# THE PHOTOVOLTAIC EFFECT

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## I. INTRODUCTION

The photovoltaic effect is defined (VIII-2) as the production or change of potential between two electrodes separated by a suitable electrolyte or other substance when the electrodes are unsymmetrically illuminated. It is also called the "Becquerel effect" in honor of its discoverer, Becquerel. Similar to this effect is the "Swensson–Becquerel effect," which is the production of a photopotential upon illumination of the electrolyte only. In this paper we shall identify both the Becquerel effect and the Swensson–Becquerel effect as the photovoltaic effect. We shall limit our investigation to the "wet" type of cell, in which the electrodes are separated by a liquid.

It is the purpose of this paper to review the results of the research published about this phenomenon and to present the theories proposed to account for the mechanism producing it.

## II. HISTORICAL

In 1839 Becquerel (IV-31) observed that an electric current was produced when he illuminated one of two similar platinum, gold, brass, or silver–silver halide electrodes immersed in dilute acid. This experiment closely followed his

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observation (IV-30) that an electric current was produced on the illumination of a system consisting of a platinum electrode in each of two stratified liquids containing two substances which reacted with each other under the influence of light; this is regarded by Lange (VIII-4) as the birth-date of the photoelements. Becquerel's discovery was followed by numerous investigations of workers with different types of "wet" cells and "dry" cells. Notably among these workers were Herz (VI-10) and Hallwachs (VI-9). The latter's discovery, in 1888, of the external photoeffect for the "dry"-type cell led to the development of the alkali photocells. The success in perfecting these cells and the interpretation of their mechanism diverted the attention of investigators from an intensive study of the "wet" type of cell originally used by Becquerel. However, since that time a number of different types of "wet" cells have been investigated and several theories have been proposed to interpret their mechanism. To date each theory seems to fit the experimental evidence for some cells but appears to be untenable as a general explanation for all types. A correlation of the available data seems to be necessary in an attempt to understand the mechanism involved in this process.

## III. CLASSIFICATION OF PHOTOCELLS

Photocells may be classified in the following three main groups:

*Group 1:* Those dependent upon the alteration of conductivity by light. The selenium cells represent this group.

*Group 2:* Those dependent upon an *external* photoeffect, i.e., an electron emission from the outer surface under the influence of radiation and an externally applied potential. The alkali photocells represent this group.

*Group 3:* Those that we shall tentatively classify as dependent upon a so-called *internal* photoeffect. In this group Lange (VIII-4) places those cells showing the Becquerel effect, the crystal photoeffect, and the barrier-layer photoeffect. He presents evidence to show that the same fundamental process underlies all three of these types.

Several general characteristics that have been used to distinguish between the cells of Group 2 (photoelectric) and those of Group 3 (particularly the Becquerel type) are the following: (*1*) The photoelectric current is directly proportional to the light intensity; the photovoltaic potential is directly proportional to light intensity at low intensities and then to the logarithm of the intensity and finally reaches a steady maximum on increasing the light intensity. (*2*) No external potential is required for the photovoltaic cells. (*3*) The photovoltaic cells show reversals of polarity, whereas the photoelectric cells do not.

## IV. CLASSIFICATION OF PHOTOVOLTAIC CELLS

The different kinds of photocells of Group 3 are of six general types:

Type I. Metal electrodes immersed in solutions of electrolytes.

Type II. Metal electrodes immersed in fluorescent solutions.

Type III. Metal electrodes immersed in organic (non-fluorescent) liquids.

Type IV. Metal electrodes coated with inorganic compounds and immersed in solutions of electrolytes.

Type V. Metal electrodes coated with a dye and immersed in solutions of electrolytes.

Type VI. Metal electrodes separated by solid semiconductors. The first five of these types are the so-called "wet" type of cell and are discussed in this paper.

## V. PHOTOVOLTAIC CELLS OF TYPE I: METAL ELECTRODES IMMERSED IN SOLUTIONS OF ELECTROLYTES

Cells of this type usually produce a relatively low photopotential unless the electrolyte is light sensitive, and even then considerable time may be required to reach the full value of the photopotential.

Becquerel (IV-31), in 1839, illuminated in turn one of two platinum, gold, or brass electrodes in a dilute acid with light of various colors and noted that (*1*) the current produced was greatest for light at the blue-violet end of the spectrum, (*2*) this current was not a thermoelectric effect, and (*3*) the illuminated electrode became positive with respect to the dark one. In 1859 Becquerel (IV-38) reported the following observations: (*1*) irradiated platinum, silver, and brass electrodes immersed in an electrolyte produced a current the direction of which depended on whether the electrolyte was acidic or alkaline; (*2*) the blue and violet parts of the spectrum were effective but not the red; (*3*) the effect was decreased if the platinum electrodes were heated and dipped in nitric acid; (*4*) the rays may have modified the state of equilibrium of the particles of the surface of the metal; and (*5*) polarization greatly increased the effect.

Grove (I-17), in 1858, reported that irradiated platinum plates in dilute sulfuric, hydrochloric, or nitric acid were sometimes positive and sometimes negative. He attributed the effect to an increase in the already existing polarization of the electrodes.

Pacinotti (I-23) illuminated copper plates in solutions of copper nitrate or copper sulfate, zinc in zinc sulfate or zinc chloride, iron in ferrous sulfate or ferrous chloride, lead in lead acetate, and silver in silver nitrate. In each case except silver, the illuminated electrode was negative. No effect was detected for platinum in copper sulfate.

Hankel (I-19) reported the following observations: illuminated copper in water became negative; copper in a slightly acid solution of copper sulfate first was negative but then became strongly positive; illuminated silver in water became negative; platinum became positive; silverized platinum became slightly positive; platinized silver became very strongly positive; and tin in water became negative. In all cases the effect was greatest in the blue region and least in the red. The sign of the thermal potential of copper in water was shown to be in the opposite direction from the potential upon irradiation.

Bose and Kochan (I-12), studying a cell with gold electrodes in sulfuric acid, found that after polarization for 17 days the anode potential was lowered by violet light, unaffected by sodium light, and raised by red light. The potential varied to the extent of 0.1 volt, according to the nature of the light.

Buisson (I-13) found that the potential between a metal and an electrolyte was changed when the metal was plunged into the liquid after having been subjected to ultraviolet rays.

Wildermann (I-29, 30, 31, 32) found that for pure, carefully polished, illuminated silver or copper electrodes the potential was usually less than $1 \times 10^{-4}$ volts. Upon irradiation the potential slowly increased to a constant value and decreased slowly to the original value when the light was withdrawn, the two periods being designated as "induction" and "deduction" periods. With irreversible cells, such as silver in potassium chloride, the photopotential changed in a complicated manner because of the action of opposing forces due to light and polarization. The potential which was calculated from the current flowing through a high resistance was directly proportional to the intensity of light and was a function of its composition. The photopotential of reversible cells, e.g., silver in silver nitrate, after the induction period, was proportional to the light intensity and independent of the salt solution. According to Wildermann (I-29), "Each kind of equilibrium between two states of matter becomes, at a constant volume on exposure to light, shifted in the direction which is accompanied by the greater absorption of light." . . . . "The law of mass action must hold good for equilibrium in homogeneous systems, when the equilibrium is shifted under the action of light to a new point in the same manner as in the dark." He concluded that the photopotential was due solely to a change in solution pressure of the electrode, on the basis that an equilibrium could be established for light as it had been set up for heat by van't Hoff.

Athanasiu (I-1) studied cells made of silver, copper, nickel, zinc, and cadmium electrodes immersed in 0.25 *N* solutions of their salts. He (I-2, 3) attributed the effect to an alteration of the electrode surface (which became visibly tarnished) and to a heat effect upon irradiation, the two effects being superimposed. Copeland (I-16), Black (I-11), and Clark (I-14, 15) investigated the thermal potential of silver electrodes and concluded that the potentials developed on illumination of silver electrodes were not the direct result of temperature effects, because long wave lengths of light were relatively ineffective in developing photopotentials, and the thermal potential developed was very often of the opposite sign to that of the photopotential.

Schlivitch (I-26) reported photopotentials of 0.7–12 millivolts when using platinum electrodes in solutions of sodium nitrate, potassium dichromate, and ammonium dichromate. When the illumination ceased, the potential changed from its negative value to zero, and for concentrated solutions to a positive value.

Sihvonen (I-27) studied cells of pure metals (e.g., platinum, silver, copper, nickel, iron, chromium, zinc, aluminum, and mercury) in solutions of inorganic acids, bases, and salts. He considered the photoeffect to be the resultant of (*1*) photoelectric effects at the electrode, (*2*) adsorbed films of gas on the electrode, and (*3*) ions in solution. He accounted for the results on the basis of five possible reactions: namely, (*1*) liberation from the metal of an electron which solvates in solution; (*2*) discharge of cations by electrons when the electrode is illuminated with current flowing; (*3*) formation of anions from the adsorbed gas on the electrode; (*4*) photovoltaic discharge of anions; and (*5*) photovoltaic formation of cations from adsorbed gas on the electrode.

Audubert (I-5, 6) reported that platinum, copper, and mercury functioned as anodes (emitted electrons to the solution) upon illumination, while silver and gold functioned as cathodes irrespective of the electrolyte. Potentials of $10^{-7}$ to $10^{-5}$ volts were developed. From these studies he drew the following conclusions: (*1*) That the potentials were not due to a layer of impurity, as proposed by Berthelot (IV-40). (*2*) That light of short wave length was more effective than that of long wave length. The threshold frequency seemed displaced toward the short wave length the higher the solution pressure of the electrode, and the sensitivities varied inversely with the solution pressure. (*3*) That the influence of the cation was small and that of the anion was apparently zero. (*4*) That positive polarization diminished the photovoltaic effect of metals acting as anodes when illuminated but negative polarization increased it, while the opposite was true for cathodes. At high polarizations the sign of the effect was reversed. This suggests a mechanism for the photovoltaic effect which closely resembles that of the photoelectric effect.

Audubert (I-8) also studied gold and platinum electrodes in solutions of various pH values and concluded that the inversion was independent of the frequency of the radiation and independent of the concentration of the electrolyte but depended mainly on the potential of the metal and also on the acidity, basicity, or neutral nature of the electrolyte. Further work (I-9, 10) with gold and platinum electrodes, using different colored light, led him to suggest that the photopotential was due to photolysis of water. The molecules of water were assumed to become fixed to the electrode, to absorb radiations not usually absorbed, and to liberate oxygen and hydrogen, which depolarized the electrodes.

The threshold values of metal electrodes were investigated by Copeland (I-16) (for silver electrodes) and by Clark (I-14, 15) (for copper, silver, and gold electrodes) immersed in solutions of potassium chloride, potassium bromide, potassium nitrate, etc. They found that light of wave length longer than 4900 Å. was ineffective in producing a photopotential; a slight effect was noted at 5500 Å., but Clark and Garrett (I-15) attributed that to a coating on the electrode. Figure 1 shows a typical curve for the wave length *vs.* photopotential for such pure metals. This threshold value is compared with those obtained for the same metals in a vacuum but at various stages of outgassing; that comparison is shown in table 1. Columns 3, 4, and 5 were compiled from those given by Hughes and DuBridge (VIII-2, page 75).

Clark (I-14) observed that most of the cells studied gave a positive photopotential (illuminated electrode the anode). Some of the cells he studied gave a negative photopotential, but all of them gave the same threshold value regardless of the sign of the photopotential. The solutions used for the determination of these threshold values do not absorb in the region of this photoactivity. The inference from this work is that the effect in the cells studied by Copeland and Clark is photoelectric in origin.

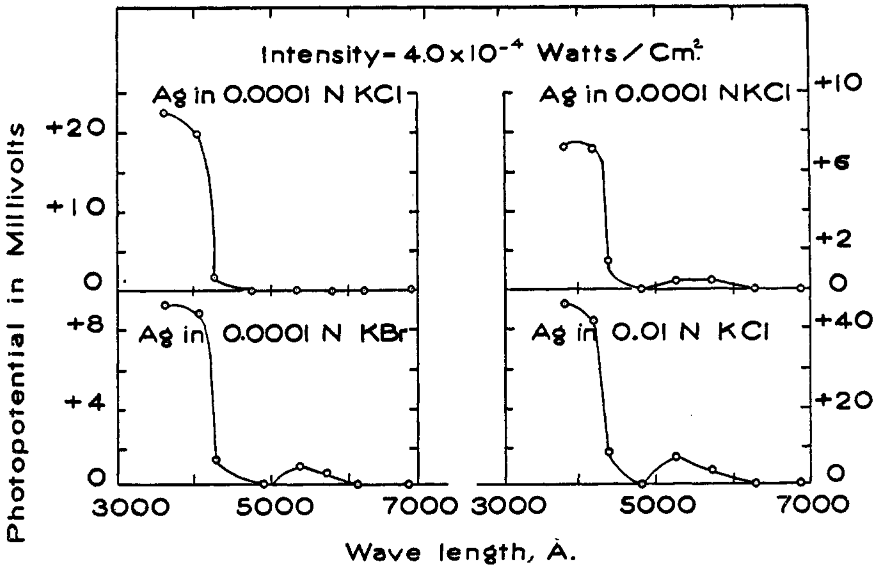


FIG. 1. Typical curve for the wave length *vs.* photopotential for pure metals

TABLE 1

*Approximate photoelectric thresholds of silver, gold, and copper*

| METAL | METAL IN SOLUTION | THRESHOLD WAVE LENGTH; METAL IN A VACUUM | | |
|---|---|---|---|---|
| | | No outgassing | Partial outgassing | Extended outgassing |
| | | Å. | Å. | Å. |
| Silver | 4900 | 3200–3400 | 2900–3100 | 2600–2700 |
| Gold | 4900 | 2625 | 2600–2800 | 2650–2610 |
| Copper | 4900 | 2700–3000 | 2700–3000 | |

Copeland and Clark detected a change in sign of the photopotential with concentration of the electrolyte. This was investigated by Black (I-11), who reported that cells containing silver electrodes in electrolytes of low concentration (below 0.05 molar for most salts studied) in general gave positive photopotentials but at high concentrations (above 0.2 molar) gave negative photopotentials (the illuminated electrode became more negative, and then the dark electrode). His results are summarized in table 2. This observation throws some doubt on the conclusions of Audubert (I-5, 6) and of Schlivitch (I-26), who reported that the illuminated electrodes were positive in solutions of some salts and negative in others, for the effect may have been due to the magnitude of the concentrations used; however, the effect of pH change on the sign of the potential should be determined for these solutions.

TABLE 2

*Sign of photopotential for silver electrodes in several electrolytes*

| ELECTROLYTE | NORMALITY | SIGN OF PHOTOPOTENTIAL (EACH SIGN IS THAT OF A DIFFERENT CELL) |
|---|---|---|
| KCl | 0.20 | −+ |
| | 0.18 | − |
| | 0.16 | −− |
| | 0.14 | −− |
| | 0.12 | ++ |
| | 0.10 | + |
| KBr | 0.15 | −−− |
| | 0.12 | −−−− |
| | 0.10 | −−+ |
| | 0.06 | −−+−−− |
| | 0.04 | −−−−+ |
| | 0.02 | ++++ |
| KI | 0.20 | −−− |
| | 0.18 | −− |
| | 0.16 | −− |
| | 0.14 | ++++ |
| | 0.12 | ++ |
| | 0.10 | ++ |
| KCN | 0.50 | −− |
| | 0.30 | −− |
| | 0.10 | −− |
| | 0.07 | +−−− |
| | 0.04 | ++ |
| | 0.01 | + |
| $KNO_3$ | 0.50 | −−− |
| | 0.35 | −− |
| | 0.20 | ++ |
| | 0.10 | ++ |
| | 0.05 | ++ |
| | 0.02 | ++ |
| $K_2CrO_4$ | 0.10 | − |
| | 0.07 | − |
| | 0.06 | − |
| | 0.05 | − |
| | 0.04 | ++ |
| | 0.03 | ++ |

Studies have been reported of several cells containing metal electrodes in electrolytes which are known to be light sensitive. Baur (II-1) reported a small positive effect on illuminating platinum electrodes in solutions containing ferrous and ferric chlorides, mercurous and mercuric chlorides, and cerous–ceric salts. Iimori (I-20) studied cells composed of platinum electrodes in potassium ferrocyanide and obtained a negative potential. This he attributed to the reaction

$$Fe(CN)_6^{-4} + 2H_2O \xrightarrow{\text{light}} Fe(CN)_5H_2O^{-3} + OH^- + HCN$$

The photochemical effect was greatest at 4400–4500 Å. He reported a positive potential for platinum electrodes in solutions of potassium nickel cyanide and potassium platinum cyanide (I-21). This he attributed to a type of complex-ion formation rather than to a photoelectric effect. Audubert (I-7) studied cells with platinum electrodes immersed in solutions of $Fe^{+++} \mid Fe^{++}$ and of $I^- \mid I_2$. In the case of the $Fe^{+++} \mid Fe^{++}$ solution the reaction

$$Fe^{+++} \xrightarrow{\text{light}} Fe^{++}$$

was used to account for the observed potential; in the $I^- \mid I_2$ solutions, the addition of iodine changed the potential from negative to positive, owing to the formation of the trihalide ion. He interpreted his data quantitatively in terms of these equilibria.

Sasaki and Nakamura (I-24) reported a photopotential for the reversible reaction:

$$Fe^{+++} + I^- \underset{\text{light}}{\overset{\text{dark}}{\rightleftharpoons}} Fe^{++} + I$$

which proceeded in the dark and reversed in the light. The change of potential with iodine concentration was identical in the light with that in darkness.

Schiller (I-25) studied the Becquerel effect of molar solutions of potassium oxalate containing varying amounts of ferrous and ferric salts. Pure ferrous salt showed a change of potential, but the potential rose faster the greater the proportion of ferric salt present. He accepted Baur's theory as fitting all the facts better than the theory of photoelectric emission.

Swensson (I-28) worked with platinum electrodes in solutions of cupric sulfate, nickelous sulfate, zinc sulfate, and sulfuric acid. He rejected Baur's (II-1) photolysis theory, because there was no formation of hydrogen, oxygen, hydrogen peroxide, or ozone, and suggested that the electrodes probably became polarized. He found an initial negative effect which changed to positive on continued illumination. He observed that a potential was produced when the electrolyte only was illuminated, and he concluded that the phenomenon did not depend on the illumination of the electrode but was due entirely to the effect of light on the solution. He assumed that light reversibly changed the molecules from form A to form B at a rate proportional to the concentration of A and the light intensity. Thus an absorption of light resulted in a change in energy content, producing a corresponding change of potential.

Mukhin and Zilberfarb (I-22) studied the influence of radiation on the electrolyte only in a cell containing a platinum electrode in sulfuric acid at various concentrations. They measured both the thermal potential (negative at all concentrations) and the photopotential. The effects due solely to the light were as follows: negative potential at 0.05 $M$, maximum positive potential at 0.49 $M$, and negative potential again at 1.24 $M$, because of the two opposing processes occurring in the electrolyte.

Adler (VI-1) has extended Kimball's (VI-11) theory of the absolute reaction rates at electrodes to the positive primary photopotential and has shown that the derived formula reduces to the equation

$$\text{Potential} = \text{Constant} + kI$$

where $I$ is the intensity of illumination, for pure metal electrodes of very low intensities and to

$$\text{Potential} = \text{Constant} + k' \ln I$$

for active electrodes such as the oxide, sulfide, or halides of copper or silver. Both of these equations are in agreement with experimental data.

Gibney and Dole (VII-16) studied the cell

$$\text{Na} \mid \text{NaI in } C_5H_{11}NH_2 \mid \text{Na}$$

using a 200-watt tungsten lamp and a mercury-vapor arc and found no photovoltaic effect for sodium in the absence of water. The energy supplied to the electrons by visible light was not sufficient to cause the transition of the electron from metal to solution. Gibney and Dole suggested that the presence of sodium ions in solution may modify the energy relation of the electrons, and that the stable energy level of electrons in monoamylamine may be so high that the electrons in metal illuminated by visible light cannot make the transition from metal to solution.

### *Summary on photovoltaic cells of Type I*

These data would suggest that the photochemical theory is probably applicable to those cells containing an electrolyte that is light sensitive. For other cells the primary effect seems to be either the photoelectric effect, the photolysis effect, or a combination of both, while the thermal effect is secondary and slight. It seems highly probable that the observed photopotential may be the resultant of more than a single mechanism.

## VI. PHOTOVOLTAIC CELLS OF TYPE II: METAL ELECTRODES IMMERSED IN FLUORESCENT SOLUTIONS

Early work with these solutions was concerned with the effect of light on their electrical conductivity (II-5, 6, 36; VII-25).

Nichols and Merritt (II-33), in studies with eosin, fluorescein, rhodamine, naphthalene-roth, and cyanin dissolved in absolute alcohol found an increase in electrical conductivity which reached its full value at once. As soon as the light was cut off, the conductivity returned to its dark value. The relation of this effect to fluorescence was indicated by the observation that only those rays which excited fluorescence changed the conductivity, and that the light that caused the most intense fluorescence produced the greatest change in conductivity.

Goldmann (II-7), in 1908, studied platinum electrodes pressed flat against the inside wall of the illuminated side of the cell and transparent platinum mirrors on glass. He reported that the changes of conductivity of fluorescent solutions were caused by the absorption of light in the solution layer in close proximity to the electrode. The current was proportional to the amount of electrode surface illuminated and to the light intensity. Goldmann concluded that the effect depended upon absorption but not on fluorescence, since solutions which did not fluoresce gave effects of the same magnitude as those which did.

Hodge (II-19) found that if the electrodes were entirely concealed from light, or if the liquid was moved rapidly past the electrode, no change of conductivity as great as 0.1 per cent was produced when the liquid was illuminated. In all cases when alcoholic solutions of fluorescent electrolytes were used, the exposed electrode became positive with respect to the unexposed one, although aqueous fluorescein produced a potential of opposite sign.

Hodge (II-20) reported an increase of 10 to 15 per cent in the conductivity of an alcoholic solution of eosin on exposure to light. He drew the following conclusions: (*1*) The effect is not thermal, for the temperature coefficient is not more than 1 to 5 per cent per degree, the light effect is about the same with the cell in ice water, and there is a quicker light and dark response than that due to heat. (*2*) There is no change in the conductivity of the liquid unless a region very near the electrodes is illuminated. (*3*) An immediate decrease of resistance followed by an increase, which is reversed on removing illumination, suggests a combination of two effects, one growing to a maximum more rapidly than the other and decreasing more slowly. (*4*) The maximum potentials with the application of no external E.M.F. are obtained at the infrared edge of the absorption band for eosin, fluorescein, naphthalene-roth, and rhodamine, the last dye showing a potential of 0.2 volt.

Rassenfosse (VII-22) noted that the electrical conductivity of eosin and fluorescein was greatest when illuminated by light of a wave length most absorbed by the solution, but Pienkowski (VII-20) observed no change in conductivity when these same materials in water, alcohol, or gelatin were illuminated by white or monochromatic light, under conditions preventing heating and polarization. Von Samsonow (VIII-10), in experiments with uranyl and quinine sulfates and with chlorophyll, found the maximum effect in the spectrum region of greatest absorption.

Baur (II-1), in 1908, reported a negative effect upon illuminating platinum electrodes in a solution containing both uranous and uranyl salts. Titlestad (VIII-14) confirmed this observation, using varied relative concentrations of uranous and uranyl sulfates acidified with sulfuric acid. The greatest effect was in the blue and violet range of 4230–4840 Å. The rate of increase of potential plotted against the potential was linear for the ascending curve, but the rate of decrease was proportional to the square of the potential and the maximum potential was proportional to the logarithm of the intensity of the light. The study of dilution, varied concentration of sulfuric acid, and addition of alcohol indicated that the mass-action law of Wildermann (I-29, 30, 31, 32) was not obeyed. Baur (VII-5), commenting on Titlestad's paper, suggested that absorption of light made uranous salts more negative and uranyl salts more positive, and that the former effect usually predominates. He derived mathematical expressions for the ascending curve during illumination and for the descending curve after extinction. He ascribed this effect to a change in thermodynamic potential resulting from the absorption of light and the subsequent induced reaction. If the absorption is high and the reaction slow, the change in potential is proportional to the logarithm of the intensity of the light, whereas if absorption is low and reaction velocity is high, the change in potential is directly proportional to the light intensity. Baur (II-2) postulated that light changed uranium ions to the octavalent and quadrivalent states; in the dark the two reunite to yield the hexavalent form, giving off absorbed light in the form of fluorescence. He found that chloride or iodide ions, ferric and vanadyl salts, vanadic acid, and quadrivalent uranium salts extinguished the fluorescence and also destroyed the Becquerel effect. In 1921 Baur (II-3) found that the photocurrent was increased by the illumination of polarized platinum electrodes in solutions of uranyl sulfate, eosin, and quinine sulfate; he suggested that the depolarization of light might have its origin in the photolysis of water. Baur and Rebmann (II-4) concluded that continuous photolysis of water can occur only if the system excludes the recombination of hydrogen and oxygen.

Trümpler (VII-27) studied the illumination of the urano-uranyl sulfate system and found that a positive or negative effect may result in the presence of small quantities of other substances. The negative effect was diminished by iodine, hydrogen iodide, hydrogen chloride, vanadium sulfate, ferrous sulfate, and ferric sulfate, and in some cases the effect appeared to be changed from negative to positive. The positive effect was diminished by sulfur dioxide, uranic sulfate, and oxalic acid. The substances which exerted either a positive or a negative influence on the Becquerel effect also decreased the fluorescence of uranyl sulfate solutions. The cause of the Becquerel effect in these cells was considered to be the result of raising the uranyl ions to a higher valence state. Hatt (II-18) studied uranyl formate and found that the uranous salt (one of the products of the light reaction) retarded photolysis (II-3). Potassium iodide, potassium chloride, ferric chloride, vanadyl sulfate, and vanadic acid also retarded the reaction.

Thompson (II-42) used thin films of metals fastened to the front wall of the cell to eliminate absorption by the fluorescein, fuchsin, etc., between the light source and the electrode. He carefully made correction for unequal dispersion and energy distribution throughout the spectrum. His results may be summarized as follows: (*1*) Curves for the growth and decay of the "photoelectric current" are similar to those for fluorescence. (*2*) There is no close connection between the photoelectric current and fluorescence, for two methods of increasing the fluorescence do not increase the current. The region for excitation extends farther into the red than for fluorescence. (*3*) The magnitude of the photoelectric current depends on the metal. Only platinum, silver, gold, and oxidized copper, of the ten metals tested, gave a measurable effect. (*4*) The effect is not the photoelectric effect of the metal in the liquid, for the position of the maximum depends on the material in solution, not on the electrode. (*5*) All curves show a maximum photoelectric current approximately in the region of maximum absorption of the solution.

Staechelin (II-41), after an extensive study of the photovoltaic effect of platinum in fluorescent dyes in the absence and presence of oxidizing agents, concluded that the effect is bilateral, its magnitude and direction depending on the reducing or oxidizing agent present, and that the behavior can be explained on the assumption of a "latent knall-gas" photolysis.

Jenkins (II-21), using identical semitransparent films of platinum sputtered on the glass walls of a cell containing alcoholic solutions of rhodamine B made the following observations: (*1*) The sensitiveness of the current increases to a maximum for 3 per cent concentration and then decreases. (This is contrary to Goldmann's observation (II-7) of a continuous increase with concentration.) (*2*) There is an apparent increase of sensitiveness, which may be due to the failure of the molecules changed by light to return to their original condition. (*3*) A stream of electrolyte flowing against an electrode causes it to become more negative, temporarily, irrespective of its previous charge. The magnitude of the negative potential is a function of the force with which the liquid strikes the electrode.

Grumbach (II-10) studied cells made of platinum electrodes immersed in solutions of fluorescent substances previously illuminated by a mercury arc and obtained an effect showing that the potential was due at least in part to the modification of the electrolyte with light. A reversal from a negative to a positive potential was noted with 0.05 per cent uranin. Grumbach suggested that the electrodes adsorb the photoproduct, forming a true concentration cell. He (II-11) further confirmed his theory of a potential due to the adsorption of light-modified molecules on the electrode surface plus a Becquerel effect of the fluorescent solution by the following observation: Illumination of a platinum electrode in sodium fluoresceinate produced a positive potential, while illumination of the liquid about 15 mm. from the electrode produced a negative potential. Using the potassium salt of sulfofluorene, Grumbach (II-12, 13) confirmed his generalization as to the rôle of adsorption and indicated the necessity of introducing the concept of electrolytic dissociation into the theory of the electromotive force of adsorption. According to him (II-14), each measured photopotential in fluorescent electrolytes is the algebraic sum of the potential of adsorption and the Becquerel effect. Grumbach (I-18) further showed these two effects by the illumination of platinum electrodes in glycerol solutions and in glycerol–sodium fluoresceinate mixtures.

Platinum electrodes in sodium fluoresceinate exposed to oxygen of the air produced a potential of 5 millivolts on illumination but no potential in a vacuum (II-15). In a cell containing sodium fluoresceinate in 40 per cent glycerol, the Becquerel effect in air was negative but much more negative in a vacuum.

Schlivitch (II-40) confirmed Grumbach's observation of the effect of air by the observation that the potential of a photovoltaic cell consisting of platinum electrodes in aqueous uranin depended on the amount of dissolved oxygen.

Grumbach and Taboury (II-16, 17) reported that the potential of the photocell

$$\text{Pt} \mid \text{fluorescein–sulfuric acid} \mid \text{Pt}$$

assumed discontinuous values given by the equation

$$E = nE_1$$

in which $n$ is a whole number and $E_1 = 1.3 \times 10^{-3}$ volts. This, the "law of equidistances," was explained on the basis of the adsorption of successive monomolecular layers.

Murdock (II-30) suggested that the equations of Goldmann (II-7) and of Thompson (II-42) have no physical significance; he showed that these equations do not represent the experimental data even after corrections are made for damping and inertia of the galvanometer. This casts doubt on Goldmann's mechanism of a photoelectric action. Murdock (II-31) made use of a device similar to Goldmann's cell, whereby the electrolyte could be illuminated before, during, and after flowing by the electrode. He also agreed with Grumbach (II-10, 11, 12, 13) that the effect was due largely to a change of the electrolyte by the light, even when the electrode was not illuminated. He thought it probable, but not certain, that illumination of the electrode resulted in an E.M.F., with polarization playing an important rôle. Later (II-32) he considered that the apparent constancy of current with external resistance was probably due to the fact that the external resistance was small relative to the internal resistance of the cell.

Rule (II-38) illuminated electrodes through the electrolyte (alkaline fluorescein solution), and concluded that variations arose because of the formation of a concentration cell by means of the photochemical changes of the electrolyte. The same electrodes in alkaline solutions in the absence of fluorescein gave no photopotential. He noted a maximum effect (II-37) for a particular concentration of electrolyte (fluorescein), which he attributed to the parallel occurrence of fluorescence. When the molecule receives a quantum of radiation it passes to a critical state from which it returns to its original stable state or another stable state by emitting fluorescent radiation. As the concentration increases, the number of activated molecules increases and the E.M.F. increases to a maximum where the "protective" effect of adjacent molecules removes a part of the energy, thus decreasing the E.M.F. During illumination he observed an initial small positive potential which changed to a negative potential and increased to a maximum value.

Russell (II-39) derived an equation for the variation of the potential with time, using the theory of photochemical modification and the effect of diffusion on the potential developed. He described in detail each step, arriving at the equation

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

where $T_i$ = time during illumination,
$t_i$ = time in the dark,
$I$ = intensity of the light,
$K = \frac{RT}{nF} \ln 10$, and
$B$ = constant.

To test his theory, Russell (II-39) used platinum electrodes (so thin as to be transparent), sputtered on glass in a 3 per cent solution of rhodamine B in absolute alcohol. He obtained a straight line by plotting photopotential *vs.* log $(T_i^{1/2} + B/I)$, as called for by the theory, except where the photopotential was small. This, he explained, was due to a small constant negative photopotential built up in the first few moments of illumination, as above noted by Wildermann (II-43), Grumbach (II-10, 12, 13), and Rule (II-38). This suggests the intermediate compound indicated by Wood (II-45). The results for decay were in better agreement with the theory than for growth, again indicating that during illumination there was present some source of photopotential not considered in the theory. A further test of the importance of diffusion was shown by the lag between the illumination and the change of potential. Russell (II-39) concluded that the material causing the photopotential is formed at or near the place where the light enters the dye and that diffusion is an important factor in controlling the potential–time relation. He found no evidence indicating the presence of the Hallwachs photoelectric effect.

Lifshitz and coworkers (II-22 to 27; VI-12) have studied the photovoltaic effect of platinum in solutions of dyes. They have drawn a number of conclusions from their own work and from discussions of the work of others:

(*1*) The results of Swensson (I-28) have been confirmed (II-22).

(*2*) The photovoltaic effect in dyes is independent of the hydrogen-ion concentration (II-23).

(*3*) The effect is ascribed to the after-effects of a photochemical change in the electrolyte (II-22 to 25).

(*4*) Both positive and negative effects are observed, dependent upon the nature of the ions (II-23).

(*5*) The Becquerel effect is the electrochemical consequence of the primary photochemical process in which some electrons are thrown into another orbit by the action of light (VI-12).

(*6*) The magnitude of the effect is greatly influenced by impurities (II-23, 25).

(*7*) The Swensson–Becquerel effect is not present at reversible metal–metal ion electrodes or at hydrogen electrodes. It is shown only at polarizable electrodes or at phase boundaries (II-23).

(*8*) It is difficult to distinguish between surface effects at the light-sensitive electrodes (effects of the first kind) and volume effects in the electrolytic solution (effects of the second kind) which are suggested by Winther (II-44); the latter does not depend on a simple photochemical displacement (II-25).

(*9*) The effect occurs in non-aqueous solutions (II-25).

(*10*) The effect depends on the nature of the solvent, the kind of ions, the wave length and intensity of the light, and the temperature (II-25, 26).

(*11*) The effect is independent of (*a*) the external and internal cell resistance, (*b*) the nature of the non-polarizable electrode, (*c*) the duration of light exposure, (*d*) the polarization and electrode potentials, (*e*) the size and shape of the electrode, and (*f*) the volume of the exposed solution (II-29, 34).

Lowry (II-28, 29) reported the results of a very precise and extensive research on the location of the seat of the photopotential with platinum electrodes in fluorescent dye solutions. He used an apparatus patterned after that of Murdock (II-30, 31, 32), whereby the electrolyte was circulated concentrically about two narrow strips of platinum sputtered on the outside of a Pyrex test tube mounted on a vertical brass tube. For illumination, a small rectangular window was cut in the lower end of the brass tube. The electrode could be turned in front or on either side of the window through a range of more than 180°, so that the electrolyte could be illuminated before, during, or after contact with the electrode. The electrolyte about the test tubes was contained in a rotating bottle, and the whole was placed in a constant temperature bath.

Lowry (II-29) formulated the following conclusions: (*1*) The photovoltaic effect for rhodamine B is due entirely to the modification of the electrolyte with light. (*2*) The effect follows the laws of the concentration theory, the concentration of the modified form B varying with the light intensity, the time of illumination, and the concentration of material A. (*3*) There is no indication of any effect due to the direct illumination of the electrode–electrolyte boundary. This is indicated by the smooth curve rather than an abrupt change of slope in going from one region to another. (*4*) There is no reversal of photopotential for rhodamine B and uranin at the beginning or end of illumination, as noted above by Rule (II-38). However, values of the potential for short periods of illumination are reported which deviate from the theory.

Ghosh (VIII-15), in a study of polished platinum electrodes in alkaline solutions of fluorescein, postulated the reaction

$$B \rightleftharpoons B^+ + e$$

at an electrode and applied the Nernst equation to the reactions at the light and dark electrodes. According to Ghosh, the excited molecule of the fluorescent substance gives with a second normal molecule an unstable intermediate B, which in turn can combine with a second molecule of B to form C. The potential depends on the concentration of the intermediate B, the velocity of formation of which is proportional to the light intensity and the deactivation velocity of which is proportional to the square of the concentration.

Rao (VII-21) illuminated platinum-foil electrodes in aqueous solutions of erythrosin and chrysoidine and found that their photopotentials (negative for erythrosin and positive for chrysoidine) varied directly as the square root of the light intensity. The wave lengths immediately following the long-wave-length limit of the absorption band of the dye were most effective. After a review of various theories of the effect, it was concluded that the diffusion of activated molecules to the electrode seemed best to explain the potential curves for various concentrations.

Pincussen, Suzuki, and Seitz (II-34) obtained curves for extract of visual purple and for the solvent, both in the dark and in the light. The reversible phenomena of the curves were attributed to the photovoltaic effect of the solvent.

### *Summary on photovoltaic cells of Type II*

The conclusions of the workers in the field indicate that the principal effect for this type of cell is probably photochemical rather than photoelectric. The thermal effect and the photoelectric effect may be present but, if so, they must be small.

## VII. PHOTOVOLTAIC CELLS OF TYPE III: METAL ELECTRODES IMMERSED IN ORGANIC (NON-FLUORESCENT) LIQUIDS

Of the many possible cells of this type, those prepared from Grignard solutions have received considerable attention. Historically, the photoeffect of such solutions was investigated as a result of the observation that luminescence is often associated with the reactions of Grignard reagents (III-6, 7, 8, 17, 21, 22, 23, 24). Moreover, it was observed by Dufford and coworkers (III-8, 9, 10) that light was emitted at the anode when potentials up to 1500 volts were applied to luminescent solutions. This observation suggested to them that the converse might be true: namely, that a potential difference might be produced upon the illumination of electrodes in Grignard reagents. Dufford (III-3, 11) prepared cells containing Grignard reagents with platinum for the electrode to be illuminated and other metals for the dark electrode; the potentials were measured with a potentiometer. His results were as follows: (*1*) Of the eight metals tested (platinum, gold, magnesium, lead, zinc, copper, aluminum, iron), the combinations platinum–aluminum, platinum–copper, and platinum–lead seem best. (*2*) Aromatic compounds give stronger responses than aliphatic. (*3*) The order of sensitivity is RMgCl > RMgBr > RMgI. (*4*) The optimum concentration seems to be 1 *M* for aromatic and 0.5 *M* for aliphatic Grignard solutions. (*5*) Some Grignard solutions show a reversal of the initial response on continued illumination. (*6*) The light sensitivity seems to spread throughout the entire visible spectrum, with a broad maximum in the green or blue. (*7*) The voltage change is not a thermal effect, for (*a*) the rate of change of voltage averages only about 0.002 volt per degree, (*b*) the direction of the thermal effect is the reverse of the light response, and (*c*) cells in ice water give about the same response as at 25°C.

With several refinements in his apparatus, i. e., fresh distillation of ether over sodium, use of sodium-free ether, preparation of the compounds in a nitrogen atmosphere, and use of an H-type of cell to make certain of illumination of only one electrode, Dufford (III-13, 16) reported the following results:

(*1*) For the initial response, the potential is proportional to the intensity. For the total response, the potential is proportional to the logarithm of the intensity.

(*2*) There is a slight photovoltaic effect with platinum–aluminum electrodes in pure ether.

(*3*) The first response is usually positive, but after two or three illuminations it becomes and remains negative.

(*4*) Depolarizers such as ethyl bromide, methyl iodide, and benzyl chloride greatly increase the current and the voltage.

(*5*) A positive response is obtained with magnesium, aluminum, copper, zinc, lead, and iron as the illuminated electrodes, but a negative response with platinum.

(*6*) The positive response is not due to occluded oxygen, for (*a*) there is no observable difference after outgassing platinum by heating in hydrogen at 80°C. for several hours and allowing it to cool in hydrogen, and (*b*) there is no observable difference after electrodes are kept between freshly cut surfaces of sodium for several days.

(*7*) An apparatus was devised for circulating the electrolyte past three electrodes, the middle one being illuminated and the "upstream" one maintained as a reference. With the solution at rest, illuminating the middle electrode did not affect the "downstream" electrode. The effect was the same when the middle electrode was removed and only the electrolyte illuminated. The solution clearly carried with it something that reduced the potential of the "downstream" electrode.

Recently it has been observed (III-14) that magnesium electrodes cleaned by reaction with organic halides are "inactive" but when exposed to oxygen they become light sensitive. A surface film appears to be necessary for light sensitivity in the case of magnesium electrodes.

Hammond (III-19) reports the following observations of Grignard photocells: (*1*) The photopotential is affected by agitation, polarization, cleaning, or brief exposure to air. (*2*) There are no noticeable temperature changes. (*3*) Oscillations of potential in the dark occur, owing to some unknown cause. (*4*) The potential changes with the age of the cell, owing to concentration changes and to slow electrolysis caused by leakage currents. (*5*) Illumination of the electrolyte alone gives very small effects, which are attributed to scattered light reaching the electrodes. Thus the seat of the phenomena is located at or near the surfaces of the electrodes, near enough to be affected by changes on the electrode surfaces. (*6*) Several types of cells give responses of 0.2 to 0.8 volt when exposed to x-rays (III-15, 19), which differ in magnitude and frequently in sign from the photovoltaic effect of the same cells with visible light. (*7*) It is impossible to trace any general interrelation between the changes in potential, resistance, and capacitance or illumination. (*8*) The photoelectric hypothesis is untenable, for it seems unreasonable to attribute a voltage variation of 10 to 50 per cent to a process causing a resistance change of only 1 to 2 per cent.

Harty (III-20) studied the influence of depolarizers on the photovoltaic effect in Grignard solutions. He used copper, zinc, aluminum, iron, lead, and platinum electrodes in ethylmagnesium bromide and phenylmagnesium bromide with ethyl bromide and ethyl iodide as depolarizers. Special care was taken to keep the Grignard solutions dry. The cells contained about 40 cc. of Grignard solution and 1 cc. of depolarizer, that having been shown to be the best concentration.

Harty drew the following conclusions: (*1*) The value of the dark voltage occurs as if it were a matter of chance, ranging from 0 to 40 millivolts, with no good reason discovered. (*2*) The data fail to reveal any uniformity in the effects due to polarizing the electrodes either anodically or cathodically. (*3*) The capacitance of cells filled with ethylmagnesium bromide is greater than for phenylmagnesium bromide, as expected if Hammond's (III-19) calculations, showing a monomolecular layer, are correct, because of the thinner layer of the former. (*4*) The direct current resistance (a function of the thickness) of phenylmagnesium bromide should be greater than for ethylmagnesium bromide, as found by Hammond and Harty.

Dufford (III-16) concluded that the photovoltaic effect in Grignard solutions is due to the formation of excited molecules by the light, either throughout the liquid or in the electrode surface layer of electrostatically strained molecules. They more or less completely replace the normal molecules on the electrode surface, being more or less regularly oriented. He further suggested that these molecules may or may not have the same dipole moments as in the solution, but should change the work function of the interface and give rise to a difference of potential. Dufford suggested that the most probable type of excitation is a vibration similar to that in the Raman effect, due to the independence of the photovoltaic effect of selective adsorption, usually associated with electron displacement.

Harty's results seem to support the theory of layers of excited molecules on or near the electrode as the cause of the photopotential in Grignard solutions. An altered potential difference would result if light produces in or near these layers a number of excited molecules having different dipole moments from the normal molecules and having the property of displacing the latter from the layers until a sort of saturated layer is built up. Since the "life period" of the excited molecules may be short, the electrode "recovers" in the dark. By assuming that the "negative ends" of the polarized molecules can attach themselves to some metals and the "positive ends" to others, the positive and negative voltage and current responses can be explained. The depolarizer probably disturbs this layer of excited molecules on or near the electrode surface. The effect would probably depend on the electrodes, electrolytes, and depolarizers. Harty suggested the need for more information on the reactions involved and especially on the structure of the molecules.

Nga (III-25) studied the photopotentials of various organic molecules and concluded that only those having a group with one or more nitrogen atoms—such as amines, amides, oximes, and semicarbazones—showed "instantaneous" photopotentials. She (III-24) found that the meta-iodoaniline derivatives always had greater photopotentials than the ortho derivatives, the para compounds having about the same values as the meta. She (III-23) further found that 1,2-naphthalenediamine was distinctly less photosensitive than the 1,8- and 2,7-compounds, which were about equally sensitive.

### *Summary on photovoltaic cells of Type III*

The best explanation for the photopotential produced by this type of cell seems to be the formation of excited molecules which are probably adsorbed in one or more layers at the electrode surface. These excited molecules probably change the work function of the interface of the metal and solution.

The Swensson effect, i.e., the photopotential produced by illumination of the electrolyte only, seems to be very small, as is the thermal effect. Thus for both Type II and Type III the effect appears to be photochemical.

## VIII. PHOTOVOLTAIC CELLS OF TYPE IV: METAL ELECTRODES COATED WITH INORGANIC COMPOUNDS AND IMMERSED IN SOLUTIONS OF ELECTROLYTES

The cells of this type that have received the most attention are those coated with silver halide or copper oxide.

### *A. The silver halide cells*

Becquerel (IV-31) in 1839, using silver plates coated with silver halides and immersed in dilute sulfuric acid, noted a photocurrent upon the illumination of one electrode. The current varied with film thickness, light intensity, and color of light, the blue-violet end of the spectrum producing the greatest effect. He found the effect much greater than for uncoated metal electrodes and again concluded that the effect was not a thermal one. In the next twenty years (Becquerel IV-32 to 39) continued his work on silver electrodes coated with silver chloride, bromide, and iodide. In a study of silver–silver iodide electrodes (IV-33, 34) he reported a maximum in the yellow-green range, a minimum at the beginning of the blue, and another maximum in the indigo-violet range. For silver–silver chloride electrodes (IV-36) the maximum effect was at the beginning of the green region of the spectrum. However, Becquerel recognized that his light source was most intense in this spectral region, and so he studied the effects of varying the intensity as a means of determining the true color sensitivity. He also recognized the possible error due to differences of reflection and absorption of light at the electrode surface.

Griveaux (IV-75), in 1883, illuminated silver–silver bromide and silver–silver iodide electrodes and measured the *potentials*, rather than the current. He (IV-76) summarized his results as follows: (*1*) Silver–silver iodide electrodes upon illumination reach a maximum value in a certain time. (*2*) Continuous circulation of solutions of iodine of increasing concentrations in the vessel during illumination progressively decreases the maximum potential to zero, the required concentration varying directly with the intensity of illumination. (*3*) At a fixed concentration of circulating liquid and at the maximum potential, the latter gradually increases if the circulation is stopped. (*4*) The above effects are observed with silver–silver bromide or silver–silver chloride electrodes, but the concentration of the solution necessary to decrease the potential to zero depends on the nature of the sensitive salt.

Luggin (IV-97), in 1894, measured the potential (0.42 volt) produced by the exposure to diffuse sunlight of a platinum–silver bromide electrode immersed in 0.1 $N$ potassium bromide. The rate of rise of potential was found to be less for weak than for strong illumination. Continuous and intermittent light of the same mean intensity appeared to have the same effect. The potentials were lowered by previous exposures to strong light. Using the same type of cell, he (IV-98) applied a stopping potential to decrease the photocurrent to zero (called the equilibrium potential). Luggin called the current normal or positive when the action of the current was to remove halogen and cause darkening of the electrode, while currents acting in the opposite manner were called solarization currents. With silver chloride electrodes, yellow light favored the latter and blue light the former.

Scholl (IV-122, 123), in 1905, reported that platinum–silver chloride, platinum–silver bromide, and platinum–silver iodide electrodes in dilute acid or alkali halides became positive when illuminated. He stated that exposed silver iodide in aqueous salt solutions underwent dissociation, producing the ions of silver iodide and probably electrons; the latter imparted metallic conductivity to the silver iodide. The dissociation was induced by light of all wave lengths but paralleled the absorptive power of the silver iodide. Scholl's experiments indicated no change in potential on illuminating the potassium iodide solution and showed that the solubility of the illuminated silver iodide was probably 15 to 20 per cent higher in violet light than in the dark. He considered the effect to be due to diffusion potentials.

Wildermann (I-29 to 33; II-43; IV-153) studied silver–silver halide cells and applied to them his theories of "induction periods" and "deduction periods," the law of mass action, and thermodynamic equilibrium under the influence of light. His conclusions were as follows: (*1*) The velocity of chemical reaction and chemical equilibrium in homogeneous systems under the action of light follows the laws of mass action. (*2*) The potential produced by light consists of: (*a*) an electromotive force due to the variation of chemical potential and solution pressure, and (*b*) a thermoelectromotive force. (*3*) The rays of all wave lengths act both "chemically" and as "heat rays," only in different amounts. (*4*) Reversals noted by Becquerel (IV-39) and Minchin (IV-101) are not surface phenomena but are due to polarization. (*5*) Each kind of equilibrium between two states of matter on exposure to light becomes shifted in the direction accompanied by the greater absorption of light.

Sichling (IV-137) studied the illumination of electrodes made by absorbing photochlorides (silver chloride and amorphous silver) in gelatin and in silicic acid and applying this paste to a platinum-gauze electrode. In potassium chloride solution positive potentials to 0.5 volt were obtained; blue and yellow light had much the same effect as white light, green light had less effect, and red light produced a negative potential. The latter may have been a thermal effect, for the temperature coefficient was found to be negative. The maximum potential increased in an approximately logarithmic manner with the light intensity.

Baur (IV-29), in commenting on Sichling's work, suggested that the increase of potential on illumination was due to the formation of the unstable photochloride $Ag_2Cl$, the decrease on continued illumination being caused by a change of color, whereupon the stimulating effect of the light diminished. The negative effect with red light was ascribed to the amorphous silver in the photochloride.

Iimori and Takebe (IV-83) studied silver–silver iodide electrodes in 0.3–5 $M$ potassium iodide and concluded (*1*) that the potential varies with the concentration of the cell liquid according to the equation

$$E = A + B \log 1/C$$

where $C$ is the concentration of the potassium iodide and $A$ and $B$ are constants depending on temperature, intensity of illumination, and the electrodes, (*2*) that an increase of temperature decreases the effect, and (*3*) that the photovoltaic effect with halide electrodes is caused by the reversible chemical reaction of silver iodide.

Athanasiu (I-4; IV-5, 8, 11, 13), in studies of silver–silver halide electrodes, made the following observations: (*1*) The maximum sensitivity of silver iodide is at 4245 ± 20 Å. (IV-5). (*2*) The positive photopotential of silver iodide in neutral potassium chloride is inverted to a negative value by adding a base, the maximum sensitivity being thereby shifted to 4300 Å. (I-4; IV-13). (*3*) For all cells studied, the photopotential increases when the temperature decreases, and *vice versa*, possibly owing to opposing photochemical reactions being differently affected by the change of temperature (IV-8, 13). *(4)* The positive photoeffect reaches saturation after a few minutes of illumination with unfiltered radiation but continues to grow if the radiation is monochromatic (IV-11). (This might be due to insufficiently intense monochromatic radiation.) *(5)* It is impossible to explain the Becquerel effect on the basis of the photoelectric effect alone (IV-8, 13). *(6)* The results may be explained as due to the electrode functioning as an "acceptor" of the hydroxyl ion of the electrolyte. The iodine liberated by the light on the electrode may temporarily form IOH, which interferes with recombinations with the silver (I-4; IV-13).

Garrison (IV-67) coated thin sheets of silver with silver iodide by the use of vapors and by electrochemical deposition, the latter giving better uniformity of thickness. The electrolyte was saturated with silver iodide, thus fixing the ion product, but the ratio $Ag^+/I^-$ could be varied by adding potassium iodide or silver nitrate. He drew the following conclusions: *(1)* The sign of the potential depends on the thickness or density of silver iodide. The negative effect increased with increase of the ratio $Ag^+/I^-$ by adding silver nitrate, and the positive effect was developed by the decrease of the ratio by adding potassium iodide. *(2)* The curves obtained by plotting potentials *vs.* intensities were of the same form, even though the negative potentials were larger than the positive ones for the same intensity. *(3)* There seems to be no simple relation between the photopotential and the frequency. The effect seems greater in the blue and violet with a slight maximum in the yellow-green.

Garrison also assumed that light tends to separate the ions, increasing the solubility. Silver coated with silver iodide can act either as a reversible silver or as a reversible iodine electrode. Since the solubility product of silver iodide is $1.0 \times 10^{-16}$, when potassium iodide is added so that $I^- = 0.01$, then $Ag^+$ must be $1 \times 10^{-14}$ in the dark. Hence $Ag^+$ could be doubled with only a slight decomposition, the $I^-$ remaining nearly constant. Hence the silver electrode ($Ag \rightleftharpoons Ag^+ + e$) may be used to measure the silver ion increase. Thus, on adding potassium iodide the electrode would become positive, as experimentally noted. Conversely, on adding silver nitrate the electrode acts as an iodine electrode ($I_2 + 2e \rightarrow 2I^-$); the potential is negative and becomes more negative on adding silver nitrate.

Garrison (IV-68) later used silver iodide deposited on gold, platinum, and palladium plates. His results were as follows: *(1)* There is a positive effect, provided the electrode does not have silver deposited from light exposure. *(2)* Changes of the electrolyte have little effect on the potential, for in 0.1 $N$ potassium iodide solution the dark potential is 0.2587 volt, compared to 0.411 volt for the dark potentials in 0.1 $N$ silver nitrate. The respective photopotentials are 0.450 and 0.432 volts. *(3)* The relation between potential and intensity is the same as before—almost linear for low intensities and constant for high intensities. *(4)* The photochemical action on silver iodide in any part of the visible spectrum diminishes as the light becomes more nearly monochromatic, the light intensity being maintained at a constant value. (*5*) Illumination in the blue is necessary to sensitize the electrode to red, after which it is most sensitive in the red.

Garrison suggests that the rise of potential of the noble metal–silver halide electrodes is due to an increased number of silver iodide molecules being made polar by the light, displacing the electrons toward the halogen. His assumptions are: (*1*) There is a probability distribution of polarity among the molecules. (*2*) The greater the degree of polarity, the longer the wave length of light absorbed by the valence electrons. Thus the blue sensitizes the silver iodide to red by increasing its polarity. However, this would not seem to account for its response being greatest in red after sensitization. (*3*) The energy of light is stored in the molecule as increased polarization and thus increases the ionization and the apparent solubility. (*4*) A molecule having absorbed a quantum of energy and become polar may return to a less polar state by giving its energy to several other molecules, thus increasing their polarity.

Garrison's theory of the loosening of the ions was somewhat strengthened by his discovery (IV-69) that silver chloride, which is slightly diamagnetic, became less so, and silver bromide and silver iodide, which are slightly paramagnetic, became more so in light.

Price (IV-111) criticized Garrison's work and suggested that light formed a photohalide, accompanied by the formation of colloidal silver, which would have a higher solution pressure than massive silver, thus producing the negative effect.

Garrison (IV-70) answered Price's criticisms, showing that Price had merely reversed his calculations and thus obtained the same constant used by the author in one of his data tables. He indicated two ways in which silver–silver iodide could act as an iodine electrode: (*1*) The salt and the electrolyte retain some iodine in solution, which may ionize. (*2*) The iodide ions may be liberated directly from the crystalline lattice, the charge being conducted directly through the crystal.

$$\mathrm{AgI} \rightleftharpoons \mathrm{Ag} + \mathrm{I}^- + (+)$$

Tucker (IV-143) studied photovoltaic cells having silver halide or copper halide on platinum and on silver or copper. His work may be summarized as follows, with the note that he designated the anode as "that electrode from which current flows in the cell solution," which is negatively charged: (*1*) In cells having photosensitive substances on platinum, illumination causes oxidation of the substance if the solution is an oxidizing one, causing the exposed electrode to behave as a cathode (positively charged). If the solution is a reducing one the electrode behaves as an anode (negatively charged). (*2*) In cells of the second type, having copper halides or silver halides on copper or silver, respectively, illumination tends to promote reduction of the photosensitive substance, "local cell" action causing a reduction of the observed electromotive force, especially if the layer is not uniform. (*3*) If these "local cells" are completely reversible, the electrical behavior of the illuminated electrode is determined by the oxidizing or reducing nature of the cell solution. (*4*) The photoeffect is in the order silver chloride > silver bromide > silver iodide, whereas the order for the photoelectric effect is iodine > bromine > chlorine, as reported by Toy, Edgerton, and Vicks (IV-141). (*5*) The results of Becquerel, Minchin, Wildermann, Case, and Garrison can be accounted for on the basis of these considerations.

Audubert (IV-14, 15, 16, 18), in a study of silver–silver halide cells, made the following observations:

(*1*) With very thin layers of silver halide, red rays give a negative charge, while blue rays initially give a higher negative charge which gradually becomes positive after several hours' exposure (IV-14).

(*2*) The effect is independent of a thermal effect and is in the opposite direction (IV-15).

(*3*) Blue radiation is much more active than red (IV-15).

(*4*) In all cases a polarization of inverse sign to that of the electrode increases the effect, while polarization of the same sign decreases it but never reverses it (IV-15).

(*5*) Experiments with buffered solutions confirm the statement that lowering the pH raises the positive photopotential and increasing the pH raises the negative potential (IV-18).

(*6*) The photoeffect diminishes when the concentration of cation is raised (IV-18).

(*7*) The photoeffect is attributed to the photolysis of water and the displacement of the resulting equilibrium by the photosensitive substance. The sign of the photopotential is negative or positive, depending upon the way hydrogen or oxygen displaces the electrochemical equilibrium (IV-18).

Goldmann (II-7) reported observations of the illumination of silver–silver chloride and silver–silver bromide electrodes in sodium chloride and sodium bromide solutions, respectively. He claimed that Wildermann's (I-30, 31, 32) hypothesis that such cells have a definite electromotive force determined by the light intensity is wrong; he suggested that selective absorbing molecules send off electrons into the solution, allowing the rest of the solution to give its positive charge to the electrode. Later, Goldmann (II-8, 9) reiterated his theory that the primary process in a photochemical process is a removal of electrons and that the Becquerel effect is analogous to the Hallwachs–Leonard photoelectric effect. He explained that solarization was a kind of polarization of the photoelectric elements, taking place when the charges appearing are not neutralized, and that it could be avoided by the use of oxidizing substances at the electrodes.

Experiments by Fajans, Frankenburger, Fromherz, and Karagunis (IV-51, 52, 53, 54, 62, 63, 64) indicated that the interaction between light and silver bromide was influenced by adsorbed ions. Fajans (IV-50, 51, 54) suggested that under the influence of the adsorbed silver ion the amount of energy required to transfer an electron from a bromide ion to a silver ion may be decreased. However, in the case of silver iodide, he asserted that one is dealing not with a change in the energy requirements but simply with an increase in the number of elementary processes. If the surface were coated with silver ions, then an equal amount of silver iodide would absorb a larger portion of the incident light and therefore more silver iodide would be decomposed. He concluded that one may therefore regard the silver ion not only as a chemical acceptor but also as a spectral sensitizer in the photolysis of the silver halides. The primary action of light on silver bromide is ejection of an electron from the bromide ion to the silver ion, forming neutral atoms of silver and bromine.

Sheppard and coworkers (IV-127 to 135, 147), in a study of the silver–silver halide electrodes (IV-147), concluded that Tucker's theory of initial negative photopotentials caused by local cell reactions on the illuminated electrode may be discarded. The precision of their work, their recognition of variables, and the testing and control thereof seem to be the best of the experimental work on the photovoltaic effect for this type of cell. To obtain rapid measurement in the first fraction of a second of exposure of a cell to light they used an amplifier–oscillograph system. Figure 2 shows a typical potential–time curve using a vacuum-tube voltmeter; it shows that the nearly inertialess negative effect is still observable after five 0.01-sec. exposures. The quasi-instantaneous negative portion probably was not eliminated on the appearance of the positive effect, but the observed potentials are the resultants.

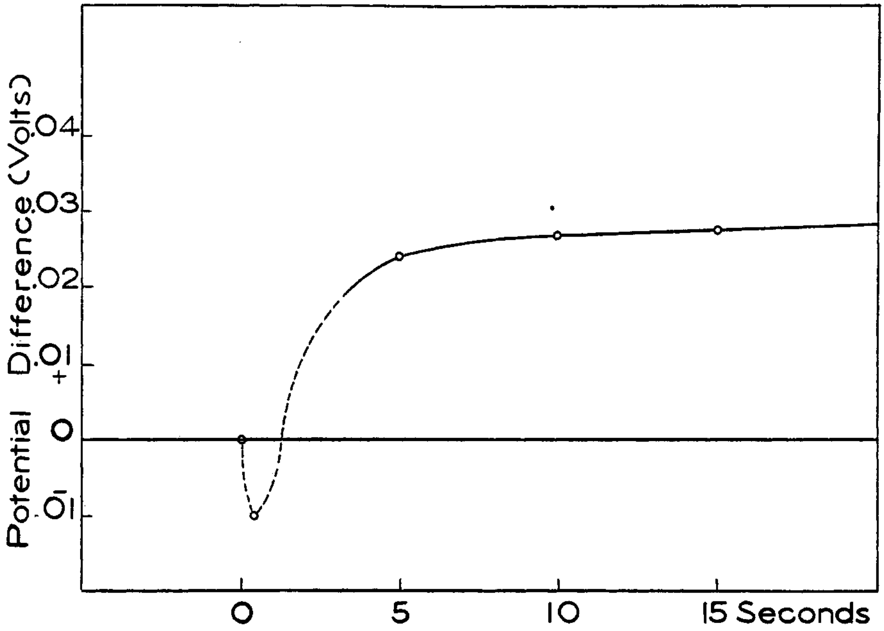


FIG. 2. Typical potential–time curves, using a vacuum-tube voltmeter. Silver–silver bromide electrodes; silver bromide thickness = 0.00039 mm.; photocell electrolyte, KBr saturated with AgBr; radiations, complete spectrum of quartz mercury arc.

They report the following conclusions from their work on silver–silver bromide electrodes: (*1*) As the thickness of silver bromide increases, the photopotentials assume a more steady potential after the first 30-sec. exposure and remain steady for at least 90 sec. (*2*) The thinner the silver bromide layer, the more marked the initial negative effect. (*3*) The time to obtain the maximum negative potential is about 0.06 sec. in all cases. (*4*) The maximum difference of potential increases with age at least for the period 2 min. to 8 days. (*5*) This change over a period of time may be due to a change in crystal structure or to removal of hydrogen bromide or bromine formed during electrolysis. (*6*) There is no Swensson–Becquerel effect on illuminating the solution (IV-132).

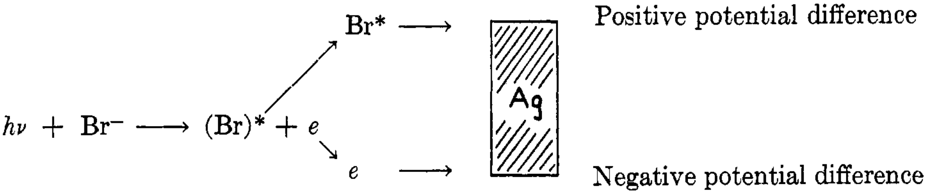
Sheppard and Vanselow (IV-147) propose the following theory: The primary photochemical process may be represented by

$$\begin{aligned} Br^- + h\nu &= Br^* + e \\ Ag^+ + e &= Ag \end{aligned}$$

Both the electrons and the bromine atoms or molecules may be supposed to move in the direction of the light ray toward the silver electrode, the former producing the initial negative surge by an increase in electron pressure. When the more slowly moving bromine reaches the electrode, it reacts to give a positive potential

$$\tfrac{1}{2}Br_2 + Ag \rightarrow Ag^+Br^-$$

so the mechanism may be represented by



Indications that this is the correct mechanism are the following: (*1*) The relation of the fall of the positive potential with time on removing illumination is in agreement with the diffusion resistance being directly proportional to the thickness of silver bromide. (*2*) Oscillograph and intermittent-exposure data demonstrate the inertialess character of the negativation. This is the order obtained in photoconductance of crystals. (*3*) Halogen acceptors, such as sodium nitrite or acetone semicarbazone, eliminate or reduce the positive effect, as shown in figure 3 (as predicted). (*4*) An increased positive potential is produced in the dark by permitting bromine to diffuse through the silver bromide of one electrode, the other being shielded by an alundum crucible.

Sheppard suggests the two possible reaction schemes:

| I | II |
|---|---|
| (1) $Br^- + h\nu \rightarrow (Br^-)^*$ | (1) $Br^- + h\nu \rightarrow (Br^-)^*$ |
| (2) $(Br^-)^* \rightarrow Br + e^*$<br>$Br^* + e$ | (2) $(Br^-)^* + Ag^+ \rightarrow Ag + Br$ or $Br^*$ |
| (3) $Ag^+ + e \rightarrow Ag$ | (3) $Ag + Br \rightarrow Ag^+ + Br^-$ |
| (4) $Br + Br \rightarrow Br_2$ | |
| (5) $Ag + Br \rightarrow Ag^+Br^-$ | |

Sheppard provisionally accepts scheme I as more probable. Evidence for the production of relatively free internal photoelectrons in insulated silver halide has been given by Arrhenius (IV-1, 2), Scholl (IV-122, 123), and Gudden and Pohl (IV-77).

Assuming the reaction to be

$$\tfrac{1}{2}Br_2 + Ag \rightleftharpoons Ag^+Br^-$$

For equilibrium

$$K = \frac{(Br_2)^{1/2}(Ag)}{(Ag^+Br^-)} = \frac{[Br_2^-]^{1/2}[Ag]}{[Ag^+][Br^-]}$$

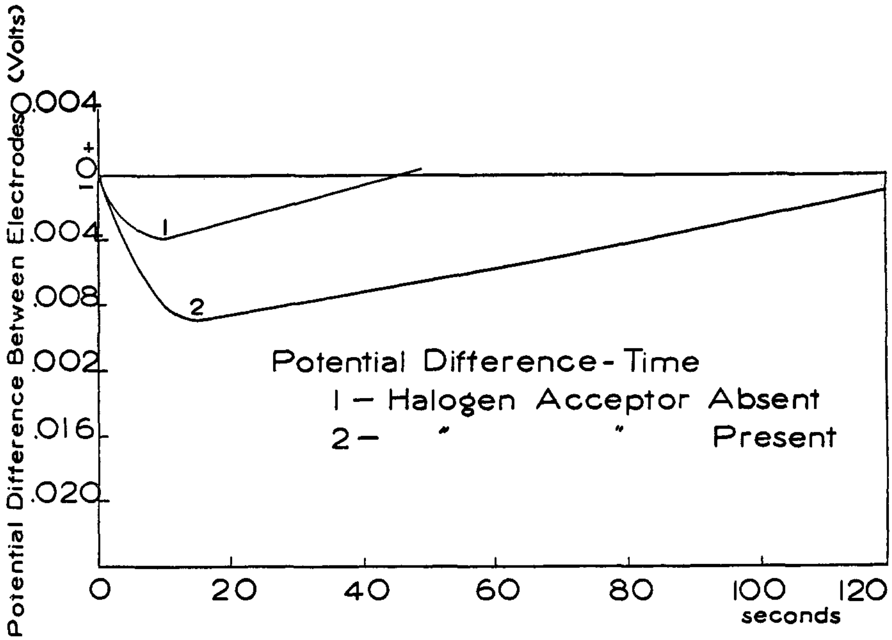


FIG. 3. Effect of halogen acceptors

Since [Ag] and [Ag⁺Br⁻] are constant,

$$K = k(Br_2)^{1/2}$$

and from Nernst's equation

$$E = E_0 - RT \log k[Br_2]^{1/2}$$

A plot of steady E.M.F. against log $(Br_2)^{1/2}$ is a straight line, until the lowest concentrations are reached.

Sheppard and Vanselow (IV-130), after considering the energy steps in the Born cycle for calculating lattice energies of silver halides, conclude that photolysis of solid silver halide may occur directly to give halogen and silver or may occur indirectly by way of separation of electrons from halide ions, followed by acceptance of electrons by silver ions. They assume that both the lattice energy and the electron affinity are lowered at interfaces, making it possible for the inner photoelectric effect to take place in the visible spectrum.

Herzfeld (IV-80) has calculated the influence of the surroundings on the work required to transfer an electron from the bromide ion to the silver ion in the silver bromide crystal. Sheppard and his associates (IV-133, 134, 135) have studied the effect of adsorbed acidic and basic sensitizing dyes on the photolysis of silver halides (this will be discussed in a later section). From present results it cannot be concluded whether the electrons are initially released from the dye by absorption of light and recovered from bromide ions of the crystal with release of bromine, or whether the dye merely transmits sufficient energy to the crystal to separate electrons and halogen. Sheppard (IV-135) also reported new values of 0.09 sec. as the time to reach the initial maximum negative photopotential and 1.23 sec. to recross the zero potential line. This work was done with an Einthoven string galvanometer with a direct-current vacuum-tube amplifier (IV-148).

Kieser (IV-91) believes that the photolysis of silver bromide according to the theories of Fajans explains regression, coagulation, the photovoltaic effect, and photoelectric conductance of the silver halides over the entire visible spectrum. He finds that the maximum photoelectric conductivity corresponds with the greatest photochemical sensitivity. He also affirms the hypothesis of Fajans and of Sheppard and Trivelli.

Winther (II-44) has concluded that (*1*) effective photovoltaic electrodes have large surface area, have a corresponding absorptive power, and are made more conductive by irradiation, (*2*) the effect depends on a primary ionization and a consequent change in the absorption equilibrium, and (*3*) the often-observed chemical processes are secondary side reactions.

Kirillow and coworkers (IV-92, 93) reported a study of the irradiation of pure monocrystalline silver chloride, silver–silver iodide, and gold–silver iodide electrodes. They interpreted the effects as photochemical rather than barrier-film effects, and offered a mechanism on the basis of the hypothesis of Fajans and of Sheppard and Trivelli.

Hartung (IV-78), using a microbalance, reported a change of weight of illuminated silver bromide, silver chloride, and silver iodide, indicating decomposition into silver and free halogen. Strömberg (IV-139), from a similar experiment with silver bromide, ascribed the loss of weight to thermal effects. Mutter (IV-106), Schwarz and Stock (IV-124), and Steiner (IV-138) have contributed data indicating that the photolysis of silver bromide and of silver chloride liberates halogen. Feldmann and Stern (IV-55, 56, 57) have used a potentiometric method to follow the splitting of chlorine or bromine from silver chloride or silver bromide during illumination, using a nitrite as a halogen acceptor. They found a quantum yield approaching 1 for precipitated silver chloride at 3130 Å. and 3650 Å. in the presence of nitrite, and for precipitated silver bromide at 3650 Å. and 4360 Å. Jouaust (IV-85) found that the maximum light sensitivity of silver iodide cells was at 4245 Å., independent of the electrolyte.

Kameyama and Kikuchi (IV-87) calculated the long-wave-length limit of dissociation of silver halides by the method of de Boer as applied to alkali halides. They found that the energy for an electron to pass from the halide ion to the silver ion and for the silver halide to be adsorbed by the lattice was 3250 Å. for silver chloride and 4100 Å. for silver bromide. The existence of crystal effects was thought to make possible photolysis at longer wave lengths of 3900 Å. and 4350–4600 Å., respectively. Trillat and Motz (IV-142) found crystalline silver on the overexposure of silver bromide–gelatin emulsion. All these data lend support to the theory of Fajans and of Sheppard.

TABLE 3

*Spectral sensitivity of silver–silver iodide electrodes*

| WAVE LENGTH | PHOTOPOTENTIAL POTENTIAL/LIGHT INTENSITY |
|---|---|
| *Å.* | |
| 5460 | 0 |
| 4358 | 30.9 |
| 4046 | 66.1 |
| 3660 | 54.2 |
| 3341 | 54.2 |
| 3130 | 40.6 |
| 3025 | 34.2 |
| 2967 | 31.9 |
| 2652 | 30.3 |
| 2536 | 38.75 |

TABLE 4

*Spectral sensitivity of silver and of silver–silver bromide electrodes*

| WAVE LENGTH | PHOTOPOTENTIAL OF SILVER–SILVER BROMIDE ELECTRODES IN 0.001 *M* KBr | PHOTOPOTENTIAL OF SILVER ELECTRODES IN 0.001 *M* KBr |
|---|---|---|
| *A.* | *millivolts* | *millivolts* |
| 6908 | 0.4 | 0.0 |
| 6234 | 0.1 | 0.0 |
| 5780 | 1.6 | 0.0 |
| 5461 | 2.8 | 0.1 |
| 4916 | 0.3 | 0.0 |
| 4358 | 3.6 | 0.5 |
| 4047 | 5.2 | 3.6 |
| 3650 | 5.5 | 4.2 |

Sanders and Kolthoff (VI-16) reported that silver bromide showed a photovoltaic effect even in the absence of all free metal. They found that the photovoltaic effect of pure silver bromide was always negative, in contradiction to prior work with metal–silver halide electrodes. Previously reported photopotentials of silver–silver halide electrodes were regarded to be complex functions of the effect, plus the oxidizing action of free halogen or hypohalite on the metal. According to Sanders and Kolthoff, the most probable mechanism for the photovoltaic effect at metal-free silver bromide is a photodecomposition resulting in the liberation of a free bromine atom and an electron. The electron may then react to produce silver atoms or take its place in the lattice, in either case playing no rôle in the potential change, since the system is non-metallic. The free bromine can diffuse into the solution and hydrolyze, giving hypobromite and bromide ions. These bromide ions give the silver bromide salt its negative potential. The fact that positive photopotentials are never observed is due to the absence of free metal which may be oxidized by the bromine or hypobromite.

The spectral sensitivities of silver–silver iodide electrodes, as determined by Athanasiu (IV-5), are given in table 3 and for silver–silver bromide electrodes, as determined by Clark and Garrett (IV-47), are given in table 4.

### *B. Copper oxide photovoltaic cells*

Hankel (I-19), in 1877, discovered that partially oxidized copper in water became negative on illumination. As the thickness of the oxide layer was increased, the potential became less negative and finally became strongly positive, blue and violet light producing the greatest effect. He showed that the effect was not a thermal one. Pellat (IV-108), in 1879, reported that a Daniell cell in which the copper plate was oxidized produced a lower potential, about 0.029 volt lower, when placed in sunlight but that if the positive plate were coated with an oxide by heating in a Bunsen flame, light increased the E.M.F. by making the anode more positive.

Gouy and Rigollot (IV-73), in 1888, found that a copper–copper oxide electrode in a solution of a metallic chloride, bromide, or iodide was very sensitive to light, even of low intensity. The cuprous oxide coating was more sensitive than cupric oxide. A positive potential of several hundredths of a volt was reported for illuminating copper–copper oxide plates in sodium chloride solution with diffuse sunlight and at least 0.1 volt with direct sunlight. Rigollot (IV-118) found the maximum in the sensitivity curve of copper–copper oxide electrodes in sodium chloride was at 5000 Å., in sodium bromide at 4850 Å., and in sodium iodide there was a broader maximum at about 5300 Å. The current was found to be proportional to the intensity of illumination except for intense illumination, where the curve flattened. Rigollot (IV-119) also found that the change in potential on illumination was eight times as large in 1 per cent potassium iodide as in 1 per cent sodium nitrate. In changing from a 0.5 per cent solution of potassium sulfate to a 10 per cent solution the sensitivity increased 300 per cent, but for sodium iodide it decreased 80 per cent. Rigollot (IV-115) noted an increased sensitivity when the copper–copper oxide electrodes were dyed with eosin, erythrosin, safranine, malachite green, and Soluble blue.

Goldmann and Brodsky (IV-72) studied oxidized copper electrodes in chlorides, bromides, sulfates, and nitrates of alkali and alkaline-earth metals. The "photoelectric characteristic" was independent of the concentration of sodium chloride in the range 0.05 $N$ to 1.0 $N$ and of the nature of the electrolyte for the above compounds. The photocurrent decreased on prolonged or repeated strong illumination. The ratio of the current to light intensity decreased with increasing intensity but remained about proportional to the intensity when the solution was stirred. The current increased when the temperature was increased.

Case (IV-44), using the cell

Cu | CuO | NaCl solution | Cu

obtained a current of 0.5 milliampere at 0.1 volt upon illuminating the oxidized electrode. Later (IV-45) he found that the cuprous oxide electrode in formic acid acted as an anode to produce a potential of 0.11 volt; upon continuous illumination the potential dropped nearly to zero, but on rotation of the electrodes so that they were alternately illuminated, a continuous alternating current was produced for 500 hr., without noticeable disintegration of the light-active material.

Case considered the cuprous oxide to be oxidized under the influence of the light to cupric oxide, which dissolves to form copper formate, this action continuing until the cuprous oxide is exhausted and the current goes to zero. On immersing polished copper in copper formate in the dark, a coating of cuprous oxide is formed. Reversing the plates gives the original condition, i.e., the cuprous oxide is oxidized to cupric oxide and the copper in contact with copper formate forms cuprous oxide.

Von Samsonow (IV-150) studied the action of depolarizers on oxidized copper electrodes immersed in sodium sulfate, bromate, iodate, and chlorate solutions. The depolarizers were ferrous sulfate and oxalate, glycine developer, *p*-aminophenol and sodium sulfide, sodium arsenite, and sodium phosphite. The potentials were higher in iodate and bromate than in sulfate and chlorate solutions.

Garrison (IV-65, 66), in an extensive study of cuprous oxide electrodes, obtained the following results:

(*1*) A cuprous oxide electrode which is positive on illumination may be changed to negative by increasing the density of the oxide coating.

(*2*) The current produced by the light flows in such a direction as to destroy the illuminated oxide film.

(*3*) An electrode having a negative effect on illumination in a neutral electrolyte may be made to have a positive effect by increasing the hydrogen-ion concentration, and *vice versa*.

(*4*) With electrodes having a negative light effect, increase in cupric-ion concentration reduces the negative effect but does not produce a positive effect.

(*5*) The initial maximum negative photopotential is approximately proportional to the intensity of the light for low intensities but beyond a certain intensity is constant. With increasing intensity the positive effect increases as the logarithm of the intensity.

(*6*) With electrodes showing both positive and negative effects, light of long wave lengths produces a negative effect, while light of short wave lengths produces a positive one.

(*7*) The conductivity of a suspension of cuprous oxide in pure water is not influenced by white light, but the conductivity of a suspension of copper coated with a thin layer of cuprous oxide is increased. This has been distinguished from a temperature effect and is explained by assuming cuprous oxide to be more soluble in light.

Garrison explained the photovoltaic effect on the basis of light increasing the solubility of cuprous oxide and shifting the equilibrium of the reaction:

$$Cu_2O \text{ (solid)} \overset{\text{light}}{\rightleftharpoons} Cu_2O \text{ (dissolved)} \rightleftharpoons 2Cu^+ + O^{--}$$

A positive photopotential results when the electrode potential is determined by the reaction

$$Cu^+ \rightleftharpoons Cu - e$$

and a negative potential results when the potential is determined by the reaction

$$2O^{--} \rightleftharpoons O_2 + 2e$$

Garrison concludes, "If we start with the assumption that light causes an increase in the solubility of cuprous oxide, then all the characteristics of the influence of light which have been found for these cells may be explained by the established laws of electrochemistry. The influence of the radiation in such cases is primarily the separation of the charged elements as ions followed by the establishment of an electrochemical equilibrium. In some instances the limit of solubility from an electrochemical standpoint is reached and a spontaneous discharge of ions takes place with the liberation of the elements."

Van Dijck (IV-144) studied cupric oxide electrodes in solutions of potassium nitrate, zinc nitrate, and sodium bromate with illumination of 4490–8500 Å. and found the "stopping potential" to be the same for all wave lengths. He concluded that the effect does not consist in the neutralization of positive ions in the liquid by electron ejection from the electrode, as had been proposed by Goldmann. Van Dijck later (IV-145) reaffirmed this conclusion and proposed that, under the action of light, cupric oxide is decomposed into copper and oxygen and that the copper reacts with the cupric oxide.

$$2CuO \overset{\text{light}}{\rightleftharpoons} 2Cu + O_2$$

$$Cu + CuO \rightleftharpoons Cu_2O$$

$$4Cu + O_2 \rightleftharpoons 2Cu_2O$$

$$2Cu_2O + O_2 \rightleftharpoons 4CuO$$

Tucker (IV-143) studied copper–cuprous oxide and platinum–cuprous oxide electrodes, using both gauze and sheet metals. He concluded that the cell solution, the nature of the metal, and "local cells" were the important factors. The "local cell" action was at a minimum for a thick or uniform layer of the light-sensitive substance and less for the sheet type than for the gauze. He found that in all reducing solutions, photochemical reduction of cuprous oxide to copper tends to take place, and in oxidizing solutions oxidation to cupric oxide tends to take place on the illuminated electrode, as postulated by Bancroft (IV-27).

Winther (IV-156; VII-29) explains the photoeffect of the cupric oxide electrode on the basis of copper acting as an oxygen electrode with an oxygen pressure far smaller than that at the surface of the oxide layer. On irradiation the cupric oxide becomes a conductor, the whole forming a concentration cell. Winther (IV-157) later added to the support of the effect as a "photoelectric conductivity" phenomenon by showing a proportional increase of conductivity of the oxide film with light intensity.

Lanyi and Theisz (IV-96) studied silver, copper, silver oxide, and cupric oxide electrodes in distilled water and in dilute solutions, both with and without foreign gases bubbled through the solutions and over the electrodes. The pure metals showed effects up to 1 millivolt, while the oxidized surfaces showed effects up to 200 millivolts. Hydrogen, nitrogen, and oxygen were without effect. Lanyi and Theisz explained the effect as due to a photochemical reaction between the electrode and solution which is reversible in the dark.

Karshulin (IV-88, 89) studied cupric oxide electrodes in sodium halide solutions and in water. With the latter there was little rise in potential; hence he concluded that there was no decomposition of the cupric oxide in light in the presence of water. The purely photoelectric interpretation was rejected, for the effect did not disappear with positively charged static electrodes. The effect was attributed to photochemical and autocatalytic processes.

Fink and Alpern (IV-59) were interested in the engineering development of photovoltaic cells and particularly for the cell

$$\mathrm{Cu} \mid \mathrm{Cu_2O} \mid \mathrm{Pb(NO_3)_2} \mid \mathrm{Pb}$$

They found a sensitivity of 150 microamperes per lumen, a maximum response at 4600 Å., and a linear relation between current and illumination for the range 0 to 100 lumens per square foot.

Fink and Fogle (IV-60) compared solid cells with liquid photovoltaic cells under varied conditions. Fink and Adler (IV-58) studied the cell

$$\mathrm{Cu} \mid \mathrm{Cu_2O} \mid 1 \text{ per cent } \mathrm{Pb(NO_3)_2} \text{ solution} \mid \mathrm{Pb}$$

under widely varying conditions and found three types of relation between the potential and the intensity of illumination. In the region of small intensities, below 10 lumens per square foot, the potential varies linearly with intensity; in the region of 10 to 100 lumens per square foot, the potential varies as the logarithm of the intensity, while at still higher values it approaches a saturation value. They explained this form of functional dependence by an application of the theory of absolute reaction rates.

Kato and Hayami (IV-90) determined the time effect of the photovoltaic effect and the change of weight of cupric oxide when exposed and unexposed. The decrease of the weight of cupric oxide on exposure was considered to be proof that the photovoltaic effect was due to a photochemical change, rather than to photoelectric emission. Hayami (IV-79) later studied the cells

$$\mathrm{Cu} \mid \mathrm{Cu_2O} \mid \mathrm{CuO} \mid 0.1\ N\ \mathrm{NaOH} \mid 3\ N\ \mathrm{NaOH} \mid 0.1\ N\ \mathrm{KCl},\ \mathrm{Hg_2Cl_2} \mid \mathrm{Hg}$$

and

$$\mathrm{Cu} \mid \mathrm{Cu_2O, CuO, 0.1}\ N\ \mathrm{NaOH, HgO} \mid \mathrm{Hg}$$

and attributed the effect to the photoreversible reaction:

$$2\mathrm{CuO} \underset{\text{dark}}{\overset{\text{light}}{\rightleftharpoons}} \mathrm{Cu_2O} + \tfrac{1}{2}\mathrm{O_2}$$

From thermodynamic calculations on the reaction system, the equilibrium constants in light and dark were in good agreement with experimental data.

Meserve (IV-100) studied the photovoltaic properties of the cell:

$$\mathrm{Cu} \mid \mathrm{Cu_2O} \mid \mathrm{Pb(NO_3)_2}\ (1\ \text{per cent}) \mid \mathrm{Cu_2O} \mid \mathrm{Cu}$$

and found that the spectral sensitivity with sinusoidally interrupted light of variable frequency checked with that of steady illumination. A similar cell, except that the electrodes were separated by a gel containing a conductive aqueous salt solution such as lead nitrate, was patented by Wilson (IV-154).

Kalita (IV-86) found that with a copper strip coated with a layer of cuprous oxide and exposed to light while being cathodically polarized in aqueous potassium chloride, the cuprous oxide layer decomposed with the separation of copper on the illuminated area. The course of the process was concluded to be:

$$\mathrm{Cu_2O} \rightarrow 2\mathrm{Cu} + \mathrm{O}$$

The rôle of the polarization depends on the removal of oxygen according to the equation:

$$\mathrm{O} + \mathrm{H_2O} + 2e \rightarrow 2\mathrm{OH^-}$$

Sheppard and Vanselow (IV-131), from their experiments with silver halide cells, suggested that the primary process of copper–cuprous oxide cells is analogous,—a transition from an internal photoelectric effect to an external one. However, the succeeding process is hindered by the rectifying layer between copper and cuprous oxide.

Athanasiu (IV-5, 8, 9, 10, 13), in his studies of copper–copper oxide cells, reported as follows: *(1)* The maximum sensitivity of cupric oxide is at 4046 Å. and the minimum at 3100 Å. (IV-5, 9). *(2)* The sensitivity of the electrodes in potassium chloride, sodium chloride, and sodium bromide diminishes in that order (IV-5). *(3)* The potential increases when the temperature decreases and *vice versa*, probably because opposing photochemical reactions are differently affected by a change of temperature (IV-8, 13). *(4)* The presence of cupric oxide in admixture with cuprous oxide displaces the maximum of the sensitivity curve toward the red and diminishes the potential produced by the light (IV-9). *(5)* The barrier-film hypothesis, as suggested to explain the behavior of the dry cuprous oxide cell, cannot give a general explanation of photovoltaic phenomena, especially where there is reason to suspect photochemical action with intervention of the electrolyte (IV-10). *(6)* The positive photovoltaic effect is increased by a decrease in pH and is decreased or reversed by increase of pH (IV-13). *(7)*

It is impossible to explain the photovoltaic effect on the basis of the photoelectric effect alone (IV-13).

Audubert (IV-15 to 23; V-1) has been one of the chief exponents of the theory of photolysis of water in the photovoltaic effect. Some of his results with copper–cuprous oxide electrodes are as follows:

(*1*) A polarization of inverse sign to that of the electrode increases the effect, while a polarization of the same sign decreases but never reverses it (IV-15, 16).

(*2*) Only very slight or no photopotentials are obtained under anhydrous conditions. Slight photopotentials are always obtained with solvents difficult to dehydrate and with porous electrodes. Studies were made of copper oxide cells in different solvents such as acetone, ether, ethyl alcohol, and methyl acetate, rendered conducting by sodium iodide. Light appears to displace the oxidation–reduction equilibrium by photolysis of water (IV-17, 21).

TABLE 5

*Spectral sensitivities of copper–copper oxide electrodes*

| WAVE LENGTH | PHOTOPOTENTIAL* | POTENTIAL/LIGHT INTENSITY† |
|---|---|---|
| *Å.* | *millivolts* | |
| 6908 | 15.0 | |
| 6234 | 2.0 | |
| 5780 | 20.0 | |
| 5461 | 30.0 | |
| 4916 | 7.5 | |
| 4386 | | 6.5 |
| 4367 | | 8.6 |
| 4359 | 24.0 | |
| 4348 | | 11.0 |
| 4324 | | 14.5 |
| 4301 | | 16.6 |
| 4282 | | 19.0 |
| 4258 | | 21.0 |
| 4236 | | 19.9 |
| 4216 | | 16.6 |
| 4197 | | 12.5 |
| 4047 | 41.4 | |
| 3650 | 41.2 | |

* Clark (I-14).

† Athanasiu (I-4).

(*3*) Photoconductance is not an essential factor in photovoltaic effects. The maximum photovoltaic effect for cuprous oxide is at 4000 Å., but the maximum photoconductance is at 5000 Å. Furthermore, the influence of variation of light intensity on the two effects is very different (IV-23).

(*4*) An increase in pH increases the negative photopotential and a decrease in pH increases the positive photopotential. Increasing the cation concentration decreases the photovoltaic effect (IV-18).

(*5*) The photovoltaic effect is attributed to the photolysis of water and the displacement of the resulting equilibrium by the photosensitive substance (IV-17, 18, 21, 22).

(*6*) A copper–cuprous oxide electrode shows a positive photopotential with a maximum at 4000 Å. in most electrolytes, particularly reducing agents, but a weak negative potential with a maximum at 6200Å. in an oxidizing medium. By choosing the proper electrolyte, photoelectrochemical effects can be dissociated from secondary electronic effects; under some conditions they may be superposed (IV-19).

(*7*) The potential of copper–cuprous oxide electrodes in solutions of copper sulfate depends on the equilibrium between the cupric and cuprous ions and on an oxidation–reduction process (IV-19, 20).

$$E = E_0 - \frac{RT}{2F} \log [\mathrm{Cu}^{++}]$$

Pastel (IV-107) studied copper–cuprous oxide electrodes in distilled water and in sodium chloride solution and concluded that water played an essential rôle; the hydroxyl ions were regarded as responsible for the reaction causing the potential. Theodoresco (IV-140) confirmed earlier reports that a negative polarization increased the positive potential of the copper–cuprous oxide electrode, while positive polarization decreased it. She concluded that the effect was due to a displacement of the oxidation–reduction equilibrium, probably by photolysis of water.

In recent years there have been some suggestions that the copper oxide photovoltaic cell closely resembles the dry "barrier-layer" type of cell. Barton (IV-28) has pointed out that the three photoeffects—change in resistance, change in potential, and photoelectric effect of cuprous oxide—begin at increasingly shorter wave lengths in the order mentioned, indicating that the least energy is required to excite electrons, a greater amount is necessary to remove an electron, and the greater the dielectric constant of the medium the less is the amount of energy needed to remove the electrons. Duhme (IV-49) concluded that the physical interpretation of the photoelectric effect in a rectifying layer in photovoltaic cells is supported by the behavior of cuprous oxide photoelectric cells. Waibel (IV-151) concluded that all the characteristics of barrier-film photocells occur also with cuprous oxide electrodes in a 5 per cent potassium chloride solution.

Müller and Spector (IV-105), in a study of copper–cuprous oxide electrodes in sodium chloride, potassium chloride, or a mixture of the two, found that the primary function of the electrolyte is to act as a conductor for the photoelectric current, although secondary chemical effects do arise. They suggested that a new avenue of approach to the solution of the photovoltaic problem has been opened by the advent of the barrier-layer cell of Lange (VII-18) and Schottky (VII-23). Griffith and Boucher (IV-74) found that upon irradiating with x-rays a "barrier-layer"-type cell of cuprous oxide and a liquid photovoltaic cell, using cuprous oxide electrodes in 0.34 $N$ sodium chloride, comparable currents were obtained.

Roulleau (IV-120, 121) noted a maximum at 3900 Å. and a second maximum at 4700–4800 Å., due to superposing the photoelectronic and photochemical effects upon illuminating a copper–cuprous oxide electrode with a blocking layer and immersed in an electrolyte. Their results point to the predominance of the photoelectrochemical explanation; the photoelectronic effect disappears if care is taken to clean the surface and so to remove the "barrier layer."

Miseliuk (IV-103) regarded the photovoltaic effect as a barrier-layer phenomenon associated with polarization of the surface. Fink and Fogle (IV-60) found that the wet type of cuprous oxide photovoltaic cells depended on electrolytic action for generation of a current, whereas the solid cuprous oxide cell converted luminous energy directly into electrical energy. Therefore, they concluded that the primary action of the solid type was distinctly different from that of the wet type.

### *C. Metal–metal sulfide photovoltaic cells*

Laur (VII-19) found in 1881 that in a cell of

$$Ag \mid Ag_2S \mid NaCl,\ CuSO_4\ \text{(solution)} \mid Hg \mid Pt$$

the silver sulfide became more positive on illumination. Bidwell (IV-41) reported that silver–silver sulfide electrodes were very sensitive to light, but that copper–copper sulfide electrodes were not. Chaperon and Mercadier (IV-46) noted an instantaneous effect on illuminating silver–silver sulfide electrodes in an electrolyte. Rigollot (IV-116) irradiated silver–silver sulfide electrodes in dilute salt solutions with infrared rays and found the illuminated plate always to be negative, an effect which he concluded could not be thermal.

Athanasiu (I-4; IV-8, 10, 11), in a study of silver–silver sulfide cells, reported (*1*) that the photovoltaic effect of silver electrodes thickly coated with silver sulfide is negative, (*2*) that the sign and magnitude of the effect can be changed by modifying the pH, and (*3*) that the photovoltaic potential increases when the temperature decreases.

Audubert (IV-22, 23) found the maximum photovoltaic effect of silver sulfide to be 10,000 Å. and the effect to be only slight or zero in non-aqueous electrolytes.

Athanasiu (IV-3, 4) found that the photopotential of mercuric sulfide was negative, with a maximum response at 4046 Å. Audubert and coworkers (IV-22, 26) reported that the cadmium sulfide electrode has a photopotential which was generally negative, and especially high in oxidizing solutions but the opposite in reducing solutions. The electrode showed maxima at 3900 Å. and at 5200 Å. with a minimum at 4100 Å. Audubert concluded that the effect was due to photolysis processes.

Fischer, Gudden, and Treu (IV-61), in 1937, found that various kinds of lead sulfide immersed in electrolytes and irradiated with light exhibited currents which were proportional to the light intensity and which were regarded to be photoelectric rather than thermionic. Schröppel (VII-24), in 1938, reported the quantum yield in photovoltaic cells of lead sulfide to be 0.03, and in those of silver sulfide to be 0.2, while antimony sulfide gave no reproducible results.

### *D. Miscellaneous types of coated-electrode cells*

Athanasiu (I-4; IV-3, 4, 8, 11) found that light increased the potential of

$$\text{Hg} \mid \text{Hg}_2\text{F}_2, \quad \text{Hg} \mid \text{Hg}_2\text{Cl}_2, \quad \text{Hg} \mid \text{Hg}_2\text{Br}_2, \quad \text{and Hg} \mid \text{Hg}_2\text{I}_2$$

increasing in the order named. The maximum sensitivities for the chloride, bromide, and iodide were at 2536, 2967, and 4046 Å., respectively. The effects of change of pH and temperature were similar to those discussed for other electrodes. Audubert (IV-17) found only a slight effect or no effect for mercurous and cuprous iodides in non-aqueous electrolytes. Rao (IV-113) studied the photovoltaic properties of eleven phototropic mercury compounds and found that short wave lengths produced the maximum potential. Dyeing electrodes with erythrosin increased the potential and shifted the maximum towards the red. The photovoltaic effects of cuprous chloride, fluoride, and iodide have been studied by Audubert and Lebrun (IV-20, 22). Copper iodide in copper sulfate, nitrate, and chloride was studied by Quentin (IV-112), who found that the effect depended on the action of light on the liquid as well as on the electrode.

TABLE 6

*Spectral sensitivities*

| WAVE LENGTH | PHOTOPOTENTIALS* METAL–METAL HALIDE | | | POTENTIAL/LIGHT INTENSITY METAL–METAL SULFIDE | |
|---|---|---|---|---|---|
| Å. | Mercurous iodide | Mercurous bromide | Mercurous chloride | Mercuric sulfide* | Cadmium sulfide† |
| 7000 | | | | | 7.0 |
| 6000 | | | | | 30.0 |
| 5460 | 0 | 0 | | 0.5 | |
| 5200 | | | | | 48.0 |
| 5000 | | | | | 40.0 |
| 4916 | 20.0 | 0 | | | |
| 4358 | 35.0 | 0 | | 3.1 | |
| 4046 | 39.2 | 4.9 | | 3.8 | |
| 4000 | | | | | 25.0 |
| 3660 | 35.0 | 8.1 | 0 | 3.3 | |
| 3130 | 30.1 | 42.0 | 1.7 | 2.9 | |
| 3025 | 25.4 | 44.9 | | | |
| 2967 | | 50.5 | 7.8 | | |
| 2652 | 32.9 | 44.1 | 27.2 | | |
| 2536 | 28.0 | 35.0 | 38.5 | | |

* Athanasiu (IV-4).

† Audubert and Stora (IV-26).

The photovoltaic effect of an aluminum–selenium electrode in enanthol was noted in 1895 by Minchin (IV-102); the cell was most sensitive in the yellow region. Swinton (VII-26) noted that an illuminated copper–selenium electrode in tap water became negatively charged. Audubert and Roulleau (IV-24, 25) discovered that the photovoltaic effect of platinum–selenium electrodes was positive, of the same order of magnitude in non-aqueous as in aqueous solutions and less in a reducing solution than in an oxidizing medium. They considered the mechanism to be photoelectric and not photoelectrochemical.

Coehn and Mykolajewycz (IV-48) explained the photoeffect of bismuth oxide electrodes in terms of reduction of $Bi_2O_4$ to $Bi_2O_3$ under the influence of light.

Grube and Baumeister (VII-16) found that platinum–platinum oxide in sulfuric acid showed a decrease in potential on exposure to light. The influence of x-rays was similar to that of light.

Pougnet and coworkers (IV-110), in 1913, noted that the potential of a Weston cell in a quartz vessel decreased from 1.0252 to 1.0192 volts when illuminated with a mercury-vapor lamp. The slowness of recovery, about 40 min., indicated a chemical rather than a physical effect.

Young and Pingree (I-34), in 1913, attributed the change in rate of migration of colloidal arsenic sulfide under the influence of light to a direct effect on the static charge carried by the suspended particles, primarily a photoelectric effect.

After the report of Winther (IV-155) on the photovoltaic effect of zinc oxide, Burgin (IV-43) studied the effect with zinc oxide suspensions in water with and without cathodic depolarizers (dyes or metallic salts) or anodic depolarizers (glucose, glycerol, or benzidine), and with and without both. The formation of zinc peroxide was postulated to account for the alteration of the sign of the photopotentials in the dark (after exposure to light). Baur's theory (VI-6, 7, 8) of sensitized photolysis was supported.

Hoja (IV-81) found that an aqueous suspension of pure zinc oxide freed from adsorbed water did not show a photovoltaic effect (in contrast to the results of Burgin (IV-43)); the presence of a small amount of hydrated zinc oxide produced the effect. If it is assumed that the hydrated compound acts as a cathodic depolarizer, the results agree with the theory of Baur (VI-8). Hoja (IV-82) found that the photoelectric sensitivity of a platinum electrode in an aqueous zinc oxide suspension depended on the liquid phase and also on the previous history of the platinum.

### *Summary on photovoltaic cells of Type IV*

Results of investigations in this field seem to indicate that the thermal potential is small and often of the opposite sign to that of the over-all potential. The results are inconclusive, but the primary effect seems to be the photochemical alteration of the electrode coating which may result in a positive or negative effect, depending upon the nature of the electrolyte ions present.

## IX. PHOTOVOLTAIC CELLS OF TYPE V: METAL ELECTRODES COATED WITH A DYE AND IMMERSED IN SOLUTIONS OF ELECTROLYTES

Moser (IV-104), in 1888, discovered that the photopotentials produced by sunlight on electrodes of silver chloride, bromide, or iodide was considerably increased by immersing the electrodes in a bath of a dye such as erythrosin. Rigollot (IV-115) studied undyed and dyed copper–cuprous oxide electrodes, using eosin, erythrosin, safranine, malachite green, Crystal green, and Soluble blue. He found a severalfold increase in the photocurrent for the dyed electrodes; the most effective light was that within the band of maximum absorption of the dye.

Stora (V-6 to 15) has made an extensive study of the photovoltaic effect produced by metal electrodes covered with many different dye films and immersed in aqueous solutions of inorganic salts. She reported the following conclusions:

(*1*) The potential is independent of the metal (V-6).

(*2*) Most photopotentials are negative except for fluorescent dyes (V-8).

(*3*) Most photopotentials are due to a reduction for which the chromophore group is responsible (V-8).

(*4*) The auxochrome group has no effect (V-8).

(*5*) There is a positive effect in the neighborhood of the absorption bands, which is probably due to a shift in the oxidation–reduction equilibrium (V-6).

(*6*) The sensitivity curve is similar to the light-absorption curve of the absorbed dye but with a lag of 100–1500 Å., which increases with the concentration. This is interpreted as an indication that only the portion of the dye in immediate contact with the electrode is photosensitive and the rest of the dye molecule merely acts as an absorbent screen (V-7).

(*7*) There is a definite relation between the photopotential and the proportion of dye reduced in the dyed layer (V-9).

(*8*) A platinum electrode with an adsorbed photosensitive dye behaves toward a reducer as an inert electrode in an oxidation–reduction medium (V-9, 14).

(*9*) The negative photopotential of dyed platinum electrodes is diminished by bubbling oxygen through the solution, is inverted by nitrogen, and becomes strongly positive with hydrogen (V-10).

(*10*) Photoelectric effect and photochemical sensitiveness both result from oxidation and reduction dependent on the chemical constitution of the dye and on the nature of the solvent (V-12). The Becquerel effect is the resultant of the positive effect due to the oxidizability of the reduced form and the negative effect to the reduceability of the oxidized form (V-14).

(*11*) The photopotentials of xanthane dyes are markedly reduced by hyposulfites, phenols, amines, and titanous chloride (V-11).

(*12*) The rules regarding the effect of pH on the photoeffect of electrodes coated with a metallic salt do not apply to dyed electrodes (V-13).

(*13*) For metal electrodes, such as copper, covered first with the oxide and then dyed, the potential of the metallic compound is superimposed on the potential due to the presence of the dye (V-6).

(*14*) An increase of temperature decreases the positive photovoltaic effect and increases the negative effect (V-15).

Schlivitch (V-5) reported that the electrodes in the cell

$$\mathrm{Cu} \mid \mathrm{CuSO_4(aq.)} \mid \mathrm{Cu}$$

became sensitized because of the presence of a dye such as methylene blue, but he attributed the sensitivity to the oxidation of the copper which is effected more rapidly in the presence of the dye. He reported that zinc electrodes are sensitized only to a very small extent by methylene blue.

Nga (V-3, 4) studied dyed platinum and copper electrodes and attributed the photovoltaic effect to a displacement of the oxidation–reduction equilibrium following photolysis of water. She found no effect on illuminating colored electrodes in glycerol containing dissolved potassium iodide of various concentrations, but the effect appeared upon the addition of water.

Sheppard and coworkers (IV-134, 135) have studied dye-sensitized silver–silver halide electrodes. Their experiments indicated the release of photoconductance electrons, either by the adsorbed dye itself or by the halide ions receiving energy from the photoactivated dye. Light which was absorbed by the adsorbed dye, but not by the silver halide itself, produced relatively large photocurrents. The adsorbed dye acted also as a halogen acceptor, diminishing the positive effect.

Kameyama and Hukumoto (V-2) studied the photoconductance of dye-sensitized silver bromide and concluded that, in the region sensitized by the dye, the electron was set free or raised to the conduction band by the energy of light absorbed by the dye adsorbed on the silver bromide.

### *Summary on photovoltaic cells of Type V*

Results of investigators seem to indicate that for metal electrodes coated with a dye the main effect is caused by photochemical alteration of the dye. This alteration may result in a shift of the oxidation–reduction equilibrium or may actually emit an electron from the dye or from the sensitive layer. The sensitivity curve is similar to the light-absorption curve of the adsorbed dye, but is slightly modified by the thermal effect and by the effect of the metal electrode itself.

## X. SUMMARY

The results of this study have presented a number of ideas with reference to the mechanism involved in the production of photopotentials in the "wet"-type of photovoltaic cells. Among these are the "local-cell" theory of Tucker, the "increased-solubility" theory of Garrison, the "photolysis" theory of Audubert, the "photoelectric" theory of Goldmann and others, the "activated-molecule" theory of Dufford, the "ion-adsorption" theory of Fajans, and the "photochemical" theory of numerous investigators.

The work of Sheppard, Vanselow, and Trivelli reveals in an interesting manner a probable cause of both the negative (inertialess movement of an electron) and the positive (slower movement of an ion or an atom) responses which so often characterize the coated-electrode type of photovoltaic cells.

Several attempts have been made to account for the photovoltaic potentials more or less quantitatively. Baur (VI-6, 7, 8; III-1, 2) developed theoretical formulas covering photolyses in different conditions of inhibition, autocatalysis, etc., on the basis of his theory of photosensitization, in which the catalyzer is assumed to act as an oxidizing and reducing agent. Bancroft (VI-2 to 5) has summarized the photophenomena in terms of the principles of the electrochemistry of light. Russell (II-39) derived an equation for the variation of the photopotential with time, using the photochemical modification theory and the effect of diffusion on the potential developed. Adler (VI-1) has applied Kimball's (VI-11) treatment of the theory of absolute reaction rates to the positive primary photopotential. Magee and Eyring (VI-13) have also used the theory of absolute reaction rates to calculate the measured potential at an electrode displaced from equilibrium by a photochemical reaction; they have compared their results with experimental results for the photovoltaic effect. Lange (VIII-4) presents evidence to prove that the observed photovoltaic effect is the same fundamental photoelectric process that is present in the crystal photoeffect and the barrier-layer photoeffect. He groups these three phenomena together as "semiconductor photoeffects". Lange's idea of the similarity in these three phenomena is illustrated by means of figures 4 and 5. In figure 4 he illustrates the "front-wall" and "back-wall" cells; the difference depends upon the position of the insulating layer. He calls attention to the fact that it is not essential that the front translucent electrode be a metal; it can also be a conducting liquid or an electrolyte. This leads him to a schematic diagram (figure 5) of a cell in which a liquid is present,—he names it an "electrolytic semiconductor photocell" (Becquerel cell).

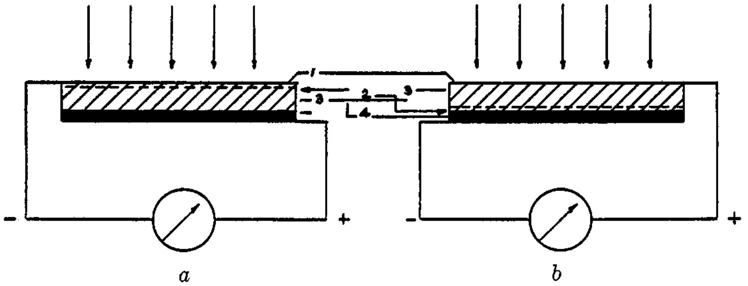


FIG. 4. Illustration of (*a*) front-wall and (*b*) back-wall cells. 1, translucent electrode; 2, insulating layer (barrier layer); 3, semiconductor; 4, supporting electrode.

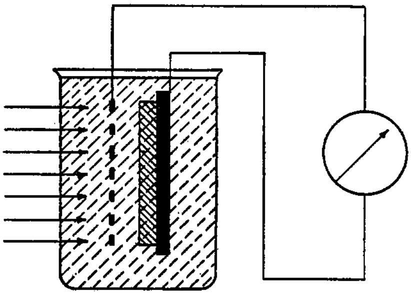


FIG. 5. Schematic diagram of a cell in which a liquid is present (Becquerel cell)

An interesting sidelight is thrown onto this topic by Lifschitz (II-22), who suggests that we refer to the "photovoltaic effect" only when it appears impossible to formulate the chemical reaction for a difference of potential caused by light. Baur (VI-8) suggests that the Becquerel effect is the symptom of a hidden photochemical change in a material system.

In general, the evidence to date seems to be sufficient to warrant the following conclusions: Certain cells seem to be very sensitive to small temperature variations; irradiation may produce sufficient heat effect to account for at least a part of the potential observed. For pure metals in inert electrolytes the photopotential may be primarily photoelectric, but these potentials are usually quite small. For metal electrodes in light-sensitive solutions the effect is primarily due to the photochemical alteration of the electrolyte. For coated electrodes the effect may be a combined photoelectric–photochemical process taking place in the coating material. The possibility of photolysis of water is not ruled out but requires more supporting evidence. It seems very likely that the observed photovoltaic effect is probably the resultant of several of these effects and that that effect which predominates depends upon the type of electrode–electrolyte system under investigation. Better data are now needed to identify and measure the separate effects.

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