro-photo-voltaic cell increased the fluoro-photopotential as discussed on page 72.

Another effect noticed here and throughout these studies was that erratic drift of the galvanometer became less as the concentration and fluoro-photopotential increased. This becomes apparent from the fact that the greater number of charged fluorescing molecules around the probe causes a greater

stability of the space charge which they form.

The _Behavior_ of _Benzoin_ and _Benzil_ in _Absolute_ _Ethyl_
Alcohol. During the study of the fluoro-photopotential
method of detecting boron by means of benzoin, according to
the procedure of White (70) and discussed below, it was found
that benzoin alone in absolute ethanol yielded very large
fluoro-photopotentials when compared with other fluorescent
substances at the same concentrations. Table VI and Fig. 22
present the concentration _versus_ galvanometer-units character-
istic. Benzoin displayed no surface fluorescence even up to
solution saturation and no maximum appears in the curve. Also,
benzoin formed a colorless solution, absorbing little light
for this reason. However, benzoin, even though it gave large
fluoro-photopotentials, did not display the same intensity of
fluorescence as other fluorescing substances which gave much
lower fluoro-photopotentials at the same concentrations.

Benzil dissolved in absolute ethyl alcohol has a pale-
yellow color. Fig. 22 indicates the fluoro-photopotential
characteristic with the variation in concentration. The
smaller fluoro-photopotentials of benzil as compared to those
of benzoin are partly due to the yellow color of benzil absor-
bing some of the light which would have given a greater amount
of fluorescent light if the benzil solution were colorless,
as in the case of benzoin. Also, the yellow color of the
benzil solution may absorb blue light but allow yellow light
to pass through giving the impression that a longer wave-length
of light yields a greater fluoro-photopotential than a shorter

wave-length, contrary to the laws of photo-electricity; this impression was given by Russell (52) mentioned on page 59 as an argument against the photo-electric theory.

The Behavior of the Boron-Benzoin Fluorescent Complex. An attempt was made to obtain a curve of the concentration of boron versus galvanometer units by means of the boron-benzoin complex which is the basis of a delicate fluorescent test for boron (70). The following solutions were prepared:

(1) saturated boric acid in ethyl alcohol
(2) 0.5% benzoin in ethyl alcohol
(3) 0.6% sodium hydroxide in ethyl alcohol   .

The benzoin solution alone displayed the fluoro-photovoltaic effect but the two other solutions did not. One ml. of the hydroxide solution with 8 ml. of the benzoin solution diluted to 100 ml. with ethanol resulted in the transient fluoro-photo-inductive effect, to be described below, as well as in a small final positive fluoro-photopotential. Addition of a few drops of the saturated alcoholic solution of boric acid developed a blue volume fluorescence but the fluoro-photopotential was too small to allow a calibration curve to be made.

If larger concentrations of benzoin were used, it would not be possible to detect the presence of boron by the fluoro-photopotential method because benzoin alone gave a large effect and sodium hydroxide decreased the effect of the benzoin to a degree which would still be larger than that obtained with boron. This is the main disadvantage of the fluoro-photo-potential method, that low concentrations of fluorescent substances which can be easily seen with the eye and detected by

external photo-electric cells can not be detected by this new
method, as stated on page 56. The probe, however, can very
well detect differences in higher concentrations where the
eye and external photo-electric cell can not be used.

The Behavior of Quinine Sulfate. One gram of quinine
sulfate dissolved in 100 ml. of absolute ethyl alcohol dis-
played a slight volume fluorescence and a small fluoro-photo-
potential. On adding two drops of concentrated sulfuric acid,
the slight volume fluorescence disappeared and intense surface
fluorescence of a blue color appeared. Dilutions of this
solution were made and fluoro-photopotentials determined to
obtain Table VII and Fig. 21.

This was repeated with concentrated hydrochloric acid
which gave somewhat similar results as shown in Fig. 21.
Sulfuric acid produces a greater fluorescence with quinine
sulfate than hydrochloric acid at low concentrations according
to the eye[V].

Fig. 21, page 73, indicates that the sulfuric and hydro-
chloric acids produced practically the same fluoro-photopoten-
tials at the lower concentrations. However, at trace concen-
trations, the eye can definitely see that hydrochloric acid
produces no fluorescence with quinine sulfate in ethyl alcohol
while with sulfuric acid fluorescence persists.

[V]Private communication of Professor White

TABLE VII

EFFECT OF CONCENTRATION OF QUININE SULFATE WITH EXCESS
SULFURIC AND HYDROCHLORIC ACIDS ON THE FLUORO-PHOTOPO-
TENTIAL AT ROOM TEMPERATURE AND WITH 1.5 MM. PROBE-POINT
AT CELL WALL

Concentration of quinine sulfate in mg. per ml.	Average fluoro-photopotential in galvanometer units	
	Excess HCl	Excess H_2SO_4
(A slight fluoro-photopotential of about 3 units was produced without the addition of acid.)		
10	27	37
5	29	35
2.5	19	12
1.25	10	3

The Behavior of the Aluminum-Pontachrome Fluorescent
Complex. This complex is the basis of a delicate fluorescent
test for aluminum (69). Pontachrome (Superchrome Blue) at a
concentration of 1% in absolute ethyl alcohol was used as the
stock solution. 2 ml. of this solution were diluted to a
volume of 100 ml. with ethyl alcohol and was found not to be
fluoro-photo-active and no fluorescence was discernible. A
1% aqueous solution of potassium alum was also photo-inactive.
Adding 2 drops of the alum solution to the above diluted
pontachrome solution resulted in a fluorescent solution which
gave a fluoro-photopotential of 2 galvanometer units. Adding
1 ml. more of the 1% alum solution yielded after a few minutes
a maximum reading of 12 galvanometer units which is also indi-
cated in Table VIII. The addition of more alum solution to
the above caused a precipitate of alum to form.

The Transient Fluoro-Photo-Inductive Effect. When sodium
fluorescein, benzoin, or benzil in ethyl alcohol were rendered
alkaline with sodium hydroxide, a peculiar photo-effect was

obtained similar to that with the metals of Part I, page 40, and shown in Fig. 14, page 41. When the resulting solution was first irradiated, the fluoro-photopotential, which usually assumed a positive value, first went to a negative value and then assumed a positive value$^{\nabla}$. On removing the light quickly, the fluoro-photopotential increased positively and then reverted to zero. As a typical example, 100 ml. of a 1% benzoin solution in ethyl alcohol yielded a fluoro-photopotential of 1070 galvanometer units at room temperature (Fig. 22). Adding two drops of a 20% aqueous sodium hydroxide solution did not affect the volume fluorescence according to the eye. However, immediately on irradiating, a maximum negative fluoro-photopotential of about 30 units resulted and then the fluoro-photopotential became positive to about 25 units which is much lower than the former 1070 units.

10 ml. of a saturated alcoholic solution of potassium acetate were added to 100 ml. of a 1% alcoholic benzoin solution in the fluoro-photovoltaic cell; a definite transient effect was again obtained. With other 1% alcoholic benzoin solutions, the addition of alcoholic solutions of potassium chloride, aluminum chloride, ammonium iodide, zinc chloride, and lithium chloride did not produce the transient fluoro-photo-inductive effect. The alcoholic solutions of these inorganic substances did not possess any photo-activity. Thus,

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$^{\nabla}$An analogous phenomenon was obtained (35) with fluorescein deflecting in a magnetic field only in the presence of oxygen (not with neon or carbon dioxide) during the study of the paramagnetism of fluorescein.

the transient fluoro-photo-inductive effect can be attributed to the presence of basic substances which in these studies were the hydroxyl and acetate radicals.

The presence of the foreign inorganic substances lowered the fluoro-photopotentials of the above 1% benzoin solutions as indicated on page 77.

The Effect of the Molecular Structure of the Fluorescent Molecule on the Fluoro-Photopotential. On comparing the molecular structure of the various fluorescent compounds used in this research, it was noticed that a carbonyl group was present in the fluorescent compounds which produced definite fluoro-photopotentials. Comparative studies were then made on organic compounds with and without a carbonyl group but fluorescence was not primarily considered. Table VIII, page 89, briefly summarizes the experimental work and theoretical considerations are made in the following chapter.

TABLE VIII

EFFECT OF VARIOUS MOLECULAR STRUCTURES
ON THE FLUORO-PHOTOPOTENTIAL

(All concentrations at 1% in ethyl alcohol
unless otherwise stated; room temperature
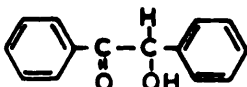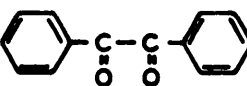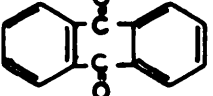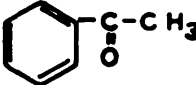and 1.5 mm. probe-point at cell wall.)

Fluorescent substance	Molecular structure	Relative fluoro-photopoten-tial in galv. units	Approximate degree and type of fluorescence (visual with u.v. filter)
Benzoin		1070	faint blue volume
Benzil		710	faint blue volume
Benzophenone		700	faint blue volume
Benzaldehyde		450	questionable blue volume
Benzhydrol		none	faint blue volume
Anthraquinone (0.5% sat.)		350 (high)	blue volume
Acetophenone		200 (fairly good)	faint blue volume
Hydroquinone	$HO-\bigcirc-OH$	none	none
Quinone	$O=\bigcirc=O$	transient effect, then 60	faint blue volume

TABLE VIII (CONTINUED)
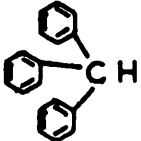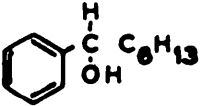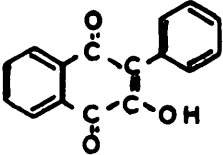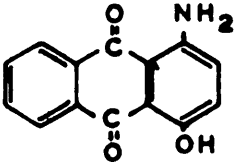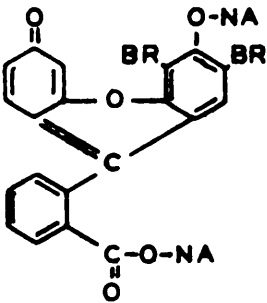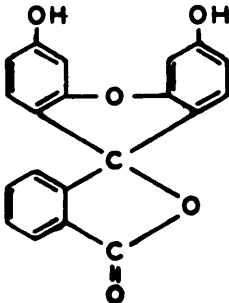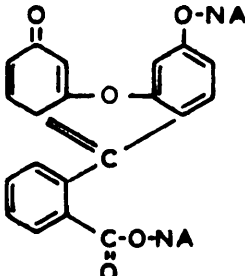
Fluorescent substance	Molecular structure	Relative fluoro-photopotential in galv. units	Approximate degree and type of fluorescence (visual with u.-v. filter)
Triphenyl-methane		none	blue volume
n-Hexyl phenyl carbinol		10	blue volume
Flavanol (0.4% sat.)		10 (sluggish)	yellowish-green surface
1-amino-4-hydroxy anthra-quinone		2	faint red surface
Sodium eosin (0.1%)		45	green volume
Fluorescein acid (0.5%)		115	greenish-blue volume

TABLE VIII (CONTINUED)

Fluorescent substance	Molecular structure	Relative fluoro-photopotential in galv. units	Approximate degree and type of fluorescence (visual with u.v. filter)
Sodium fluorescein (0.5%)		9	intense yellow-orange volume
Rhodamine B Reference (24)		100	intense red surface
Quinine sulfate		37	blue surface
Aluminum-pontachrome complex (0.02%)		12	blue volume

CHAPTER XIII

THE NATURE OF THE FLUORO-PHOTO-ACTIVE MOLECULE
AND THE THEORY OF THE FLUORO-PHOTOVOLTAIC EFFECT

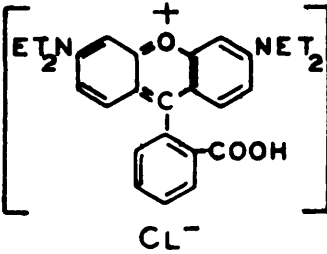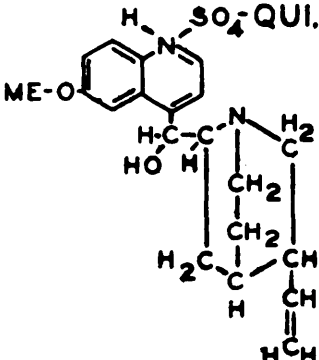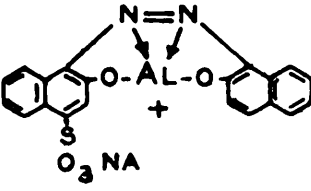Table VIII indicates that certain fluorescing and non-fluorescing substances such as benzaldehyde in solution can produce a fluoro-photopotential. The same considerations can therefore be made for both types in the following discussion.

That the probe-point is detecting a fluorescence type of activation and not a photochemical activation type seems to be true because the fluoro-photopotentials are stable and reproducable and return to zero when the light is removed. The fluorescing or non-fluorescing fluoro-photo-active substance does not suffer any permanent change in its overall electronic energy content, as pointed out by Wolfenden (72) as follows:

"An electronically excited molecule does not suffer degradation of its electronic energy before it emits fluorescence; on the other hand, a molecule which is photochemically activated has in general undergone degradation of its electronic energy. The lifetime of a fluorescent and of a photochemically activated molecule must not be confused."

The probe is always rendered positive when in the fluorescing region. This positive photo-effect on the probe-point may occur by two methods: (1) according to Thompson (62), by actual contact with the fluorescing molecule which would indicate the charge of the molecule to become positive or less negative and (2) according to Gilbert (17), by induction at the probe-point which would also show that the fluorescing molecule becomes more positively or less negatively charged. Thompson's explanation (footnote page 62) is more acceptable;

there are two examples that a probe-point or electrode placed
in a space charge assumes the polarity of the space charge:
(1) the production of oxidation-reduction potentials according
to the Nernst equation and (2) the so-called "contact potential"
in vacuum tubes containing an electron-emitting filament and
a plate. In any event, the electrometer assumes the same
polarity as that of the space charge.

The positive charge from the fluoro-photo-active molecule
may probably arise from an unsaturated group, perhaps chromo-
phoric (6), such as the carbonyl, ethylene, azo, nitroso, azoxy
acting as a low electron-density point or area to which electrons
can move from the solvent or from an electron-donating group
such as a benzene ring which become positively charged. Kasha
(29) indicated that carbonyl compounds have characteristic
long wave-length absorption bands probably due to loosely
bound electrons. This explanation is similar to the electro-
meric shifts encountered with meta-directing groups such as
the nitro, sulfonic, and carboxylic, attached to a benzene
ring.[V] Benzoin, benzil, benzophenone, benzaldehyde, and several
other molecular structures from Table VIII, which contain the
carbonyl group produced large positive fluoro-photopotentials
whereas benzhydrol and hydroquinone which possess no electron-

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[V]Hammick and Illingworth (21, 59) formed a rule given as
follows: "If in the benzene derivative ⬡XY, Y is in a
higher group of the periodic table than X, or if, being in
the same group, Y is of lower atomic weight than X, then the
group is meta-directing. In all other cases, including that
in which the group XY is a single atom, it directs into the
ortho- and para-positions."

sink groups yielded no fluoro-photopotential. Other organic compounds possessing electron-donating groups attached to a benzene ring so as to be ortho, para-directing (according to Hammick and Illingworth's rule) have not been studied.

Perrin (45) theorized that with fluorescein, fluorescence is due to a quinoid grouping in the molecular structure which may be in equilibrium with another colored or colorless structure, the equilibrium depending on the pH of the medium, as follows:

FORM 1   FORM 2
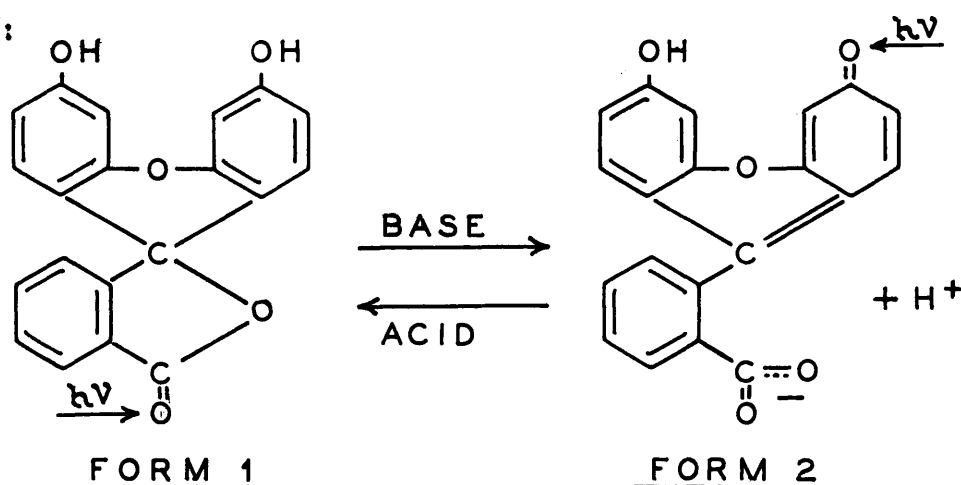
According to Table VIII, fluorescein in an acid medium produced a fairly large fluoro-photopotential while the sodium salt produced a very small effect. Since the basic Form 2 produced bered ring of Form 1 seems to be/the active electron-sink for 5-membered ring of Form 1 seems to be/the active electron-sink for producing the large positive fluoro-photopotential of the acid Form 1, and the carbonyl group of the quinoid structure of Form 2 probably produced the very small fluoro-photopotential in basic solution. The carboxyl group of Form 2 probably has little effect in producing a fluoro-photopotential because the marked overall negativity of this carboxyl group may screen

out the effect of the light on its two resonant carbonyl groups.

The production of the positive polarity may indicate that the overall charge on the organic molecule or solvent where irradiated has decreased negatively. The solvent may probably enter into the production of the fluoro-photopotential as indicated by the transient fluoro-photo-inductive effect. It was mentioned on page 76 that non-polar solvents such as benzene and carbon tetrachloride have extremely high electrical resistances and can not be used for fluoro-photopotential measurements with the vacuum-tube electrometer. However, there were definite experimental indications that these non-polar solvents produced no fluoro-photopotential at all with benzoin, even with their very low dielectric constants. This points to the idea that polar solvents may be attracted to a charged area of the fluoro-photo-active molecule, or that a hydrogen bridge may be formed between the alcohol and, for example, the oxygen atoms of the carbonyl electron-sinks after they have "borrowed" their electrons from the fluoro-photo-active molecule or the solvent. The line-up of the polar solvent molecules around the larger fluoro-photo-active molecule may be considered as if the solvent molecules array themselves on a dielectric plane with their positive ends facing the probe-point, thereby forming the positive charge on the probe-point and electrometer.

The presence of the carbonyl or similar group in a molecule containing an aromatic ring seems to determine whether it is fluoro-photo-active but its position in the molecular structure may determine the degree or magnitude of the fluoro-

photopotential. It may appear that benzil should produce a much larger fluoro-photopotential than benzoin or benzophenone. However, resonance may occur between the two oxygen atoms of the carbonyl groups of benzil or the two nitrogen atoms of the aluminum-pontachrome complex to give a lesser fluoro-photovoltaic effect.

n-Hexyl phenyl carbinol contains no carbonyl or similar group yet it produced a small fluoro-photovoltaic effect as indicated in Table VIII. This may be due to the unsaturated benzene ring at the end of the molecule acting as an electron-sink. The positive fluoro-photopotential would indicate that electrons are probably tending to move into the benzene ring from the hydroxyl and/or saturated hexyl group or from the solvent. The positive polarity in this case appears to be formed from the positive charge remaining on the projecting electron-source hexyl or hydroxyl group or solvent molecule. Similarly, with projecting electron-sink groups, such as the carbonyl, nitro, and sulfonic, the positive charge formed on the benzene ring as the electron-source group seems to cause the positive fluoro-photopotential.

The behavior of quinine sulfate with sulfuric and hydrochloric acids, shown in Table VII and Fig. 21, is distinct in that at the higher concentrations a lower fluoro-photopotential is produced with hydrochloric acid than with sulfuric. The addition of hydrochloric acid may tend to affect the unsaturated ethylene group by addition according to Markownikoff's rule more so than the addition of the sulfuric acid, or the negative

chloride ion may tend to block any effect that the solvent molecule may have in donating electrons to the unsaturated ethylene group and becoming less negative.

Positive colloidal ferric hydroxide or negative colloidal arsenious sulfide produced no potential when their dispersions surrounded the probe-point. The colloidal particle assumes its charge by adsorbing ions from the dispersion medium, and the zeta-potential is concentrated only in the Helmholtz double-layer so that no electric field from the charged particle can exist remote from it; thus no charge was detected by the probe in the colloid. But on irradiating the fluoro-photo-active molecule, the probe was rendered positive. If ions are present in the solution, adsorption of them apparently does not take place by the excited fluoro-photo-active molecule. If a fluoro-photo-active molecule is sufficiently large to be of colloidal size, the electron-source still seems able to influence the probe-point steadily regardless of the electrical double-layer which might exist around the molecule.

Dimerization or polymerization might also occur between two or more fluoro-photo-active molecules at oppositely charged groups or between a negative group of one molecule and an accepting electrophilic group of another of the same kind. This may account for the slow precipitation which occurs with certain fluorescent substances in solution on standing as mentioned on page 59.

CHAPTER XIV

GENERAL SUMMARY

The studies of the photovoltaic effect with metals were made with copper, iron, zinc, tin, and magnesium. Of these metals, copper produced the largest photopotentials when directly illuminated with the incident light which was intended for fluorescence excitation. The mode of experimentation was to paraffin the sensitized copper electrode completely except where the light struck the electrode squarely. A glass membrane was also introduced in these studies as the unirradiated glass electrode to allow any electron concentration difference across it to be measured by a sensitive vacuum-tube electrometer. The glass membrane and paraffin coating aided in producing large photopotentials with the incident light but very poor photopotentials were obtained with fluorescent light from solutions in which the photo-element was immersed.

The light-sensitizing of the metal electrode was attempted by two methods: (1) by heating the metal in air and (2) by chemical treatment by immersion in a suitable oxidizing solution. Copper produced good photo-elements by both of these methods which, however, gave opposite effects; heating in air produced a photopositive element while immersion overnight in a cupric nitrate solution produced a photonegative electrode. The other metals were light-sensitized by chemical means.

Although the external dry photo-e.m.f. cell has been shown (33) to be sensitive to fluorescent light down to 5×10^{-5} mg.

of sodium fluorescein per ml. of solution, these photovoltaic studies with metals did not produce sufficiently light-sensitive electrodes which could be immersed directly into the fluorescent solution. This part of the research with metals was therefore abandoned and full attention given to the photovoltaic effect of fluorescent solutions.

The studies of the fluoro-photovoltaic effect with fluorescent solutions gave promising results. An especially sensitive vacuum-tube electrometer was used and the irradiated electrode was merely an inert platinum point which was placed in the fluorescing volume. It was found that non-fluorescing substances could also produce a large fluoro-photopotential and this led to the conclusion that it was the peculiar structure of the fluorescent molecule which produced a fluoro-photopotential and not the fact that it was merely fluorescent. Those organic substances, whether fluorescent or not, which produced a fluoro-photopotential appear to have an unsaturated group to which photo-electrons can move either from the organic substance or the solvent.

The following are conclusions derived from the experimental work on fluorescent solutions:

1- Fluoro-photopotentials are obtainable with organic fluorescing and non-fluorescing substances and not with solutions of acids, bases, salts, other organic solutes, etc. (any effect with inorganic electrolytes as in group 3, page 2, is too small to be of any significance in these studies).

2- Fluoro-photopotentials are obtainable with organic compounds which contain an unsaturated electron-sink group and probably an electron source from the molecule or the solvent.

3- Surface fluorescing solutions can yield no fluoro-photopotentials 1 mm. or more away from the surface; volume fluorescing solutions can yield fluoro-photopotentials throughout the fluorescing volume.

4- The pure solvents used in these studies, such as water, ethyl alcohol, methyl alcohol, benzene, etc., produced no fluoro-photopotential at the wave-lengths of light. The solvent must be polar to produce a fluoro-photopotential with a fluoro-photo-active molecule. USED

5- Removal of the incident light results in the fluoro-photopotential returning to zero.

6- The polarity of the fluoro-photopotential is positive in all of the cases studied here.

7- The aluminum-pontachrome fluorescing complex provides a fluoro-photopotential while its non-fluorescent components do not. The aluminum ion which can coordinate with the two chromophoric nitrogen atoms may induce photo-electrons to move from the aromatic rings towards the nitrogen atoms.

8- Stirring prevents a maximum fluoro-photopotential from being formed due to equalization effects.

9- The dielectric constant of the solvent can affect the fluoro-photopotential according to electrostatic and electrolytic theory.

10- The fluoro-photopotentials are reproducable and the effect is stable.

11- The fluoro-photopotential is proportional to the concentration of the fluorescing molecule in volume fluorescence and not in surface fluorescence.

12- The fluoro-photopotential decreases as the temperature increases, as with fluorescence.

13- Using a B. & S. No. 24 gauge platinum wire, a 1.5 mm. length is the optimum size for the point.

14- The greater the intensity of the light, the greater the fluoro-photopotential for all fluoro-photo-active substances, indicating the photo-electric nature of the effect.

This fluoro-photopotential method can be used as a

quantitative tool for the determination of the concentration

of certain fluorescent substances in solution which display

volume fluorescence. The concentration of non-fluorescent

fluoro-photo-active substances can also be determined by this method. Other uses for this fluoro-photovoltaic effect, which can at present merely be suggested, are the checking of the molecular structure of organic compounds, rapid dielectric constant determinations of solutions, and studies on the mechanism of chelation.

The probe-point assumes a charge of the same polarity as that of a "space charge" in a solution. There may be a relationship between the excess oxygen atoms of the cuprous oxide semi-conductors of Part I and the oxygen atoms of the carbonyl photo-active negative nuclei of the fluoro-photo-active molecules of Part II. In Part I, copper when heated in air absorbed excess oxygen atoms in the resulting light-sensitive cuprous oxide layer and a photopositive electrode resulted. In Part II, the fluoro-photopotential was found to be positive in every case. In both cases of semi-conductor and fluoro-photo-active molecule, light probably causes electrons around the oxygen atom to become activated.

This research indicates that this "small effect", which Zworykin and Wilson (73) claimed in 1934 to be "only of academic interest" (page 60), may be a useful analytical tool as well as a promising research phenomenon.

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