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PHOTOELEMENTS
and Their Application

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Translator's Preface

This book should be of interest to the layman, thinking of the possible use of photoelectric devices for his own purposes, as well as to the engineer or scientist, thinking of new uses and new devices. Hence in several instances an everyday word familiar to the layman has been preferred to the more precise technical term, and occasionally the author's thought rather than his mode of expression has been translated.

The original illustrations have been used for the most part, hence in some cases the reference letters differ from our customary usage. Since all are defined in the text or the captions they should cause no difficulties. A few illustrations have been redrawn, and a new index has been prepared.

The translation was reviewed by E. F. Kingsbury, of Bell Telephone Laboratories, who suggested several improvements in terminology and a few in phraseology which have been incorporated in the text. Some comments on units have been included as footnotes with his initials. This painstaking attention is greatly appreciated by the translator and by the publisher.

ANCEL ST. JOHN.

New York, 1937.

Preface

When three years ago the publisher approached me about writing a book concerning barrier layer photocells, a digest of the few original works in this new domain was thought of. But in the meantime nearly every number of the technical journals has brought further articles about this new photoeffect, and not only Science but also Engineering were interested in it. The scope of the photoelements already exceeded that of alkali photocells and selenium resistances. Thus the need increased for a digest of our present knowledge, and lack of knowledge, the more so as, during the increase in experimental material, clarity and simplicity in presentation threatened to be lost. Barrier-layer photoeffect, crystal photoeffect and Becquerel effect were treated as distinct photoeffects in addition to the internal and external photoeffects and were explained by different theories.

In the following treatment a presentation will be sought which groups these phases, differing only in externals, as semiconductor photoeffects, and traces the phenomena back to the internal photoeffect, with the difference only that in the semiconductor photoeffect an external potential is set up through a concentration gradient of electrons, the magnitude of which is obtained from the electron diffusion theory here presented.

I have sought, in connection with the theoretical treatment, to present the physical properties of the photoelements as completely as possible and to describe the methods of measurement exhaustively, so that those even slightly acquainted with this domain can carry on by themselves the measurements of interest to them. In a later chapter

the historical development of the photoelements will be discussed, with citations of the original works.

The proposition that the Physics of today is the Engineering of tomorrow, is only in a few cases demonstrated with so few exceptions as by the phenomena of photoelectricity. This was already valid for the alkali photocells, but it proved correct in still higher measure for the photoelements. Plant scale working technique has been developed successfully from laboratory scale experiments in only a few years. In the second part of this book the numerous applications of the photoelements will be described in the most elementary way possible, so that the engineer, machinist, doctor or other person who may be interested can evolve a practical use.

A substantial supplement was made from some hitherto unpublished articles and further contributions which other professional colleagues have graciously placed at my disposal. If in certain places I have discussed a particular work in detail, this happens only because it seemed to me the more natural arrangement in theory and practice. Even if I have stressed personal opinions at the risk of being refuted, the presentation seems thus to be simpler, more forcible and more interesting. If my point of view toward the problems should give rise to investigations which will better explain the phenomena concerned then I will consider that also as a gain on my part.

I thank the publisher for his sympathetic patience at the before mentioned delay in completion of the book and for his great cooperation in the enlargement.

B. LANGE.

Berlin-Dahlem, September, 1935.

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PART I

DEVELOPMENT AND PHYSICAL PROPERTIES

Introduction

An Historical Comparison

Galvanic Elements and Photoelements

The heroic age of electrical research began with the discovery of the galvanic elements. Next the idea of the electric current became clear, then followed all the great events. With the help of the galvanic elements Oersted discovered the connection of the magnetic field with the electric current, Michael Faraday in 1832 discovered the law of induction, and Georg Simon Ohm laid the foundation of our present system of electrical measurements with the fundamental quantities, electric current and electric potential.

Today chemical sources of current are still indispensable aids of Electrical Engineering. Besides the galvanic elements, the thermoelements discovered by Theobald Seebeck in 1822 have become important for all sorts of measurements of temperature and radiation. The subject matter of this book is another kind of electrical element in which the current is produced by neither chemical processes nor heat, but by light. As this is also a question of spontaneous sources of current, we will designate this sort of photocell as photoelements, using a similar word construction as for galvanic elements and thermoelements. We hope that their significance for Science and Engineering will be just as great as that of the galvanic elements.

Almost 100 years ago E. Becquerel [1] in 1839 made the discovery that two metal electrodes immersed in an electrolyte showed a difference of potential upon illumination of one of the electrodes. Although the photoelectric char-

acter of this process was not made clear until much later, we must mark 1839 as the birth-year of the electrolytic photoelements. The appearance of an electromotive force upon the illumination of various crystals was first observed at the beginning of this century, and only during the last five years has the technical development of selenium and cuprous oxide photocells of lamellar form been successful. Different as are Becquerel, crystal and barrier-layer photocells outwardly, still the same primary photoeffect and the same spontaneous production of an EMF when illuminated underlies them. Therefore we designate these three externally different photoelectric systems as "Photoelements," and in the course of the further elaboration will have repeated occasion to draw a parallel between the mechanisms of current and potential production in galvanic elements and in photoelements.

It is always interesting to realize in what direction a newly discovered physical phenomenon develops and which of its special properties finds a technical use. It often happens that a side branch which seems not at all the essential part of the new physical process will be developed first, and the particular fundamental process only very much later. We find parallelism between Galvani's discovery and Becquerel's even in this respect.

Let us recall briefly the basic experiment which Aloysius Galvani carried on in the year 1791. Galvani produced sparks from an electrostatic machine in a spark-gap with two antenna-like brass rods. At some distance from these were two other antenna-like brass rods, between which a frog's legs were suspended. At every spark the frog's legs contracted very noticeably. That was undoubtedly the basic experiment of wireless telegraphy, the transference of mechanical signs by means of electric waves. Nothing was lacking. Galvani also established the effect of atmospheric disturbances by a similar receiver. He led his antenna from the roof of the house to a spring and observed a twitch of the frog's legs at every distant lightning flash. At this the inven-

tion of the electric telegraph might have begun with its wireless form. But the historical development ran otherwise. Galvani's experiments led to the development of chemical sources of current, the elements. Similarly Becquerel's discovery by no means led directly to the development of dry photoelements, of crystal and barrier-layer photocells. Rather, the discovery of the external photoeffect by W. Hallwachs followed in 1887 and led to the development of alkali photocells.

Looking backward it seems to us almost incomprehensible why the crystal photoeffect in lead sulfide, molybdenite, cuprite and numerous other crystals which nature offers us in abundance, was not discovered first. For an alkali photocell is an extremely complicated technical structure and requires considerable skill in glass-blowing and evacuation. Only in recent times has the essential sameness of the Becquerel effect, the crystal photoeffect and the so-called barrier layer photoeffect been generally recognized. But as in a physical treatise it is a question of essentials, and not of the externals of the varying modes of performance, it seems to us legitimate to designate Becquerel as the discoverer of the photoelements.

The Basic Photoelectric Phenomena

Although we have learned that, considered historically, photoelectricity at first took place in electrolytic elements, it is more lucid to study first the external photoelectric effect, as in the electrolytic cells secondary actions greatly obscure the picture of the primary photoeffect.

The External Photoeffect and Alkali Photocells

When Wilhelm Hallwachs[2] discovered the external photoeffect in 1888, neither the discoverer himself nor scien-

tists interested in it anticipated that it would present to research, applied and technical physics an aid of extraordinarily versatile usefulness. As early as the beginning of this century technical applications of the new effect were proposed. But they were all wrecked by the very small photoelectric current, and partly by the difficulty of constructing constant photoelectric cells. Boundless scientific labors and untiring research were necessary to study the characteristics of this effect and to learn all the factors upon which the photoelectric effect and the behavior of photoelectric cells depend. Foundations must first be laid and experience gained, with the help of which it would be possible on the one hand to increase the electron yield, and on the other to construct an unobjectionable and stable cell. When this was successful the photoelectric cell in combination with an amplifying tube found a variety of uses as a technical tool. Thus it is to be explained that the triumphal progress of the photoelectric cell combined with the amplifying tube began only during this century.

The impulse for the discovery of the external photoelectric effect was given by the classical experiment of Heinrich Hertz.[3] During investigations on the resonance of electrical oscillations he observed that the sparking distance of the discharge in a spark-gap was influenced by ultraviolet light. Moreover, Hallwachs found a remark of A. Schuster[4] "that even the smallest electromotive force in a gas can produce a current." These two suggestions led to the first classical "Basic experiment of photoelectric discharge." If a negatively charged metal plate, Figure 1, which is connected to an electroscope is illuminated with the light of an arc lamp the electroscope leaves collapse, that is, the metal plate loses electrons under the influence of the illumination, whereas a positive charge on the metal plate, on the other hand, is not affected by irradiation. Elster and Geitel[5] made a further remarkable step in the development through the use of alkali metals in an evacuated glass bulb, Figure 2. If the alkali layer is connected to the negative pole of a battery

and the wire net with the positive pole an electron current flows from the photocathode to the anode upon irradiation of the alkali metal. When the influence of the wave-length of the light is investigated it is shown that the long-wave infrared and red portion of the spectrum is inactive for most of the metals, and that the photoeffect begins only at a par-

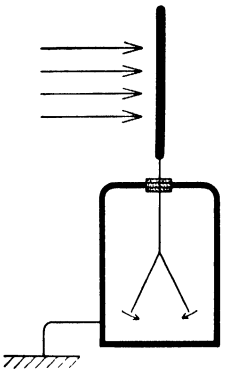


FIGURE 1.—Basic Experiment on the External Photoelectric Effect

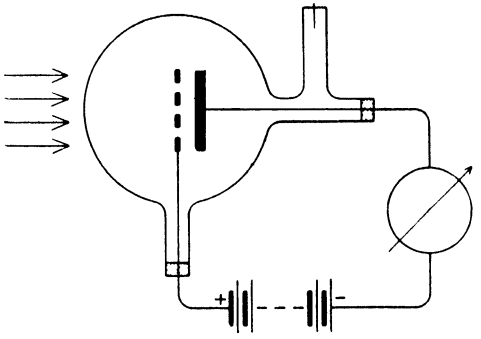


FIGURE 2.—Diagram of the Alkali Photocell.

ticular wave-length, the so-called threshold wave-length, and increases toward the short-wave region of the spectrum. In the case of caesium, the heaviest alkali metal, the threshold wave-length lies in the infrared at about 1000 mμ, and in the case of lithium, the lightest alkali metal, it is moved

over into the green region of the spectrum, whereas for the heavy metals the threshold lies in the ultraviolet. The alkali metals owe their technical significance to the property of being sensitive within the visible spectrum.

The external photoeffect, accordingly, consists of an electron emission from the outer surface under the influence of radiation. It is present not only in metals, but also in all solid, liquid and gaseous substances, but the threshold wavelengths for these materials lie in the very short-wave ultraviolet region accessible only with difficulty, and in the case of gases are displaced to still higher frequencies so that an electron emission occurs only through x-ray or cosmic radiation.

To complete our discussion of the external photoeffect, we will mention briefly its freedom from time lag, and the linear ratio of the photocurrent to the intensity of the incident light, two properties which were decisive for the use of the alkali cells for sound films and television.

The Internal Photoeffect. Photoelements and Photoresistances

While in the external photoeffect the photoelectrically liberated electrons escape through the surface of the material, the internal photoeffect, as the name indicates, is concerned with a process in the interior of an irradiated substance. We will describe this effect also by a basic experiment. A cuprite (Cu_2O) crystal is clamped between two electrode plates, Figure 3, and the electrodes are connected to a battery through a sensitive galvanometer. In the dark the crystal is almost an insulator, so that no current flows. As soon, however, as the crystal is illuminated, a current flows, which possesses all the characteristic properties of an electron stream, starts without lag, and increases linearly with the illumination.

The selenium resistance cells already discovered in 1873 by Willoughby Smith [6] depend upon this photoelectric alter-

ation of conductivity. But here the lagless primary photoelectric effect was masked by the sluggish secondary effect of ionic conduction.

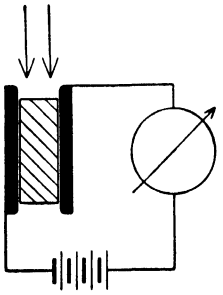


FIGURE 3.—Basic Experiment on the Internal Photoelectric Effect. Illumination perpendicular to the electric field (Transverse illumination).

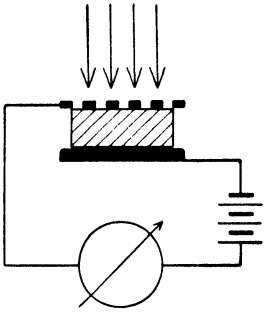
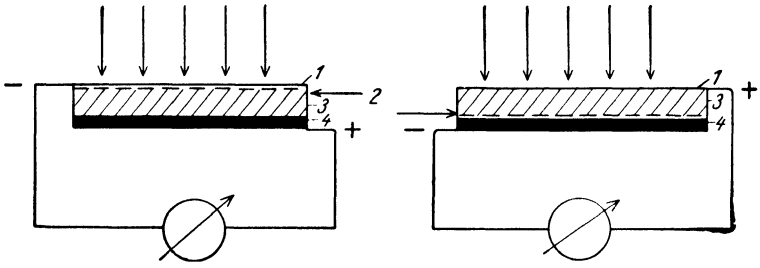


FIGURE 4.—Basic Experiment on the Internal Photoelectric Effect. Illumination parallel to the electric field (Longitudinal illumination).

In the basic experiment illustrated in Figure 3 the illumination takes place perpendicular to the direction of the current (transverse illumination). In Figure 4 we have shown the same experiment in a somewhat modified form so that the illumination of the crystal takes place through the translucent front electrode. In the case of this longitudinal illumination we also observe a current upon irradiation, and, what is noteworthy, under suitable conditions even without external exciting potential. These phenomena, observed in 1901 for lead sulfide and other minerals by J. C. Bose and later on investigated thoroughly for various semiconducting crystals, were recently detected also for cuprite by H. Dember and called the crystal photoeffect. This effect of the development of a spontaneous EMF under the influence of radiation is shown not only by single well-formed crystals, but also by crystalline layers. Thus we come to the lamellar semiconductor photocells (barrier layer photocells), with which

we will be chiefly occupied. The layout of these semiconductor cells is shown in Figure 5, in which we indicate a high resistance layer, the barrier layer or insulating layer, between the semiconductor and one electrode, which is of special importance for the production of the photo-EMF. According as this insulating layer is placed toward the front or



a. Frontwall cell b. Backwall cell

FIGURE 5.—Diagram of the Semiconductor Photocell.

1. Translucent electrode
2. Insulating layer (barrier layer)
3. Semi-conductor
4. Supporting electrode

toward the back, we distinguish between "Vorderwand" or "frontwall" cells and "Hinterwand" or "backwall" cells.

In the form of semiconductor photocell illustrated in Figure 5 it is not absolutely necessary that the front translucent electrode be a metal, it can also be made of a conducting liquid, an electrolyte. We come then to the third basic type of the photoelements, the Becquerel cell shown in Figure 6, with which the discovery of the photoelements began.

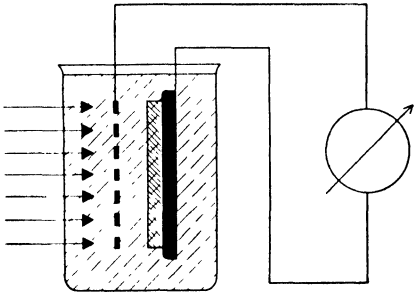


FIGURE 6. — Electrolytic Semiconductor Photocell (Becquerel Cell).

It will be the purpose of this book to present proof that the same fundamental photoelectric process underlies the Becquerel effect, the crystal photoeffect, and the barrier-layer photoeffect. We group these three phenomena, differing only outwardly, together as "semiconductor photoeffects" and designate the various photocells depending thereon as "photoelements," so as to emphasize thus their characteristic property of acting as spontaneous sources of current.

We thus exclude alkali cells, that is, photocathodes, depending upon the external photoeffect, and photoresistances, depending upon photoelectric changes in resistance. We have made this demarcation not only in the mode of expression but also in the content, since very many productions concerning alkali and selenium-resistance cells are already published.

Chapter 1

Historical Development of the Photoelements

Electrolytic Photoelements

In the year 1839 E. Becquerel [1] discovered that when one of two electrodes immersed in an electrolyte is illuminated changes of potential appear. Such a potential change appears when a metal electrode is in a solution of its salts. But where these changes amount to only a few millivolts, those of several hundred millivolts are obtainable when brominated, iodated, oxidized or sulfided electrodes are used. Addition of organic or inorganic dyestuffs increases the sensitivity.

The explanation of the Becquerel effect was originally purely chemical. A. Goldmann and J. Brodsky [7] were the first to give a photoelectric interpretation. They concluded from measurements on oxidized copper in various solutions that the source of the current is the oxide layer itself, not perhaps, a reciprocal action between electrode and electrolyte. A. Garrison [8] and C. W. Tucker [9] considered the phenomenon photochemical for cuprous oxide and silver halides. If the photosensitive substance is oxidizable it becomes the cathode. If the photosensitive substance is photochemicaly reducible and is placed in a reducing solution it becomes the anode. According to I. Liftschitz [10] there are two kinds of Becquerel effect. The effect of the first kind arises from the electrons in the contact surface between electrode and electrolyte, and an effect of the second kind or volume effect results from the photochemical process in the electrolyte itself.

R. Sabine [11] described in 1878 an electrolytic selenium cell with a platinum wire covered by a thin layer of selenium opposite a platinum electrode in distilled water. In the dark the selenium electrode showed a positive potential of 0.1 volt toward the platinum electrode, that dropped about 0.15 volt when illuminated. Unfortunately the photoelectric change of potential proved to be variable, so that a practical application of this cell to measurement of light did not result. G. M. Minchin [12] obtained more favorable results with a cell devised by him in 1893. His cell consisted of a small glass bulb of the form shown in Figure 7. A small glass tube

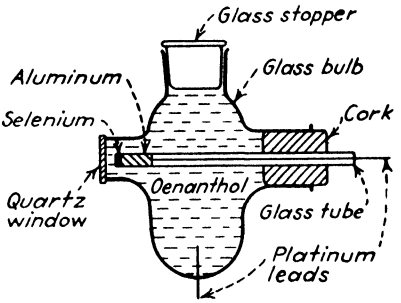


FIGURE 7.—Electrolytic Selenium Cell of Minchin.

projects into this from one side through a cork, carrying an aluminum wire with some selenium on its front surface. The selenium is illuminated through a small quartz window which lies close before it. The glass bulb is filled with acetone, methyl alcohol, or preferably oenanthol and closed with a glass stopper. Two platinum wires serve for connection of the lead wires, one dipping into the fluid through the glass bulb, the other attached to the aluminum wire. The seat of the EMF is the surface of the selenium, which becomes positive when illuminated. Through test of such a cell on the spectrum of a calcium light Minchin showed that it is sensitive for all radiation from the infrared to the ultraviolet. It produces the greatest EMF in the yellow, which, however, does not decrease greatly up to the violet. The EMF increases

as the square of the light intensity. Minchin recommended this cell for astronomical measurements, for which it is mounted directly on the telescope.

In recent years electrolytic cuprous oxide cells have found considerable technical use. The "Rayfoto" consists of an oxidized copper plate in an electrolyte of lead nitrate with a lead anode. A still wider use has been secured, especially in America, by the Arcturus Photolytic cell, Figure 8, which

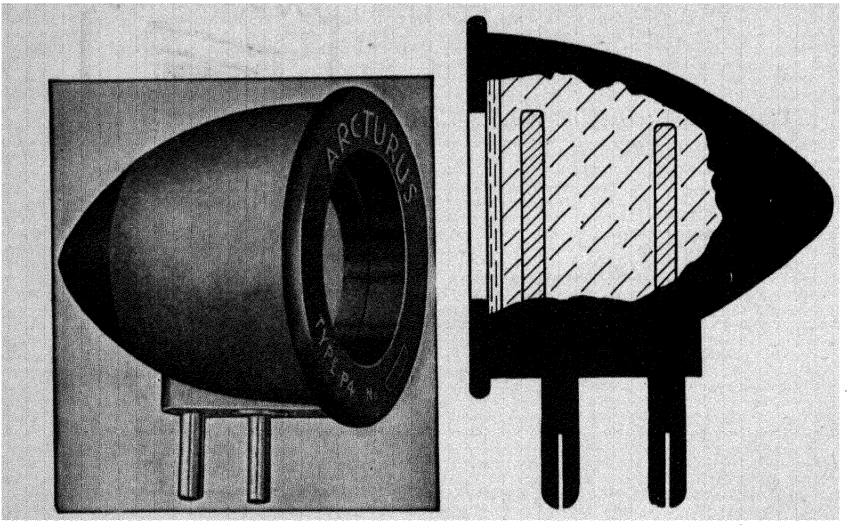


FIGURE 8.—American Arcturus Photolytic Cell.
(Electrolytic Cuprous Oxide Cell).

differs from the "Rayfoto" in that the lead anode is replaced by a second cuprous oxide electrode, so that the annoying dark potential of the cell drops from 0.5 volt to below 0.1 volt. Efforts were made to replace the fluid electrolyte of this cell, which became cloudy through products of precipitation, by a solid electrolyte, and were successful through the use of gelatine or agar-agar. The use of a moist sodium chloride crystal as a solid electrolyte, as shown in Figure 9, is also interesting.

The physical data of the electrolytic cell will be discussed in the next chapter. Here we will be content with the remark that these cells have been displaced almost entirely by semiconductor photocells, barrier layer photocells, with which we at present occupy ourselves.

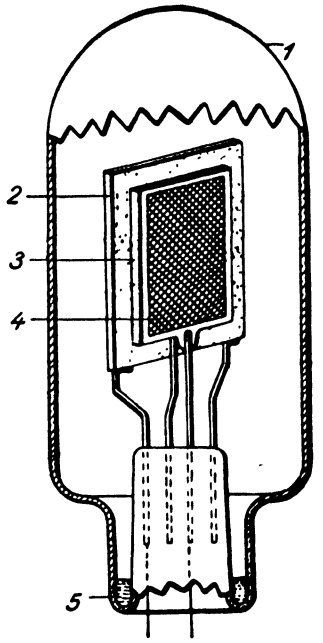


FIGURE 9.—Electrolytic Arcturus Cell with Solid Electrolyte.

1. Glass bulb
2. Cuprous oxide plate
3. Rock salt crystal
4. Wire electrode
5. Saturated sodium chloride solution

Semiconductor Photocells (Barrier Layer Cells)

The development of these cells originated from an observation about the appearance of a spontaneous EMF upon the illumination of a selenium rod, concerning which Adams and Day [13] reported in 1877, only three years after the discovery of the light sensitivity of selenium. Their work was carried on for the purpose of investigating accurately the unipolar conductivity of selenium, upon which they had already reported the previous year, and to clear up the question whether light was able to produce an electric current in

selenium. For this investigation they used a round bar of amorphous selenium one inch long and ¼ inch thick with annular electrodes of platinum wire at each end, which had been pressed into the heated bar. This selenium bar was heated to about 200° C. in an iron bulb filled with sand, and thus enclosed was cooled slowly so that the amorphous selenium was converted into the light sensitive crystalline modification. The selenium cell prepared in this manner was set, for protection, in a small glass tube closed with cork stoppers. Although no illustration is presented in the original communication we can, from the description therein, reconstruct the first selenium cell to yield a current by itself, as shown in Figure 10.

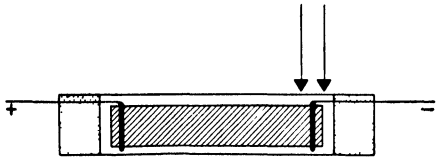


FIGURE 10.—First Selenium Photoelement of Adams and Day (1876).

While carrying on resistance measurements on this type of cell Adams and Day noticed on exposure to light a variation in the galvanometer throw indicating a reversal of the current. This observation was immediately explained correctly by the investigators as an additional EMF produced by the incident light. The proof of this assumption followed through the detection of an EMF with no external source of current. This experiment was repeated under the most varied conditions and it was clearly proved that the observed current was produced by the light, and started and stopped with the light without lag. Just as in the present day selenium photoelements, the illuminated electrode became negative. Adams and Day laid the appearance of the EMF to an additional crystallization produced by the light. They assumed that the selenium bar had not been heated equally throughout during the crystallization process, and besides that the outer part had cooled more quickly than the inner

and that hence differential crystallization had taken place. Since light, as they concluded, assisted the crystallization a stream of electrical energy thus proceeded from the parts of the selenium crystallized by the light to those not so influenced. They also explained the decrease of resistance of selenium when illuminated as due to this crystallization process, since crystallized selenium is a better conductor. This attempt at explanation now seems as original as it is false. Apart from this the experimental results are indeed very considerable and deserve full recognition, since an entirely new effect, namely the appearance of a spontaneous EMF, was detected from small deviations in the readings of galvanometer deflections.

Apparently without knowledge of these observations of Adams and Day the same effect was discovered for the second time by Charles Fritts in 1884 in New York, and indeed under more favorable conditions with respect to the cell construction. Fritts [14] had already described in 1883 a new form of selenium resistance cell with longitudinal illumination, after the manner of a modern barrier layer cell, consisting of a metallic supporting plate covered with a thin layer of selenium upon which the light fell through a sheet of gold leaf. Whereas Werner Siemens had obtained a reduction of resistance of 14.8 times in his selenium wire cell when illuminated by sunlight, Fritts with his cell attained a resistance change of 40 times under similar conditions. Not only is the magnitude of this change notable, but also the lower resistance of these cells, which lay between 500 and 5000 ohms, and could even be made substantially lower, for Fritts reports one cell with only 9 ohms resistance. At such low resistances the available current changes were correspondingly large and could be used directly for the control of mechanical relays.

We have already seen in the Introduction that longitudinal illumination is favorable for the observation of a spontaneous EMF. Therefore it is not surprising that Fritts in 1884 reported on the current production of his cells in an

English patent specification 3249, and in addition, in the same year sent some cells to Werner Siemens for test. Werner Siemens [15] reported on these in the Proceedings of the Prussian Academy of Sciences of 1885, and confirmed that these cells produced a continuous current when illuminated, which was excited by light and not by dark heat radiation. In the report Werner Siemens further showed that the photocurrent increases approximately linearly with the intensity of illumination and is not confused by a polarization effect. Siemens also referred to the use of this cell as a photometer for the determination of varying daylight. Siemens could thus fully confirm the statements of Fritts and comment to him thereon in his own enthusiastic way, as follows: "We have here in fact to do with an entirely new physical phenomenon, which is of greatest scientific importance—since here for the first time appears the direct transformation of the energy of light into electrical energy."

The similar discovery already made by Adams and Day in 1877, as well as communications of S. Kalischer [16, 17] with data concerning a repetition of the experiment described by Adams and Day had escaped Siemens.

Fritts himself was also thoroughly clear about the significance of his novel selenium cell and published in 1885 [18] in various places complete accounts of the preparation and use of these cells, which showed also the special suitability of these selenium layer cells for rectifier purposes. Thus Fritts had observed a current ratio of 1:200 for different directions of the current, a value which corresponds to the modern dry rectifier. Unfortunately there are in Fritts' work no exact data concerning the relation of the photocurrent to the intensity of the illumination. From the remark that Fritts had measured moonlight we get a certain hold on the sensitivity of the cells, and likewise from the statement that he used needle instruments in daylight measurements. In this astonishingly bountiful work Fritts showed the extensive freedom from lag of his cells by an experiment with a rotating perforated disc, which rapidly interrupted the light beam

falling on the cell. The variations in the photocurrent thus set up gave tones in a telephone corresponding to the light frequency. In connection with these experiments Fritts disclosed the use of these cells for the transference of music and speech through a corresponding modulation of the light, the cell supplying the currents for the operation of the telephone.

If we survey the works of Fritts collectively we find as the essential advance the selection of an improved arrangement in the construction of the cell, the use of longitudinal illumination. In addition it is to Fritts' credit that he gave methods for securing lower cell resistance, according to which the selenium layer is put on the supporting layer under pressure at high temperature. Through this method of preparation he secured selenium layers which were firmly joined to the supporting plate. The disadvantage of this cell is the loosely attached gold electrode which does not touch the layer uniformly and produces a considerable contact resistance, which reduces the photocurrent.

It might be expected that, after the various interesting publications of Fritts and the notice which Werner Siemens gave these new cells, their technical utilization began at once. But this by no means happened. Except for a more complete investigation by W. Uljanin [19] and some measurements by A. Righi [20] on the potential from illuminating a selenium plate with an insulated wire electrode in front of it, we find prior to the new articles beginning in 1928 no communications about this interesting semiconductor photoeffect.

Uljanin chose for his work a somewhat modified form of cell, in which he replaced the front loosely attached translucent gold leaf of Fritts' cell with platinum leaf burned onto glass. Moreover he improved the contact by melting the selenium directly between two platinized glass plates and letting it solidify under pressure. The current flow took place, as can be seen from Figure 11, from both platinum electrodes P of the glass plates G.

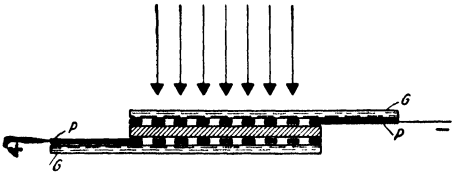


FIGURE 11.—Selenium Photoelement of Uljanin (1888).
G. Glass plate
P. Translucent platinum layer

In agreement with the earlier statements Uljanin, too, found a lagless appearance of EMF upon illumination of the cell, in which the illuminated electrode became negative. If both sides were equally illuminated, no current ordinarily flowed in the external circuit. To be sure Uljanin's cell showed a disadvantage compared with Fritts' cell, namely the lack of intimate contact with a roughened copper or brass supporting plate. Hence his cell had very high resistance and showed a correspondingly small photocurrent, even though an EMF as high as 0.12 volt was measured. In addition Uljanin investigated the best method of tempering for transforming the amorphous selenium into the light sensitive crystalline modification. He proved that the method given by Adams and Day for heating in a sand bath was too uncertain and produced cells of widely varying properties. Uljanin secured the best results by the method suggested by Siemens of heating in a paraffin bath, which was maintained at exactly 195° C. by means of a thermostat, and by slow cooling. Uljanin further proved microscopically that the light sensitive cells showed fine particles of crystalline selenium on their surface and that the strength of the light sensitivity depended upon a suitable proportion in the mixture of the two modifications. For the smaller intensities of illumination Uljanin found a linear increase of the photocurrent with the light intensity. These results according to our present knowledge depend upon external resistance, which apparently was high in Uljanin's experiments and so caused a falling off in the photocurrent at relatively small light intensities. We owe to Uljanin also the first, more exact data on the spectral sensitivity of the cells through measurements in light resolved into a spectrum. In

agreement with present day measurements he found the maximum sensitivity in the orange and a decreasing sensitivity on both sides to the ultraviolet and infrared thresholds. The investigations of Uljanin, compared with the work of Fritts, had a more academic character and lead to no technical use. It seems rather that the work of Uljanin, through the proof of various complications in preparation and use, was not exactly encouraging for a practical application of these cells.

During the next four decades only isolated measurements of the photoeffect in crystals were published, but nothing about layer built or lamellar cells. In 1929 R. L. Hanson [21] communicated an investigation concerning the EMF from the illumination of cells made in accordance with the structure chosen by Uljanin, although without any technical improvements, which were suitable for the production of stronger photocurrents. It is valuable to refer to the photoelectric observations made in the meantime on crystals, about which we will report in the next section.

In Gudden's fundamental book on "Photoelectric Phenomena," appearing in 1928, we find accordingly the prominent published discoveries, and various other measurements on the appearance of an EMF when a crystal is illuminated, briefly summarized in a chapter with the title "Earlier Phenomena with Probable Photoelectric Basis." We take the following quotation from this section:

"According to this a thermoelectric conception does not seem to follow necessarily, although the substances concerned are characterized by uncommonly high thermoforce. . . . From that it results almost certainly, that the phenomenon does not depend upon thermopotential, as the relations of temperature to illumination are unexplained. . . . The fundamental process in all these phenomena would be photoelectric on account of certain similarities of spectral distribution with that of photoelectric conduction. But nothing further can be said at present."

The results of the interesting measurements of Adams and Day, of Fritts and of Uljanin, which had already quite plainly shown the photoelectric nature of the effect, had thus been so completely forgotten that it is not surprising a rediscovery of these phenomena was necessary. The origin of this discovery was, however, not selenium but cuprous oxide.

A. H. Pfund [22] in 1916 investigated the changes of resistance of cuprous oxide under the influence of radiation, in a detailed study. It is important, that Pfund did not start with natural cuprite crystals but with polycrystalline cuprous oxide strips, which he made from sheet copper strips through oxidation in an electric furnace at about 900° C. The surfaces of these strips consisted of black cupric oxide, CuO, which was etched off so that the brilliant ruby red cuprous oxide, Cu_2O, crystals were laid bare. For his investigations Pfund used the double cell illustrated in Figure 12. The cell consisted of a cuprous oxide plate 1.2 mm thick, 5 mm wide and 12 mm long with three cathodically sputtered gold electrodes. It should be noted that Pfund always applied a transverse illumination, which is unfavorable for the production of a spontaneous EMF. Pfund could not, therefore, detect any spontaneous photocurrent and limited himself solely to the determination of the photoelectric conductivity in relation to the wave-length of the light. Upon illumination of the edge of the cuprous oxide plate in the direction I, with current connection to the front and back electrodes 1 and 2, the current lines penetrate more deeply into the body of the crystals; upon illumination in direction II, with current connection to the two front electrodes 1 and 3 on the other hand, they are more in the surface. Accordingly, Pfund found differences in the spectral sensitivity of the resistance change. For case I a maximum appeared at 630 mμ, for case II the maximum lay in the green spectrum at about 500 mμ. Pfund thus established the same difference in color sensitivity that we later also were to recognize for cuprous oxide backwall and frontwall photoelements. Pfund

explained this difference by the filtering action of the overlying cuprous oxide layers for case I, but overlooked that, for case II then, a red maximum must also be present in addition to the maximum in the green. Later on we will recognize chemical differences of the photoelectrically active centers as the basis for this difference.

The works of Pfund are not only noteworthy for the investigation of a new substance, cuprous oxide, but are also clearly novel with reference to the method of constructing the electrodes. With Fritts we have gold leaf electrodes pressed on, with Righi wire electrodes, with Uljanin we find platinized glass electrodes fused on, and with Pfund, for the first time, gold electrodes which were put on by the newer procedure of cathode sputtering. We will see that this process is notably superior to the earlier procedures and is used exclusively in the industrial construction of barrier-layer photocells.

After these essential preliminary works of Pfund only a single further step was required to detect also a photo-EMF in layer type cuprous oxide cells. For this it is only necessary to alter the cell illustrated in Figure 12 so that the front

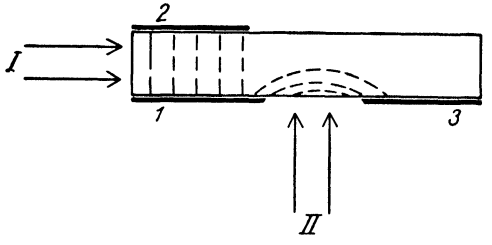


FIGURE 12.—Cuprous Oxide Resistance Cell of Pfund (1916).

gold electrode is translucent, and that the light falls on this. A cuprous oxide cell of this type, according to Figure 5, was described by B. Lange.[23] While carrying on thermoelectric measurements on tellurium, cuprite and other minerals in 1928 B. Lange observed deviations in the deflections of a mirror galvanometer used in the measurement of the thermocurrents, which he was able to trace back to an effect of the

light. By blackening the light sensitive surface the information could be gained that the effect was not caused by heating set up by the light, as the sooted surface generally gave no current when illuminated. Also through a determination of the spectral sensitivity and an oscillographic record of the extreme freedom from lag, the proof of a primary photoelectric effect could be brought out. Had the observations of Lange remained limited to minerals they would have had only an academic interest, just as the previously published investigations on lead sulfide and molybdenite. A discovery made in a neighboring field of electrical engineering, the development of cuprous oxide dry rectifiers, helped the work decisively.

We have already mentioned that Pfund [22] in his investigations had started with copper sheet which he oxidized in an electric furnace through the action of atmospheric oxygen. Correspondingly L. O. Grondahl and P. H. Geiger [24] set themselves the task of producing a photoelectric resistance cell that would deliver currents sufficient for actuating mechanical relays. For this purpose they started, as had Pfund, with a copper strip, oxidized this only about half, so that there was on each face of the 0.5 mm thick mother copper a thin coating of cuprous oxide with an outer layer of black cupric oxide, which was ground off. On one side the cuprous oxide layer was also fully removed and the mother copper was used directly as one of the electrodes, while for the second electrode lead sheet was pressed against the cuprous oxide. Grondahl and Geiger had hoped that on illumination of this arrangement a particularly large change of resistance would occur, since the cuprous oxide layer was thin and would be completely penetrated by the light. Their expectation was entirely disappointed. Still they made another observation, that of the unipolar conductivity of their system. They found that the resistance of the system is much less when the current flows from the mother copper to the cuprous oxide than conversely. Grondahl and Geiger followed this secondary observation further and developed thus, from the

search for a practical photoresistance, the cuprous oxide dry rectifier which in a few years spread a million-fold over the whole earth. Starting with copper plates, developed cuprous oxide and a partially translucent metal front electrode B. Lange [23] succeeded in producing photoelements which gave currents of a few milliamperes in sunlight and which on account of their simple construction and their stability were useful for technical purposes, and which became the point of departure for numerous scientific and engineering investigations.

Grondahl and Geiger in a work published in 1927 made known the observation of a small EMF upon the illumination of the edge portion of a cuprous oxide rectifier, and in a British patent specification 277,610 published in 1928 described a photoelement, Figure 13, which consisted of a copper plate with developed cuprous oxide and a wire spiral pressed on for taking off the current. Still this cell lacked

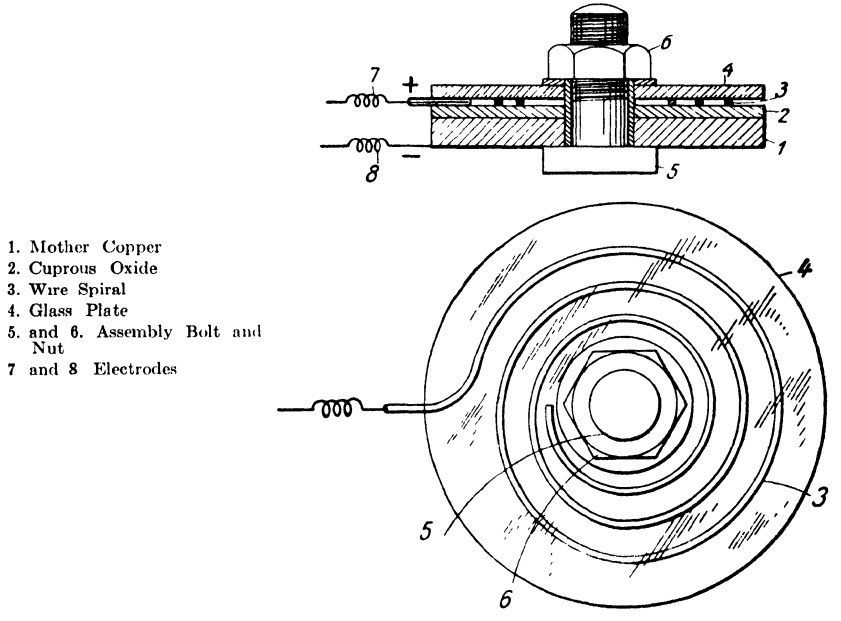


FIGURE 13.—Cuprous Oxide Cell of Grondahl and Geiger.

the sheet-like, translucent front electrode which gives a notably higher efficiency, since in this arrangement the photoelectrons released at every point of the surface find a path through the front metal film, whereas in the arrangement of Grondahl and Geiger only the electrons released in the neighborhood of the spiral are measurable. In addition the contact resistance of the impressed spiral is much greater than that of a front electrode cathodically sputtered, or built up by chemical reduction. These circumstances brought it about that in America the electrolytic cuprous oxide cells were introduced, while nothing was known of technical applications of rectifier cells with impressed wire electrodes.

Whereas B. Lange, and also Grondahl and Geiger, made the discovery of the cuprous oxide photoelements through the evaluation of secondary observations during experimental investigations of other physical problems, W. Schottky,[25] on the basis of purely theoretical considerations concerning the unipolar behavior of dry rectifiers succeeded in observing the primary photoeffect in this system. In common with F. Waibel and other co-workers in the Siemens concern he pursued from 1928 an exact investigation of this system, particularly as to the point of origin of the photoelectrons and the quantum yield. Schottky advanced the following considerations: If in analogy with the known external photoeffect in alkali photocells it can be reckoned that a photoeffect appears also at the boundary of two solid conductors, this effect can only be observed and utilized if the electrons, in penetrating the interface, have filtered through a special barrier layer resistance limited to a very thin boundary surface. Otherwise the effect would be undetectable on account of internal short circuiting. All further work of this circle of investigators was, consequently, based on the barrier layer hypothesis, which proved to be very fruitful from many considerations, and led to the development of the cuprous oxide "Vorderwand" or "frontwall" cell,[26] in which the electrons were released in the uppermost surface of the cuprous oxide and, just as in the selenium photoele-

ments, flowed to the translucent front electrode, whereas the electrons in the previously mentioned cuprous oxide rectifier cells originated at the interface between the copper base and the developed cuprous oxide. As a particular example of experimental skill the detection by F. Waibel [27] of the material nature of this barrier layer by spectral analysis, and the determination of its thickness as about 5×10^{-6} cm is noteworthy. On the basis of this barrier layer hypothesis and the experimental detection of an activated surface layer, the selenium and cuprous oxide photoelements have frequently been called barrier layer photocells. To what extent the barrier action of this highly insulating surface layer is really necessary for the appearance of the EMF will be discussed in detail later on, page 56, etc.

The independent development of the cuprous oxide photoelements just described, occuring at different places, offered something new in contrast with the work of Adams and Day, Fritts and Uljanin, as it made known the effect of a spontaneous EMF in a new type of semiconductor system constructed in layers. From the way the older works fell completely into oblivion, it is again not surprising that a rediscovery of the selenium photoelements became necessary. B. Lange gave a description of this type of selenium photoelement in a demonstration lecture the latter part of 1930, and in a subsequent publication.[28a] Here too, as for the cuprous oxide cells, the plate of the selenium dry rectifier was shown to be a suitable starting material, as E. Merritt [28] had already hinted. An independent description of the selenium photoelement followed later on from L. Bergmann.[29]

The development here given, shown by the published literature, ran parallel with the technical developments in the cells, concerning which only very little was published, as these have found their resting place in patent specifications, which for the most part have not yet been published. A German patent application of E. Falkenthal, of June 8, 1930/21 gF 1536,[29] published in the meantime needs particu-

lar mention, the essential content of which is concerned with various technical procedures for rational manufacture of selenium photoelements through internal connection of all layers, so that low resistance cells were produced that delivered sufficient currents for technical uses without the aid of a battery. Experiments had not been lacking, to prepare lamellar, or layer-built, photoelements with other semiconductors, the photoeffect of which was known for natural crystals, such as lead sulfide and molybdenite. Nevertheless systems with higher photoelectric efficiency than in cuprous oxide and particularly in selenium have not thus far been presented. Similarly as in the alkali photocells, pains were taken to reach a greater efficiency by activation of the light-sensitive boundary layer, R. Rother and H. Bohmke.[30] A still greater interest has been given to the use than to the preparation of these cells, concerning which we will report in detail in part II.

Crystal Photoelements

The difference between the polycrystalline semiconductor photoelements and the so-called crystal photocells is purely external, since only a difference in degree and not in kind exists between the physical properties of the pure crystal and most of the artificially prepared crystalline systems. Engelhard[31] was able to show experimentally for cuprous oxide that large single crystals and crystalline fragments generally have the same mechanism of photoelectric conductivity. From purely external considerations, cells with large sheet-like electrodes are called semiconductor photocells, and the label crystal photocell is limited to cells with well developed crystal-like semiconductors. The first selenium photoelement of Adams and Day, illustrated in Figure 10, according to this, would no longer be called a crystal photoelement, since superficially it shows no crystal structure. Considered physically, however, it shows the same effect as the crystal photoelements now to be described.

The first observations on galena (lead sulfide), tellurium and other detector minerals were made in the Far East, in Calcutta, by Jagadis Chunder Bose [32] and described in U. S. patent 755,840 of the year 1901. The Indian physicist was perfectly clear about the applicability of this discovery and so compared his light detector with an artificial eye, and in support of this comparison gave the typical embodiment in the patent specification the external form of an eye, as shown in Figure 14, in which the light is concentrated by the lens 3

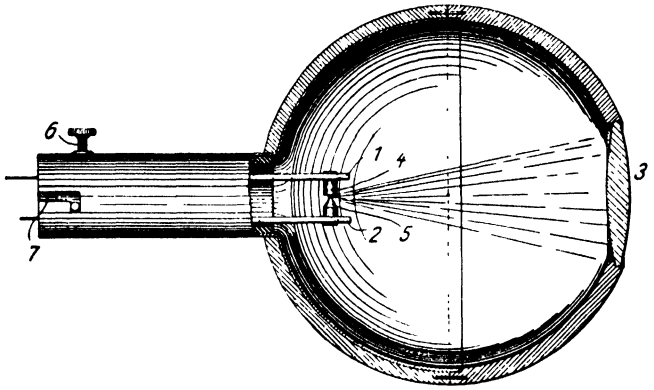


FIGURE 14.—Tejometer, First Crystal Photocell of Bose (1901).

on the point of contact of the crystal 4 with the opposite electrode 5. Through a lever shaped crystal-holder 1 and a setscrew 6 the most favorable contact pressure could be produced as in an ordinary detector. Bose also proposed to fill the detector sphere with a liquid filter, so that his artificial eye should have the spectral sensitivity of the human eye. Inventively and fantastically, Bose named his light detector a "Tejometer," derived from the Sankrist word for radiation "tej."

However, these "artificial eyes" found just as little use as had Fritts' cell in its day. Because of the rather difficult accessibility of Bose's publication, a rediscovery of the crystal photoeffect was likewise needed, which followed in

1917 through Coblentz,[33] who, with various co-workers, described the light sensitivity of molybdenite, silver sulfide, proustite, pyrargyrite and other substances, and particularly investigated that of the molybdenum sulfides more closely and suggested the use of the crystal cells for radiation measurements. Independently of Coblentz, D. S. Steinberg[34] also described "photoelectric phenomena and unipolar conductivity in molybdenite crystals." Steinberg determined the EMF in relation to the intensity of illumination and found the linear increase at small light intensities typical of all crystal photocells, that for most of them approached a limiting value, which lay under 0.4 volt for molybdenite. Steinberg and Coblentz found a well marked maximum of the sensitivity in the infrared at about 1 μ. In addition Steinberg investigated the unipolar conductivity of the crystal and found that the current flowed in the higher resistance direction.

Further, H. H. Sheldon[35] and P. H. Geiger[36] describe the appearance of the photo-EMF in natural argentite (Ag_2S). The maximum of spectral sensitivity here also lies in the infrared at about 1 μ. The illuminated contact part became negative for the time being, whereas symmetrical illumination of the middle of the crystal gave no external EMF. The electromotive force of the selenium crystals was investigated by R. M. Holmes and N. L. Walbridge,[37] who in fact applied a translucent platinum layer to the single crystal by cathode sputtering, and thus produced a selenium crystal photocell in miniature form.

B. Lange[38] in 1931 described the light detector illustrated in Figure 15. The light sensitive crystal was fused into Wood's metal in a metal bowl within a glass guard tube. By means of the supporting bow the finest possible filament was suspended so that it touched the crystal only at a point. Through a brief spark discharge of a small induction coil it was possible to weld this contact point with the crystal, so that not only was the constancy increased, but also, through the reduction of the contact resistance, the photocurrent was

raised. B. Lange investigated the spectral sensitivity of such a light detector of lead sulfide (French galena) more exactly, and for it found a threshold wave-length displaced into the infrared at 4.5 μ, with a maximum of light sensitivity at 1.1 μ.



FIGURE 15. — Light Detector. According to B. Lange (1931).

With the investigation of a well developed natural single crystal of cuprite, Figure 16, H. Dember [39] became occupied in a series of different investigations of cuprite, proustite and zinc blend.[40] R. Robertson [41] and a co-worker also noticed

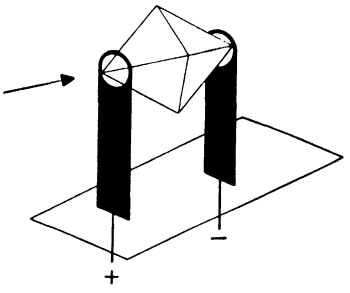


FIGURE 16.—Cuprous Oxide Crystal Photocell, Dember (1931).

the appearance of a spontaneous EMF in diamond upon illumination, and St. Pelz [51] observed it in a sodium chloride and a potassium chloride crystal colored yellow by x-rays.

In the well developed cuprite crystal Dember investigated the photo-EMF in relation to the illuminated point and showed that for the photo-EMF to appear it is not at all necessary to illuminate the contact point, but that the photocurrent is produced through absorption of light within the crystal itself, even when the electrode is insulated from the crystal.[42] This determination is of special significance as it can no longer be explained by the barrier layer hypothesis suggested by Schottky, and thus leads to the proposal of a new theory concerning the origin of the photoelectrons in semiconductor photocells.

Review of the Historical Development

From the very first the interest in the photoelements was not merely academic. Particularly through the work of Fritts there was a general technical interest with regard to the use of the photoelements as instruments of unbiased judgment for measuring light. Much, which one is accustomed to evaluate only from the appearance, can be determined numerically in a convenient way through the simple connection of a photoelement with an electrical measuring instrument. But not only on technical grounds can photoelements claim a general interest, perhaps they are even more interesting for the far from small community of those who find pleasure in tracing out the play of natural phenomena. The question, in fact, is not as to the application for technical purposes of well known natural laws, as in the case of the incandescent lamp and the telephone, but of a physical process not even today fully investigated and explained.

Looking backward it seems to us as if the road was not so very long from the first electrolytic photoelement of Becquerel, by way of the photoelectromotive selenium cell

of Adams and Day, to the present day commercial barrier-layer photocells, and every step in the historical development seems simple and obvious. The circumstances did not appear quite so simple to the individual investigators, who, in ignorance of the very scattered literature, buried in old patent specifications, had to go through all the steps in the development themselves. In order to make a single stride in actually new territory, a long road had to be retraced through already discovered realms, as again, orientation was made difficult by missing or insufficient data. Hence the numerous rediscoveries and inventions running side by side, so that it almost seems a principle of nature to form continuously more crystallization centers for new ideas, so as to give thereby a certain assurance of their discovery. On another ground, also, the natural piling up of concurrent discoveries seems important to us, namely, for the observation of the same effect from the most different viewpoints. Only through this do we get a panorama-like view, which lets us realize the coherence of externally different realms. Becquerel effect, barrier layer and crystal photoeffect, outwardly very different, appear to us through this consideration as thoroughly coherent. The disclosure of inner agreement and the preparation of a regional survey is just as important as the investigation of further details and we must give the greatest recognition to those who prove to us deeper agreements in the interesting play of nature between light and electricity.

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Chapter 2

Various Theories Concerning the Semiconductor Photoeffect

Having become acquainted with the basic photoelectric phenomena and the historical development of the photoelements in the two preceding sections, we now come to the chief part of the book, to the discussion of the semiconductor photoeffect and to the description of the various physical properties of semiconductor photocells. Beforehand, however, we will in this chapter become acquainted with the different theories about the semiconductor photoeffect, so as to be able to test, in the next chapter, how well the physical properties are explained by the theoretical ideas. One of the outstanding characteristics of the photoelements is their semiconducting property. We begin, therefore, with the question of the special properties of the semiconductors.

Properties of Semiconductors

Lattice Distortion Points and Their Constitution

Just as the machine builder must be acquainted with the properties of his working materials, the steels, just so are the properties of the semiconductors important for the understanding and the further development of the semiconductor photoelements. Only a good command of the properties of materials can lead to their fruitful use. In the attempt to answer this important question as to the properties of the semiconductors, however, we meet with difficulties. For we must admit that there is really no semiconductor with

strictly defined properties. The properties of the metallic conductors are known the best, those of the insulators notably less, and those of the semiconductors most incompletely. Even the demarcation between semiconductors and insulators is entirely arbitrary, so that we designate materials with a resistance of more than 10^{10} ohms per centimeter cube as insulators. Almost all materials that are good insulators at room temperature, show a considerable conductivity at higher temperatures, so that our arbitrarily fixed value of the boundary between semiconductor and insulator is itself dependent upon temperature.

The conduction of electricity in semiconductors can take place in two completely different ways, either through ionic migration, we speak of an electrolytic conduction, or through an electron migration, as in the metals. Finally a mixed conduction by both ions and electrons is possible. Since ionic conduction is bound up with a transfer of matter, it is recognized by disintegration and precipitation at the electrodes in accordance with Faraday's Law. Furthermore, for ionic conduction a negative temperature coefficient and the absence of the Hall effect are characteristic. But in many cases, particularly with mixed conduction, a clear decision is difficult, and still debatable as to which conduction is effective. In the case of the semiconductor photocells we are, however, interested only in the electron semiconduction, which takes place without disintegration phenomena and which has a positive temperature coefficient of conductivity. So from now on we will limit our treatment of semiconductors to this subdivision.

From the work of Gudden [43, 44] and his colleagues especially, it appears that the electron conduction in crystallized semiconductors is not a property of the material itself, but depends upon points of deficiency and distortion in the crystal lattice. The same crystals with completely regular ideal lattice structure are highly insulating, and according to the number of deficiency and distortion points we find quite different conductivities. For example, in the case of

cuprous oxide E. Engelhard proved that according to the thermal treatment variations of conductivity of more than a thousand-fold were obtained, without a chemical change of the substance being observable. As a result, all investigations of semiconductors with electron conduction were made very difficult, since the same material presented quite different properties according to the previous treatment and probable contamination in "homeopathic doses." Since the photoelectric properties also depend upon these deficiency and distortion points of the lattice, the same material can, similarly, show a strong photoeffect or even none at all, depending upon the previous thermal treatment. This must always be kept in mind in all statements about the photoelectric properties of semiconductors, as otherwise entirely contradictory results are secured. The number of free electrons in a semiconductor, the work in detaching an electron, the spectral sensitivity, and even the arrangement of the photoelectrons in the semiconductor are not constants of the material, but are very different according to the previous history of the material. Only through the accumulation of measurements on like materials, and painstaking study of the conditions of preparation is it possible to detect conformity to law. Fortunately these troublesome tasks have already been begun, so that we have at least secured exact data for a few substances. In the first place should be mentioned cuprous oxide, which is producible in crystalline form of high purity from pure copper by oxidation at about 1000° C. Thus, starting with a copper single crystal, it can be transformed by this process into a single crystal of cuprous oxide, and in this way crystals with edges more than 1 cm long can be produced, which are shown to be homogeneous by x-ray analysis. One would expect that at least in this sort of pure crystals thermal and photoelectric conductivities would have definite values. This is not the case, however. We have already learned, at the beginning of the preceding chapter that Dember [39] has measured the photo-EMF of natural and artificial

crystals. As he established, the natural cuprite crystals from Tsumeb showed the greatest effect, whereas artificial crystals were at times entirely insensitive; moreover, in turbid polycrystalline crystals the current direction is also reversed, that is, the electrons flow opposite to the direction of the incident light. E. Engelhard [31] found a similar great difference in conductivity for artificial cuprous oxide crystals according to the previous thermal treatment. Fortunately, however, single crystals show the same regularity as polycrystalline cuprous oxide, so that investigations were feasible with this more easily producible material. As F. Waibel [45] had shown, the partial pressure of the oxygen during the tempering is of decisive importance. Tempering in a vacuum yields crystals of extremely low conductivity, tempering in the presence of oxygen gives material the conductance of which may be a million times greater. To explain the influence of the oxygen during the tempering, the chemical processes must be born in mind. For copper and oxygen form two different oxidation products; cuprous oxide, Cu_2O, and cupric oxide, CuO. At temperatures over 1000° C. the equilibrium is displaced almost completely to the side of cuprous oxide, at lower temperatures more cupric oxide is produced. To produce cupric-oxide-free crystals they must be tempered at high temperatures and cooled rapidly, to avoid establishing a new equilibrium during slow cooling. During subsequent tempering of the cuprous oxide in oxygen CuO is formed in it, whereas during tempering in a vacuum CuO is transformed back into Cu_2O through liberation of O_2. The vacant places in the cuprous oxide lattice are formed directly out of the lattice units through transformation into material of a different valence. Proof of these lattice distortion points, therefore, by pure chemistry is extremely difficult, since the distortion points do not consist of foreign atoms, which are for instance detectible in extremely small quantity by sensitive spectral analysis methods, but there is merely the possibility of deducing the presence of cupric oxide from a change in the

stoichiometric proportions of copper and oxygen. If we bear in mind further that a single distortion center among 10^7 normal lattice atoms makes itself felt in the conductivity, there seems no prospect of using chemical methods for the determination of lattice distortion points. Besides, it happens that oxygen separated during the tempering process can remain within the lattice, so that a crystal with thermally produced distortion points appears to have exactly the same atom proportions stoichiometrically, as a highly insulating crystal with the ideal lattice. L. Dubar,[46] nevertheless, by chemical means succeeded in proving that in well-conducting cuprous oxide the presence of minor quantities of cupric oxide is probable. B. Lange [47] reached the same result on the basis of optical measurements of the threshold wave-lengths of the photo-effect in cuprous oxide according to a relation between threshold wave-length and molecular weight.

So we find that the thermal and photoelectric conductivity of cuprous oxide is caused by lattice distortion points, and that these probably consist of Cu^{++} ions and O^{--} ions. If a certain energy, for instance light or heat, is applied to these lattice distortion points, a splitting off of electrons takes place at these points, which makes itself felt by increased conductivity, or even in suitable cell structures as a spontaneous photocurrent. As here, in contrast to the metals, we have a comparatively small electron concentration, this can be calculated according to the electron theory of van't Hoff and Königsberger as dependent on the temperature. The number n of free electrons per cubic centimeter available at the temperature T is, according to this

$$n = n_o e^{-\frac{\varepsilon}{kT}} \qquad (1)$$

in which n_o is the number of detachable electrons on the whole, ε the work of freeing one electron and k the Boltzmann constant. The number n_o of the electrons at all detachable corresponds to the number of lattice distortion

points which are capable of electron emission. At very low temperatures, for instance, in liquid air the conductivity of semiconductors decreases exponentially according to the foregoing expression. The semiconductors turn to insulators and, conversely, crystals, which still insulate at room temperature, become conducting at high temperatures. The preceding equation can be somewhat transformed and the resistance R introduced in place of the number of free electrons, so that we get:

$$\log_e R = \frac{\varepsilon}{kT} - \log_e n_o \qquad (2)$$

If, accordingly, log R is plotted as ordinate and $1/T$ as abscissa a straight line is secured, from the slope of which the work of freeing an electron ε can be calculated.

Engelhard[31] carried out this sort of measurement on a great number of cuprous oxide specimens treated in various ways. He determined, for instance, that a specimen glowed in vacuum had 0.1×10^{17} atoms per cubic centimeter able to give off electrons, and after tempering in oxygen 230×10^{17}. Bearing in mind that the number of cuprous oxide molecules per cubic centimeter is 2.5×10^{22} it follows from this that in the untreated specimen there is only one atom capable of losing an electron (lattice distortion point) for 2½ million molecules and that even in the substance tempered in oxygen there is only a single distortion point for about a thousand molecules. We will see later (page 79) that the concentration of these distortion points, which corresponds to the maximum number of detachable electrons, is fundamental to an understanding of the photo-EMF. We will once more take up the preceding measurements of Engelhard, which give the value 2300 for the ratio of the atoms capable of losing an electron in a specimen tempered in oxygen to those in a specimen annealed in vacuum, and from that calculate the maximum photo-EMF.

Thus through the application of purely physical methods we have succeeded in making an exact representation of electron conduction in crystals and even in calculating the number of lattice distortion points essential for the conduction of the electric current. Through determination of the Hall constant for the same materials, furthermore, the mobility of the electrons and their free path, amounting to $2\text{-}3 \times 10^{-6}$ cm at room temperature, can also be determined. On cooling to the temperature of liquid air the electron mobility and the free path increase about tenfold.

Nothing about the construction of the atoms or the atom groups able to give off electrons results from these data, however. The possibility exists, that these distortion points, capable of losing electrons, are the lattice units themselves, in the case of cuprous oxide the Cu^+ ions and O^{--} ions, so that individual places in the lattice are occupied by O^{--} ions instead of by Cu^+ ions. C. Wagner[48] calls this faulty arrangement the Substitution Type. But the possibility also exists that excess copper atoms are in between fully occupied lattice positions. An Inter-lattice or Interstitial Type is thus presented. And as a third possibility we mention the Vacant-place Type in which individual Cu^+ ions are missing (deficiency conduction), whereas all O^{--} ion positions are fully occupied. For the illustration of deficiency conduction in the Vacant-place Type, C. Wagner used the picture of a fully occupied chess board, on which, because of the existence of a vacant place, movement of the men was possible by a neighboring man moving into the vacant place. In crystals a conduction of electricity can take place correspondingly through displacement of the ions, or also through electrons alone going from one deficiency point to another. The latter possibility alone interests us here, as in the case of cuprous oxide, lead sulfide, and other photoelectrically efficient semiconductors only electron conduction takes place, at least at room temperature. Dünwald and Wagner[49] further succeeded in

proving that at temperatures 800-1000° C. copper ions are missing and correspondingly there is an excess of oxygen, so that we get the atom configuration illustrated in Figure 17.

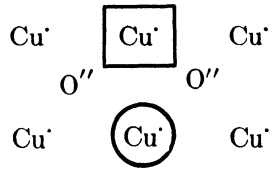


FIGURE 17.—Cuprous Oxide Lattice Distortion Points. Vacant-place type. The [Cu·] is lacking in the lattice (Deficiency conduction).

The Cu^{+} ion enclosed in the rectangle in Figure 17 should be missing. Hence the influence of the electrostatic fields of the O^{--} ions upon a neighboring Cu^{+} ion, enclosed in the circle, would be increased and its second valence electron would be loosened, or lost by the addition of energy through heat or radiation, so that the cuprous ion goes over to a cupric ion. Thus the field action of the O^{--} ions is overcompensated and the same Cu^{++} ion will upon the addition of a conduction electron again go over into a univalent Cu^{+} ion. This reversible process can be somewhat expressed by the following equation:

$$Cu^{+} + \text{Energy} = Cu^{++} + \text{Electron}.$$

We can also make exact statements as to the energy required for detaching electrons, in the case of cuprous oxide about 0.3 electron volt is necessary. If the quantum energy of the radiation is less than ε then generally no electron emission results. The transformation of univalent copper ions into bivalent thus becomes the source of electrons and the light the driving force of the electron pumping station, in which the cuprous ions through the addition of light energy are transformed into cupric ions with liberation of electrons, whereat we once more recall, that these processes only take place at vacant lattice positions. In the foregoing treatment we have assumed that

the lattice distortion points were caused by missing Cu^+ ions, since it was a question of electron deficiency conduction.

According to measurements by W. Schottky and F. Waibel [50] we have, however, no electron deficiency conduction in cuprous oxide at low temperatures, but rather an excess conduction. Through measurement of the Hall constant they succeeded in proving experimentally that at an intermediate temperature of about 500° C. a sudden change from an electron deficiency conduction to an excess conduction took place. As is evident from Figure 18, the Hall con-

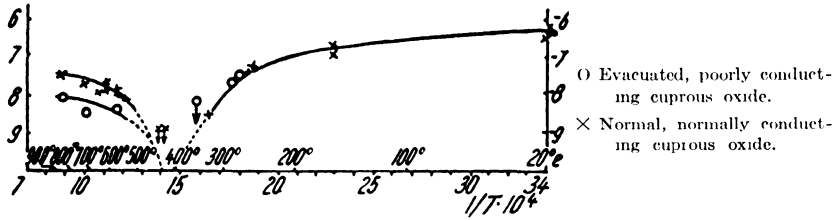


FIGURE 18.—Logarithm of Hall Constant R in relation to $1/T$. According to Schottky and Waibel.

stant changes its sign between 400° and 500° C., for normally conducting cuprous oxide as well as for the oxygen-poor, slightly conducting cuprous oxide. Hence we find ourselves compelled to assume another configuration of distortion points, somewhat after the interstitial type, for excess electron conduction.

According to Figure 19 a neutral copper atom, enclosed in parenthesis, is embedded within the lattice. This neutral atom can be excited thermally or photoelectrically and loses its valence electron, which had already been loosened by the neighboring O^{--} ions.

As we assumed for electron deficiency conduction that the free electron became free during the transformation from the lower to the higher valence material, we are here forced to the assumption that the electrons arise during

the transformation from neutral to univalent Cu^{+} ions. Hence we have two different elementary processes, for which we can expect two completely different configurations of distortion points and different spectral sensitivities, namely, the detaching of the first and second valence electrons. The question arises, whether such a difference can really be observed.

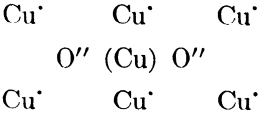


FIGURE 19. — Cuprous Oxide Lattice Distortion Points. Interstitial type. (Cu) atom entrapped. (Excess conduction).

"Frontwall" and "backwall" cells display an entirely different spectral sensitivity (see p. 116 seq.). The assumption that the backwall effect has another spectral sensitivity only because the intervening cuprous oxide layer acts as a red filter is refutable, as then in the frontwall effect alongside the maximum at 500 mμ the maximum of the backwall effect at 630 mμ must be present. As, however, this maximum is completely lacking we find ourselves compelled to assume other photoelectrically efficient centers for the frontwall effect. The differences result from the recently discussed different constructions of the lattice distortion points, with electron deficiency conduction or electron excess conduction, by the escape of the first or the second valence electron.

As we have made it plausible, on the ground of the different spectral sensitivities, that different elementary processes apply the question arises whether we can explain such an enclosure of neutral copper atoms chemically. At first sight this does not seem very intelligible, since we could prove an oxygen treatment with formation of cupric oxide as favorable for the genesis of distortion points. However, we reach a comprehension through consideration of an occurrence increasingly observed during oxidation

processes, disproportionate oxidation and reduction. In this, oxidation is associated simultaneously with a reduction process, so that according to the following equation:

$$Cu_2O = CuO + Cu$$

CuO and Cu appear side by side. If, for example, a polished Cu_2O layer is etched in diluted hydrochloric acid a disproportionate oxidation and reduction takes place according to the following equation:

$$Cu_2O + 2\,HCl = Cu + CuCl_2 + H_2O,$$

and a spongy copper layer separates from the crystal surface. After removal of this layer small particles of copper can be detected microscopically in the upper crystal layer, using dark field illumination. Surfaces treated in this way show a distinct primary photoeffect which is many times stronger than in unetched sheets. For the production of efficient cuprous oxide frontwall cells such a reduction is above all indispensable, indeed it is desirable to carry it out in a glow discharge to avoid the secondary effects of acid residues.

Through this the experimental information can also be adduced that the photoelectrically efficient centers in frontwall cells are not cupric oxide molecules, but entrapped Cu atoms after the manner of the interstitial type.

From the relation already mentioned concerning the dependence of the threshold wave-lengths (see p. 143) we reach the result that in the frontwall cells Cu atoms constitute the photoelectrically efficient centers, whereas from the considerably longer infrared limit of the backwall cells a eutectic mixture of cupric oxide and cuprous oxide is indicated. Since cuprous oxide cells can be produced which show the frontwall effect when illuminated with short-wave light and the backwall effect when illuminated with red light, we are led to the conclusion that Cu atoms and Cu^+ ion vacancies are present in the same substance, and that deficiency or excess conduction takes place according

to the mode of preparation and the temperature; circumstances which also explain the inversion point of the Hall constant at 500° C. as well as the break in the resistance curve according to the Königsberg equation at $73 \pm 5°$ (see p. 107).

Similar relations exist for sodium chloride and potassium chloride as for cuprous oxide. The development of lattice distortion points can be brought about in these substances by x-rays through formation of alkali metal atoms, which produces a yellow color of the crystal. As St. Pelz [51] proved, crystals colored in this way show not only photoelectric conduction but also a crystal photoeffect, so that with irradiation which is unsymmetrical with respect to the electrodes a photocurrent flows in the external circuit. We find here a lattice distortion by the enclosed alkali atoms which give off their valence electrons. There is also an electron excess conduction. In contrast to this we can make the chemically interesting statement concerning electron deficiency conduction that this appears especially in those compounds in which the cation can be transformed into a higher-valence material very readily through the loss of another electron. In suitable cases it can actually be observed for Cu_2O, CuS, NiO, and PbS that excess of the electronegative component produces a loosening of the second valence electron and thus increases the conductivity, see LeBlanc and H. Sachse.[52]

For selenium the relations are less clear than for cuprous oxide, for here one and the same element can assume a metalloid or a metallic character and thus a chemical investigation is made difficult. But this much is known about it, that a concentration of the one modification in the element through suitable tempering processes is necessary for producing photoelectric properties.

Electron excess conduction and electron deficiency conduction will first be explained in terms of the corpuscular theory. This picture seems the simpler and more suitable for the proposed investigation. Entirely similar considera-

tions appear also for treatment of the phenomena in semiconductors by wave mechanics, see L. Nordheim [53] and F. Bloch.[54]

Having thus far tried to picture the formation of photoelectrons, it would be natural to ask where the electrons originate in semiconductors. For the present, however, we will be content with the brief statement that in crystal photocells the photoelectrons arise in the interior of the crystal, in accordance with the depth of penetration of the light, whereas in barrier layer cells they arise in the immediate neighborhood of the boundary layer. On closer consideration it appears that exactly this boundary layer is of decisive significance for the action of the semiconductor photocell. Several theories concerning the influence of this boundary layer on the photoeffect have been proposed, which we will now discuss.

The Barrier Layer Theory

It has already been mentioned in the chapter on the historical development of the photoelements (p. 37) that with Schottky a theoretical consideration was the starting point for the observation of the semiconductor photoeffect. If, concluded Schottky, in analogy with the known external photoeffect, it can be supposed that a photoeffect also occurs at the boundary of certain solid conductors, this effect could only be observed and used provided the electrons, in penetrating the boundary layer, had to traverse a certain barrier resistance layer restricted to a very thin boundary film. Otherwise the effect would not be observable because of "internal short circuits." This consideration led to the assumption that this sort of special "Barrier Layer Photoeffect" would appear at the contact of all such conducting substances as showed an electric barrier effect toward each other, hence in detectors and dry rectifiers.

According to the barrier layer theory the rectifying effect is not at all a material property of pure cuprous

oxide. It has been clearly proved through numerous exact investigations that pure cuprous oxide behaves as an ohmic resistance and has no rectifying action. The rectifying action is only conditioned by the type of contact between the cuprous oxide and the metal electrode. Metal electrodes evaporated in a vacuum show no barrier action in contrast to cathodically sputtered electrodes. The greatest barrier effect is present in cuprous oxide films which have been developed at high temperature upon copper. In agreement with the fact that the cuprous oxide itself has no unipolar behavior, the rectifying effect does not decrease when the developed cuprous oxide sheet is made thinner by grinding or etching. It can be proved further through measurements with probes that the seat of the rectifying effect is the boundary layer itself. Furthermore, it can be proved that the resistance of the boundary layer is very dependent upon the applied voltage and its direction. For low voltages the resistance in both directions is not very different, whereas for higher voltages a ratio of 1:100 or more is reached, the electrons traveling more readily from the copper to the cuprous oxide than in the opposite direction. If it could be imagined that this resistance is a high purely ohmic boundary resistance, the great dependence of this thin insulating layer upon the voltage must be explained. This sort of insulating layer seemed improbable to Schottky, for it was a difficult matter to put an extremely thin homogeneous layer of high resistance between two highly conducting materials; in the case of inorganic substances even 5 μ thick, short circuits had to be expected. Schottky therefore laid aside the hypothesis of a homogeneous contact between copper and cuprous oxide and assumed only a contact of individual little surfaces separated from each other somewhat as if the fine crystals of cuprous oxide touched the mother copper only with their corners and that this purely geometric effect of a "resistance sieve" caused the rectifying. From the ratio for the two directions of current and from experiments with very small electrodes on

cuprous oxide films Schottky came to the conclusion that these little elementary contact surfaces were to the whole surface of the mother copper as 1:100, possibly even as 1:1000.

According to Schottky's theory the presence of such a rectifying barrier layer, dependent upon the voltage, is a condition for the appearance of a semiconductor photoeffect, and so leads to calling these cells "barrier layer photocells." Furthermore, Schottky was able to prove that only those photoelectrons that had traversed the barrier layer before being reabsorbed were the effective source of an external photocurrent, and that these electrons originated in the immediate neighborhood of the barrier layer. For this proof a cuprous oxide cell was used which had a narrow sputtered gold electrode as front electrode. If the surface of the cell was touched with a fine line of light, going parallel to the gold electrode, the photocurrent varied with the distance from the line electrode as illustrated in Figure 20.

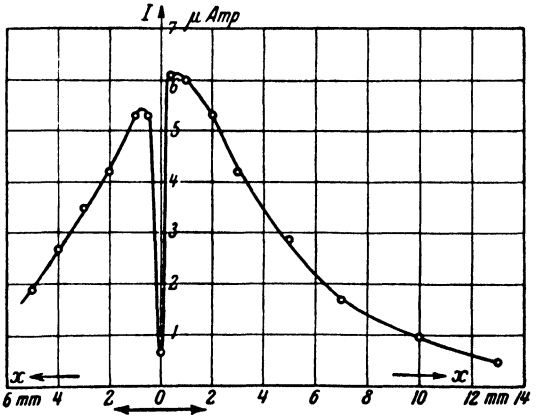


FIGURE 20.—Dependence of the Photocurrent on the Distance Between Light Strip and Electrode Strip in a Cuprous Oxide Backwall Cell. According to Schottky.

If the line of light covered the gold electrode almost completely a small photocurrent flowed which reached a maximum as soon as the light probe spread its whole width over the pure cuprous oxide layer next to the gold electrode. With increasing distance the photocurrent decreased exponentially, the distance d corresponding to the decrease of the photocurrent to $1/e$ of its maximum value amounting to about 4.2 mm. This finding supported the assumption that the primary photoelectrons were driven from the cuprous oxide through the barrier layer to the mother copper throughout, as shown schematically in Figure 21. The light falls through the cuprous oxide sheet onto the barrier layer between cuprous oxide and mother copper

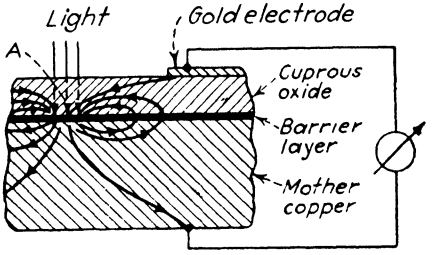


FIGURE 21. — Diagrammatic Course of the Photoelectron Path in a Cuprous Oxide Backwall Cell, cross section. According to Schottky.

and in this way loosens electrons. This photoelectron stream has two ways of completing a circuit, as in Figure 21. One path leads through the mother copper and the measuring instrument back to the cuprous oxide on the barrier layer. In addition a short circuit path leads from the mother copper through the barrier layer back to the cuprous oxide. The external part of the current will depend upon the proportion in which the current as a whole is divided. Hence the further the light ray is from the gold electrode, the smaller will be the external current, since an increasingly great fraction of the photocurrent flows through the barrier layer and is lost to the external circuit. The course of the decrease in current can be calculated

from the theory of conducting networks with longitudinal and transverse resistances and can be proved with sufficiently exact independent measurements of the resistance of the darkened cell. If, namely, an external potential is applied the current flows not only perpendicularly through the cuprous oxide layer but also spreads throughout the cuprous oxide on account of the high boundary resistance. Thus each electrode seems, as it were, to be broadened, and according to the theory of conducting networks, to a marginal zone of the width *d*. In good agreement with the half value width determined photoelectrically for the same cell this marginal zone was 3.8 mm.

A well-founded result of the Schottky theory is, accordingly, the statement concerning the point of origin of the photoelectrons, a result which can also be reached by an etching experiment on cuprous oxide backwall cells. Thus, if the thickness of the cuprous oxide layer is reduced by grinding or etching, there results almost no reduction in the photocurrent, as would be expected for a volume effect, but an increase in the same. A falling off in the current occurs only at a very slight layer thickness, comparable with the boundary layer. The capacity of the cell is comprehensible according to the barrier layer theory, which Schottky explained through the "distance keeping layer" of the barrier layer. Accordingly the barrier layer theory has a purely physical character. No assumptions were made concerning a particular material structure of the barrier layer. The barrier layer theory explains the unipolar behavior of the boundary layer and also the photoelectric effect under the assumption of chemically pure, completely homogeneous semiconductor layers, solely through the special formation of a sieve contact with numberless extremely small elementary contact surfaces.

There are cuprous oxide rectifiers which consist of two copper electrodes with a cuprous oxide layer lying between them, and similar cuprous oxide semiconductor photocells with a copper front electrode, cathodically sputtered or

produced by chemical reduction. Such rectifiers and photocells really present a symmetry paradox. It is not understood how such a symmetrical arrangement transmits the current better from one side than from the other, and the less as the cuprous oxide present between the electrodes possesses no rectifying properties in itself. The barrier layer theory will explain this symmetry paradox for us through its statement about the different geometrical structure of the boundary layers. According to this, one side of the rectifier consists of a completely homogeneous contact, the other, on the contrary, of a sieve contact limited to extremely small elementary surfaces, nevertheless with the assumption of a chemically homogeneous cuprous oxide. The fine structure of the contact, alone, causes the completely different behavior.

Before we investigate how far the barrier layer theory agrees with the physical properties of semiconductors, we will discuss some theories presented from other sides for explaining the semiconductor photoeffect, which supplement the barrier layer theory or occupy themselves with other properties of the cells.

The Field Funnel Theory

The field funnel theory of H. Teichmann [55] gives a more detailed picture of the boundary layer, and thus presents an extension of the barrier layer theory. According to Schottky the sieve contact between mother copper and cuprous oxide can perhaps be so represented that the individual little oxide crystallites touch the mother copper only with their corners. This rather rough material notion was refined by H. Teichmann through the assumption of a particular arrangement of the lattice units in the boundary layer as a kind of field funnel.

Teichmann derived his field funnel theory from a comparison with the flow of very rare vortex-free gas through a system of funnels, as illustrated in Figure 22.

If there is an alternating difference of pressure between the two spaces A and B, which produces an alternating flow between A and B, more gas particles go from A into B, and remain in space B, since particles are reflected at the slanting funnel walls, thereby altering their direction as indicated in Figure 22 by the arrow. Teichmann transferred

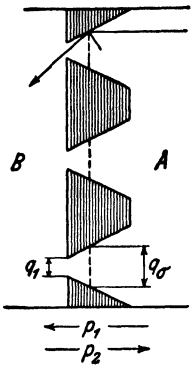


FIGURE 22.—Flow of a Rarefied, Vortex-free Gas Through a System of Funnels. According to Teichmann.

this conception to the crystal structure of the barrier layer and replaced the "material funnels" of this illustration with a special configuration of the electric field in the barrier layer through "field funnels." Copper has a face-centered cubic lattice. The copper ions are located at the corners of the elementary cubes as well as at the intersections of the face diagonals. Cuprous oxide also has a cubic ion lattice. Oxygen atoms are located at the corners and at the intersections of the diagonals of the elementary cube. Each oxygen ion is surrounded by a tetrahedron with copper ions at the corners. Teichmann started from the purely physical theory of Schottky and assumed that in the boundary layer there is no longer pure cuprous oxide but mixed crystals of copper and its two oxides. Thus, for instance, in the development of cuprous oxide from copper some of the oxygen ion positions at the corners of the elementary cubes of cuprous oxide could be occupied by copper, producing a

deformation of the lattice. If we consider, continued Teichmann, that the zone of formation of mixed crystals (10^{-7} to 10^{-8} cm), the thickness of the barrier layer (10^{-6} to 10^{-8} cm), and the free path of the electrons (10^{-7} cm) have the relative dimensions known to be necessary for the funnel idea, it is natural to look for the seat of the field funnels in this zone. If we choose as an example an elementary cube of copper on which cuprous oxide has been developed the position of the field funnel can result, Figure 23.

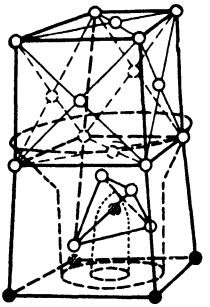


FIGURE 23.—Location of the Field Funnel in a Copper-Cuprous Oxide Mixed Crystal. According to Teichmann.

Thus Teichmann's theory has converted Schottky's individual contact points into field funnels, but otherwise has not altered the mechanism of the semiconductor photoeffect. The characteristic of the field funnel theory is the formation of an atomically oriented boundary layer. As we will see later (p. 111) atom layers deposited with preferred orientation cause a selective photoeffect, which exhibits a vectorial behavior toward polarized light. Therefore Teichmann sought such an effect in various semiconductor photocells, and was able to prove a dependence of the photocurrent upon the direction of vibration of the incident light (see p. 126), a behavior that is also explainable from the optical constants of the semiconductors.

Teichmann's field funnel theory presents thus a valuable supplement to the barrier layer theory, but it makes no statements concerning the mechanism of generating the

photoelectrons, or concerning the dependence of the photopotential upon the light intensity, and explains just as little as the barrier layer theory these same spontaneous photoeffects in crystals free from barrier layers.

The Crystal Photoeffect and the Electrochemical Theory

H. Dember [39] had observed that an external photocurrent flowed upon illumination of a pure cuprite crystal, free of barrier layers. Dember [42] had further observed, that this photocurrent flowed in the direction of the light, and vanished for illumination that was symmetrical with respect to the two electrodes. He was able to prove clearly and unobjectionably that the photocurrent also flowed when only the crystal, and no electrode, was illuminated. Hence there could be no question of a barrier layer photoeffect, as it was not bound up with the presence of barrier layers conducting in but one direction and dependent upon potential. It was thus found necessary to interpret this effect as a new independent photoeffect, which Dember called the crystal photoeffect. The relation between the direction of the light and the photocurrent in this effect was particularly striking. In cuprous oxide backwall cells the electrons also flow just in the direction of the light, in the frontwall cells, however, in the opposite direction, so that for these two cells, there is evident no characteristic influence of the direction of the light. The action of the light direction in the crystal photocells seemed thus a characteristic of the crystal photoeffect and von Laue [56] took the influence of light pressure upon the electron motion into account.

R. Deaglio [57] investigated this phenomenon in cuprite crystals from Chessy, and in doing so modified the arrangement as illustrated in Figure 24. A prismatic piece was cut out of the cuprite crystal and translucent gold electrodes free from barrier layers were evaporated onto the ends. When the crystal was illuminated through these gold elec-

trodes a photocurrent flowed, corresponding entirely to the discovery of Dember.

The arrangement used by Deaglio also permits, as can be seen from the illustration, illumination of the upper crystal surfaces parallel to the electrodes. If the direction of the light is decisive for the crystal photoeffect, if perhaps the electron current arises from the impelling pressure of the light, no current should, on the whole, appear with this arrangement. Dember had in fact already observed that a symmetrical illumination parallel to both electrodes produced no photo-EMF. Using a narrow light probe, Deaglio could observe this phenomenon only when the illuminated part lay in the middle of the crystal. If the light probe approached one of the electrodes, however, a photocurrent flowed, the direction of which varied with approach to the left or the right electrode. Since the light direction is here normal to the direction of the electron stream, directed light pressure cannot be the source of the crystal photoeffect. H. Th. Wolff [58] was able to prove theoretically that the influence of the light pressure is very much smaller than is necessary for explaining the photocurrent. Deaglio thus saw himself forced to look for a new

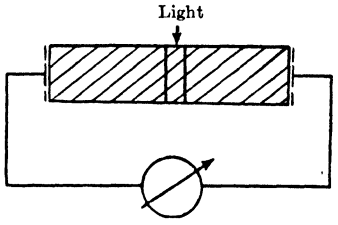


FIGURE 24.—Prismatically Sectioned Cuprous Oxide Crystal with Translucent Gold Electrodes. The left or right electrode becomes negative according to the position of the light probe.

explanation of the crystal photoeffect and proposed his electrochemical theory. According to this the electronic dark conduction of the cuprous oxide is changed into an electrolytic conduction upon exposure to light. Only thus, concluded Deaglio, could an EMF appear in a closed circuit, something impossible with conductors of the first class.

As experimental support for his theory Deaglio carried on a fatigue experiment. That is, if the crystal is illuminated for a long time with a constant light intensity, after a few hours the photocurrent falls more than one half. According to Deaglio this decrease is caused by a transport of the Cu^+ ions to the cathode and a deposit there of metallic copper. This light-absorbing copper layer should cause a decrease in the photocurrent. If the same current is sent through the unilluminated crystal with the help of an external source of current, no copper transport takes place, in agreement with Deaglio's assumption that the dark crystal conducts electronically. Transport of copper and therewith decrease in the photocurrent results only from continuous illumination.

G. Mönch and R. Stühler [59] took issue with this theory of Deaglio. They showed that the fatigue effect appears also for crystals with thin open ring electrodes, for which the eventual copper transport cannot cause any light absorption, since the illumination takes place through the open ring electrode.

Furthermore the recovery of the crystal contradicted the chemical concept of a copper transport. A crystal kept in the dark for several hours shows very nearly the original photocurrent upon renewed illumination. Besides, the fatigue observed during static potential measurements contradicted the copper transport. Finally cuprite crystals from Cornwall and Tsumeb showed no fatigue effect. Thus the electrochemical theory is not suitable for explaining the crystal photoeffect.

We have already mentioned that Dember was able to exclude the crystal photoeffect as a barrier layer effect, that he proved the photoeffect appeared also without illumination of the electrodes. This proof was not, however, compelling as light can reach the boundary surfaces through internal reflections within the crystal and thus cause a boundary surface effect. This objection is no longer possible on account of an experiment of Dember [42] with fully

isolated crystals and a proof of the electron flux under exposure to light, through inductive action on the insulated electrodes. If the crystal is illuminated with pulsating light the potential variations in the electrodes are amplifiable and detectable in a loudspeaker. Bergmann [60] has prepared such crystal cells, free from electrodes and barrier layers, with Cu_2O, Se, Ag_2S, PbS and various other substances. Thus it has been proved beyond objection that the electron stream caused by the light is not produced by the light pressure, nor traceable to a barrier layer effect.

The Semiconductor Photoeffect and the Einstein Relation

The previously discussed theories concern themselves exclusively with the structure or the chemical composition of the semiconductors, but do not touch upon the elementary process of the splitting off of the electrons under the influence of the radiation.

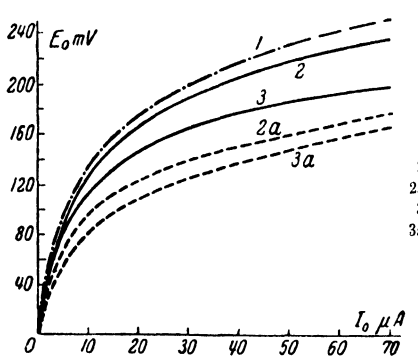
B. Lange [23] mentioned already in his first communication concerning semiconductors, that the primary electron separation, as in the internal photoeffect, was governed by Einstein's fundamental photoelectric law:

$$\frac{m}{2} v^2 = eV_o = h\nu - h\nu_o \qquad (3)$$

so that above a threshold frequency ν_0 characteristic of each substance electrons will be released with a velocity determined solely by the frequency of the light. Since the infrared threshold wave-length of the cuprous oxide backwall cells lies at about 1.4 μ corresponding to a work function of 0.88 volt, the velocity of the electrons for red light must amount to about 1.2 volts and for blue light about 2.0 volts. However, potentials only about one-tenth as large are observable.

Investigations concerning the applicability of the Einstein relation to semiconductor photocells were carried out by F. von Körösy and P. Selenyi.[61] According to their con-

cept the velocity of the primary electrons would be retarded through the fall of potential in the external resistance and the fall of potential in the barrier layer resistance. As, however, the velocity of the electrons depends upon the color of the light, for the same primary electron current a difference should be detectable between the external open circuit potential of the cell for red and blue light.



1. Dark characteristic
2. Blue light, calculated
2a Blue light, measured
3 Red light, calculated
3a. Red light, measured

FIGURE 25.—Open Circuit Potential of a Selenium Photoelement for Red and Blue Light. Light intensity measured as the primary current I_0. According to Selenyi and von Körösy.

As evident from Figure 25, such a difference could be detected in selenium photoelements. For blue light the open circuit potential is somewhat larger than for red light, but falls short of the calculated difference. For cuprous oxide frontwall cells this difference of the open circuit potential for blue and red light is much smaller and sometimes is in the opposite sense. An influence of the color on the open circuit potential was on this account denied by A. Goldmann and M. Lukasiewitsch,[62] and by P. R Gleason.[63] Körösy and Selenyi assumed further, that the primary photocurrent would be decreased, as in a vacuum photocell, by the retarding effect of the potential E adjacent to the barrier layer, in such a way that it would vanish for $E = E_0$. According to measurements in a vacuum

photocell the decrease of the photocurrent is to a first approximation proportional to the retarding potential. For the unretarded photocurrent also

$$I = I_o - I_o \frac{E}{E_o}. \tag{4}$$

This photocurrent is divided into the external current

$$i = \frac{E}{r + r_e} \tag{5}$$

in which r is the semiconductor resistance and r_e the external resistance, and into the current flowing back through the barrier layer, the value of which is not linear but depends in form upon an empirical characteristic to be determined, which is to be inferred from resistance measurements of the unilluminated cell, and will be called $I'(E)$. As the sum of the external and the internal currents is equal to I, the following equation is obtained:

$$I_o - I_o \frac{E}{E_o} = \frac{E}{r + r_e} + I'(E). \tag{6}$$

This equation can be solved for E with the help of the barrier layer characteristic $I'(E)$, and from this the external photocurrent i and the potential E across the external resistance can be calculated. In this way the calculated cell potentials of Figure 25 for red and blue light were derived, which show a much greater dependence upon the color of the light than was observed.

As the essential result of these considerations it follows furthermore that the short circuit current of the cell does not increase linearly with the intensity, but more slowly.

Figure 26 confirms this action, although the observed departure from linearity is considerably larger than the calculated.

A similar examination of the relation of photocurrent and potential in a semiconductor photocell to the illumina-

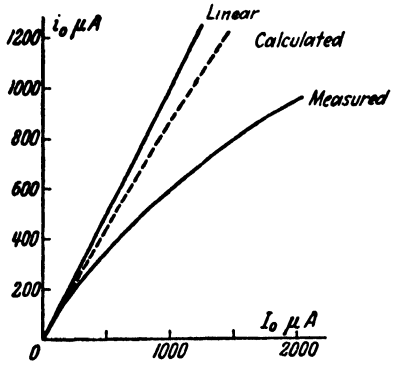


FIGURE 26.—Relation Between Light Intensity (measured as the primary current I_o) and the Short Circuit Current (i_o) of a Selenium Photoelement. According to Selenyi and Körösy.

tion was carried out by E. Perucca and R. Deaglio.[64] They proceeded on the assumptions that the velocity of the photoelectrons is given by the Einstein relation and that the external cell potential depends upon the fall of potential in the external resistance. Whereas Selenyi and Körösy describe the unretarded photocurrent by the empirically discovered equation

$$I = I_o - I_o \frac{E}{E_o} \tag{4}$$

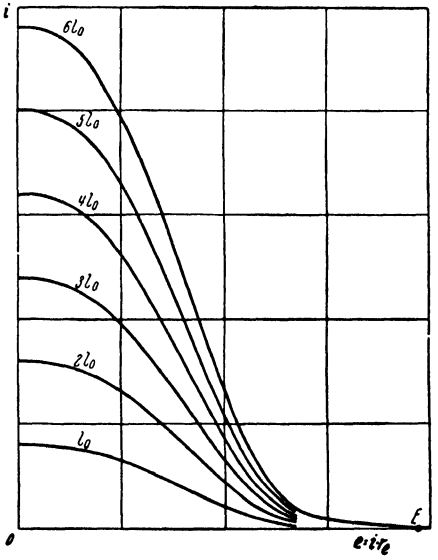


FIGURE 27.—Dependence of the Photocurrent on the Potential Drop

$$e = ir_e$$

for Various Intensities of Illumination l_o.

After Ramsauer on the distribution of velocities of photoelectrically liberated electrons.

According to Perucca and Deaglio.

Perucca and Deaglio take the relation between the photocurrent and the potential from Ramsauer's[65] measurements of velocity distribution among the liberated electrons, and so arrive at the family of curves for different light intensities illustrated in Figure 27.

With increasing illumination the fall of potential $e = ir_e$ approaches the Einstein limiting value E_o asymptotically. Also for a given value of the external resistance r_e the current i is an increasing function of the illumination. If r_e is taken as a parameter which differentiates one curve from another, the curves of Figure 28 are obtained. Bergmann

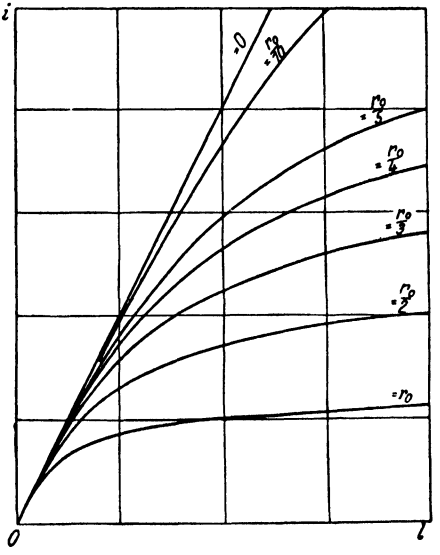


FIGURE 28.—Dependence of the Photocurrent upon the Intensity of Illumination for Various External Resistances.
According to Perucca and Deaglio.

has tested these relations for selenium photoelements and has found an extensive agreement between the course of the curves according to the preceding calculations and the actual measurements.

The derivation of Perucca and Deaglio was, however, made on the assumption that the internal resistance of the cell is constant, entirely contrary to the barrier layer theory,

which contains as an essential constituent the assumption of a boundary resistance dependent upon the potential. Hence Perucca discarded the barrier layer theory and explained the semiconductor photoeffect as a Hallwachs effect.[64]

The Insulating Layer Theory

Already in the discussion of the barrier layer theory the question has arisen as to how far the blocking, or unipolar, action of the high resistance boundary layer is characteristic for the occurrence of the semiconductor photoeffect. In this section we will present this question in somewhat enlarged form, as follows:

1. Is the barrier layer a high resistance layer (insulating layer) structure?

2. Is the blocking action of the insulating layer necessary for the semiconductor photoeffect?

B. Lange [47] has investigated these questions thoroughly with the result that neither a barrier layer nor an insulating layer is necessary for the occurrence of the semiconductor photoeffect, and that insofar as an activated surface or boundary layer of special chemical structure has been found favorable its blocking action is only a secondary effect that is not essential for the semiconductor photoeffect. As the name "Barrier Layer Photoeffect" emphasizes a property not essential to the occurrence of this photoeffect, B. Lange grouped these phenomena together as semiconductor photoeffects and showed that in crystal and Becquerel cells it is a question of the same photoelectric effect.

According to the barrier layer theory the barrier layer is necessary for the prevention of internal short circuits. This would be more plausible if the photoelectrons really were released in the direction of the flow and their return flow through the barrier layer were hindered, which does not prove correct. Rather, in all semiconductor photocells the

electrons are liberated in the reverse direction, so that their return flow takes place in the direction of the lower resistance. The presence of a unipolar conducting layer is thus not necessary for the prevention of an internal short circuit, rather such a short circuit would be favored by the sense of the blocking direction, and a thin highly resistant insulating layer would act more favorably. B. Lange therefore has investigated the blocking action of various cuprous oxide photoelements and secured the static characteristics repre-

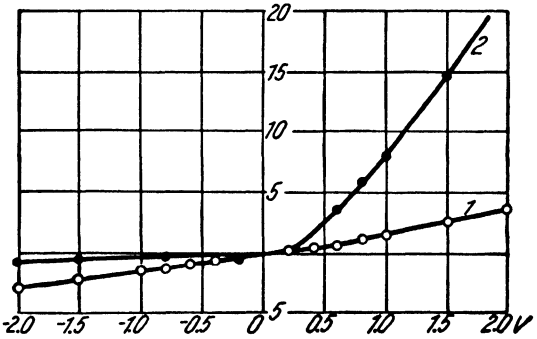


FIGURE 29.—Static Characteristic of (1) a Cuprous Oxide Frontwall Cell, and of (2) a Cuprous Oxide Backwall Cell.

sented in Figure 29. Curve 2 refers to a cuprous oxide backwall cell and curve 1 to a frontwall cell of the same size with a front electrode sputtered with special care. As can be seen the unipolar conductivity of the frontwall cell is vanishingly small. Nevertheless the photocurrent of the frontwall cell is almost ten times greater than that of the backwall cell. Thus we find that a cuprous oxide cell with vanishingly small rectifying action produces considerably more favorable photoelectric phenomena than a cuprous oxide backwall cell with decided unipolar conductivity. Likewise P. R. Gleason [66] was able to prove that a cuprous oxide frontwall cell that showed no rectifying effect, still had 10% of the normal frontwall effect. These two experiments are still not entirely persuasive, as a slight unipolar conductivity of the frontwall cell might still be assumed. Hence B. Lange [47] provided a massive cuprous oxide layer with barrier-

free metal electrodes on two opposite ends, so that the illuminated middle surface was entirely free from electrodes and barrier layers. If the whole surface of the cell together with the electrodes was illuminated, no photocurrent could be observed. If the cell was illuminated only in the vicinity of one electrode, then a photocurrent flowed, the direction and magnitude of which corresponded to the currents in cuprite crystal photocells. This photocurrent could be intrinsically increased by a chemical treatment of the cuprous oxide surface.

If the ground cuprous oxide layer was etched with dilute acid there resulted, as already mentioned on page 54, a disproportionate reduction and oxidation of the cell surface and thus a substantial increase in the sensitivity. According to this a photoeffect is also detectible in a cuprous oxide plate without a barrier layer, which can be considerably increased by chemical treatment of the cell surface. A further proof of the special chemical structure of the barrier layer results in the following way:

If copper discs are oxidized completely or partially at 1000° C. and suddenly quenched in mineral oil, formaldehyde or other reducing agent, the outer cuprous oxide layer will be reduced. If the reducing agent is sufficiently weak the outer copper film is translucent and permits the detection of a proportionally larger frontwall effect. If the copper film and partially reduced cuprous oxide layer beneath it are removed and a new metal layer revealed the photoelectric activity vanishes almost completely. If the copper film, on the contrary, is replaced topochemically by another metal film, as silver, the photoeffect is retained, as in this way the insulating layer has not been damaged.

A third method of increasing the sensitivity consists in the treatment of the cell in the glow discharge. Here, too, an activated surface of about 5×6^{-6} cm thickness is formed, as F. Waibel [27] was able to prove by etching off the surface layer and determining the copper concentration spectroscopically.

From all these experiments the material nature of the barrier layer appears clearly, so that Schottky was forced to give up the purely geometric barrier layer theory. Futhermore we have seen, that a blocking action is not at all essential for the occurrence of the semiconductor photoeffect, as this effect takes place in polycrystalline cuprous oxide just as in cuprite single crystals. Finally we have seen that a particular surface layer increases this photoeffect substantially. A special characteristic of this surface layer is its extremely high resistance, so that it possesses the character of an insulating layer and this sort of cell could be called an insulating layer photocell. We prefer the name "Photoelement," as in this is expressed the nature of these cells as spontaneous sources of current, and because in the crystal cells neither an insulating layer nor a barrier layer is present.

We have already mentioned (p. 56) that the assumption of a material insulating layer was challenged on the ground that the formation of such thin homogeneous insulating layers without short circuits seemed impossible. This might prove correct for the artificial production of such insulating layers on metal plates, but not for natural crystal growth. For a comprehension of this process the recent works of R. Rother and H. Bohmke [67] on the thermal formation of cuprous oxide layers are valuable. According to these, the formation of the Cu_2O is accomplished after the manner of a Tammann [68] reaction in the solid state by diffusion of the oxygen through the Cu_2O layer already formed. Thus several zones of different conductivity are produced. In the immediate vicinity of the mother copper the cuprous oxide is permeated with copper particles and so has a high conductivity, zone 1 in Figure 30. Outside of this the concentration of the copper becomes ever smaller, zone 2, until a layer of the purest Cu_2O with extremely small conductivity, zone 3.

According to our experiments on semiconductors we know that a layer of the purest Cu_2O of this sort insulates highly, as the conductivity is only caused by embedded lattice distortion points. So Rother and Bohmke find that on the

thermal oxidation of the copper a highly insulating layer of pure Cu_2O is formed. Subsequently the conductivity increases in zone 4, since here lattice distortion points are formed in profusion through the oxygen diffusing inward.

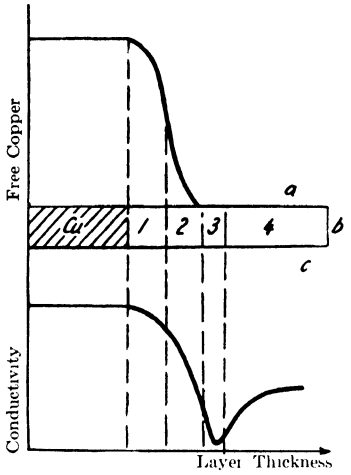


FIGURE 30.—Dependence of the Content of Free Copper and of the Conductivity on the Layer Thicknesses in the Thermal Oxidation of Cuprous Oxide.

b. Various zones 1-4
3. Barrier layer.

In the frontwall effect, in a quite similar fashion, there seems to be a thin completely pure cuprous oxide zone, since on evaporation of the metallic front layer in a high vacuum no frontwall effect appears, but only upon a partial reduction of the surface layer, as heretofore described, through the glow discharge or in a chemical manner. From the different modes of formation of the insulating layer in frontwall and backwall cells is explained also the different spectral sensitivities of the photoelectric cells, since as we have already seen, in the backwall cells monovalent copper ions are photoelectrically active and in the frontwall cells neutral copper atoms. According to a purely physical barrier layer theory these differences would not be comprehensible.

Altogether we see that proof has been adduced in several ways that the semiconductor photoeffect is bound up only with the existence of photoelectrically active centers and

that the photoeffect can be substantially increased by special surface layers. It could be assumed that these surface layers are particularly rich in the photoelectric centers, and that the increase of the photoeffect results from this, yet opposed to this is the fact that these layers are highly insulating and thus according to our concept poor in lattice distortion points. From this we see that the insulating layer theory needs a supplement, which will now be developed in the next section.

The Electron Diffusion Theory of the Semiconductor Photoeffect. Photoelements as Electron-concentration Elements

The theories presented up to now handle only individual phenomena of the semiconductor photoeffect. They are still unsatisfactory, since they give us no complete picture of the whole behavior of the cell as to generation of the photoelectrons, action of the insulating layer, production of a photocurrent and dependence of the photopotential upon the light intensity. The electron diffusion theory will facilitate this coordination.

As a safe basis we can assume in agreement with the various theories that photoelectrons appear at certain centers of the semiconductor under the influence of the light. The electrons thus released enter the semiconductor with a certain velocity given by the $h\nu$ relation, traverse here a distance of about 10^{-4} to 10^{-5} cm and are then again reabsorbed, while the life of the free electrons amounts to about 10^{-5} to 10^{-6} sec. If we illuminate an insulating layer cell, then the light releases electrons in the insulating layer, whose number, N_0, however, is small, since these insulating layers, corresponding to their slight conductivity possess only a few photoelectrically active centers. In comparison, the number N_l of electrons liberated photoelectrically in the semiconductor is substantially greater. Accordingly there is a difference in the electron concentration in the two layers, corresponding to the difference in the number of lattice dis-

tortion points, which as we have seen, can amount to more than a million-fold. We now make the assumption that the EMF of the photoelement results from the difference in concentration of the electrons in the insulating layer and the adjacent semiconductor layer, similarly to galvanic concentration elements, and will now have to prove that the photo-EMF measured in semiconductor photocells agrees with that calculated in this way. For the calculation of the EMF we use Nernst's formula for the diffusion potential. If N_1 and N_0 are the ion concentrations of two solutions and u and v the mobilities of anions and cations, then the potential of this concentration cell is:

$$E = \frac{u - v}{u + v} RT \log_e \frac{N_1}{N_0}. \tag{7}$$

Since in semiconductor photocells the mobility of the positive ions is very small compared with the mobility of the electrons

$$\frac{u - v}{u + v} = 1 \tag{8}$$

and the potential of our photoelement will be

$$E = RT \log_e \frac{N_1}{N_0}. \tag{9}$$

If we express the gas constant R in the electrical system of units and introduce Briggs instead of natural logarithms, it follows that:

$$E = 2.30 \frac{k}{\varepsilon} T \log_{10} \frac{N_1}{N_0} \tag{10}$$

in which k is Boltzmann's constant and ε is 1 electron-volt. For a temperature of 18° C. therefore we get

$$E = 0.0577 \log_{10} \frac{N_1}{N_0}. \tag{11}$$

As we have already mentioned (p. 49) E. Engelhard has determined the number of atoms capable of liberating an electron for a cuprous oxide specimen glowed in vacuum as $N_0 = 0.1 \times 10^{17}$ and for a specimen tempered in oxygen as $N_1 = 230 \times 10^{17}$. The ratio of these two values, which interests us, is 2.3×10^3 and from this $V = 0.0577 \log_{10} 2.3 \times 10^3 = 183$ millivolts, a value which agrees absolutely with actual measurements of the open circuit voltage of cuprous oxide cells. This calculated voltage shows, to be sure, a limiting value for the most intense illumination, which occurs when all emission centers have lost their electrons. For finite light intensities the electron concentrations n_1 and n_0 in semiconductor and insulator are smaller and show the course illustrated in Figure 31.

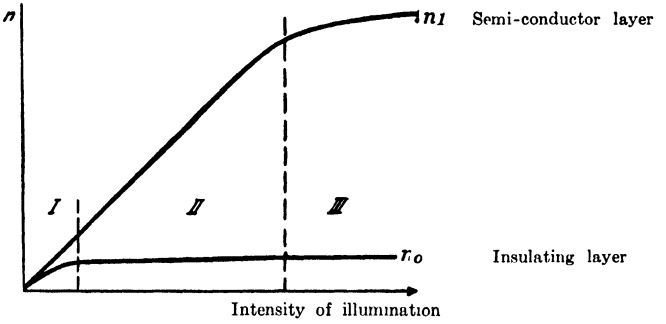


FIGURE 31.—Dependence of the Photoelectrons n Produced in a Semiconductor and Insulating Layer upon the Intensity of Illumination.

At small intensities of illumination electrons whose number increases with increasing intensities of illumination are released in semiconductor and insulator. In the insulator, n_0 approaches the saturation value N_0 at low intensities of illumination corresponding to the comparatively small number of points able to liberate electrons. In the semiconductor on the other hand the saturation value will be reached only

at very great intensities of illumination corresponding to the very great number of centers for liberating electrons.

In the course of the n_1 and n_0 values we can distinguish three sections. In region *I* of small intensities of illumination the ratio n_1/n_0 increases only slowly and at very small intensities approaches the value 1. In region *II* of medium intensities of illumination n_0 is nearly constant and n_1 increases linearly with the intensity. Accordingly the cell voltage increases according to the following logarithmic relation:

$$E_{II} = 0.0577 \log_{10} k L \qquad (12)$$

in which k is a constant of the cell and L is the intensity of illumination.

In region *III* n_1 approaches the saturation value and in the limiting case becomes N_1, so that for this the maximum voltage

$$E_{III} = 0.0577 \log_{10} \frac{N_1}{N_0} \qquad (13)$$

is reached, a value which is determined by the quotient of the photoelectric centers in semiconductor and insulating layers.

Besides the test of the limiting value E_{III} for high intensities of illumination the possibility further exists of determining the dependence of the photo-EMF on the intensity in the region of medium illumination. According to the theory of photoelectron concentration cells there will be a logarithmic relation of the EMF to the light intensity. Corresponding measurements on a selenium photoelement in the region from 1-1000 Lux are shown in Figure 32. As can be seen there is complete agreement according to curve *I*. For these measurements a cell with very high resistance insulating layer was used so that the electron concentration in the insulating layer reached the saturation value at very small intensities of illumination. In cells of lower resistance, curve *II*, n_0 reached a saturation value only at intensi-

ties of several hundred lux, so that only beyond this point was the linear course established in the logarithmic representation, whereas at small intensities the voltage increased approximately linearly with the intensity.

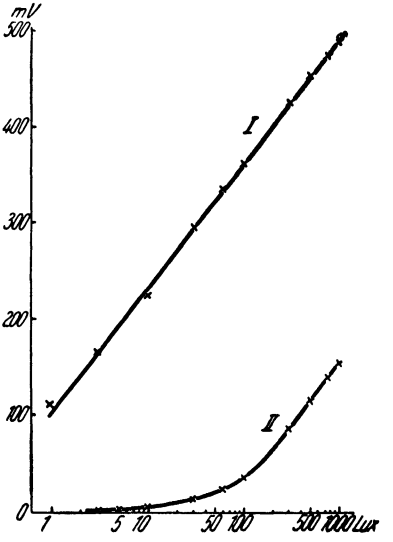


FIGURE 32.—Dependence of the Open Circuit Potential on the Logarithm of the Intensity of Illumination for two Selenium Photoelements *I* and *II*.

The relation between the photo-EMF and the logarithm of the intensity of illumination for a larger region has accordingly the course illustrated schematically in Figure 33. Here, too, three sections can be distinguished, a lower part *I*, a middle part *II* with linear dependence of the photo-EMF on the logarithm of the illumination, and an upper part *III* of saturation. We have a curve form quite similar to curves of photographic density, or blackening.

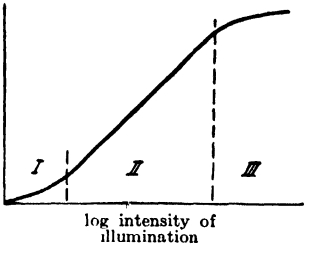


FIGURE 33.—Schematic Course of the Open Circuit Potential of a Photoelement as Dependent upon the Logarithm of the Intensity of Illumination.

For elucidation we will consider as a concrete example cuprous oxide frontwall cells. We have seen that in cuprous oxide frontwall cells the photoelectrically active centers are interstitial Cu atoms. Let their number in the photoelectrically active semiconductor layer be N_1. For an intensity of illumination L a number n_1 of these Cu atoms will liberate an electron and so transform to Cu^+ ions, so that $(N_1 - n_1)$ Cu atoms remain.

During the time dt there arise from these $(N_1 - n_1)$ Cu atoms, through splitting off of electrons under the illumination L,

$$a_1 (N_1 - n_1) L \, dt$$

Cu^+ ions in which a_1 is a constant of the material. Further, it will be assumed that the number of these n_1 Cu^+ ions which in the time dt again become Cu atoms through addition of an electron is

$$b_1 n_1 \, dt$$

in which b_1 is another constant of the material. In the equilibrium state the quantity of Cu^+ ions produced and of Cu atoms again reconstructed must be equal, so that

$$a_1 (N_1 - n_1) L \, dt = b_1 n_1 \, dt$$

whence

$$n_1 = \frac{N_1}{1 + \frac{c_1}{L}} \tag{14}$$

in which $c_1 = \frac{b_1}{a_1}$ has been introduced for simplicity.

For the insulating layer, analogously, is obtained:

$$n_0 = \frac{N_0}{1 + \frac{c_0}{L}} \tag{15}$$

from which the quotient $\frac{n_1}{n_0}$ is given

$$\frac{n_1}{n_0} = \frac{N_1}{N_0} \frac{1 + \frac{c_0}{L}}{1 + \frac{c_1}{L}} \tag{16}$$

and according to the theory of concentration cells

$$E = 0.0577 \log_{10} \frac{N_1}{N_0} \frac{1 + \frac{c_0}{L}}{1 + \frac{c_1}{L}} \tag{17}$$

Since for zero illumination the potential will also be zero, we get equations for determining the constants:

$$\log \frac{N_1}{N_0} \frac{L + c_0}{L + c_1} = 0; \quad \frac{N_1}{N_0} \frac{L + c_0}{L + c_1} = 1; \quad \frac{N_1}{N_0} = \frac{c_1}{c_0}. \tag{18}$$

If $N_1 > N_0$ then we have $c_1 > c_0$.

Equation 17 expresses the dependence of the photopotential on the intensity of illumination for the whole range.

In the region of medium illumination, however,

$$1 + \frac{c_0}{L} \approx 1 \text{ and } 1 + \frac{c_1}{L} \approx \frac{c_1}{L}$$

approximately, since according to equation 18 $c_1 > c_0$.

For this region equation 17 becomes approximately:

$$E_{II} = 0.0577 \log_{10} \frac{N_1}{N_0} \frac{L}{c_1} = 0.0577 \log_{10} k L \tag{19}$$

in which $k = \frac{N_1}{c_1 N_0} = \frac{1}{c_0}$.

There appears also as we have already illustrated a logarithmic relation of the photopotential to the intensity of illumination. For great light intensities, that is, for the region *III* it follows that:

$$lim_{L\to\infty}\frac{n_1}{n_0}=\frac{N_1}{N_0}lim_{L\to\infty}\frac{1+\frac{c_0}{L}}{1+\frac{c_1}{L}}=\frac{N_1}{N_0} \tag{20}$$

and for the maximum potential $E=0.0577\ log_{10}\frac{N_1}{N_0}$, that is, the potential is given by the maximum number of free electrons in the semiconductor and insulating layers, corresponding to the number of lattice distortion points, as we have seen at the beginning of our discussion.

In the preceding derivation we have assumed that the number of lattice distortion points is different in the insulating layer and the semiconductor layer. This assumption, as we will now show, is not essential for the appearance of a photo-EMF in semiconductors. We can according to the same idea likewise explain the photo-EMF in cells with homogeneous semiconductor, in which the concentration gradient of the electrons arises solely from the differential intensity of illumination in different layers of the semiconductor. So we come to the calculation of the photo-EMF in crystal photocells. If L is the intensity of illumination in the front layer of the crystal, we get by analogy

$$n=\frac{N}{1+\frac{c}{L}}. \tag{21}$$

For simplicity we will assume that the crystal is so large, or that the light absorption in the crystal is so great, that the intensity of illumination at the rear of the crystal is vanishingly small. The concentration of free electrons on

this side is then independent of the intensity of illumination and given solely by a constant of the material m. Hence we get for the photo-EMF

$$E = 0.0577 \log_{10} \frac{N}{(1 + \frac{c}{L})\, m} \tag{22}$$

and for $L = \infty$

$$E = 0.0577 \log_{10} \frac{N}{m} \tag{23}$$

that is, here too the maximum EMF is given by the concentration of lattice distortion points in the crystal, so that an ideal crystal without distortion points shows no photo-EMF at all.

Likewise in analogy with the insulating layer cells there is here, in agreement with experiment, a linear increase of the EMF with the logarithm of the intensity of illumination.

So we find the same far-reaching similarity for crystal and insulating layer cells, only with the difference that the electron concentration gradient is produced by the different intensities of illumination on the front and rear of the crystal in crystal cells and by the lower concentration of photoelectrically active centers in the insulating layer of the insulator cells. Accordingly in the crystal cells the photoelectrons flow in the direction of the light from the front face to the rear face of the crystal, from the point of entry of the light where the number of emitted electrons is the greatest to the back, with its slighter light intensity and correspondingly slighter electron concentration. In the semiconductor photocells with forward insulating layer (frontwall cells), on the contrary, the layer of lower electron concentration is in just the opposite situation on the front of the semiconductor and the electron flow accordingly takes place in the opposite direction. So we find that the direction of the light is a secondary matter, and that the direction of the photocurrent is determined solely by the

location of the layer of least electron concentration. Hence the possibility exists of changing the direction of the current in a crystal cell by producing a front electrode with insulating layer on the front face of the crystal by means of a special cathodic sputtering. Also in crystals with inclusions and internal cleavage surfaces, which act as insulators, a reversal in the direction of the photocurrent is found, entirely in agreement with the theory of electron concentration cells.

Our conception of the semiconductor photocells as electron concentration cells permits yet further statements concerning photo-EMF and photocurrent.

We have seen that the normal photo-EMF in insulator cells is determined by the concentration ratio of the electrons in the insulating layer and the semiconductor layer, corresponding to the emission centers therein, whereas in crystal cells it is determined by the ratio of the emission centers at the place of incidence of the light to the electron concentration at the unilluminated rear wall. In the insulating layer there are no, or at least very few, emission centers available to lead to an increase of the electron concentration through the illumination. At the rear of the crystal there are, indeed, emission centers available, but no light for releasing electrons. Hence the photo-EMF of both cells, as far as experience shows, is not essentially different for crystal and insulating layer cells.

Yet the photocurrent in crystal and insulating layer cells is very different, since in crystal cells the resistance path is great, corresponding to the great layer thickness of the crystal, whereas in insulating layer cells the resistance path of the slight layer thickness is correspondingly very much slighter and accordingly the photocurrent is stronger. The photocurrent then will be the largest when the light absorption in the semiconductor is so great that almost all the light is absorbed in a very thin layer and the diffusion path of the photoelectrons corresponds almost to this layer thickness. In this case all the electrons released photoelectrically

flow as an external photocurrent and the full quantum equivalent will be reached.

Thus the electron diffusion theory traces the semiconductor photoeffect back to the internal photoeffect and explains the spontaneous photo-EMF as the diffusion potential of an electron concentration element. A consideration of the light direction and the barrier layer is not necessary in this treatment, nor a direct relation between light frequency and photocurrent, according to Einstein's equation. Indeed the primary liberation of the photoelectrons takes place according to the fundamental photoelectric law, notwithstanding that the external photo-EMF corresponds to the potential of an electron concentration element. Here also we find a parallel with the galvanic elements already brought up for comparison, except that in the latter the ions and in the photoelements the electrons themselves cause the concentration gradient.

Chapter 3

Physical Properties of Semiconductor Photocells

The Cell Characteristic

Photocurrent, Photopotential and Cell Resistance in Relation to the Intensity of Illumination

We have already calculated in the last section the course of the open circuit potential of a photoelement in relation to the intensity of illumination as the potential of an electron concentration element, and have found that in the region of medium intensities of illumination the photo-EMF increases linearly with the logarithm of the intensity of illumination, in the region of small intensities, on the other hand, increases almost linearly with the intensity, and at high intensities approaches a limiting value. Furthermore, it was mentioned that the primary photocurrent I increases linearly with the intensity of illumination. In this section we will now see how far the experimental facts agree with this and learn the exact course of the photocurrent, the photopotential and the cell resistance in relation to the intensity of illumination.

In Figure 34 we have illustrated the photocurrent, which was measured as short circuit current, and the open circuit potential for a selenium photocell (Electrocell System, Type S 50), and have introduced as a broken line the values calculated according to the preceding hypothesis. As we see, the values for the photopotential agree completely with the calculated values* whereas the photocurrent at high

*(Translator's Note: The theoretical curve for the photopotential seems to be masked in Figure 34.)

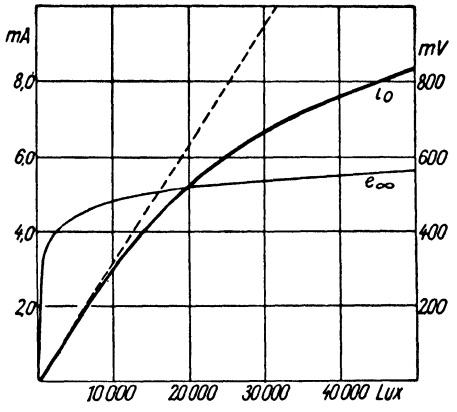


FIGURE 34.—Open Circuit Potential e_∞ and Short Circuit Current i_0 of a Selenium Photoelement Type S 50 No. 400 (10 cm² Light Sensitive Surface).

intensities of illumination departs considerably from the linear course. The preceding measurements consist of the short circuit current i_0 and the open circuit potential e_∞, that is, the photocurrent with vanishing external resistance and the external potential with infinite resistance. The results with finite resistances are essentially different. As is evident from Figure 35, with increasing external resistance the photocurrent departs more and more from the linear course and at very high external resistances shows a course similar to the open circuit potential. In Figure 36 we have illustrated the cell potential for various external resistances and we see from this that the cell potential, just as the photocurrent, increases almost linearly at small external resistances and with increasing external resistance approaches more and more the logarithmic form.

To understand these complicated relations with finite resistances we will investigate more closely the primary photocurrent in the cell and in the external circuit, and for this will make an equivalent diagram of the cell. The crystal photocells are the simplest in construction and their equivalent diagram is correspondingly simple, Figure 37a.

According to the electron diffusion theory the illuminated crystal behaves as a concentration element, which we have indicated in our diagram by our usual symbol for an

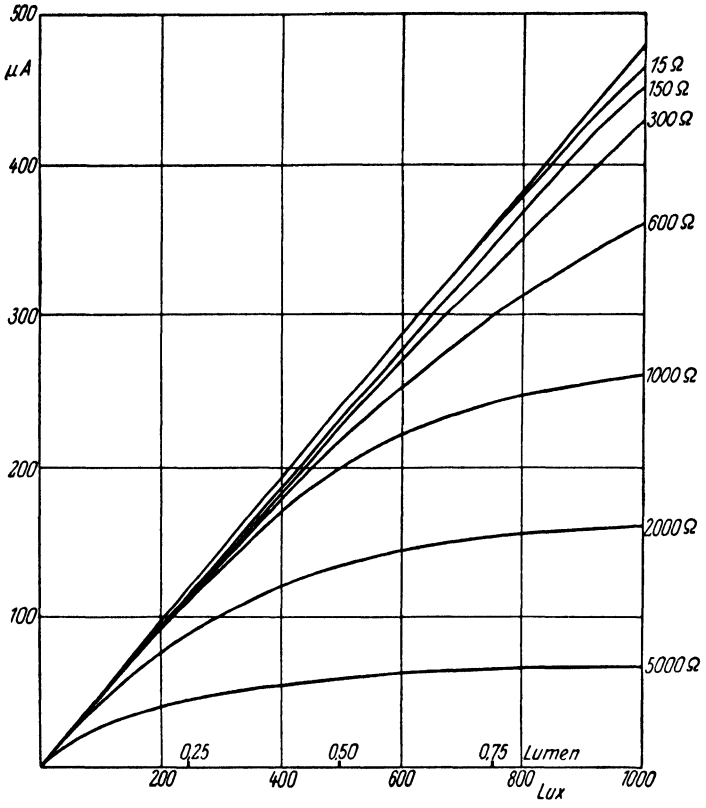


FIGURE 35.—Dependence of the Photocurrent on the Intensity of Illumination and on the External Resistance. For a selenium photoelement type S 50, No. 400.

element E. Parallel with the source of current lies the internal resistance r_i of the crystal. We now present the question of the relation of the external photocurrent i to the intensity of illumination L and the external resistance r_e.

From the equivalent diagram it is evident that the primary photocurrent I branches through the internal resistance r_i and the external resistance r_e so that

$$\frac{i_o}{i} = \frac{r_e}{r_i}. \tag{24}$$

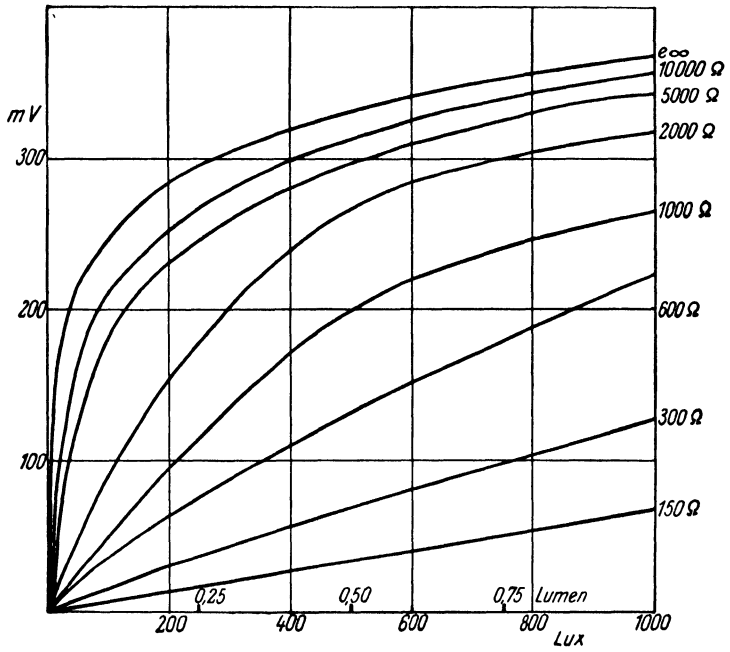
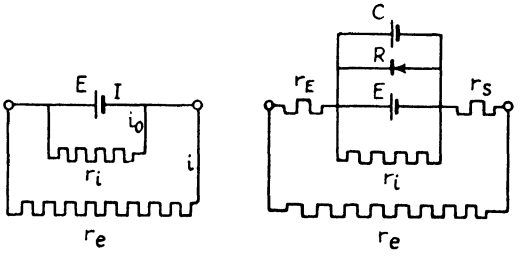


FIGURE 36.—Dependence of the Photopotential on the Intensity of Illumination and on the External Resistance. For a selenium photoelement type S 50, No. 400.

If the internal resistance r_i is large compared with the external r_e the internal photocurrent i_o will be small so that almost the whole primary photocurrent flows through the external circuit.



a. Crystal Photocell b. Insulating Layer Cell

FIGURE 37.—Equivalent Circuit of a Photoelement.

Since, furthermore, the relation

$$I = i + i_o \tag{25}$$

exists, and since

$$I = I_o \cdot L \tag{26}$$

the relation we are seeking is obtained:

$$i = \frac{I\,L}{1 + \frac{r_e}{r_i}}. \tag{27}$$

If r_i is large with respect to r_e, that is, if the external resistance is vanishingly small, the denominator of the foregoing equation approaches the value 1 and the external photocurrent increases linearly with the intensity of illumination. This description needs, however, a supplement. For the internal resistance r_i is not a constant but depends upon the intensity of illumination.

For insulating layer cells we must enlarge our diagram considerably. With these cells the potential gradient is produced in the extremely thin insulating layer so that a considerable capacity C exists between the front electrode and the semiconductor, Figure 37b. Furthermore we have the unipolar behavior of the semiconductor layer to consider, which we have indicated in our equivalent diagram by the symbol of a rectifier R, and finally we must not leave out the resistance of the translucent front electrode r_E and of the semiconductor r_S.

For direct current measurements, which alone interest us in this section, we can neglect capacity effects as well as the unipolar conductivity of the insulating layer, which, as we have seen in the preceding chapter, is not essential for the semiconductor photoeffect. Hence it is sufficient to extend equation 27 by including r_E and r_S. So we obtain:

$$i = \frac{I_o L}{1 + \frac{r_e + r_E + r_S}{r_i}} \tag{28}$$

But from this it follows that the true short circuit currents are not determinable, since even with an external short circuit the resistance of the leads and of the semiconductor, which together amount to about 10 to 100 ohms, act as series resistances for the internal source of current. Hence there is no sense when determining the short circuit current to go below an external resistance of several ohms or to use artful circuits which make it possible to determine the photocurrent at zero external resistance. Thus there is on the whole no great linearity between the external photocurrent and the intensity of illumination. The departure of the short circuit current from a linear course already mentioned and illustrated in Figure 34 thus becomes comprehensible, and also that this relation increases with increasing intensity of illumination, since r_i falls with the light intensity and hence the quotient of the resistances become greater.

Thus we find that the photocurrent and photopotential really depend upon the cell resistance, so that the course of this resistance in relation to the intensity of illumination belongs to the characteristic properties of the cell.

For simplifying the calculation of the cell resistance we will assume r_E and r_S as small compared with r_i, which agrees sufficiently well for small and medium intensities of illumination and larger external resistances. So we solve equation 27 for r_i and obtain

$$r_i = \frac{i\, r_e}{I_0 L - i} \tag{29}$$

According to this the cell resistance is particularly dependent upon the intensity of illumination and also upon the external resistance. This has different causes. We have, for one thing, neglected r_E and r_S in our calculation, which must be considered in addition to the external resistance. Furthermore we have not considered in the calculation the unipolar conductivity, for which the internal resist-

ance depends upon the cell potential. To keep the influence of the extra resistances r_E and r_S as small as possible when determining the resistance, it is expedient to carry on the measurements with an external resistance of about 1000 ohms. Moreover this resistance lies in the region of values occuring in practice.

However, we mention still another method of determining the resistance, which has the advantage of special simplicity and thus is suitable for practical measurements. According to this method the photocurrent is measured with a low resistance instrument, that is, the short circuit current of the cell is determined, and then the external resistance for which the photocurrent falls to the half value is found. If the cell possesses no unipolar conductivity, the external resistance thus determined corresponds exactly to the resistance of the cell. But with unipolar conduction the resistance determined in this way is characterized thus, that it presents the most favorable adjustment of resistance for producing the maximum power. Moreover, the resistance data thus ascertained correspond to the external resistance with which the measurements were carried out and permits an addition to the resistance determined according to equation 29. However, it must always be kept in mind that the resistances determined according to the preceding formula or the procedure described above are only apparent resistances that are limited by the true high resistance of the insulating layer, and the lower electrode and semiconductor resistances. In the region lying between these there will be an apparent resistance, similar to that in a gas discharge tube, which depends upon the electron stream.

To examine the course of the resistance in a large region we have, in Figure 38, plotted the cell resistance R in kilohms (1000 ohms) against the logarithm of the intensity of illumination. As can be seen, the resistance varies linearly with the logarithm of the light intensity over a considerable range and at small intensities, as exact investigations have shown, approaches a definite limiting value

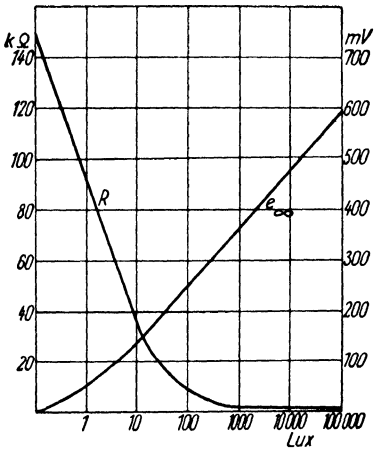
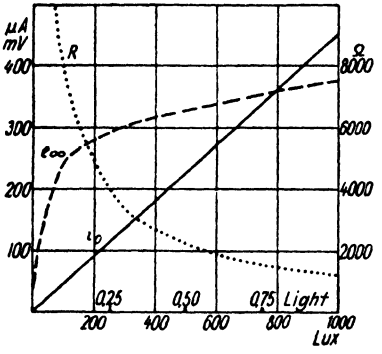


FIGURE 38.—Dependence of Resistance and Open Circuit Potential on the Logarithm of the Intensity of Illumination. For a selenium photoelement type S 50, No. 400.

According to B. Lange.

of 150 kilo-ohms, and at very high light intensities a lower limiting value of 60 ohms. The open circuit potential of the same cell, in comparison, increases almost linearly with the logarithm of the intensity of illumination above 100 lux.

Summing up, we find that for the characterization of a cell the short circuit current, the open circuit potential and the resistance must be known in relation to the intensity of illumination. In Figure 39, accordingly, the characteristic

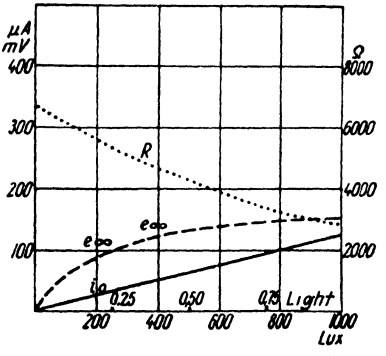


a. Selenium photoelement type S 50, No. 400

e_∞ = 365 millivolts

i_o = 450 microamperes

R = 1400 ohms at 1 lumen



b. Selenium photoelement Weston Photronic No. 594

e_∞ = 150 millivolts

i_o = 130 microamperes

R = 2800 ohms at 1 lumen

FIGURE 39.—Cell Characteristics. According to B. Lange.

curves for a selenium photocell type S50, (a), and for an American selenium photoelement, Photronic Cell No. 594, (b), are illustrated. In place of the characteristic, for the sake of brevity, the statement of the open circuit potential, the short circuit current and the resistance for a particular intensity of illumination is often sufficient. Based on many practical measurements an intensity of illumination of 1000 lux has proved appropriate. For one thing the current and potential are in this case sufficiently large and measureable with simple instruments. Furthermore up to 1000 lux the short circuit current increases linearly enough with the illumination and besides the linear relation between open circuit potential and the intensity of illumination holds in this region, so that the current and potential for a considerable range can be calculated from the values at 1000 lux. The characteristic data for 1000 lux (1 lumen) determined in this way are likewise given in the subtitles of Figure 39 a and b. It is more convenient to refer the data, not to the intensity of the illumination, but to the light flux in lumens since this takes into consideration the area of the cell. As the area of the most commonly used cell, type S50, amounts to about 10 cm^2, the measurement at 1 lumen corresponds to an intensity of illumination of 1000 lux.

Our picture of the physical properties of the photoelements with regard to the dependence of the photocurrent and the photo-EMF on the intensity of illumination will be supplemented by measurements of H. Dember [39] on cuprite crystal photocells, as shown in Figure 40, and by measurements of Fink and Alpern [69] on electrolytic cuprous oxide cells with lead anode in lead nitrate, Figures 41 and 42.

Figure 41 especially shows very clearly the reduction of the photocurrent with increasing external resistance, so that we find for crystal photoelements and Becquerel cells exactly the same characteristic course as for insulating layer cells.

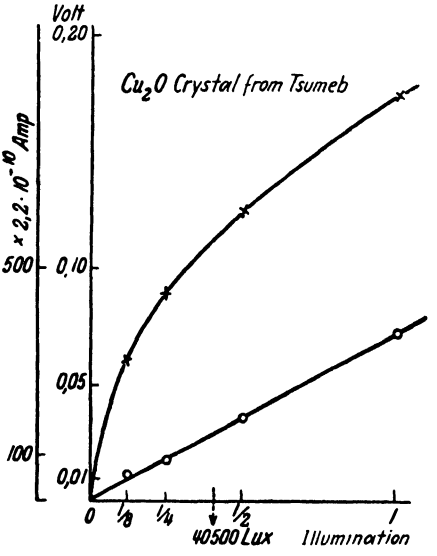


FIGURE 40.—Photocurrent and Photopotential of a Cuprous Oxide Crystal Cell. According to Dember.

FIGURE 41.—Dependence of the Photocurrent on the Intensity of Illumination and on the Resistance. For an electrolytic cuprous oxide cell.

According to Fink and Alpern.

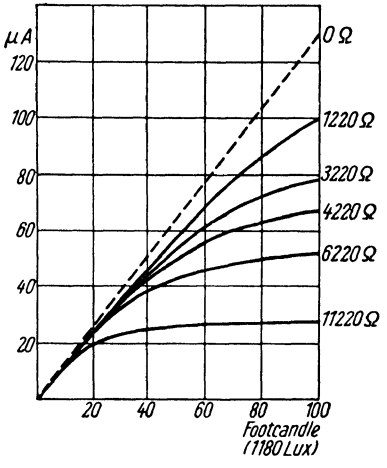
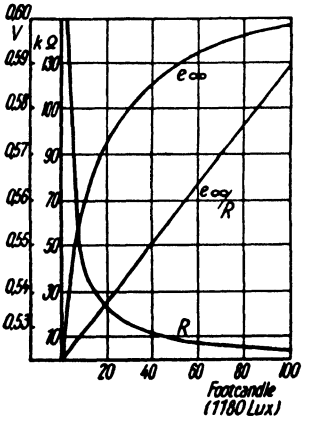


FIGURE 42.—Characteristics of an Electrolytic Cuprous Oxide Cell. In contrast with the dry photoelements the darkened cell has a potential of about 0.52 volt.

e_∞ = 597 millivolts
i_o = 110 microamperes
R = 5400 ohms at 1000 lux



Dependence of the Photocurrent and the Photopotential on the Temperature

The first investigations concerning the temperature relations of the semiconductor photoeffect in cuprous oxide backwall cells were published by H. Teichmann.[55] Teichmann described an impressive demonstration experiment, Figure 43, in which the cell was fastened in the end of a brass tube, which was filled with liquid air. The cell was illuminated by a 500-watt lamp. When the lamp was turned on the galvanometer showed a current which decreased slowly with the warming of the cell by heat radiation from the lamp. When the cell, however, was cooled with liquid air there was a rapid increase of the current to about 3 or 4

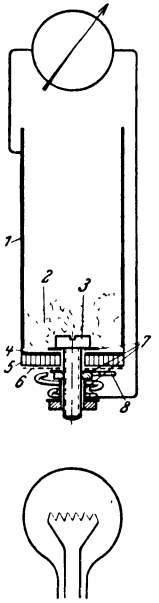


FIGURE 43—Demonstration Experiment of H. Teichmann for Showing the Temperature Relations of a Cuprous Oxide Backwall Cell.

times its value and on further cooling a quick decrease of the photocurrent to the value zero and even a reversal of the current direction. If the liquid air is evaporated the process is repeated in the reverse sense through heating by radiation

from the lamp. According to Teichmann the maximum of the photocurrent occurred at a temperature of about —108° C.

However beautiful this demonstration experiment seems, the conclusion to be drawn from it is unfavorable for the use of these cuprous oxide cells for photometric measurements; for according to this circumstance there is the risk of measuring the temperature of the cell rather than the illumination. Hence more exact measurements of the temperature relations of the semiconductor photoeffect were urgently desired. Measurements of this sort were made by B. Lange [70] with the arrangement illustrated in Figure 44

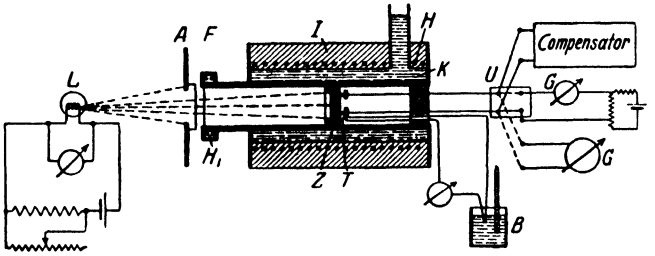


FIGURE 44.—Set-up for Determining the Temperature Relations of the Semiconductor Photoeffect in the Range from + 100 to — 185° C. According to B. Lange.

for a considerable temperature range from —180° to 60° C. As thermostat he used a double wall cylindrical copper vessel, *K*, which carried an electric heating coil, *H*, and which was well insulated thermally. For measurements at lower temperatures the copper shell was cooled with liquid air, whereas for higher temperatures it was filled with water and heated electrically. One end of the copper tube was closed with wadding and cork for heat insulation, the other end was provided with a window *F* cemented on, which was heat insulated in a glass tube and could be heated electrically, to prevent fogging. In the middle of the copper tube was the photocell *Z* in a frame with a spring collar which

assured a good contact even with strong temperature changes. The short circuit current was observed with a mirror galvanometer G of 50 ohms resistance and a sensitivity of 3×10^{-9} amperes per scale division, and the photopotential was measured with a Wolf's compensator, C. Thus the resistance of the cell was determined independently, from current measurements at small external potentials.

The measurements on a cuprous oxide backwall cell, which had for front electrode only a cathodically sputtered gold ring, are represented in Figure 45. These measurements show, like those of Teichmann, an extremely strong dependence of the photocurrent and the photopotential upon

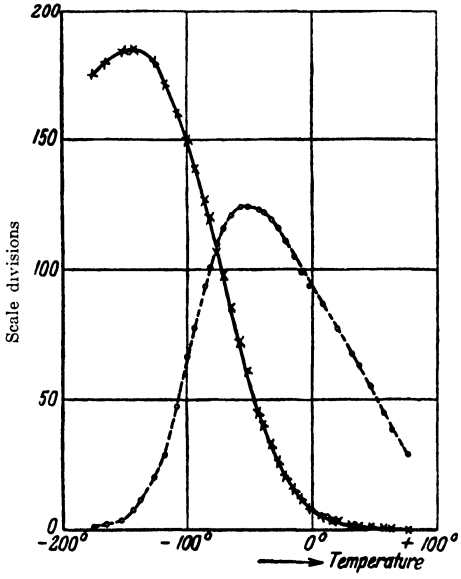


FIGURE 45.—Temperature Relations of the Photoeffect of a Cuprous Oxide Backwall Cell.

Potential: 1 scale division = 2 millivolts.
Current: 1 Scale division = 3×10^{-8} ampere.
× = Potential
O = Current

According to B. Lange.

the temperature. Only in this case the maximum of the photocurrent was reached already at —75° C. and the further decrease did not occur so rapidly. Besides no reversal in the direction of the photocurrent at very low temperatures was found. These differences are to be traced back to the fact that the cuprous oxide cell used by Teichmann had

a translucent copper electrode over its whole front surface, so that a frontwall effect was superposed, which explains the rapid decrease at —110° C. as well as the reversal of the photocurrent found by Teichmann. The simultaneous observation of a frontwall and a backwall effect in cuprous oxide is found frequently when, and only when, cuprous oxide cells with sputtered front electrodes are used. For the study of the pure backwall effect it is necessary to use cells without any front electrode, only a sputtered metal ring around the edge, as was done in the foregoing investigation.

Since the variation of the photocurrent runs almost linearly in the region from —20° to 80° and amounts to about 0.86% of the value at 0° per degree the photocurrent in this region can be represented by the equation

$$i = i_o (1 + \alpha t) \tag{30}$$

with a temperature coefficient $\alpha = -0.0086$. For other cells values were found which increased to $\alpha = -0.0116$. The average value for α is about —0.01, that is, in the vicinity of room temperature the change of the photocurrent amounts to about 1% per degree.

The rise of the photopotential E is related exponentially to the absolute temperature for the region down to $T = 150°$ and can be expressed approximately by the following equation:

$$E = E_o e^{-\beta T}$$

The foregoing measurements were made with the unresolved light of the incandescent lamp so that we learn nothing from this concerning the dependence of the spectral sensitivity on the temperature. As indicated in Figure 46, the maximum is displaced about 30 mμ for a temperature variation from 65° to —150°. This displacement of the spectral sensitivity of the photoeffect is according to B. Gudden explained by a displacement of the optical absorption constant of cuprous oxide about 0.17 mμ per degree.

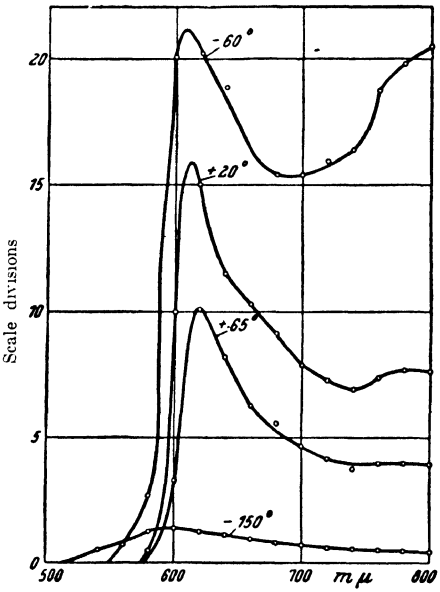


FIGURE 46.—Variation of the Spectral Sensitivity of a Cuprous Oxide Backwall Cell with the Temperature. Referred to a Constant Energy Spectrum.

According to B. Lange.

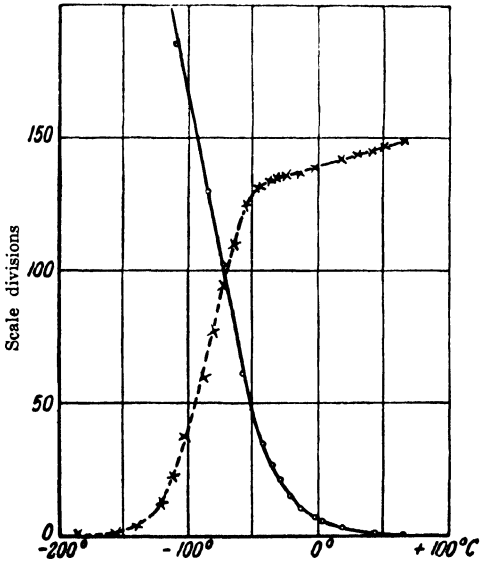


FIGURE 47.—Temperature Relations of the Photoeffect of a Cuprous Oxide Frontwall Cell.

Potential: 1 Scale division = 2 millivolts.
Current: 1 Scale division = 3×10^{-8} ampere.
O = Photopotential
× = Photocurrent

According to B. Lange.

The temperature dependence of the cuprous oxide frontwall cells is essentially smaller, as was determined with the same arrangement. As indicated in Figure 47, the variation of the photocurrent is about one tenth as great, and in the straight line region from —20° to 60° the temperature coefficient is positive and amounts to only 0.001.

W. Bulian [71] has investigated cuprous oxide cells with cathodically sputtered translucent front electrodes of gold, silver, platinum and nickel, for various temperatures, Figure 48. Bulian finds a peculiar influence of the electrode material on the temperature relation. At room tempera-

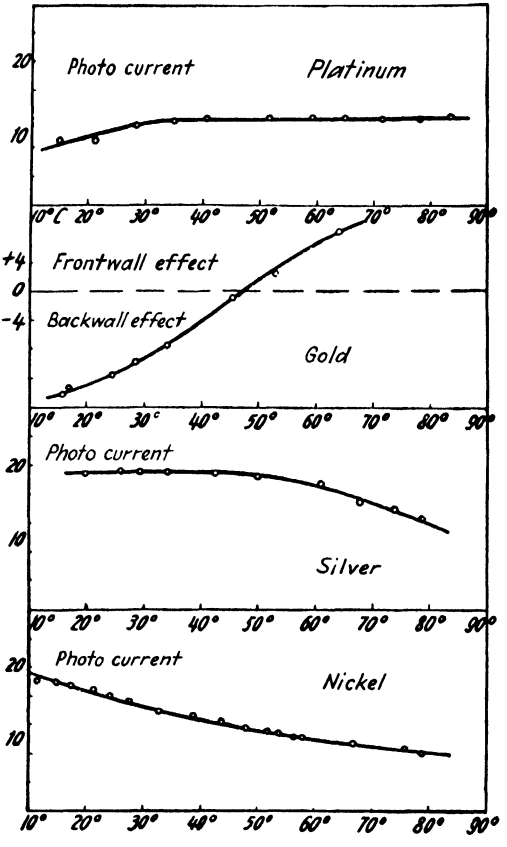


FIGURE 48.—Temperature Relations of the Photocurrent of Cuprous Oxide Frontwall Cells with Different Front Electrodes.

According to Bulian.

tures cells with silver electrodes show by far the least temperature influence, whereas cells with a gold layer have a much greater temperature error. It is not to be assumed that these differences are conditioned by the merely slight difference between the temperature coefficients of silver and gold, for then platinum sputtered cells must have a still greater temperature dependence than gold cells, quite contrary to the results of measurement. As Bulian did not work with spectrally resolved light one would suppose that according to the filter action of the sputtered materials frontwall and backwall effects occur simultaneously. Since these two effects possess opposite temperature coefficients, they can compensate each other. We see a confirmation of this idea in the reversal of the photocurrent for the gold-sputtered cell, Figure 48, which shows the backwall effect below 45° and the frontwall effect above.

Selenium photocells have the smallest temperature errors. As can be seen in Figure 49, the photocurrent has a flat maximum at room temperature with a temperature

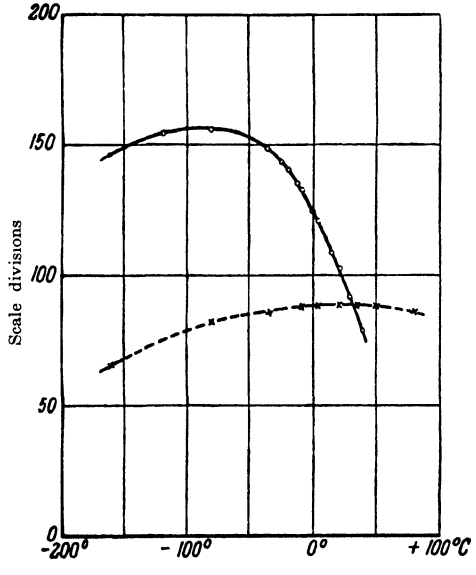
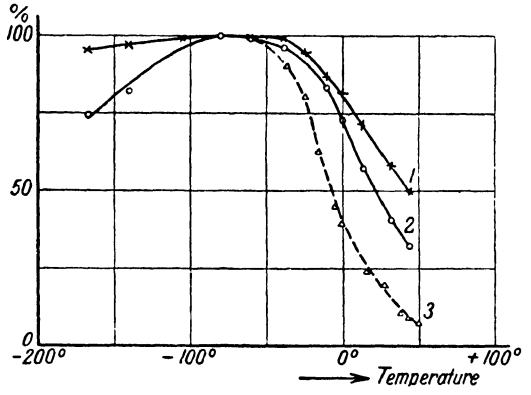


FIGURE 49.—Temperature Relations of the Photoeffect of a Selenium Photoelement.

Potential: 1 Scale division = 1 millivolt
Current: 1 Scale division = 3×10^{-8} ampere
O = Photopotential
× = Photocurrent

According to B. Lange.

coefficient of about 0.0003. The open circuit potential measured with the compensator on the other hand, shows a greater dependence on temperature, which, moreover depends upon the intensity of illumination, as indicated in Figure 50. The far-reaching independence of the spectral sensitivity from the temperature in selenium photoelements, Figure 51, is favorable.



Curve 1, 100 lux
Curve 2, 10 lux
Curve 3, 1 lux

FIGURE 50.—Percentage Temperature Variation of the EMF of a Selenium Photoelement at Various Intensities of Illumination. According to B. Lange.

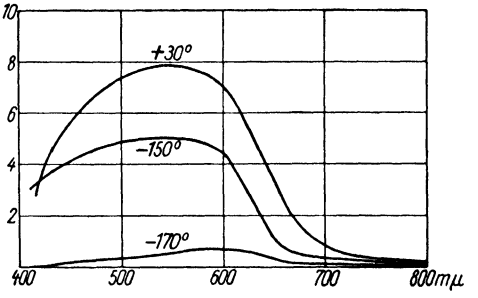


FIGURE 51.—Spectral Sensitivity of a Selenium Photoelement at Different Temperatures. According to B. Lange.

The doubts suggested by the measurements of Teichmann on cuprous oxide backwall cells as to their applicability for more exact photometric measurements accordingly

no longer exist for selenium photoelements, since the temperature variation of the photocurrent of these cells is less than that of a moving coil galvanometer with copper winding without a compensating resistance. This sort of favorable relation is present only for external resistances that are small with respect to the resistance of the illuminated cell. If the external resistance is larger quite complicated relations arise, as is evident from Figure 52 for measurements

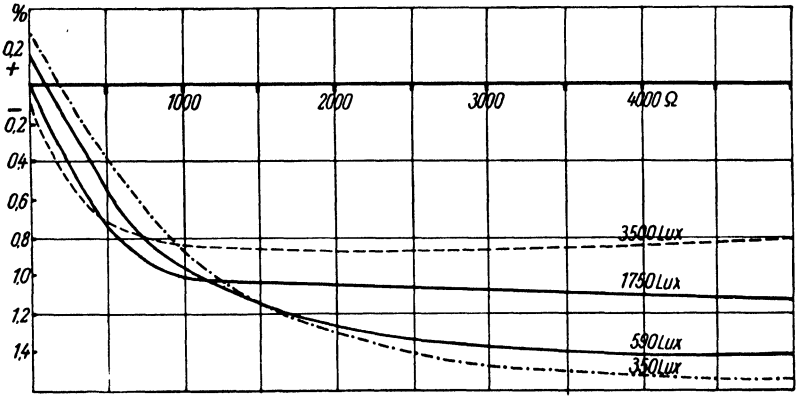


FIGURE 52.—Percent Variation of the Photocurrent of a Selenium Photoelement (Weston Photronic No. 594) in Relation to the Intensity of Illumination and the External Resistance. According to Weston.

on a Weston selenium photoelement (Photronic cell). According to this at low intensities of ilumination and low external resistances an increase of the photocurrent with the temperature can take place, and for a suitable choice of resistance the influence of the temperature can entirely vanish. For external resistances over 1000 ohms on the contrary there is always a decrease of the photocurrent of about 0.8 — 1.5% per degree rise in temperature. For practical use one will thus always have to examine which resistance is permissible and to endeavor to keep this resistance as small as possible, since a smaller resistance is not only favorable for a slighter temperature variation but also for the

linear variation of the photocurrent with the intensity of illumination, and as we shall see later, even for a small fatigue in the cell.

The dependence of the photocurrent upon the temperature is, however, not only important for practical measurements, but also is interesting for the determination of the work of liberating an electron. We have already mentioned on page 55 and thereafter the relation between the resistance of a semiconductor and the temperature according to van't Hoff's equation. B. Lange has carried on such measurements in cuprous oxide backwall cells in a temperature range of —180 to 80° C. and thus secured the results illustrated in Figure 53. The measured points lie very well on

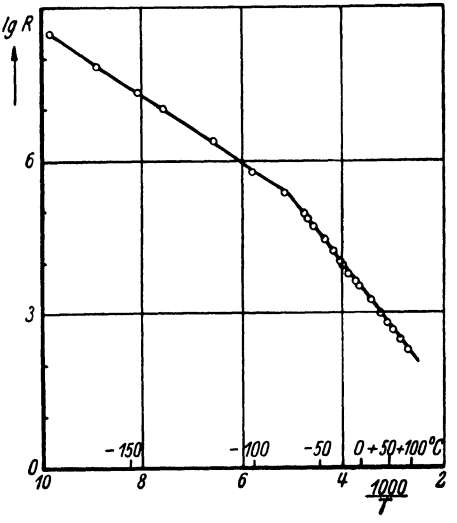


FIGURE 53.—Temperature Variation of the Resistance of a Cuprous Oxide Backwall Cell.

According to B. Lange.

a straight line, as required by the van't Hoff equation. At a temperature of —73 ± 5° the resistance curve however shows a significant break. That this point could be displaced a few degrees according to the rate of cooling was always found and could be reproduced at will. This break can be

explained by a transformation point in the cuprous oxide. E. Englehard,[44] who recently repeated such measurements on cuprous oxide, likewise found this break and explained it by the assumption that the work of liberating an electron has no firmly defined value, but is represented by a distribution function, so that the van't Hoff equation is to be extended correspondingly. There is, however, a third possibility for explaining the break in the resistance curve, namely, through two different work functions for the first and second valence electrons of the Cu atoms. According to our description of the properties of semiconductors (p. 55) the frontwall and backwall effects are explainable as photoeffects of the metallic copper atoms and the monovalent copper ions. According to this conception, above the break a frontwall effect is noticeable which is also manifested in agreement with the experimental finding in that the photocurrent decreases above this temperature and according to Teichmann's measurements even shows a reversal of the direction of flow. Lange calculated from the slope of the resistance curve to —73° an electron work function of 0.25 to 0.32 volt and above —73° a work function only half as great. The first value corresponds to the work function of the second valence electron (backwall effect) and the smaller value of the work function the first valence electron (frontwall effect). W. Vogt[72] has determined the electron work function in a pure cuprous oxide preparation and in a cuprite single crystal from the Hall constant, and thus has secured quite similar values.

The preceding values were calculated from resistance measurements on the unilluminated cell. However, the same values are obtained for the work function from measurements on the illuminated cell without external potentials. Hence the same work function exists for conduction electrons and for photoelectrons, corresponding to our assumption that the same lattice distortion points cause the conductivity and the photoeffect. E. Engelhard[44] and B. Schönwald[73] succeeded in proving through other meas-

urements that electrons liberated thermally and photoelectrically have the same free path and the same mobility.

If we consider finally once more the whole result concerning the temperature relations of the photoelements investigated it appears that an increase as well as a decrease of the photocurrent is observable during a temperature change. Only the photopotential shows always an increase down to very low temperatures. This very different behavior is only comprehensible if we assume that the primary photoeffect itself is independent of the temperature and that the observed effect of temperature is entirely conditioned by secondary processes, especially the marked dependence of the conductivity of semiconductors upon the temperature. We find a support for this assumption in the behavior of the threshold wave-lengths, which are found to depend upon the temperature (see p. 141 seq.). According to the electron diffusion theory the external photo-EMF is determined by the electron concentration in the insulating layer and the adjacent semiconductor layer. According to this it is understandable that the photo-EMF increases with decreasing temperature. For a temperature change of 200°, that is, the electron mobility and the free path increase almost tenfold, so that more electrons diffuse to the boundary layer and through the increase of the electron concentration at the boundary layer the photo-EMF increases with falling temperature.

Sensitivity in the Visible Spectral Range

In the liberation of electrons by light the energy as well as the number of the electrons has been investigated with respect to dependence upon the wave-length of the light. Both questions find an answer through Einstein's equations. The relation between the kinetic energy of the electrons and their linear dependence upon the frequency of the light is

governed by the first Einstein equation

$$\frac{mv^2}{2} = h\nu - h\nu_o. \tag{32}$$

The second Einstein equation

$$N = \frac{Q}{h\nu} \tag{33}$$

says that the number of electrons emitted is inversely proportional to the frequency, that is, increases with the wave-length. Experiment brilliantly confirmed the first statement made by Einstein in 1905 and proved with all clearness that the photo-EMF is independent of the intensity of the radiation and increases linearly with the frequency.

Hitherto it was quite otherwise with the second question of the dependence of the number of electrons upon the wave-length of the light, that is, the spectral sensitivity. Neither the increase in the yield with wave-length, Figure 54(a), demanded by the second equation, nor the order of magnitude of the quantum yield corresponded with the equation.

Two characteristic types have been found for the number of electrons per unit of absorbed light energy: for the first, Figure 54(b), the number of electrons increases contin-

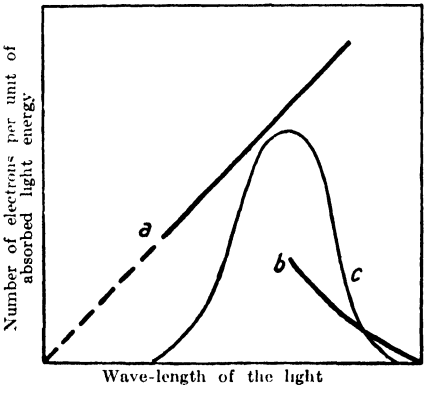


FIGURE 54.—Electron Yield in Relation to the Wave-length of the Light. According to R. Pohl.

uously with the wave-length of the light, the "normal photoeffect." For the second, Figure 54(c), a sharp maximum, reminiscent of a resonance curve appears in a narrow range of wave-lengths, the "selective photoeffect." It is the merit of Pohl [74] and Gudden,[43] to have proved in numerous works that "the electrons of the selective photoeffect do not originate in the atoms or molecules of the solid or liquid metal, but from the metal in a state of molecular or atomic division." In this condition, for example, are the sodium atoms in NaCl that has been colored yellow by x-rays, or the atoms in the interface of a metal and an insulating support. The selective effect takes place in these atomically distributed atoms in two ways: either through optical absorption corresponding to the color or through optical absorption caused by a regular arrangement of the atomic surface layer. In the latter case the light absorption of this layer is different for the two principal directions of vibration of polarized light, and the selective photoeffect can be suppressed if the electric vector is given no component normal to the metal surface, as is illustrated in Figure 55.

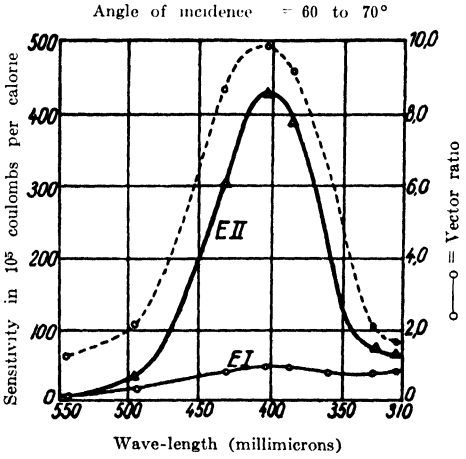


FIGURE 55.—Selective Photoeffect of a Potassium Film on a Platinum Mirror.

According to Suhrmann and Theissing.

In both cases, therefore, the optical absorption of the photoelectric centers is decisive for the spectral course. The

optical absorption spectrum of the active atoms or molecules is measured solely in an electrical manner.

Since in the semiconductor photoeffect the interstitial lattice distortion points act as emission centers for the photoelectrons, we will from the outset expect less influence of orderly surface layers. Rather we would suspect a sensitivity like a resonance curve, Figure 51c, according to Pohl's conception, similar to the internal photoeffect in yellow colored rock salt with embedded sodium atoms. The experimental results correspond fully with these expectations.

The first statements concerning the spectral sensitivity were made by Uljanin [19] in 1888. For his measurements he dispersed the light with a glass prism or with a diffraction grating and measured the photocurrent for the different spectral regions. From this he came to the conclusion that the greatest sensitivity occurred in the orange part of the spectrum, and that the sensitivity fell off toward both ends of the spectrum, more rapidly toward the infrared than toward the ultraviolet, as he could still detect here a relatively large sensitivity with the grating spectrograph.

According as the investigation was carried on with calcium light, Nernst glower or incandescent lamp a different spectral sensitivity was found, corresponding to the energy distribution for the light source used.

For exact investigations it is thus indispensible to refer the photocurrent to a constant energy spectrum, that is, to determine for every individual spectral region the energy content in calories or watts, either thermometrically or bolometrically, and to recalculate the photocurrent measured in each spectral region on the basis of unit energy. In measurements on alkali photocells it is customary to define the photocurrent in coulombs per calorie. For semiconductor photocells, however, the short circuit current, which is authoritative for the yield, is not measured, but the photocurrent, which depends particularly on the resistance of the galvanometer. Hence one is often content with a relative state-

ment of the sensitivity through the galvanometer deflections, referred to a constant energy spectrum.

Such determinations were carried out by B. Lange on several selenium photoelements. As indicated in Figure 56, these three cells show a marked maximum in the orange, as

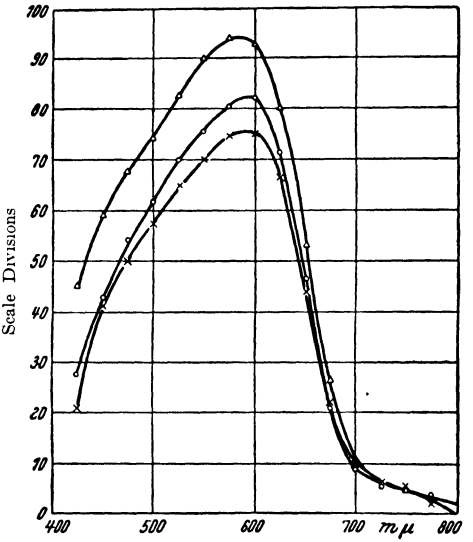


FIGURE 56.—Spectral Sensitivity of Selenium Photoelements Referred to a Constant Energy Spectrum
According to B. Lange.

Uljanin had already stated. To elucidate the differences in spectral sensitivity of the different cells the value measured at 600 mμ was taken as 100 and the values for the individual spectral regions were calculated and the average of a large series of measurements stated, as indicated in Table 1. According to this the maximum lies somewhere between 550 and 600 mμ. Between 800 and 1000 mμ the sensitivity curve begins quite flat, reaches its maximum at 580 mμ and falls off slowly toward the ultraviolet region. According to recent measurements the sensitivity at 400 mμ amounts to about 40%, at 300 mμ about 18%, and at 200 mμ about 6%. Apparently the sensitivity continues still further, since selenium photoelements are sensitive in the x-ray region.

TABLE 1. Spectral sensitivity of various selenium photoelements, referred to equal sensitivities at 600 millimicrons = 100.

λ (mμ)	S_1	S_2	S_3	S_m
425	34.1	27.6	48.5	36.6
450	52.4	55.1	63.5	57.0
475	66.9	67.1	73.0	69.0
500	76.0	76.5	80.0	77.5
525	86.2	86.4	89.4	86.9
550	93.0	93.1	97.2	94.4
575	99.3	99.4	101.5	100.1
600	100.0	100.0	100.0	100.0
625	88.2	88.9	86.7	87.9
650	57.4	59.2	57.3	58.0
675	25.7	29.6	28.6	28.0
700	11.5	12.7	11.0	11.7
725	8.9	9.1	6.2	8.1
750	7.7	7.1	5.6	6.8
775	4.9	3.2	3.6	3.9
800	3.1	3.0	2.1	2.7

TABLE 2. Series of measurements for determining the spectral sensitivity of a selenium photoelement, referred to a constant energy spectrum.

mμ	II	III	IV	V
400	5.6	1	1	100
425	9.92	3	3	100
450	13.35	7	9	130
475	16.10	14	22	160
500	18.32	24	44	180
525	20.19	38	79	210
550	21.78	60	128	214
575	23.13	86	194	227
600	24.32	120	259	216
625	25.35	156	280	179
650	26.27	201	218	108
675	27.06	257	93	36
700	27.76	322	35	11
725	28.40	396	19	5
750	28.98	471	12	2.5

On account of the importance of the determination of spectral sensitivity, the entire course of a measurement given in Table 2 will be described. The measurements refer to a selenium photocell, type S50, with platinum front electrode. They were carried out with a double monochromator according to Bechstein from the firm of Schmidt & Haensch and a Zernicke galvanometer type Zd with a current sensitivity of 2×10^{-10} amperes per scale division. The wavelength is given in the first column of the table, in the second the accompanying drum setting of the double monochromator, in the third the galvanometer deflection for a vacuum thermoelement according to Moll, in the next column the galvanometer deflection for the selenium cell and in the last the spectral sensitivity referred to a constant energy spectrum, calculated as the quotient of the galvanometer deflections for thermocurrents and photocurrents.

If the spectral sensitivity is not referred to a constant energy spectrum, a markedly different curve form is secured, as well as a displacement of the maximum. As an example of this a measurement of Bergmann [29] on selenium photoelements is represented in Figure 57. According to this there

Curve 1: Selenium photoelement with lead alloy electrode
Curve 2: Selenium photoelement with transparent gold electrode
Curve 3: Cuprous oxide frontwall cell for comparison

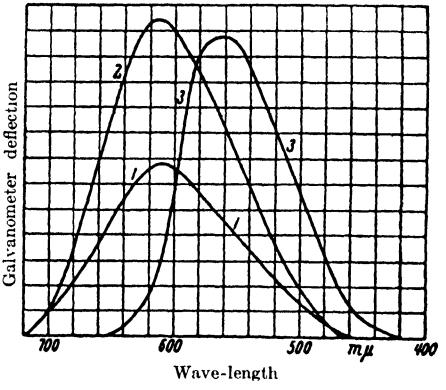


FIGURE 57.—Spectral Sensitivity of a Selenium Photoelement Referred to the Spectrum of a Tungsten Arc Lamp. According to Bergmann.

appears to be a maximum at about 610 mμ and an ultraviolet limit at about 460 mμ entirely contrary to the true limit below 200 mμ. The measurements of Bergmann are interesting in still another respect: *i. e.*, curve 1 was measured for a cell with sprayed lead alloy as front electrode and curve 2 for a cell with cathodically sputtered gold electrode. As evident from the figure, the photoelectric action is extremely independent of the material of the front electrode, a result that was fully confirmed by Bulian [71] for cuprous oxide cells with gold, silver, platinum and nickel electrodes. Platinum electrodes are, however, preferable, as these are almost a neutral gray, whereas gold electrodes have the least absorption in the green, and silver electrodes show a particular ultraviolet transparency, so that with increasing thickness of the electrode a slight displacement of the sensitivity maximum or a change of the ultraviolet sensitivity can occur, for instance with silver electrodes. Measurements by O. Knoll [75] on selenium cells of different makes, Figure 58, show how slight is this influence of the choice of electrode and of the manufacturing process.

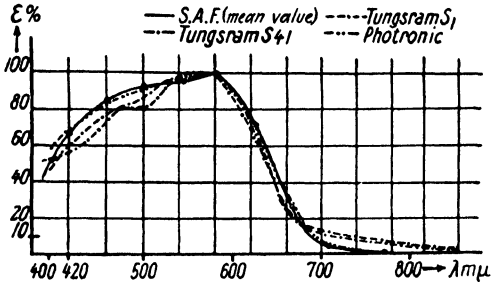


FIGURE 58.—Spectral Sensitivity of Selenium Photoelements of Different Makes. According to O. Knoll.

The property of the selenium cell that its spectral sensitivity is widely independent of temperature, as already shown on page 105, by Figure 51, is valuable.

B. Lange made the first data concerning the spectral sensitivity of cuprous oxide cells. According to these, Figure

59, the maximum at room temperature lies at 615 mμ and is displaced, as we have already seen in the preceding section on page 102, Figure 46, toward shorter wave-lengths with decreasing temperature. Besides the red maximum there is, however, also an infrared maximum at about 800 mμ, that appears particularly clear at a temperature of — 60°, while at room temperature it is quite strongly marked.

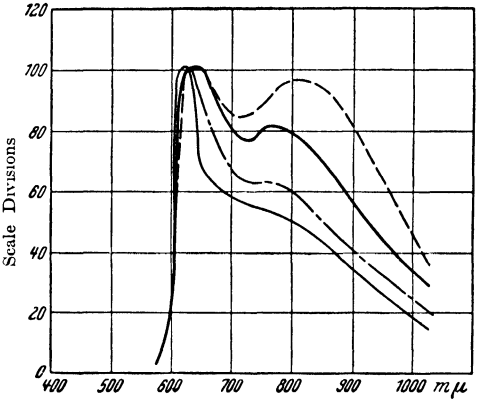


FIGURE 59.—Spectral Sensitivity of Various Cuprous Oxide Backwall Cells. According to B. Lange.

According to R. Pohl [74] a photoelectric effect is to be expected in crystals with strong coloration only on the long-wave side of the absorption region, since in this region only those molecules absorb as are distinguished from the great mass by lattice distortions. Hence it is to be assumed that the maximal photoeffect in cuprous oxide lies on this absorption edge, as B. Lange [70] has also proved through determining the light absorption of a cuprite crystal. At 620 mμ the ultrared side of the absorption curve shows a very steep rise.

Essentially different are the relations for cuprous oxide frontwall cells, in which neutral copper atoms are the photoelectrically active centers. The maximum of the photoeffect here lies at about 500 mμ. The first determination of the spectral sensitivity of the cuprous oxide frontwall cell referred to a constant energy spectrum was carried out by

P. Auger and C. Lapique [76] for cells with silver and with gold electrodes. As might be expected, the silver cell is somewhat more blue sensitive than the gold cell and shows a maximum displaced somewhat toward shorter waves. Detailed investigations concerning the sensitivities of cuprous oxide cells with respect to the material, and the thickness of the front electrode and the thickness of the cuprous oxide layer were carried out by W. Bulian.[71] A part of his results are illustrated in Figures 60, 61 and 62.

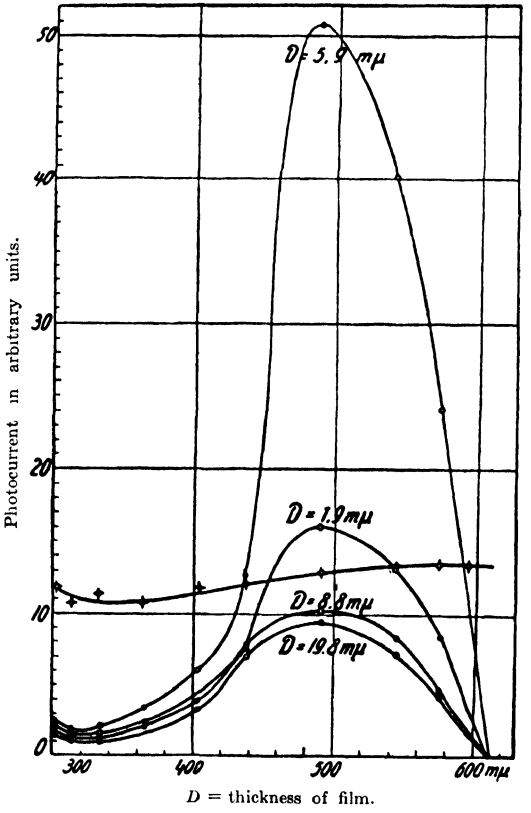


FIGURE 60.—Spectral Distribution of Sputtered Platinum Cuprous Oxide Frontwall Cells. According to Bulian.

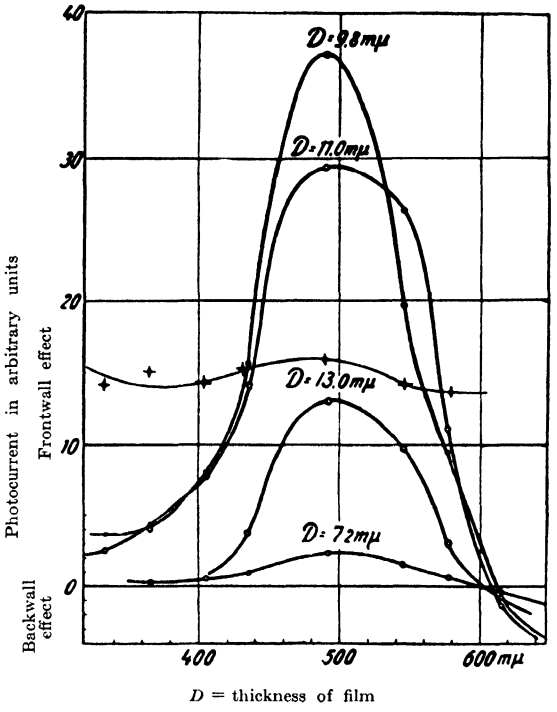


FIGURE 61.—Spectral Distribution of Sputtered Gold Frontwall Cuprous Oxide Cells. According to Bulian.

These results confirm the finding of Auger and Lapique that the spectral sensitivity is influenced only immaterially by the kind of front electrode, as Bergmann [29] had already proved for selenium photocells with gold and lead alloy layers.

E. Duhme and W. Schottky [26] found on touching the surface of a backwall cell at the edge of a cathodically sputtered gold strip a reversal in the direction of the photocurrent. If frontwall cells consist of mother copper with thermally developed cuprous oxide, the backwall effect can be observed upon illumination with red light. This reversal of the current direction above 600 mμ is very distinct as in the cuprous oxide cells with gold electrode illustrated in Figure 61, above.

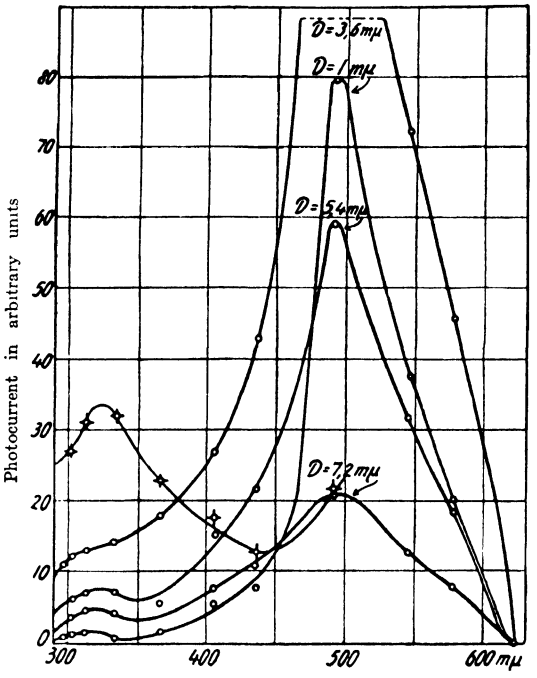


FIGURE 62.—Spectral Distribution of Sputtered Silver Cuprous Oxide Frontwall Cells. According to Bulian.

The spectral sensitivity of Dember's cuprite crystal photocell has not yet been measured. We would, however, expect no noticeable difference from the results for cuprous oxide insulating layer cells. For diamond crystal photocells R. Robertson, D. F. Fox and A. E. Martin [41] have found the maximum spectral sensitivity at the ultraviolet absorption edge. B. Lange has determined the sensitivity maximum of the lead sulfide light detector already illustrated in Figure 15 at 1100 mμ corresponding to Figure 63. The sensitivity of mineral silver sulfide was measured by Geiger and Sheldon,[35] Figure 64.

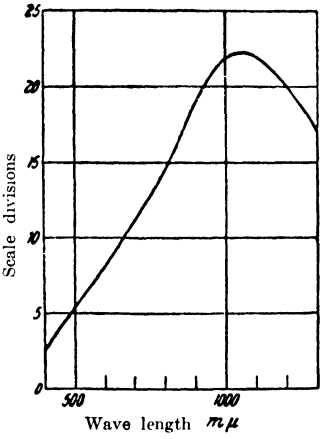


FIGURE 63.—Spectral Sensitivity of a Lead Sulphide Light Detector. According to B. Lange.

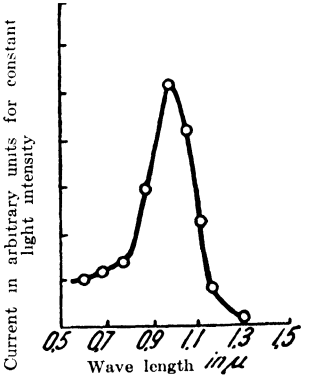


FIGURE 64.—Spectral Sensitivity of a Crystal Photoelement with Mineral Silver Sulphide. According to Geiger and Sheldon.

According to a statement of F. Waibel [77] cuprous oxide Becquerel cells have a maximum spectral sensitivity between 470 and 500 mμ and a similar curve form as cuprous oxide frontwall cells. On these grounds, too, we can assume the same elementary process in both cells.

After we have now reported on the material facts, we will in conclusion submit the question whether we can draw conclusions from the course of the spectral sensitivity as to the mechanism of originating the semiconductor photoeffect. Comparison with the spectral sensitivity of photoelectric conductivity is here suggestive.

The first measurements concerning the photoelectric conduction of cuprous oxide were made by A. H. Pfund [22] on a cuprous oxide piece, which had two adjacent gold electrodes on the front face, as already illustrated in Figure 12 II. If the front face of this cell is illuminated, the maximum of the sensitivity lies in the green, Figure 65, curve 1;

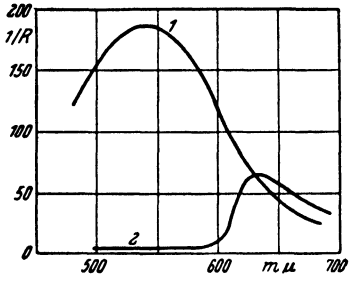


FIGURE 65. — Conductivity $1/R$ of Cuprous Oxide in Relation to the Wave-length of the Incident Light. According to A. H. Pfund.

on the contrary, if the back face is illuminated the maximum lies in the red, curve 2. Pfund explained this difference by the filter action of the intervening cuprous oxide layer for illumination on the back face. Still this explanation did not seem sufficient to him, since the red sensitivity of the backwall effect is greater than that of the frontwall effect. He therefore brought into consideration a "transmitted effect," as had been observed by F. C. Brown [78] for selenium crystals, and which consisted in this, that a change of conductivity also occurred when parts of the crystal far removed from the electrodes were illuminated. In this "transmitted" effect a displacement of the sensitivity maximum toward longer waves would occur simultaneously, similar to Pfund's measurements, curve 2. Such a "transmitted" effect was sought in many other materials, but always without result. Apparently this effect was caused by scattered light with an internal or external light transmission, so that no new property of the material is here exhibited, and this "transmitted effect" is to be stricken out of the verified factual material of experimental physics.

More obvious to us seems the explanation of the difference in spectral sensitivity through the assumption of different photoelectric centers. In front illumination we have the action of the copper atoms, the frontwall effect, in rear illumination that of the copper ions, the backwall effect.

Pfund's measurements have only a guiding character as in them the photoelectric secondary current was not cut out and also no constant energy spectrum applied. Unobjectionable on both counts are recent measurements of Schönwald,[73] which eliminated the influence of the secondary effect by the use of fluctuating light. The spectral sensitivity of the primary photoeffect measured in this way as variation in conductivity of the cuprous oxide showed a course entirely similar to the spectral sensitivity of the cuprous oxide cells illustrated in Figure 59. Beside the red maximum the infrared also shows clearly. Thus the proof is brought out that the electrons of the internal photoeffect originate in the same way as those of the semiconductor photoeffect and are on the whole identical with them, only with the difference that in the semiconductor photoeffect an external potential arises from a concentration gradient of these electrons.

Influence of Polarized Light

According to our earlier discussion, see p. 111, the selective photoeffect is conditioned either by the selective absorption of thin regularly spaced layers or by the absorption of the photoelectric centers themselves. Its behavior in polarized light is characteristic of a regularly spaced surface layer. The photoeffect and the absorption of light are both different for the two directions of vibration of the light. The selective photoeffect can be suppressed, when the electric light-vector is given no component normal to the cell surface, see Figure 55.

An investigation of semiconductor photocells in polarized light offers the possibility of distinguishing whether in

these cells a particular regular structure of the surface layer is essential for the photoeffect or whether, as in the case of rock salt, the selective sensitivity can be traced back to the embedded photoelectric centers.

The first investigations on the influence of polarized light on selenium photoelements were published by L. Bergmann.[79] The schematic layout of his experimental set-up is represented in Figure 66. The light of a projection lamp

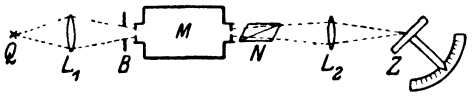


FIGURE 66.—Experimental Arrangement According to L. Bergmann for Determining the Influence of Polarized Light on Photoelements.

Q was concentrated by the lens L_1 on the entrance slit of the monochromator M, while the exit slit was focused by the lens L_2 on the surface of the selenium cell Z. In the light path was a Nicol prism N. The photocell is rotatable about an axis parallel to the image of the slit, so that the image falls exactly on the axis of rotation. The angle between the optical axis of the incident light and the cell was read from a graduated arc. Since a partial polarization of the incident light takes place at the prism surfaces in the monochromator the effective intensity of each component can be made the same by the iris diaphragm. At a wave-length of approximately 615 mμ Bergmann found the relation of photocurrent to angle of incidence illustrated in Figure 67, that is, a noticeably different photocurrent for light vibrating perpendicularly and parallel to the plane of incidence. The photocurrent is independent of the condition of polarization of the light only for perpendicular illumination or grazing incidence. R. Pohl had secured already in 1909 an entirely similar course for the relation of the external photoeffect to the angle of incidence and the direction of polarization in copper and platinum. Pohl was able to explain this behavior by means of the optical constants of the metals. If polarized light falls on a metal surface

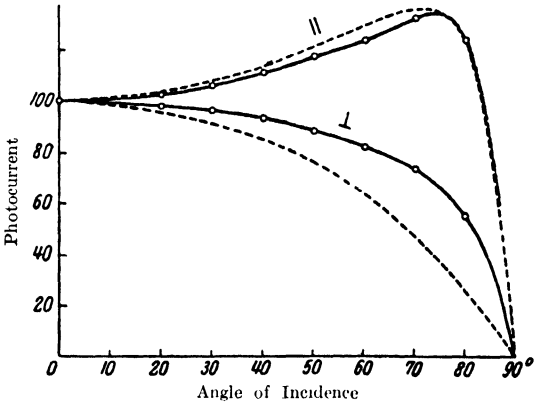


FIGURE 67. — Photocurrent of a Selenium Photoelement for Electric Vector **E** Parallel (II) and Perpendicular (⊥) to the Plane of Incidence at $\lambda = 615$ Millimicron for Various Angles of Incidence. According to L. Bergmann.

only a definite fraction will be reflected while the balance enters the metal as a refracted ray and is there absorbed. The intensities of the reflected and refracted rays depend upon the size of the angle of incidence and the position of the plane of polarization with respect to the plane of incidence. In general the intensity of the refracted ray, for light in which the electric vector vibrates parallel to the plane of incidence, is greater than the intensity of light polarized at right angles to the plane of incidence. The index of refraction n and the absorption coefficient k of the metal are determinative. If I_i indicates the intensity of the incident light, I_r the intensity of the refracted light, and ϕ the angle of incidence, the following equations hold, according to Drude:

$$I_r \perp = I_i \frac{4n\cos\phi}{n^2(1+k^2) + 2n\cos\phi + \cos 2\phi}; \qquad (34a)$$

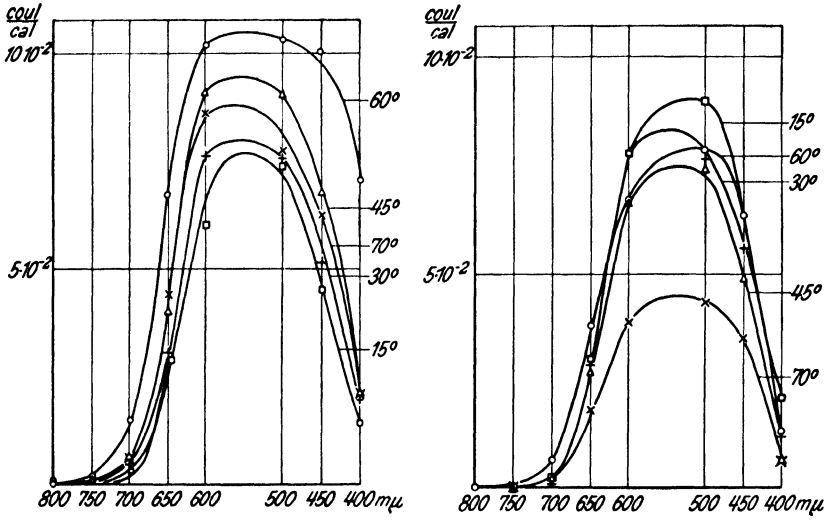
$$I_r \parallel = I_i \frac{4n\cos\phi}{n^2(1+k^2)\cos^2\phi + 2n\cos\phi + 1}. \qquad (34b)$$

An exact calculation is not possible for selenium photocells as the index of refraction and the absorption coefficient are not known for the form of selenium used in the cell;

but if one calculates with $n = 3.2$ and $k = 0.25$ one secures a similar curve form, the broken lines in Figure 67.

Bergmann has thus made it probable that the vector relation of the selenium photoeffect can be explained from the optical constants without requiring the assumption of a photoelectrically active surface layer with a particular structure.

A more exact analysis is possible, however, through an investigation of the spectral form of this vector relation. H. Teichmann [55] has carried out such an investigation on selenium and cuprous oxide photoelements. The results of his measurements on selenium photoelements are exhibited in Figure 68.



a. Electric vector parallel to plane of incidence

b. Electric vector perpendicular to plane of incidence

FIGURE 68.—Spectral Sensitivity of a Selenium Photoelement at Various Angles of Incidence. According to Teichmann.

As can be seen the curves do not show the typical form of a selective photoeffect, since a marked maximum is present for each direction of vibration. If there is a slight influ-

ence of a selective action it cannot be distinguished in the present inexact knowledge of the values of n and k for the modified selenium.

In order to test the nature of the structure in the surface of selenium photocells in another way, H. Teichmann carried out the following interesting experiments. He distilled a thin layer of potassium onto the surface of the photoelement and followed up the changes of spectral sensitivity thus produced. For breath-thin alkali layers, which were directly observable through the appearance of interference colors over the selenium base a weak selective maximum showed in the ultraviolet, Figure 69 *I*, which is traceable to a selective absorption in the thin layer of potassium. A thicker layer of potassium recognizable as a white coating, however, gives a yield that really shows the expected selectivity at the place where the selenium photocell has its maximum sensitivity, as represented in Figure 69 *II*.

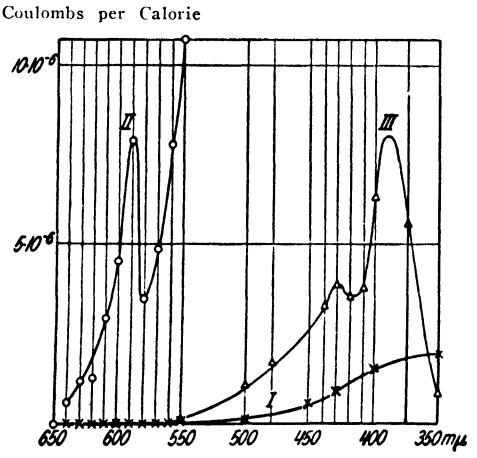


FIGURE 69.—Spectral Sensitivity of the External Photoeffect of a Potassium Layer on the Surface of a Selenium Photoelement.

Electric vector parallel: Angle of incidence 70°.

According to Teichmann.

In the course of a few hours, however, the sensitivity is displaced toward the ultraviolet, curve *III*, apparently as the result of a formation of K_2Se in the meantime, as the spectral sensitivity now corresponds to the value which

W. Kluge [80] observed for cells with a thin potassium layer on a K_2Se base. According to Teichmann cuprous oxide cells show an entirely similar relation as selenium photoelements.

Teichmann saw in these displacements of the sensitivity a confirmation of his "field funnel theory." This conclusion, however, presupposes certain assumptions as to the dependence of the selective photoeffect upon the permeability of the intermediate layer for electrons. A final conclusion seems possible to us only after further experimental confirmation. For the present, we find a sufficient explanation of the results with polarized light in the effect of the optical constants of the semiconductor, and account for the formation of the spectral photoeffect just as in the example mentioned in the beginning, of NaCl with embedded sodium atoms, through the selective absorption of these inclusions.

Sensitivity in the Region of X-Ray Radiation

According to the quantum theory of photoelectric phenomena a photoeffect is present for electromagnetic radiation of all wave-lengths beyond the ultrared threshold frequency, and hence also for the short wave x-ray region. The photoeffect in the region of the x-ray frequencies has also been the subject of numerous works and has led to particular results in fog track experiments in the Wilson chamber and the Geiger point counter. Ultimately every method of measuring x-rays is based upon a photoelectric process, be it the photochemical process of the photographic plate, or the fluorescence of the light screen, or the change in conductivity in the ionization chamber. It is natural therefore to look for a photoelectric primary current in semiconductor photocells in the region of x-ray radiations. P. Selenyi and B. Lange [81] were actually able to establish such an action for a cuprous oxide cell as well as for selenium photoelements. At 12 cm distance from the copper anticathode of a line focus x-ray tube, operating at

40 kilovolts and 12 milliamperes a photocurrent of several microamperes could be observed with a selenium photocell. K. Scharf and O. Weinbaum [82] subsequently carried out exact measurements as to the dependence of the photocurrent and the photopotential upon the intensity and fre-

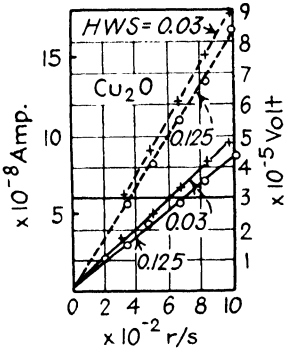


FIGURE 70.—Photo-EMF and Photocurrent of a Cuprous Oxide Frontwall Cell in Relation to the Intensity of X-rays.

Intensity in terms of half value.

Thickness of copper: O = 0.125 mm.
× = 0.03 mm.

——— Photopotential.
- - - - Photocurrent.

According to Scharf and Weinbaum.

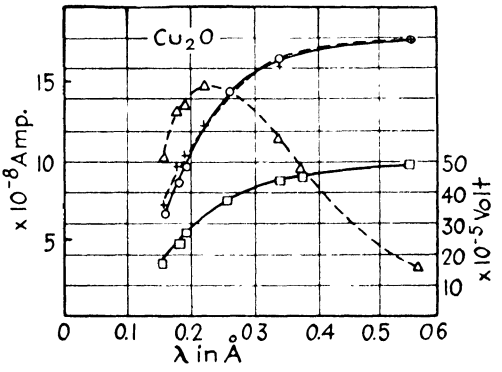


FIGURE 71.—Photo-EMF and Photocurrent of the Cuprous Oxide Cell, Referred to Constant Dosage, in Relation to the Wave-length of the Incident X-rays.

O———O Photocurrent
□———□ Photopotential
×— —× Calculated for half value thickness of copper = 6×10^{-6} cm
△———△ Calculated for half value thickness of copper = 6×10^{-2} cm

According to Scharf and Weinbaum.

quency of the incident x-rays. As indicated in Figure 70 their measurements show that the current and potential increase with the intensity of illumination for cuprous oxide frontwall cells. The photo-EMF, which is produced by x-rays with a half-value thickness of 0.03 mm copper, amounts for an intensity of 0.1 *r*/sec to about 5×10^{-5} volts and the photocurrent in external resistance of 300 ohms comes to 1.8×10^{-8} amperes. As is also evident from Figure

70, for shorter wave-lengths of the x-rays, half-value thickness 0.125 mm copper, at the same intensity the photocurrent and photopotential are likewise smaller. The exact course of the spectral sensitivity is exhibited in Figure 71. Photo-EMF and photocurrent referred to the same dosage of 1 *r*/sec increase to a limiting value with increasing wavelength. Furthermore Scharf and Weinbaum establish that the photocurrent and photopotential increase linearly with the illuminated surface and do not change perceptibly under long illumination. According to Bergmann selenium photoelements, in distinction to these, show a decrease of the photocurrent that only reaches a constant value after a period of illumination of about 30 minutes, at about 25% less than the original current. The fatigue depends upon the intensity of the x-rays and is, as can be seen in Figure 72, slighter for small intensities, similar to visible light,

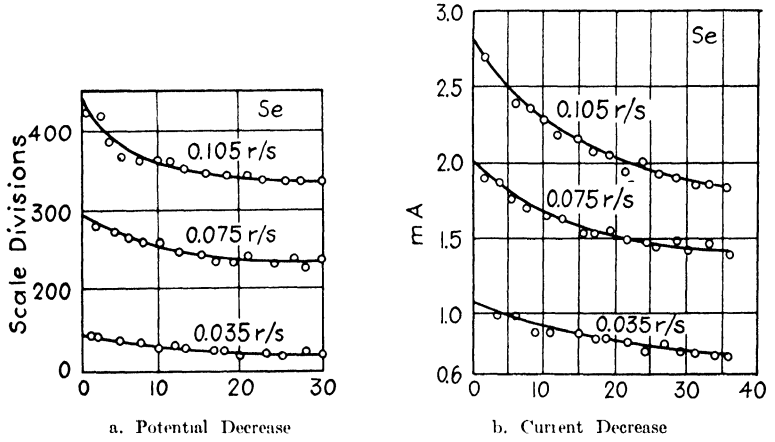


FIGURE 72.—Fatigue of a Selenium Photoelement, According to Bergmann, During Irradiation with Different Intensities of X-rays (r/s). According to Scharf and Weinbaum.

see p. 116, and decreases with successive illuminations. Besides this fatigue under illumination a darkening lag was observed such that the galvanometer deflection did not

return at once to zero upon darkening, but only reached zero again after the course of several minutes. The spectral sensitivity of the Bergmann cell, referred to equal dosages, is fairly constant between 0.2 and 0.6 Å, Figure 73, and hence it is really more suitable for dosage measurements at

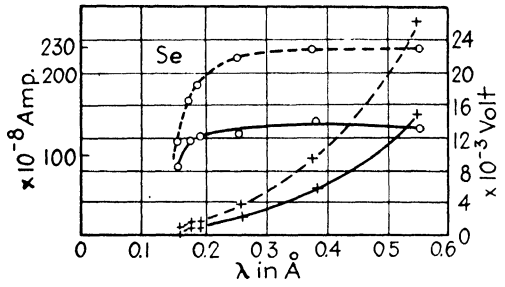


FIGURE 73.—Spectral Relation of the Photo-EMF and the Photocurrent of the Bergmann Selenium Cell Referred to:
Constant Dosage (0) or to Constant Incident energy (×)
——— = Photopotential
– – – – = Photocurrent
According to Scharf and Weinbaum.

different hardnesses of the x-rays. A further advantage of the selenium cell is its considerably greater sensitivity, which is about 24 times as great as the cuprous oxide cell for the photo-EMF and attains about 13 times the photocurrent. For 1 *r*/sec the initial value of the photo-EMF amounts to 1.2×10^{-3} volts and the initial value of the photocurrent 2.25×10^{-7} amperes.

P. R. Gleason [83] has recently carried out measurements with Weston and Tungsram selenium photoelements at x-ray potentials of 600 kilovolts and wave-lengths under 0.45 Å, and even in this short wave region has found no important decrease in the sensitivity. In addition the fatigue was always small, so that rest periods of 15 seconds were sufficient. According to these results and those reported below the impression is gained that the selenium photoelements used by Scharf and Weinbaum were very low resistance or partially had internal short circuits. As we will see later, p. 165, just such low resistance cells show an abnormally high fatigue.

According to a private communication, which R. Jaeger most kindly placed at the author's disposal, a further real increase in the current sensitivity of almost ten times was

secured by a selenium photoelement developed especially for x-ray measurements by E. Falkenthal. R. Jaeger was able to obtain a nearly constant relation of the photocurrent to the hardness of the rays by use of a copper filter 0.17 mm thick in this cell, Figure 74.

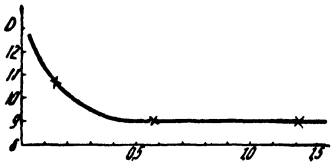


FIGURE 74.—The Relative Dosage D Required to Produce a Given Photocurrent for a Special Selenium Photoelement according to Falkenthal. According to R. Jaeger.

Mirror galvanometers were hitherto necessary for determining the small photocurrents from x-ray irradiation, in which the reading of the light pointer is cumbersome for technical purposes. This inconvenience is done away with by a newly developed Multiflex galvanometer, as this instrument with the sensitivity of a mirror galvanometer is just as easy to manipulate as a needle galvanometer, see Part II.

The Falkenthal cell has no metal plate as support for the selenium, but a thin disc of graphite which absorbs little x-rays, hence this cell can be introduced during the illumination between the x-ray tube and the irradiated object, so that, for example, the x-ray dosage in short time irradiation, perhaps for therapeutic purposes, can be determined from the throw of the galvanometer. With the comparatively large photocurrent which the Falkenthal cell supplies and the high sensitivity of the Multiflex galvanometer, about 3×10^{-9} amperes per scale division, the possibility exists of determining even smaller x-ray intensities in a simple way. An overloading of the cell and the consequent lag phenomena can thus be avoided.

From the behavior of the semiconductor photocells with x-rays we can draw in addition interesting conclusions concerning the origin of the photoelectrons in semiconductors. Visible light is already absorbed in the topmost layer of the semiconductor. Since we cannot measure the depth of penetration of the light exactly the photoelectric efficiency can likewise not be determined. The relations are more easily visible for x-rays, which penetrate the entire semiconductor and whose absorption can be calculated from the mass absorption coefficients and the weight percentages of the atoms of the semiconductor. Scharf and Weinbaum have made these calculations for cuprous oxide and so reach the interesting result that, on the assumption of a photoelectrically active layer thickness of only 6×10^{-6} cm a spectral sensitivity is secured from the relation of the absorption to the hardness of the rays that agrees well with the measured values so that the photo-EMF v and the photocurrent i are approximately proportional to the absorbed energy E_a. The curves exhibited in Figure 71 can thus be represented qualitatively by the relation

$$\frac{v}{r/sec} = k\frac{i}{r/sec} = C\frac{(E_a)_{Cu_2O}}{(E_a)_{air}} = C\frac{1-e^{\tau s}}{\tau_a} \approx C\frac{\tau t}{\tau_a} \quad (35)$$

where τ is the absorption coefficient and t is the thickness of the absorbing layer of copper oxide since the thickness of the layer is very small and the absorption of the air τ_a can be neglected. As evident from Figure 71, the broken line curve calculated from this equation conforms well with the one found experimentally. However, if the calculation is made with the cuprous oxide layer thickness of 6×10^{-2} cm really present the course of the broken curve shows a marked maximum at a wave-length of about 0.24 Å and does not agree at all with the form of the curve found experimentally.

From this it follows that in spite of the great penetrating power of the x-rays and the great energy of the liberated

electrons only a very slight thickness of the cuprous oxide is active in the production of a photo-EMF through x-raying, just as Schottky and Waibel in their etching experiments on cuprous oxide frontwall cells were able to prove directly an effective thickness of 6×10^{-6} cm.

According to the electron diffusion theory the photo-EMF arises from the difference of the electron concentrations in semiconductor and insulating layer, and the thickness of the photoelectrically active layer is not given by the thickness of the insulating layer but by the diffusion path of the electrons. The effective diffusion layer and the insulating layer existing before it possess, however, comparable thicknesses.

Scharf and Weinbaum have furthermore calculated the absolute value of the photoelectric yield. The energy absorbed in the semiconductor layer E_a, is

$$E_a = 0.1\, A \frac{1 - e^{-\tau t}}{\tau_a} \text{ erg/sec}, \tag{36}$$

in which A is the illuminated area of the semiconductor cell in square centimeters. For an effective layer thickness of 6×10^{-6} cm the yield for a wave-length of 0.476 Å amounts to 17.5 coulombs per calorie corresponding to 10^5 electrons per light quantum, and for a wave-length of 0.157 Å, 16.0 coulombs per calorie corresponding to 3×10^5 electrons per light quantum. The quantum equivalent is here, as in all x-ray photoelectric phenomena, far exceeded as a result of secondary ionization by the primary liberated electrons. Nevertheless the energy efficiency, the ratio of the electrical output to the absorbed radiant energy, is only about 1–2%.

H. Dember [42] has observed that in clear cuprite and proustite crystals the photoelectrons always flow in the direction of the incident light. If the crystal is illuminated from the rear there results a reversal in the direction of the photocurrent. The performing of a similar experiment with semiconductor photocells is impossible on account of the

opacity of the semiconductor and the metallic supporting electrode in the region of visible light, but easily possible with x-rays. In this way R. Jaeger was able to observe that the photocurrent always flowed in the same direction for illumination from the front or the rear, a behavior that follows immediately from the electron diffusion theory, since the size and direction of the EMF is given by the position of the insulating layer and the concentration gradient of the photoelectrically liberated electrons independently of the direction of the radiation. In clear semiconductor crystals, free from insulating layers, the potential fall is, on the contrary, set up in the direction of the absorbed radiation, and so the surface turned toward the radiation becomes positive. In the case of rear illumination of such a crystal cell a change of the direction of the photocurrent must be observable. On account of the smallness of the x-ray photoeffect in crystal cells this reversal of current has hitherto not been detectable.

Influence of Cathode Rays

In addition to investigations on the crystal photoeffect in lead sulfide and cuprite single crystals E. Rupp [84] also investigated the action of impinging electrons with the experimental arrangement illustrated in Figure 75. The

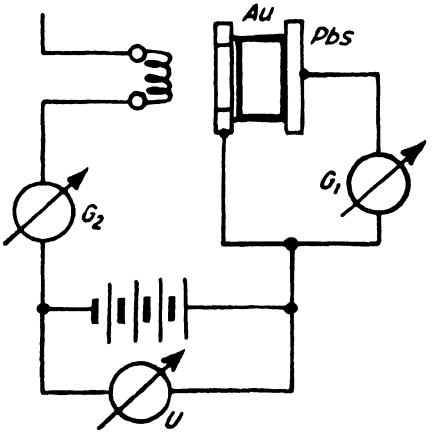


FIGURE 75.—Arrangement for Investigating the Action of Cathode Rays on Lead Sulfide Cells. According to E. Rupp.

electrons emitted in a high vacuum from the filament were accelerated by the potential U and struck a thin layer of gold Au which had been distilled onto the crystal of galena. The galvanometer G_1 measured the current of electrons liberated in the crystal by the impinging electrons, the galvanometer G_2 the current of impinging electrons. With this experimental arrangement, for one thing, the dependence of the crystal current i upon the stream of impinging electrons I at constant potential was investigated, and for another, the dependence of the electron current i upon the potential U of the impinging electrons with the current I as parameter. Figure 76 shows that for a small impinging current I the electron current i in the crystal increases linearly with I. If the impinging current I is greater than 100×10^{-6} amperes then i increases somewhat stronger than linearly, apparently the impinging electrons release secondary electrons in the crystal.

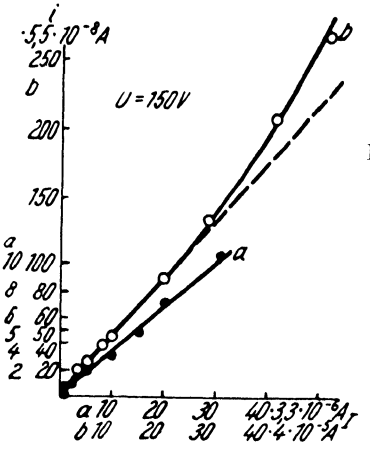


FIGURE 76.—Dependence of the Electron Current i in a Lead Sulfide Crystal on the Current of Impinging Electrons I at 150 Volt Accelerating Potential. According to E. Rupp.

In Figure 77 the dependence of the electron current i in the crystal upon the potential U is illustrated, with the current I as parameter.

For small currents I the crystal current i increases linearly with the potential U. For larger currents I the crystal current i first increases steeply with U, then bends and afterwards increases slowly, without reaching saturation.

An attempt could be made to explain thermoelectrically the phenomena observed during the bombardment of the crystal with electrons. The cathode rays produce a temperature increase in the gilded surface, so that a thermocurrent flows between this and the cooler rear part of the crystal. On this point Rupp suggested, however, that an ordinary thermoeffect at the contact surface of gold and galena did not suffice for explaining the EMF arising in the crystal, since the thermocurrent must increase linearly with the incident energy IU, which did not happen. Apparently a crystal thermoeffect also cooperated, and ultimately a direct production of an EMF by the impinging electrons is to be taken into account.

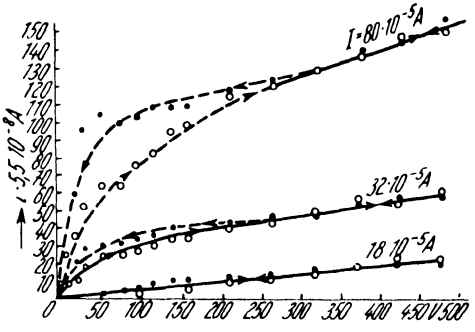


FIGURE 77.—Dependence of the Electron Current in the Crystal on the Potential U of the Impinging Electrons.
○ Potential Increasing
● Potential Decreasing
According to E. Rupp.

Recent investigations of the action of rapid cathode rays on selenium photoelements were carried out by F. Lange and A. Waly. According to a private communication the cells, through the impact of highly accelerated cathode rays, supply a photocurrent which, on short time periods of action of the radiation, is measurable with a ballistic needle galvanometer.

Threshold Wave-lengths, Their Dependence Upon Temperature, and Their Relation to the Atomic Weight

Since the threshold wave-lengths make possible a determination of the energy balance of the elementary processes from the quantum relations of the photoelectric phenomena, they are particularly important for characterizing the photoeffect. The electron work function is derived from the threshold wave-length, and the influence of temperature from measurements at different temperatures, so that the temperature relations of the primary photoelectric processes are determinable independently of external influences and variations in resistance of the semiconductor. At the close of this section we will mention a relation between the threshold wave-length and the molecular weight from which we can draw conclusions as to the constitution of the photoelectrically active centers.

The threshold wave-length is determinable from the long-wave intercept of the spectral sensitivity curve. As these curves often intercept at a very small angle a spectrophotometric determination of the threshold wave-length is difficult and inexact. But the threshold wave-length can be calculated from Richardson's formula for the emission of thermoelectrons. Since there has been no publication concerning the use of this method for semiconductor photocells an investigation of B. Lange and Th. W. Schmidt with respect to this will be described fully.

With reference to investigations of Richardson and Compton [85] and of Ramsauer [65] concerning the emission velocity of photoelectric electrons, A. Becker showed [86] that the relative distribution of the voltage velocities of the photoelectrons liberated from platinum by the light of a blackbody is the same as the velocities of thermoelectrons at a temperature corresponding to that of the black body. Accordingly the electron current for both processes must follow the same fundamental law, so that

$$i = c\, T^2\, e^{-\frac{b}{T}} \qquad (37)$$

where T is the absolute temperature of the black body and c and b are constants of the material. According to the theory of thermoelectrons the work function is

$$\Phi = \frac{b \cdot k}{\varepsilon} = b \times 0.862 \times 10^{-4} \text{ volts} \tag{38}$$

where ε is the charge of an electron, and further according to Einstein's quantum relation

$$\Phi = \frac{h\nu_0}{\varepsilon}; \nu_0 = \frac{\Phi_0 \varepsilon}{h}; \lambda_0 = \frac{1236}{\Phi_0} \text{ m}\mu. \tag{39}$$

If the current of liberated electrons i is measured for different temperatures of a black body as the source of radiation, whose energy at the time is known from Planck's radiation formula, then

$$i = \int_{\nu^1}^{\nu^\infty} f(\nu)\, E(\nu T)\, d\nu = c\, T^2\, e^{-\frac{b}{T}} = c\, T^2\, e^{-\frac{h\nu_0}{kT}}. \tag{40}$$

In this $E(\nu T)$ is the energy of the radiator at the temperature T according to Planck's radiation formula. The validity of this relation was established by R. Suhrmann [87] and S. C. Roy [88] for platinum, silver, and gold as well as for the alkali metals. B. Lange and Th. W. Schmidt show that Richardson's equation is applicable to the electron emission of semiconductor photocells and agrees well with threshold wave-lengths hitherto calculated and measured optically. A transformation of Richardson's equation is suitable for calculating the threshold wave-lengths. By taking logarithms it assumes the form

$$\log i = \log c + 2 \log T - \frac{b}{T} \log c \tag{41}$$

and after further transformation:

$$\log \frac{i}{T^2} = \log c - \frac{b}{T} \log e. \tag{42}$$

But this is the equation of a straight line, if $\log \frac{i}{T^2}$ is

plotted as ordinate and $\frac{1}{T}$ as abscissa. The slope of this equation then is $b \log e$, which gives the quantity b necessary for calculating the work function, from which the threshold frequency ν_o, and the threshold wave-length λ_o, interesting us, appear as

$$\nu_o = \frac{b\,k}{h} = \frac{3 \times 10^{10}}{\lambda_o}. \tag{43}$$

The experimental arrangement used for the measurements is shown in Figure 78. In place of the black body

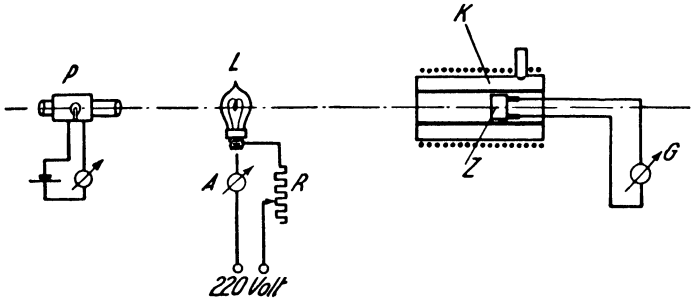


FIGURE 78.—Arrangement for Determining the Photoelectric Linearity. According to B. Lange and Th. W. Schmidt.

a carbon filament lamp was used as a gray body and its departure from the radiation of an ideal black body was taken into consideration in the calculation. By means of a series resistance the incandescent filament could be brought to different temperatures which were measured directly with a Holborn-Kurlbaum pyrometer P and likewise calculated from the lamp current I measured with the ammeter A. As the influence of the temperature upon the threshold wave-length was to be investigated simultaneously, the photocell Z to be studied was arranged in a doublewalled copper vessel K that could be heated electrically as well as cooled by filling it with liquid air.

The photocurrents were measured with a high sensitivity, low resistance mirror galvanometer after Zernicke, with a sensitivity of 2×10^{-10} amperes per scale division. The whole arrangement was set up rigidly on an optical bench, the carbon filament lamp L in the middle with the pyrometer and cell on either side, so that the filament temperature and the photocurrent could be determined simultaneously.

The photoelectric straight line was determined in this way for 5 cuprous oxide backwall cells. As indicated in Figure 79, the measured points, as required by the theory,

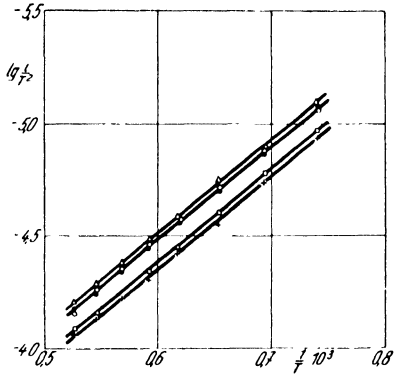
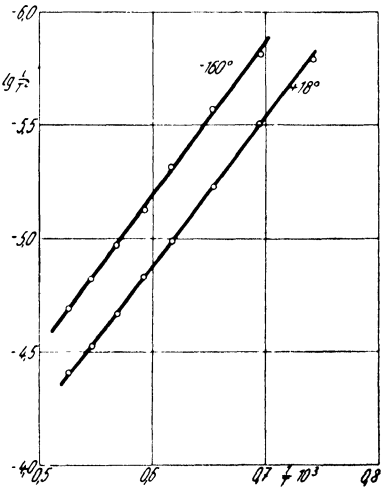


FIGURE 80.—Photoelectric Linearity for a Selenium Photoelement at Different Temperatures. According to B. Lange and Th. W. Schmidt.

FIGURE 79.—Photoelectric Linearity for Various Cuprous Oxide Cells. According to B. Lange and Th. W. Schmidt.



lie on parallel straight lines, from the slope of which is derived a threshold wave-length of 1.4 μ corresponding to an electron work function of 0.88 volt. Similar results were obtained for selenium photoelements, Figure 80, and from

the slope of the straight lines a threshold wave-length of 840 mμ and an electron work function of 1.46 volts were calculated. With the same measuring system the temperature relation of the electron work function was determined for a selenium photoelement at — 160° C. The photoelectric line thus found is likewise illustrated in Figure 80, it runs parallel to the photoelectric lines measured at 20° C. From this, accordingly, the elementary photoelectric process is independent of the temperature, quite in contrast to the external photoeffect and the photo-EMF, which are extremely dependent upon temperature on account of the great variation of resistance in semiconductors with temperature, and other influences of a secondary character.

The larger work function of the electrons stands in apparent contradiction to the greater photoelectric output of the selenium photoelements. However, it must be borne in mind that the quantum relation, which was the basis for determining the work function, represents only the energy balance of the individual elementary processes, but not the external efficiency; or expressed otherwise, if a photoelectric process takes place it proceeds according to the quantum relation, even if it occurs dependent upon other processes, often not fully understood.

In addition the photoelectric line was determined for a lead sulfide light detector, after Figure 15. For this, too, the Richardson relation was confirmed, and the very high threshold wave-length of 4.53 μ was found.

Pohl and Pringsheim [89] have already suggested that the threshold wave-lengths must be in some sort of agreement with the atomic constants of the material. Hitherto, however, no one has succeeded in discovering a clear relation.

For the threshold wave-lengths determined from the photoelectric lines Th. W. Schmidt found the following empirical relation:

$$\lambda_o = 0.384\, e^{\frac{M}{100}}\ \mu \qquad (44)$$

according to which the threshold wave-length is a function

of the molecular weight M (atomic weight). As Figure 81 shows, in a logarithmic representation the measured points for various alkali and semiconductor photocells lie on the line according to the equation above, with great exactness. The value for cuprous oxide, which shows a great departure,

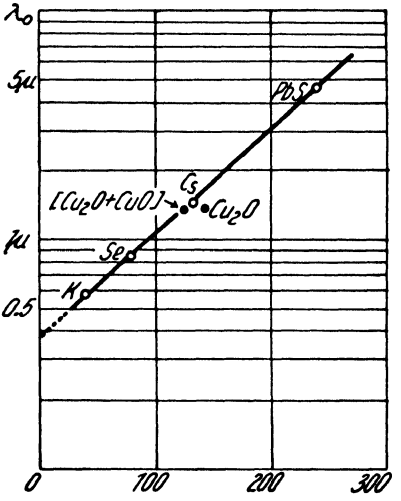


FIGURE 81.—Molecular Weight and Threshold Wave-lengths. According to B. Lange and Th. W. Schmidt.

forms an exception. If one assume, after R. Vogel and W. Pocker,[90] that a eutectoid of 32% CuO and 68% Cu_2O arises upon oxidation of the copper above 1000° C. the molecular weight corresponding to this mixture ratio shows a good agreement of the measured threshold wave-length with the calculated. We have already seen in our discussion of semiconductors, p. 54, that in cuprous oxide back-wall cells the photoelectrically active centers are embedded CuO molecules. In agreement with this the influence of the CuO is shown also in the determination of the threshold wave-length according to the preceding relation. We can, however, make the further statement concerning the photoelectrically active centers, that they consist of a eutectic mixture of cupric oxide and cuprous oxide according to the mixture ratio found by W. Pocker and R. Vogel.

In the discussion of the properties of semiconductors we have, moreover, suggested that Cu_2O not only shows lattice distortion points with CuO, but that neutral Cu atoms can be embedded within the lattice. We have already suggested that it is probable that these Cu atoms are the photoelectrically active centers of the frontwall effect. We also find a confirmation of this from the position of the copper point on the curve according to the preceding relation for atomic weight and threshold wave-length. From this is derived a threshold wave-length for copper atoms of about 720 mμ in good agreement with optical measurements on cupric oxide frontwall cells.

It should be mentioned that the foregoing relation, however, holds only for the selective photoeffect, as this is displayed in alkali and semiconductor photocells, in which finely dispersed atoms are photoelectrically active. Compact metals, which show no selective effect, do not obey this relation.

Influence of a Magnetic Field

Since the semiconductor photoeffect is conditioned by the flow of photoelectrically liberated electrons it was assumed that magnetic fields produce a deflection of the electron path and thus cause a change in the photocurrent. E. Rupp [91] has confirmed this assumption and has proved that in cuprous oxide frontwall cells the photocurrent and the cell resistance vary with the field strength, Figure 82,

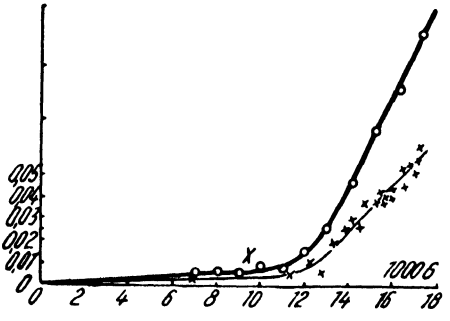


FIGURE 82.—Proportional Variation of the Photocurrent I (×) and the Resistance R (0) of a Cuprous Oxide Frontwall Cell under the Influence of a Magnetic Field.
According to E. Rupp.

but that this effect is only noticeable at high field strengths. In a further work Rupp [91] investigated cuprous oxide backwall cells and lead sulfide crystals and proved that the photocurrent varies approximately with the square of the field strength. According to Rupp the greatest change of the photocurrent and of the cell resistance is present in cuprous oxide frontwall cells when the illumination falls at 45° on the cell surface, and when this makes an angle of 45° with the lines of the magnetic field.

B. Lange and C. Schusterius have investigated the influence of magnetic fields upon selenium photoelements with an iron supporting plate and have here found a notably different behavior. For this the maximal change of the photocurrent is observable with the selenium layer placed at right angles to the lines of magnetic force and with diffuse illumination, which decreases relatively fast on rotation of the cell and reaches its minimum when the cell lies parallel to the lines of force. As is evident from Figure 83

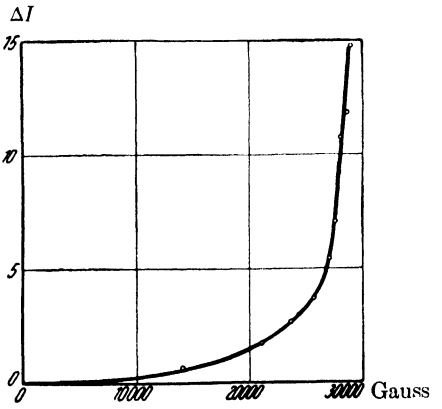


FIGURE 83.—Percent Decrease of the Photocurrent of a Selenium Photoelement under the Influence of a Magnetic Field.
According to B. Lange and C. Schusterius.

the decrease of the photocurrent does not take place with the square of the field strength but considerably faster. The field strengths given in the figure were determined by means of a bismuth spiral without a cell. The effective density of the lines of force was increased by the cell, which filled two-thirds of the pole space.

G. Groetzinger [92] has carried out investigations on the influencing of the crystal photoeffect by a magnetic field. If the direction of the light and of the photocurrent coincide and if the magnetic field is at right angles to the direction of the light (the longitudinal effect) then even at field strengths of 34,600 gauss a scarcely noticeable reduction of the photo-EMF from 64.0 to 63.6 millivolts is perceptible. For a modified arrangement, as in Figure 84, in which

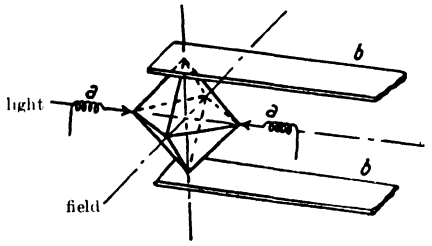


FIGURE 84.—Scheme of the Magnetic Transverse Effect of the Crystal Photoeffect.
According to G. Groetzinger.

light, magnetic field and the direction of the leads are mutually perpendicular, a current which increases linearly with the field strength flows between the leads, which were at the same potential without the field. If the crystal is viewed along the direction of the light and the magnetic field runs from right to left a positive potential appears on the upper side of the crystal. On reversal of the magnetic field the direction of this potential changes. Groetzinger called this the "transverse magnetic effect of the crystal photoeffect."

This phenomenon has a similarity to the Hall effect, except that in distinction to that no external potential is needed, but the electron flow in the crystal is caused by the light. Groetzinger also investigated the Hall effect with the same arrangement; Figure 84, by applying an external potential to the crystal through the wires *a* and at a light intensity of 50,400 lux and a field strength of 27,000 gauss determined the variations of the secondary current in dependence upon the primary current. The results of these measurements are illustrated in Figure 85. Curves 1, 1, refer

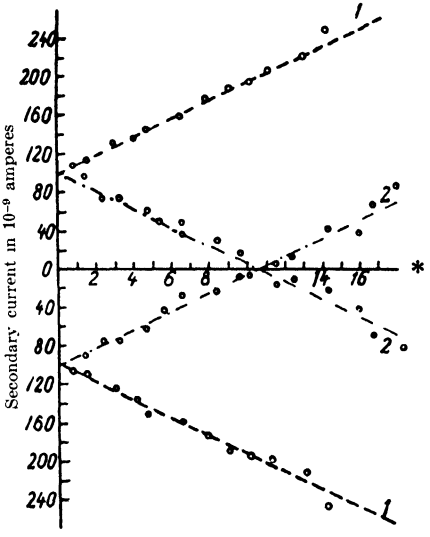


FIGURE 85.—Dependence of the Hall Effect on the Primary Current in a Cuprous Oxide Crystal Irradiated in the Direction of the Photocurrent.

According to G. Groetzinger.

*Primary current in 10^{-6} amperes.

to the case in which the direction of the primary current agrees with the photocurrent, while curves 2, 2, hold for the opposite direction. At the primary current strength $I = 0$, that is, without potential in the leads to the crystal, secondary currents are present which correspond to the transverse effect. If now a potential is applied in the direction of the photocurrent the secondary current increases linearly with the primary current. But if the applied potential is directed oppositely the secondary current decreases and vanishes for a primary current of 1.1×10^{-5} amperes. It seemed noteworthy to Groetzinger that such a considerable primary current strength is required to compensate the current produced by the transverse effect. In other words, to explain the transverse effect by means of a Hall effect the photocurrents in the crystal must be just as strong as the compensation current needed, whereas Groetzinger measured photocurrents only one hundredth as large. However, it must be kept in mind that the external photocurrents correspond merely to the potential gradient in the crystal, whereas the primary photocurrents

flowing in the crystal are considerably greater and can amount to as much as 10^{-5} amperes and accordingly the transverse effect is to be explained as a Hall potential of the photoelectric primary current.

Magnetic measurements permit us yet another conclusion as to the nature of the semiconductor photoeffect.

Rupp,[91] namely, has investigated not only the influence of the magnetic field upon the photocurrent but also the magnetic alteration of resistance for a conduction current in the same semiconductor system, and has thus come to the result that the electrons liberated photoelectrically show the same behavior as the conduction electrons, and that the mechanism of the movement of electricity in the two cases is very similar.

Capacitive Properties

One of the most outstanding properties of the insulating layer cells is their capacity, which arises from the thin insulating layer which exists between the semiconductor and the metal electrode, corresponding to our discussion of the equivalent circuit diagram of this cell, Figure 37b.

W. Schottky and W. Deutschmann [93] some time ago determined the capacitive properties in a cuprous oxide rectifier plate and on the basis of these measurements secured the results illustrated in Figure 86 with an alternating potential

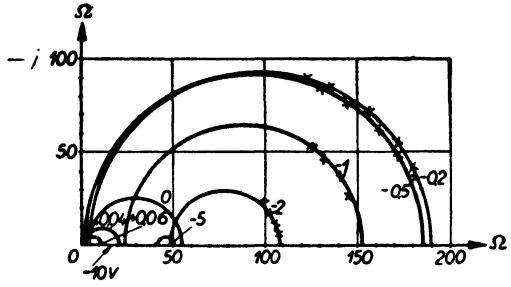


FIGURE 86.—Apparent Resistance Diagram of a Cuprous Oxide Rectifier Plate at 20° C.

According to Schottky and Deutschmann.

of 20 millivolts on the rectifier plate. The points of the curve begin at negative applied potentials with small coordinate

values, increase to relatively large values with a maximum at about —0.3 volt and then shrink together very much. At 0.08 volt the values are already so small that their measurement is difficult. From these measurements the apparent capacity c can be calculated, for a plate with 11 cm^2 surface and at the applied potential 0 it amounts to about 0.3 microfarad. If K is the dielectric constant of the insulating layer, d the distance between the plates of a condenser of equivalent layer thickness, this is calculated from the relation

$$c = \frac{K}{4\pi d}. \tag{45}$$

Since the dielectric constant of cuprous oxide is about 12 this gives an insulating layer thickness of about 3×10^{-5} cm on the condition that the insulating layer covers the metal electrode without voids. We mentioned already that F. Waibel [27] by etching experiments on cuprous oxide front wall cells had shown a layer thickness of 6×10^{-6} cm. The foregoing experiments were conducted with only cuprous oxide

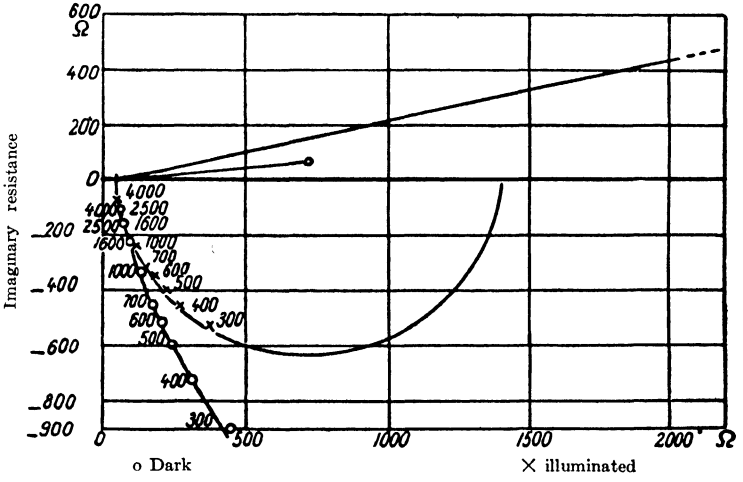


FIGURE 87.—Apparent Resistance Diagram of a Selenium Photoelement. (Weston Photronic).

rectifier plates and hence give no conclusion as to the cell capacity in relation to the illumination and the frequency, interesting to us. Measurements of this kind were made by L. A. Wood[94] on Weston (Photronic) selenium photoelements. As was expected, Figure 87, there was for the real and imaginary components of the complex apparent resistance an entirely similar behavior as in the cuprous oxide rectifier sheets, except that there is a noticeable difference between the dark and bright values, and that the center of the measurement circle does not lie on the abscissa, but above it, corresponding to a phase angle of about 10° between photocurrent and photopotential. The dependence of the capacity on the illumination and on the frequency in Hertz, or fluctuations per second, is illustrated in Figure 88. As

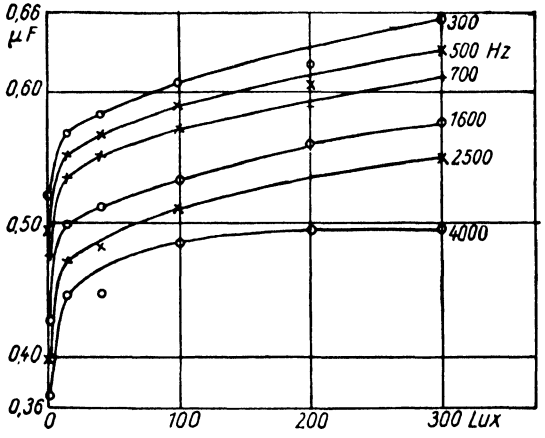


FIGURE 88.—Capacity of a Selenium Photoelement (Weston Photronic) in Relation to the Frequency and to the Intensity of Illumination. Hz = Hertz = Fluctuations per Second. According to L. A. Wood.

can be seen from this, the capacity of the cell increases with the illumination and decreases with the frequency, just the opposite of the resistance of the insulating layer which decreases with both illumination and increasing frequency.

The capacity of the photoelements makes itself particularly annoying in the transformation of high light frequencies, for instance in sound films and television. We will go further into the effect of the capacity upon the frequency action in the next section.

Frequency Relations

The extensive freedom from lag of the external photoelectric effect is sufficiently proved by numerous investigations on vacuum photocells. But there is no sort of ground for the assumption of a lag in the electron liberation of the elementary photoelectric process. So E. Marx and K. Lichtenecker could show that even at illumination times of 1.8×10^{-7} sec there was no sign of a lag. In gas-filled cells on the contrary, on account of the formation of unstable atoms during illumination and the associated ionization, a noticeable lag is present at frequencies of 10^4 hertz, which depends upon the accelerating potential. For a technical caesium cell, for instance, the lag at 10^4 hertz and 60 volts accelerating potential amounts to only 10%, but at 150 volts reaches almost 50%.

For semiconductor photocells the relations are essentially different. In addition to the lagless liberation of electrons we must here take into account the return of the electrons, that is, their re-inclusion in the photoelectrically active centers. So there arises, as we saw already in the preceding chapter, an apparent lag, caused by the capacity of the cell, which depends upon the thickness of the insulating layer situated between the semiconductor and the front electrode.

P. Görlich [95] carried out exact investigations concerning the frequency action in cuprous oxide and selenium photoelements with the circuit arrangement illustrated in Figure 89. The light ray incident on the cell was interrupted by a rotating perforated disc or light siren, and a resistance coupled amplifier with a tube voltmeter in the output circuit was used for measuring the small photopotential. As indi-

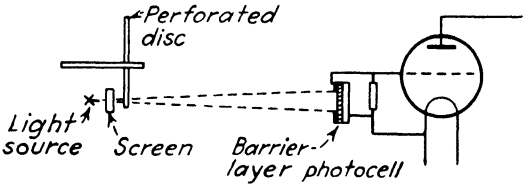
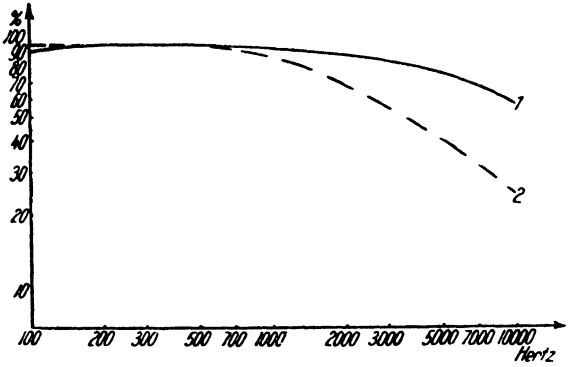


FIGURE 89.—Schematic Experimental Arrangement for Determining the Frequency Relations of Photoelements. According to P. Görlich.

cated by Figure 90, a cuprous oxide frontwall cell shows only a slight decrease of the amplitude of the photo-EMF, similar to a good gas-filled alkali cell. But a selenium photoelement showed a stronger dependence upon frequency.



1. Cuprous oxide frontwall cell (Siemens)
2. Selenium barrier layer cell (Tungsram)

FIGURE 90.—Frequency Curves of a Cuprous Oxide Frontwall Cell and a Selenium Photoelement. According to P. Görlich.

W. Leo and C. Müller [96] have recently made similar investigations with an ideal apparatus and in this way have found a considerably greater dependence upon frequency, Figure 91, which, moreover, depends markedly on the contact resistance and is thus very different for individual cells. The frequency curves secured at any time are thus extremely

dependent upon arbitrary external relations. Moreover errors in measurement could easily occur through uneven operation of the perforated disc or distorted sine form of the light flux. Leo and Müller therefore worked only with a decelerating perforated disc on a switched off motor.

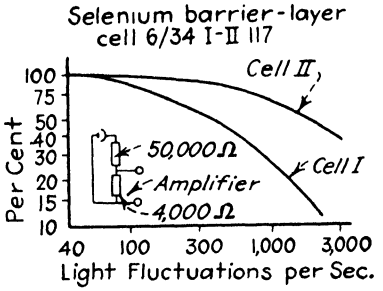


FIGURE 91.—Frequency Curves of Different Selenium Photoelements. According to Leo and Müller.

Plainly, residual stray frequencies from transference of motor vibrations to the perforated disc wave or from a perforated disc running unsteadily can distort the result completely. As indicated by Figure 92, on superimposing 50% of a frequency of 60 hertz a completely different frequency action exists. This rounding off, which simulates a really improved frequency action, takes place because the cell follows only the lower frequencies, especially if the siren frequency and the superposed frequency are more separated and when the superposed amplitude is larger.

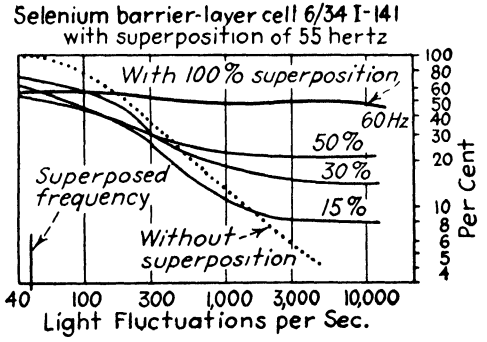


FIGURE 92.—Influence of Superposed Frequencies. According to Leo and Müller.

Müller and Leo could not show any influence of the light intensity upon the frequency action for a change of brightness of 1:5, but probably an influence of the illuminated cell surface, since the resistance of the cell depends upon the cross-sectional area of the illuminated surface. If this is not taken into account, and if the illuminated surface of the cell is altered at the same time as the intensity a strong dependence of the frequency upon the light intensity is shown. A greater dependence of the frequency curve upon the intensity appears, however, when loading resistances are used, which are large compared with the internal resistance of the cell. Through the choice of sufficiently small external resistances this influence can be avoided, but, to be sure, with reduction of the sensitivity.

The lag of the cell, as already mentioned, is for the most part to be attributed to the capacity of the cell. If it is assumed that the photoelectric process itself takes place without lag, an assumption that does not prove wholly correct, then the capacity of the cell can be calculated from the frequency action. If we suppose that the load resistance r_e of the cell is sufficiently small with respect to its internal resistance, and if A_ν is the ratio of the residual amplitude at the frequency ν to the original amplitude at the lower frequency, then

$$c = \frac{1 - A_\nu}{2\pi\nu A_\nu r_e}. \tag{46}$$

Leo and Müller, according to this formula, calculate capacities of from 0.03 to 0.2 microfarad for various semiconductor photocells, which agree well with the data in the preceding chapter.

L. Bergmann [97] investigated the influence of a continual supplementary illumination of 1000 hertz in relation to the resistance in series with the cell. If the cell is lighted additionally the amplifier current is reduced the more as the resistance in the cell circuit is greater and as the supplementary continuous illumination is higher, Figure 93.

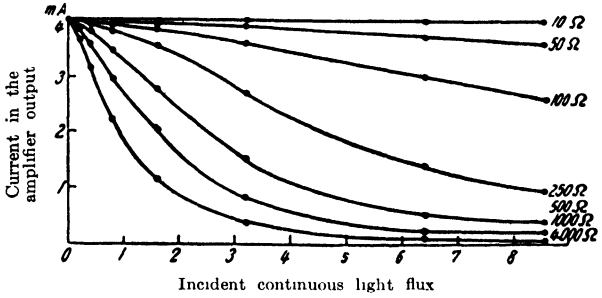


FIGURE 93.—Influence of Continuously Irradiated Light on the Photocurrent at 1000 Hertz for Different Resistances in the Cell Circuit. According to L. Bergmann.

As we have already reported, for gas-filled alkali cells the photocurrent increases with increasing accelerating potential, and simultaneously the lag of the cell increases. The relations are similar for semiconductor photocells. Here, too, an applied potential causes an increase of the photocurrent along with a simultaneous real enlargement of its lag through photoelectric secondary currents. These secondary currents mask completely the primary photocurrent, so that such cells behave as photoelectric resistance cells. If the potential applied to the cell is small, however, and the semiconductor photoeffect outweighs it, then the fluctuating photopotential is markedly dependent upon the direction of the applied potential. A small applied potential in the direction of the photoelectrons retards these and thus reduces the fluctuating photopotential. A positive applied potential, on the other hand, acts to increase the photocurrent, as is evident from the measurements of H. Kerschbaum [98] on a cuprous oxide frontwall cell illustrated in Figure 94. The simultaneous increase of the lag of the photoeffect with the applied potential is indicated in Figure 95. A noticeable increase of the photopotential through an applied potential is produced only at low frequencies, whereas the efficiency decreases rapidly with increasing frequency, and at 10,000 hertz becomes for the most part smaller than with no applied potential. For selenium cells the increase of the lag with the applied potential is even greater. If we keep in mind

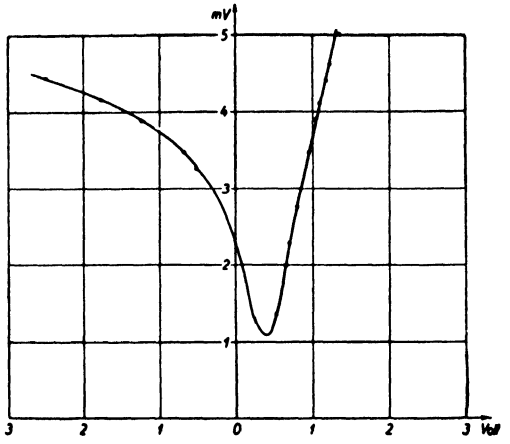


FIGURE 94.—Dependence of the Fluctuating Photopotential of a Cuprous Oxide Frontwall Cell on the Auxiliary Potential. According to H. Kerschbaum.

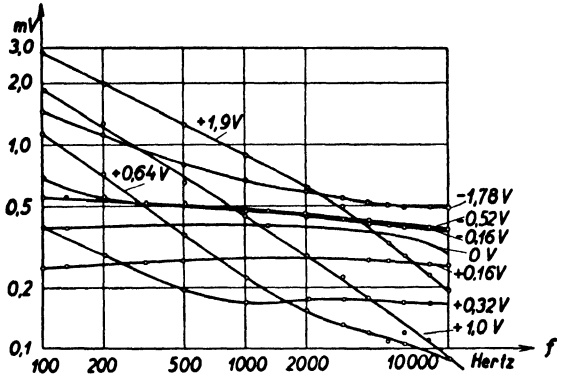


FIGURE 95.—Frequency Relations of the Fluctuating Photopotential of a Cuprous Oxide Frontwall Cell for Various Auxiliary Potentials. According to H. Kerschbaum.

the reduction of the stability of the cell with increasing applied potential, the danger of a perforation of the insulating layer, the necessity of a battery for the applied potential, and above all the increasing inconstancy, we come to the conclusion that the use of an applied potential with semiconductor photocells is generally inexpedient. In contrast to

the photoresistances and alkali cells the very applicability of the semiconductor photocells without any auxiliary potential, as spontaneous light elements, is their characteristic and valuable distinction.

As to the frequency action of the crystal photocells there are thus far no measurements; it is to be expected that this is slighter than for insulating layer cells, since the capacity of the crystal cells is small.

The frequency action of the electrolytic Arcturus cuprous oxide cell is known and is similar to that of a cuprous oxide frontwall cell.

The frequency action of the semiconductor photocells is interesting, however, not only for their technical application. Of interest to physics is the question of the real lag of the photoelectric process. We mentioned already that the release of the photoelectrons takes place with no perceptible lag, but that the recoil of the electrons, and particularly their inclusion in the photoelectrically active centers, takes place with lag. Naturally, too, the primary released electrons can be recaptured, so that our question runs into the determination of the life of the photoelectrons in the semiconductor.

B. Schönwald [73] has carried out investigations concerning this on cuprous oxide, and has determined the life of the photoelectrons in cuprous oxide from the frequency action of the changes in conductivity. From the slight dependence of the frequency Schönwald calculated a mean life of the photoelectrons of 2×10^{-5} seconds.

Stability and Fatigue

Since the beginning of the use of photoelectric cells for photometric purposes the question of their stability and their fatigue has been frequently and heatedly disputed. Thus W. Hallwachs [99] had already carried out in 1906 an exhaustive investigation concerning the "photoelectric fatigue" in copper, platinum, zinc and iron. At that time Hallwachs succeeded in proving that in the observed fatigue phenomena it was not a question of a photoelectric process,

somewhat comparable with the wasting of chemical elements in taking off a current, or of arrangement, but entirely of external influences upon the cell. He was able to show that it is particularly the ozone content of the air which affects the surface of the metal and thus causes a decrease in its photocurrent. In a vacuum the cells remain constant. Later on the same results were reached for the alkali cells.

The relations are similar for semiconductor photocells. Here, too, from the physical standpoint no change of the photoelectric effect with time is to be expected, except for chemical alteration of the semiconductor layer, which can be prevented by enclosure in a vacuum or by good lacquering.

In distinction to the alkali cells, along with the very slow alteration of the sensitivity with the time a temporary reversible fatigue is observed, that starts at once upon illumination and trails off in a few minutes. Upon darkening the process is repeated in the opposite sense.

Hence we will consider stability and fatigue separately and will turn first to the question of stability, that is, constancy over long periods of time.

As we have already recognized a chemical change of the cell as a basis for a temporary inconstancy the same change would not be expected in all semiconductor cells, but rather a different stability would be anticipated according to the chemical resistivity of the semiconductor and the front electrode. Experience has confirmed this. Thus a cuprous oxide backwall cell with a compact metallic rim electrode is considerably more constant than a cuprous oxide frontwall cell with cathodically sputtered silver electrode. The thin silver layer as well as the insulating layer suffer from atmospheric effects. Such a cell can deteriorate to half its sensitivity in a few days, as Bulian [100] has shown by an investigation of cuprous oxide frontwall cells. According to this the fatigue was the greatest during the first 50 hours of irradiation. After about 150 hours the photocurrent seemed to assume a constant value, which also did not change upon cutting off the light, but on renewed illumination set in again

with the same value. Also there appeared no reversible fatigue, but an actual change of the sensitivity of the cell. On the other hand a similar cuprous oxide frontwall cell enclosed in a vacuum or in a vessel filled with argon remained completely constant. Thus the chemical origin of the change is plainly shown. Cuprous oxide backwall cells, on the other hand, remain constant without exclusion of air.

Durability experiments with selenium photoelements are not performed so simply as the above described measurements on cuprous oxide cells, since the selenium photoelements show a much greater fatigue effect than the cuprous oxide cells, especially at high illuminations. As we will first discuss the question of the constancy over long periods of time we must separate the two effects. To accomplish this we can proceed so that continuous illumination and control measurements take place separately, so that the cell is darkened for 1 or 2 hours before every control measurement and is then measured with a lamp whose intensity of illumination is carefully controlled.

Such investigations concerning the changes of selenium cells with time were communicated earlier by B. Lange.[101] As indicated by Figure 96, for a continuous illumination with

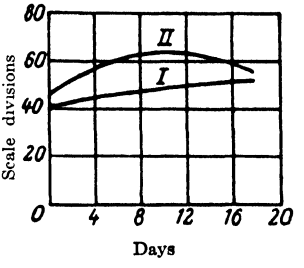


FIGURE 96.—Temporary Change of the Photocurrent of a Selenium Photoelement on Continuous Illumination with 3000 lux.

Curve I cell without load.

Curve II cell loaded with 25 milliamperes. According to B. Lange.

3000 lux for 18 days merely an increase of the photocurrent was observed, curve *I*. In contrast to the cuprous oxide frontwall cell no decrease of the effect occurred, but even an improvement of the cell. In order to get a picture of the stability in a shorter time some cells were loaded by an

applied potential with 25 milliamperes. In this case also an increase of the photoeffect was shown at first, which gradually decreased again, so that after a total illumination of 1,440,000 lux-hours the final value still exceeded the initial value. This experiment showed that the variation of the photoelectric properties of the cell depended upon its load. It could be expected that cells would behave more constantly at smaller illumination. Such experiments were recently repeated by B. Lange with improved selenium photoelements, type S 50 with platinum electrode, for cells on open circuit, short-circuited and loaded with 2000 ohms. The results of these measurements are presented in Table 3. The control measurements were carried out at 1000 lux and the photocurrent was measured at external resistances of 100 and 1000 ohms so as to check simultaneously the cell resistance calculated according to the formula of Equation 29, p. 93. As Table 3 indicates, except for the experi-

TABLE 3. Long-time test of various selenium photoelements, Type S 50.

Intensity of Illumination	500 Lux	500 Lux	500 Lux	Daylight [1]	Sunlight [2]	Dark
Load/Circuit	2000 Ohm	Short	Open	Short	Short	Open
Cell No.	391	395	396	386	385	401
Day/Current [3]	i	i	i	i	i	i
0	$\frac{21}{45}$	$\frac{21}{42}$	$\frac{23}{43}$	$\frac{23}{43}$	$\frac{21}{41}$	$\frac{21}{45}$
1	$\frac{22}{45}$	$\frac{22}{40}$	$\frac{23}{41}$	$\frac{23}{43}$	$\frac{22}{40}$	$\frac{22}{45}$
2	$\frac{22}{44}$	$\frac{21}{40}$	$\frac{23}{41}$	$\frac{23}{42}$	$\frac{22}{41}$	$\frac{21}{45}$
4	$\frac{21}{44}$	$\frac{21}{41}$	$\frac{23}{41}$	$\frac{23}{43}$	$\frac{21}{41}$	$\frac{21}{45}$
8	$\frac{23}{44}$	$\frac{22}{42}$	$\frac{22}{41}$	$\frac{23}{43}$	$\frac{21}{41}$	$\frac{21}{44}$
16	$\frac{22}{44}$	$\frac{21}{41}$	$\frac{22}{41}$	$\frac{22}{42}$	$\frac{21}{40}$	$\frac{21}{44}$
32	$\frac{23}{43}$	$\frac{21}{41}$	$\frac{23}{41}$	$\frac{22}{42}$	$\frac{19}{36}$	$\frac{21}{44}$
50	$\frac{22}{44}$	$\frac{22}{41}$	$\frac{22}{41}$	$\frac{22}{42}$	$\frac{19}{36}$	$\frac{21}{44}$

[1] At north window, maximum 10,000 Lux.
[2] At south window, maximum 100,000 Lux.
[3] Photocurrent in microamperes. Control measurement with 1000 Lux for 1000-ohm and for 100-ohm external resistance.

ment in sunlight there is no clearly observable change of the photocurrent. The daily fluctuations observed are to

be traced to differences in the darkness pause and to slight fluctuations of the intensity of illumination of the light source. As far as the merely slight changes permit a certain conclusion, it is shown by these experiments that for all the cells the photocurrent increases in the beginning and that the change is smaller for lower external resistances and frequently is not at all detectable. Apparently the observed changes depend merely upon an unimportant change of the cell resistance. For the cells set in sunlight, to be sure, a gradual decrease in the photocurrent is evident, apparently caused by the simultaneous action of atmospheric influences and the strong warming of the cell by the sunlight. For medium and small intensities of illumination, on the other hand, the cells show a good constancy with time, which is extremely independent of the external resistance. Grundmann and Kassner [102] come to an essentially different conclusion. They find an entirely uneven and inconstant behavior, which, however, finds its explanation, because there was no darkness pause introduced between illumination and control measurements. Consequently reversible fatigue and variation with the time are superposed in a completely uncontrollable way. These unfavorable results were already contradicted by L. Bergmann [103] and R. Sewig [104] and it was suggested that the cells used by Grundmann and Kassner probably possessed contact errors.

We return once more to the reversible fatigue. This process reminds one of the sluggish response of selenium resistance cells, which is caused by secondary currents. In the primary semiconductor photoeffect such a sluggish response does not seem comprehensible. Hence one seeks another cause and supposes a temperature influence such that a slow change of the photocurrent takes place through the slow fatiguing of the cell according to the magnitude of the temperature coefficient. The changes observed at large intensities of illumination were certainly caused in part by heating. But even with the most painstaking exclusion of heat rays a fatigue is likewise perceptible. B. Lange [70] was

able to show that this fatigue effect is caused by a slow change of resistance of the insulating layer. In Figure 97 the percent decrease of the photocurrent of a selenium photoelement at 1000 lux is illustrated, and the change of resistance of the darkened cell is appended. The cell resistance had

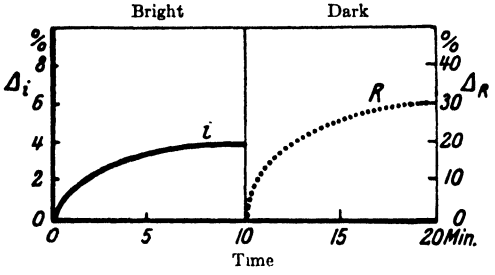


FIGURE 97.—Decrease of the Photocurrent on Exposure of a Selenium Photoelement, and Change of the Cell Resistance after Darkening. According to B. Lange.

dropped during the illumination and increased by 30% in 10 minutes after darkening. Superimposed upon the primary photoeffect, accordingly, was an internal change of resistance, which consequently caused a reduction of the external photocurrent. Since the change in resistance of selenium has its maximum at 700 mμ, but the semiconductor photoeffect at 580 mμ, this phenomenon, disturbing for photometric measurements, can be reduced by a filter, that absorbs the wave range which causes the change in resistance. Thus the percent fatigue can be reduced to about one third for a selenium photoelement through the use of a heat protecting glass which is already absorbing at 700 mμ. G. Liandrat [105] reached a similar result, and recommended the use of Corning glass filters, light alko 396 or medium alko 397.

The preceding investigations do not indicate how the fatigue depends upon the intensity of illumination or upon the properties of the cell, or how it varies with time; questions whose answers are particularly important for the photometric use of the cells. Recent measurements for clearing up these questions will be reported below.

We have seen that the release of electrons takes place at lattice distortion points. There exists, however, no basis

for this process to show fatigue phenomena. But the possibility does exist that the atoms, which have given up their valence electron and so have been transformed into ions, change their position in the lattice or even penetrate into the insulating layer and here capture photoelectrons. In this way the difference of electron concentration in the semiconductor and in the insulating layer is reduced, so that the photo-EMF falls. On the other hand if the displacement of the emission centers is very slight and if the insulating layer is strong enough, an enrichment of centers can result at the boundary layer and thus an increase of the photo-EMF can take place. We will likewise see that such an increase of the photo-EMF is in fact observable in high resistance cells. For low resistance cells on the contrary there is always a decrease of the photocurrent and the photo-EMF with the time, which moreover is proportionally much larger than for high resistance cells. These great changes in the low resistance cells are explainable since the external photocurrent (see Equation 27, p. 92) depends upon the ratio of the external and internal resistance.

The fatigue rests thus upon a displacement of the emission centers which move close to the boundary between semiconductor and insulating layer or penetrate into the insulating layer, manifesting itself as a decrease of resistance. An increase or decrease of the photo-EMF follows according to the magnitude of these displacements. If we make the obvious assumption, that the number of liberating centers is proportional to the intensity of illumination, then a logarithmic dependence of the fatigue upon the intensity of illumination follows, since the photo-EMF, according to the electron diffusion theory, depends upon the logarithm of the emitting centers. We will now see how well the measurements correspond to these considerations.

In Figure 98 are illustrated the variations of the photocurrent with time for a low resistance cell with particularly heavy fatigue, in relation to the intensity of illumination. According to this the percent fatigue is extremely dependent

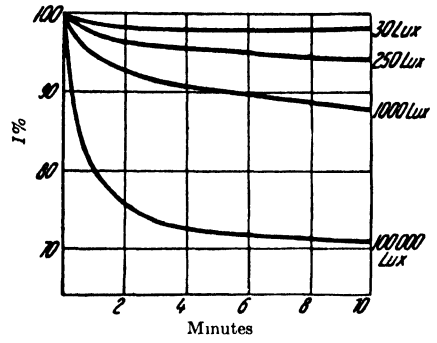


FIGURE 98.—Temporary Decrease of the Photocurrent of a Selenium Photoelement for Various Intensities of Illumination. According to B. Lange.

upon the intensity of illumination and indeed the fatigue reached after 10 minutes increases, as was to be expected, approximately as the logarithm of the intensity of illumination. As is further evident from the curves, the variation of the photocurrent with time has an exponential character, indeed the half-value time depends essentially upon the intensity of illumination. Thus at 100,000 lux (sunlight) the half-value time lies under 1 minute, but increases for small intensities of illumination to about 3 minutes. Since the variation of the photocurrent at high intensities of illumination accordingly occurs very rapidly it is necessary to measure the initial current ballistically at short illumination times (1/10 second). As the half-value times are short for selenium photoelements the fatigue can be very exactly characterized by stating the variation of the photoeffect in the first 10 minutes. The dependence of the fatigue thus determined upon the intensity of illumination and upon the external resistance is illustrated in Figure 99 for a normal cell, type S 50, with a resistance of 1400 ohms, and for a special low resistance cell. According to this the fatigue of the high resistance cell is not only essentially slighter but also shows a very different behavior inasmuch as the open circuit potential and the photocurrent do not decrease for high external resistances but become noticeably greater.

As the most important result for practical purposes it follows from this that the fatigue is extremely dependent

upon the resistance of the cell and that through the choice of a suitable external resistance the fatigue phenomena can be almost completely eliminated, at least in the region of small and medium intensities of illumination.

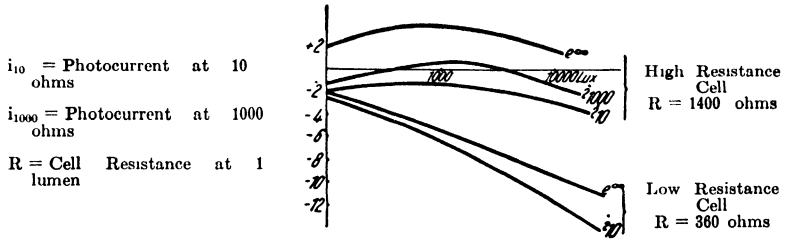
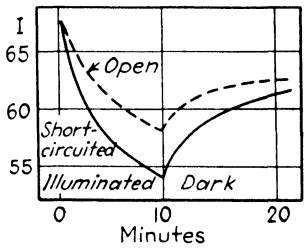


FIGURE 99.—Percent Fatigue of Selenium Photoelements of Various Resistances in Relation to the Intensity of Illumination (Logarithmic) and to the external resistance. According to B. Lange.

FIGURE 100.—Temporary Course of the Fatigue and Recovery of a Short-circuited and an Open Selenium Photoelement. According to B. Lange.

I =Photocurrent measured ballistically.



Hitherto we have described the course of the fatigue. Finally we will also make some statements concerning the recovery of the cells. In Figure 100 are illustrated the photocurrents determined ballistically for a low resistance cell during fatigue and after cutting off the illumination, that is, during the subsequent recovery. As is evident from this, the photocurrent displays a similar exponential form but with noticeably larger half-value time, so that the recovery occurs essentially slower than the fatigue. Interesting also is the difference exhibited in the fatigue of cells on open circuit and short-circuited. The fatigue of the short-circuited cell takes place more rapidly since the electron flux through the semiconductor is greater.

We have already reported that similar fatigue and recovery phenomena occur in the x-ray region (p. 130) which also depend upon the intensity of the radiation.

The practical result of the investigations concerning the constancy and the reversible fatigue can be summarized, that both phenomena are extremely dependent upon the intensity of illumination and that with avoidance of strong illumination favorable results will be secured in both respects.

That every mechanical, thermal and electrical measuring apparatus has limits to its capacity (loadability) is known. Kilograms cannot be weighed on a precise analytical balance without bending its balance beam, and high voltages cannot be measured with a pocket voltmeter without real damage to the insulation. Likewise it must be kept in mind that photoelements also have limits to their capacity, like every other measuring instrument, and even the human eye. The range of measurement is even greater than for most other measuring instruments, but it naturally is not infinitely great but bounded by an upper limit. The unfavorable results which have been mentioned are thus to be explained merely by an overstepping of this limit with abnormally high intensities of illumination.

An assumption as to the correct use of the photoelements is appropriate for delimiting this domain of physical properties. Since this has been presented in the foregoing chapter, we will now, in Part II of this book, turn to the many sided possibilities of applying the photoelements to scientific and technical ends.

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PART II

TECHNICAL USES OF PHOTOELEMENTS

Foreword to Part II

The use of photoelectric cells for illumination meters, twilight switches, light barriers and the like has been on the program of engineers for decades, but for a long time merely as projects and individual laboratory performances, as long as the development remained in its baby shoes. The introduction of sound films, however, created simultaneously a worldwide market for photocells, and from that time they began to penetrate more and more into other fields of application. The transition from a laboratory device to an article of industry, which has gradually been consummated in the realm of photoelectric cells, has been hastened materially by the rediscovery of the photoelements by Lange and Schottky. The photoelement, compared with the photoresistance, has the advantage first of all of linearity and freedom from lag, moreover, it supplies a greater current than a photocathode, and in contrast to both types of cells it requires no auxiliary potential. This last factor was decisive for the possibility of making photographic exposure meters in pocket form, which have found wide distribution. In this way, large circles have become conversant with the photoelements, and so the use of the new aid increases in other photometric apparatus and for other purposes.

The publication here presented, which gives a survey of the status of the technical uses of photoelements, has for its author the man who, in addition to the rediscovery of the effect, is to be thanked for important contributions to the study and technical development of photoelements and accessory equipment for photoelectric apparatus. This quite justifies the circumstance that a not inconsiderable part of the book is devoted to the description of the author's own contributions, which have indeed throughout been ingenious

and standing at the height of engineering. The natural reproach of bias does not prove correct for the case in point, as one can convince himself by reading the thoroughly objective and true to fact presentation. It is safe to count as an advantage of the monograph in question that the author, as the outstanding specialist in the field, has been conversant with all the details of the problems through his own active observation.

We accompany this first publication concerning the young and struggling technique of the photoelements with the wish that it may provide the stimulus to further applications of the new aid.

Hans Thirring.

Vienna, May, 1936.

Preface to Part II

In the preface to the first part I characterized the development in the realm of the photoelements with the saying: "The science of today is the engineering of tomorrow." In this second part I will now report on the technical development of the photoelements and upon their use.

I have sought to keep the presentation as simple and clear as possible, and have often omitted intentionally the derivation of the physical relations and mathematical formulae. For these I can refer to the first part of my book, and would here make possible a quick orienting for those who are interested merely in the use of photoelectric apparatus. For not every one who uses a tool needs to know its development, but every one must know as exactly as possible just what can be done with the tool. Accordingly I have taken pains chiefly to describe the many sided uses of the photoelements.

The great interest that has already been displayed in photoelectric apparatus has given me manifold stimuli for new devices. Yet it seems even more interesting to present a vision of the possibilities of development, of the engineering of tomorrow. At least I have sought to refer to existing possibilities, and nothing would give me greater pleasure than to learn of their actual realization. To all who co-operate in this, and who perhaps find a stimulus in this presentation, I wish the same enjoyment in the creation of new and useful aids to science and engineering.

Bruno Lange.

Berlin-Dahlem, May, 1936.

Chapter 1

Construction and Performance of the Photoelements

Cell Structure

After having learned, in Part I, the history of the development and the physical properties of the photoelements, we now turn to the great field of their use. We begin with the cell housing, as the satisfactory functioning of the cell depends upon a suitable housing.

The simple internal structure of a photoelement corresponds in principle also to a simple housing. As can be seen in Figure 1 the two poles of the cell are the metallic base plate 1 and the translucent front electrode 4.

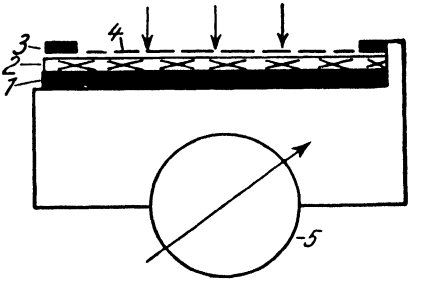


FIGURE 1.—Schematic Structure of the Photoelement.

1. Metallic base plate
2. Semi-conductor
3. Metal ring for current connection to the front electrode
4. Translucent front electrode
5. Measuring instrument

The technical production of a good cell housing, however, is not so simple as this diagram. For there are difficulties in taking the current from the front electrode. This can be done by pressing on a metal ring. But if the ring is pressed too heavily the translucent front electrode will be injured, or the thin layer of semiconductor will be ruptured so that

a short circuit between the two electrodes occurs, occasionally developing only after long use of the cell, through plastic deformation of the semiconductor. It therefore required numerous improvements and long experience in working out the cell housing so as to avoid these defects. Thus, to improve the contact, a reinforced metal ring is applied by cathode sputtering or by a metal spraying process and the cell plate is pressed elastically against a metal ring in the housing. Figure 2 shows such a structure with an insulating

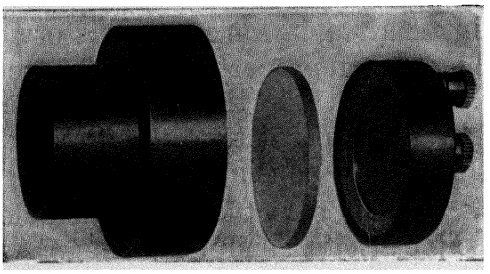


FIGURE 2.—Ocular Photocell. According to B. Lange.

ring for receiving filters. This insulating ring fits in the tube of a standard microscope, so that the cell, an "Ocular Cell," can be used in place of the microscope ocular for quantitative measurements. The flat edge of the cell housing is important to avoid shadowing. The arrangement of the binding posts on the back has also proved to be convenient.

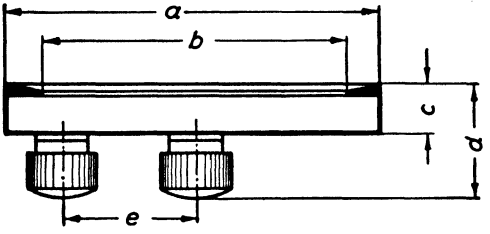


FIGURE 3.—Schematic Section of the Cell Housing. According to B. Lange.

In Figure 3 a schematic section of the cell housing is illustrated, while the different dimensions and the electrical data of the selenium photoelements are given in Table 1. The

TABLE 1

Type	a	b [1]	c	d	e	μA [2]	μW [3]
S 28	28	20	8	16	10	150	25
S 50	50	38	10	20	17	450	60
S 75	75	60	10	24	25	750	100
S 145	145	134	12	24	63	3000	420

[1] Diameter of the light sensitive layer.

[2] Photocurrent in 10^{-6} amperes at 1000 lux.

[3] Output in 10^{-6} watts at 1000 lux.

The open circuit photopotential is independent of the size of the cell and amounts to about 200 millivolts at 100 lux.

largest cell, of 145 mm diameter, shown also later in Figure 61, is distinguished from the other cells in being assembled from seven individual cells of type S 50. For it has been found expedient to assemble large cells from small cell plates, since the larger cells make difficulties in fabrication, and because the resistance of the large translucent front electrode becomes too high and the output thus drops while the photocurrent no longer increases linearly with the intensity of illumination.

An advantage of the photoelements is that they can be given any plane shape. Accordingly, rectangular cells are used for certain photoelectric apparatus.

For accurate, constant performance a housing is required in which all parts, particularly the springs, are correctly proportioned. Indeed, the construction of the housing calls for particular attention, since a faulty frame can introduce distortions which, through ignorance of the cause, mask an erratic behavior of the cell,—see **Stability and Fatigue,** Part I, Chapter 3.

In conjunction with the simple cell assemblies we will now describe a few special models for particular uses. In

Figure 4 is illustrated a two-faced differential cell after B. Lange [1] and H. Teichmann [2] with a rider pin, for the comparative measurement of two light sources on an optical bench. The rider has a spring housing with a groove and notches for turning through exactly 180°. The base plates of the two cells in this assembly are connected by springs, making a single pole of the cell, while the current is taken off from the front electrodes through the two binding posts on the cell frame. With such a differential cell P. R. Gleason [3] was able to make photometric measurements exact to 0.1%, and even for heterochromatic photometry with filters attained an accuracy of 0.5%.

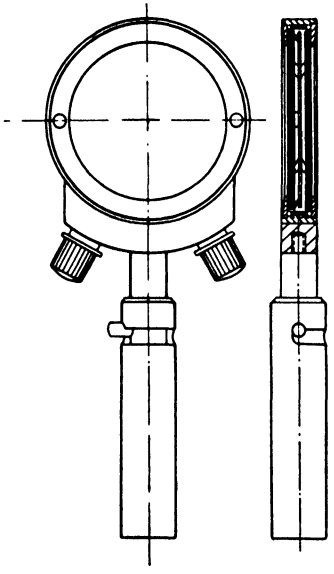


FIGURE 4.—Differential Cell. According to B. Lange.

Whereas in the differential cell just described the two light-sensitive layers stood back to back, A. V. Hill [4] and L. Bergmann [5] describe similar cells in which two half cells stand close alongside each other. The layout and connections of such a cell are shown in Figure 5. This embodiment of the differential cell is particularly adapted to the measure-

ment of the displacement of a light ray, as well as for comparing the brightness of two adjacent photometer fields.

As a particular model of the photoelement should be mentioned the cell body of the photoelectric reflection meter with ring shaped cell, as will be described in detail on page 245.

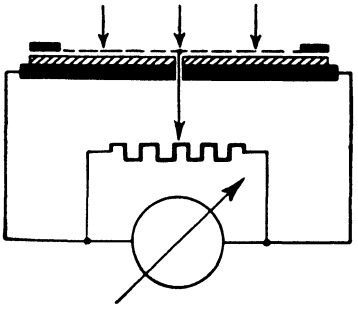


FIGURE 5.—Differential Cell. According to L. Bergmann.

Sensitivity and Output

The sensitivity of the photoelements is of the greatest importance for their use. A closer consideration, however, shows that the question of their sensitivity must be defined more exactly. The statement, for instance, that a selenium photocell is more sensitive than an alkali photocell, is wholly indefinite. It is essential to distinguish between current and potential sensitivity, and between spectral and load sensitivity. But before we go into these different sensitivities of the photoelements more thoroughly we will first discuss the dependence of the photocurrent and the photopotential upon the intensity of illumination. A detailed presentation has already been made in the first part of this book on pages 88-97.

It is particularly characteristic of the photoelements that the photocurrent and the photopotential depend not only upon the intensity of illumination but also upon the external resistance. In Part I these relations were exhibited in Figures 35 and 36 through families of curves. Among these

many curves, however, two have a special significance, namely, the curve for the photocurrent at vanishing external resistance, that is, the short circuit current I_o, and the curve for the photopotential for infinitely high external resistance, the open circuit potential e_∞.

For both of these curves there are mathematically simple relations. The short circuit current I_o of the cell varies linearly with the intensity of illumination L up to intensities of 1000 lux, and with the cell area f, so that the relation

$$I_o = i_o f L \tag{1}$$

holds, in which i_o is the photocurrent for unit intensity and unit area. Since fL corresponds to the light flux Φ it follows that

$$I_o = i_o \Phi. \tag{2}$$

If in determining i_o the cell area is measured in square centimeters and the intensity of illumination in lux then in terms of the light flux measured in lumens (lm):

$$I_o = i_o \times 10000 \text{ lm}. \tag{3}$$

For the dependence of the open circuit potential e_∞ on the intensity of illumination L the relation

$$e_\infty = a \log_{10} L \tag{4}$$

holds, in which a is a constant of the cell, a relation which can not only be confirmed experimentally over a range of about 10-100,000 lux, but which can also be deduced theoretically by the electron diffusion theory presented in Part I, pages 77-87. We assume, indeed, in equation (4) that the cell potential is independent of the cell area. Hence the open circuit potential e_∞ cannot be calculated from the light flux. A cell of 10 cm^2 area takes a light flux of 1 lumen at 1000 lux, whereas the same light flux for a cell of 1 cm^2 area corresponds to an intensity of illumination of 10,000 lux. From the relation above it is clear that in the preceding example the two cells have different potentials for the same light flux.

We are now come to the discussion of cell sensitivity and begin with the current sensitivity. W. Kluge and H. Briebrecher [6] have defined the current sensitivity σ_i of a photocell as the variation of the photocurrent with the intensity, and have expressed it mathematically as the differential coefficient

$$\sigma_i = \frac{dI}{d\Phi}. \tag{5}$$

For the short circuit current of the photoelement this relation becomes particularly simple, since according to equation (2) I_o varies linearly with Φ. Thus we obtain for the current sensitivity

$$\sigma_i = \frac{d(i_o\Phi)}{d\Phi} = i_o, \tag{6}$$

that is, the current sensitivity is constant and independent of the intensity of illumination. The current sensitivity of a good selenium photoelement amounts to about 500 microamperes per lumen.

The potential sensitivity can be defined analogously to the current sensitivity. For simplicity we will only consider the open circuit potential e_∞ and will refer this to the intensity of illumination L. Then it follows that

$$\sigma_e = \frac{de_\infty}{dL} = \frac{d\,(a \log_{10} L)}{dL} = \frac{a'}{L}, \tag{7}$$

that is, the potential sensitivity varies inversely as the intensity of illumination. Represented graphically this corresponds to an hyperbola with the coordinate axes as asymptotes. The logarithmic increase of the potential and also the sharp decrease of the potential sensitivity with increasing intensity of illumination are evident in Figure 6. At 1 lux σ_e amounts to about 50 millivolts per lux, at 100 lux only 2.5 millivolts per lux. Hence if a high potential sensitivity is required, say for the grid control of an electron tube,

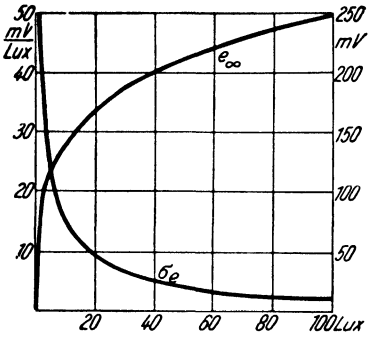


FIGURE 6.—Open Circuit Potential e_∞ and Potential Sensitivity σ_e in Relation to the Intensity of Illumination. According to B. Lange.

it is recommended to work at low intensities of illumination and perhaps to place several cells in series.

Since photoelements act as spontaneous sources of current their electrical output is decisive for most applications. We will calculate the output as I^2R, where I is the photocurrent measured in the external resistance R. The output of a selenium photoelement Type S 50 calculated thus for intensities of illumination of 300, 500, 700, and 1000 lux is illustrated in Figure 7 in relation to the external resistance R.

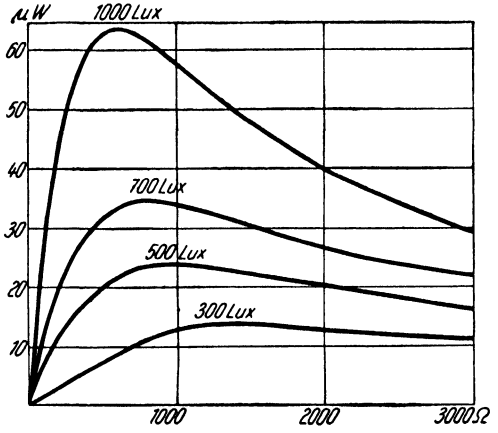


FIGURE 7.—Output of a Selenium Photoelement S 50 in Relation to the Resistance and the Intensity of Illumination. According to B. Lange.

As evident from this, the output has a marked maximum for a particular resistance, which is displayed toward smaller resistances for increasing intensities, since the cell resistance decreases with increasing intensity of illumination.

To obtain the maximum output it is therefore important to choose the resistance adjustment that is most favorable for the time being. We now present the question of the size of this resistance.

To answer this we use the relation of the external photocurrent I to the external resistance R and the cell resistance r derived in Part I, p. 92. According to this,

$$I = \frac{i_o L}{1 + \frac{R}{r}}. \tag{8}$$

For the output we get from this

$$I^2 R = \frac{i_o^2 \, L^2}{(1 + \frac{R}{r})^2} R. \tag{9}$$

To obtain the maximum of this expression we differentiate according to R

$$\frac{d(I^2 R)}{dR} = \frac{i_o^2 \, L^2 \, r^2 \, (r - R)}{(r + R)^3}, \tag{10}$$

set the differential coefficient equal to zero and solve for R. Thus we secure the simple relation

$$r = R, \tag{11}$$

that is, the maximum output will be secured when the external resistance is equal to the cell resistance.

The relation above, however, is good only when r is independent of R, which holds pretty well for cuprous oxide cells, but not for selenium photoelements.

C. H. Bartlett[7] therefore makes the following addition for the relation of the photocurrent I to the intensity of illumination L and the external resistance R;

$$I = i_o L - KL^n R. \tag{12}$$

Under these circumstances the maximum output is yielded for

$$R = \frac{r}{2}. \tag{13}$$

L. A. Wood[8] has tested this relation for American selenium photoelements (Photronic) and thus has found as a mean value $R = \frac{r}{1.6}$. From the measurements illustrated in Figure 7 and also from other investigations approximately the same value was obtained. For selenium photocells, accordingly, the maximum output will be secured if the external resistance is about ⅔ the cell resistance, that is $R = \frac{2r}{3}$.

In Part I it was shown on page 88 that the important data for each cell can be presented by means of the cell characteristic. In the cell characteristic the short circuit current, the open circuit potential and the cell resistance in the range 0-1000 lux are represented. Frequently the statement of these values for 1000 lux is sufficient. In this section we have recognized the output of the cell as a further important quantity. These values for several different sizes of selenium photoelements are stated in Table 2.

Of course pains are always being taken to increase the output of the photoelements, and contributions have not been lacking during recent years concerning new-fangled systems with allegedly much greater sensitivity. On account of the indefiniteness of such statements, however, they often prove to be unreliable. For the purpose of comparison therefore some characteristic data of different photocells are stated in

TABLE 2. Output of various photoelements at 10 cm² area and 1000 lux (1 lumen)

Type of Cell	i_∞ micro-amp.	e_∞ millivolt	R ohm	P micro-watt
Selenium S 50	450	350	1000	60
Selenium Weston	130	150	3000	12
Cu_2O frontwall	100	10	400	1
Cu_2O backwall	10	1	500	0.02
Cu_2O Photox	160	300	2000	20

Table 2. According to this the output of the selenium photoelement exceeds all other systems so far that it will be almost exclusively used.

The foregoing data concerning the output refer only to white sunlight or incandescent light. Of scientific interest also is the question as to the quantum yield in the individual spectral regions, that is, the relation between the number of photoelectrons liberated and the number of incident light quanta. For this there are measurements of F. Waibel,[9] who investigated the quantum yield of cuprous oxide frontwall cells in the region of their greatest sensitivity at about 500 mμ and found a quantum yield of 25-50%, so that about every second light quantum liberates an electron. K. Scharf and O. Weinbaum [10] have investigated the behavior of similar cells for x-rays and found for a wave-length of 0.157 Å 16 coulomb per calorie corresponding to 3×10^5 electrons per light quantum. The quantum equivalent is accordingly far exceeded, so that we must reckon with a secondary ionization by the primary liberated electrons. Hence, while the energy efficiency of the photoelement, that is the ratio of the electric output produced to the absorbed radiant energy is very small, the possibility certainly exists that in selenium photocells the quantum equivalent may also be exceeded in the visible region. At present the output of the selenium photoelements for unresolved sunlight amounts to about 100 microwatts per lumen, whereas the energy of the visible sunlight is about 5 milliwatts per lumen, so that an energy efficiency of scarcely 2% is shown.

After discussing current, potential and output sensitivity, there only remains the spectral sensitivity, concerning which we have reported in detail in Part I, page 109 (**visible spectral region**) and page 128 (**sensitivity in the x-ray region**). Hence we can here be contented with a brief comparison of the different types. In Figure 8 the spectral sensitivity of

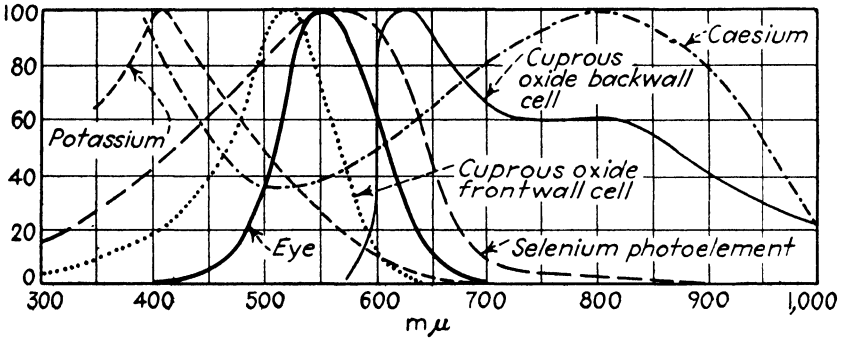


FIGURE 8.—Spectral Sensitivity of Various Photoelements and Alkali Cells.

various photoelements and alkali cells is illustrated, with the maximum sensitivity for the time being set equal to 100. As is evident from this illustration the selenium photoelement excels in its spectral sensitivity inasmuch as it comes nearest to the sensitivity curve of the eye and extends over the same completely, so that it is possible with suitable filters to make the spectral sensitivity of the cell the same as that of the eye. Added to this is the high current sensitivity of this cell, so that even in the spectral regions where the percent sensitivity is smaller the photocurrents are comparatively large. Thus selenium photoelements furnish greater photocurrents at a wave-length of 700 mμ than cuprous oxide backwall cells, although their percentage sensitivity in this region is actually smaller.

Finally we raise the question as to the choice of the most suitable cell, which is of decided importance for all applications. As indicated by the foregoing presentation, the

answer to this question depends entirely upon the various demands which will be made upon the cell. If merely a high potential sensitivity is desired, then an alkali cell or a photoresistance (Selenium or Thalofide cell) which has a potential sensitivity of about 5-10 volts per lumen is suitable. But if at the same time emphasis is placed upon special freedom from lag, for instance for television, photoresistances are eliminated. With regard to current sensitivity on the other hand the selenium photoelements are superior to the alkali cells, and offer also further advantages, namely, the simple use without auxiliary potential and a spectral sensitivity which comes nearest to that of the eye. In addition the extreme constancy and the linear dependence of the photocurrent on the intensity of illumination make selenium photoelements particularly valuable for photometric measurements.

Chapter 2

Photoelectric Illumination Meters

Since the human eye is not able to determine the intensity of illumination directly, much attention has been paid to the construction of optical illumination meters, in which the brightness to be measured is compared with a lamp of known light intensity or is so far weakened by a gray wedge that the ability to distinguish it disappears. Both methods, however, are dependent upon the visual ability of the observer. Pains are therefore taken to make objective illumination meters which permit rapid and reliable measurements. Elster and Geitel used their first alkali photocells for photometric purposes. Photoelectric illumination measurements are a great deal simpler with photoelements. For this requires merely a cell connected in series with a moving coil galvanometer of suitable sensitivity.

In the knowledge that better light promotes production, the illumination meters have acquired special significance in recent times. But before we handle the various embodiments of these instruments we will first learn the requirements which must be set up for them on physical grounds.

Fundamentals

Constancy

A basic requirement which must be set up not only for objective illumination meters, but also for all adjustable apparatus, is its continued constant performance. The question of the constancy of photoelectric cells was frequently and hotly disputed from the beginning of their use for photo-

metric purposes. Hence it is intelligible that various opinions were also expressed as to the constancy of the photoelements.

The simplicity of their structure and use soon gained numerous friends for the photoelectric illumination meters, who emphasized the advantages of these instruments and made favorable statements about their continued constancy.

Sometimes technologists who were accustomed to the use of optical photometers and who could rely on their eyes had a different opinion. These critics asserted a quite considerable inconstancy in individual cases and defended their idea with several polemics. In this it is by no means merely a matter of optimistic representation on the one hand and exaggerated criticism on the other. As we will see shortly, both parties were right and it depends entirely upon a decision as to the limits of the measuring range.

As was shown fully in Part I, page 157, we must distinguish between a reversible fatigue, and a constancy over long periods of time, and indeed both properties depend very greatly upon the intensity of illumination. For instance, if a selenium photocell is illuminated with 100,000 lux, in a few minutes a reduction of the photocurrent to 30% can be observed. In the dark, however, the cell recovers and on renewed illumination furnishes the same photocurrent. If this fatigue is not taken into consideration, and if strong and weak intensities of illumination are measured one after another, values can be found which are certainly not constant and which furnish a very confused picture, according to the rapidity and the sequence of the measurements, cf. W. Grundmann and L. Kassner,[11] and the criticism of this by R. Sewig [12] and L. Bergmann.[13] Similar erroneous results can be reached likewise in an investigation of the constancy over long periods of time. According to the intensity of the illumination and the way the measurements are made, values are secured which depend upon the reversible fatigue. It has now been shown that all these phenomena depend greatly upon the intensity of illumination. While the reversible

fatigue at low intensities of illumination amounts to only 1-2%, the same cells above 1000 lux show fatigue phenomena of more than 5%. As we will see in the next section, in the latter region the departure from a linear increase of the photocurrent with the intensity of illumination becomes great. From this it follows that to secure sufficient constancy we dare measure only to about 1000 lux. For greater intensities of illumination, filters must be used which reduce the intensities of illumination suitably.

TABLE 3. Long-time test of selenium photoelements. Photocurrent in milliamperes.

Time; Months	Intensity of Illumination			
	Dark	500 lux	Daylight	Sunlight
0	0.45 *	0.42 *	0.43 *	0.41 *
1	0.44	0.41	0.42	0.39
2	0.44	0.41	0.41	0.39
3	0.44	—	0.40	0.38
6	0.44	—	0.39	0.35
9	0.44	—	0.39	0.35

* Control measurements at 1000 lux.

In Table 3 are presented the results of continuous experiments, in which the control measurements were made at an intensity of illumination of 1000 lux after a darkness pause of several hours. As indicated by this, the cells kept in the dark show only unimportant changes in the course of half a year, just as the cells illuminated with 500 lux. The cells set up in diffuse daylight at intensities of illumination up to 10,000 lux show a decrease of the photocurrent of about 8%, while the change in sunlight is almost twice as great. From these experiments it follows furthermore that the short time action of high intensities of illumination does not affect the constancy markedly, and that even at intensities of illumination of 10,000 lux the cell can be counted on for a year of service, if high constancy is not important, for instance, in the operation of a relay. An illumination meter that was

used daily for control measurements in the laboratory, showed, in the course of a year, deviations that lay under 1%.

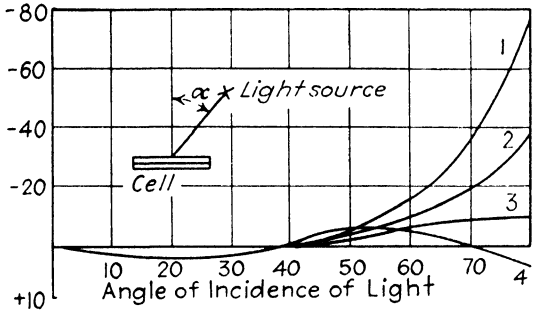
Linearity

The linear dependence of the photocurrent upon the intensity of illumination has already been emphasized as an advantage of the photoelements. As was shown in detail in Part I, pages 88-97, however, a linear relation exists only if the external resistance is small compared with the cell resistance, which depends upon the intensity of illumination. But even the short circuit current of the cell shows considerable deviations from a linear course at high intensities of illumination, since the resistances of the semiconductor and the electrodes are unavoidable. As practical experiments show, for an S 50 cell and an external resistance of 600 ohms the deviations up to 100 lux lie under 1%. For extension of the range of measurement to 1000 lux the sensitivity of the measuring instrument can be reduced by a shunt, without the deviations becoming greater than 1%. Experiments have been made to attain a greater range of measurement through the use of a non-linear scale calibrated empirically. For small demands this procedure is sufficient. For exact measurements, however, fatigue and inconstancy with time make themselves annoyingly noticeable. For these reasons all direct measurements above 1000 lux should be avoided, and for these suitable filters should be used, as E. Lux[14] suggested already in the first illumination meters.

Cosine Law

The Lambert cosine law says that the intensity of illumination of a surface depends upon the angle of incidence, so that, for example, the intensity of illumination falls to one half for an angle of incidence of 60°. Since a perpendicular incidence of the light is seldom present, illumination meters must evaluate obliquely incident light according to the cosine law.

From the foregoing it is clear that the height of the cell rim is of decisive significance for the dependence of the photocurrent upon the intensities of illumination, since a high rim gives a large shadow at glancing illumination. Accordingly the S. A. F. cell, as can be seen from Figure 9, curve 1, shows



1. S.A.F. cell.
2. B. Lange's type.
3. Like 2 with platinum opal glass filter.
4. Cell with paper screen according to R. Sewig.

FIGURE 9.—Percent Deviation from the Cosine Law of the Photocurrent of Various Selenium Photoelements.

a great departure. The deviations for photoelements in a metal housing with flat rim, curve 2, are considerably smaller. These cells behave still more favorably with a platinum opal glass filter, that consists of a dull ground opal glass plate of high light scattering power and a platinum layer applied by cathodic sputtering, see Figure 12. The correction filter for eye sensitivity (page 197) with a cover of opal glass also behaves favorably in the same way.

Another way to correct the departures from the cosine law has been described by R. Sewig and W. Vaillant[15]; they use a truncated cone made from transparent paper, that is set over the cell. As can be seen from curve 4, Figure 9, there are thus produced positive deviations * between 0 and 30° and between 70 and 90°, which, however, always remain small.

* Positive deviations also appear at high intensities of illumination. If the intensity of illumination is decreased at oblique incidence of the light the decrease of the photocurrent corresponds to the curved photocurrent characteristic.

If the large departures of curve 1 in Figure 9 are disregarded, which are caused merely by an unsuitable cell housing, it can be said to sum up that for most illumination meters the cosine error even without means of correction is not important, since the percentage of the intensity of the radiation incident at a glancing angle, for which the cosine error becomes greater, is low. However, if it is a matter of measuring sharply directed illumination, then it becomes appropriate to use a platinized opal glass filter, which in addition so far reduces high intensities of illumination that the cell remains constant and troublesome fatigue effects are prevented.

Sensitivity of the Eye

In all photometric measurements the spectral sensitivity of the measuring device is of decisive significance, since an agreement with visual measurements occurs only if the measuring device has the same or at least a similar spectral sensitivity as the human eye. For instance, if thermoelements or bolometers are used as radiation receivers then merely the total energy of the radiation is measured, and no conclusion can be drawn as to the visual brightness of the radiator. A soldering iron which is not glowing visibly but which radiates more energy than an incandescent lamp, would give a larger thermocurrent than the lamp.

We have already mentioned on page 188 that the spectral sensitivity of the selenium photoelement extends over the whole range of sensitivity of the eye, so that by means of a filter of suitable absorption complete equivalence to the sensitivity of the eye is possible. As can be seen from Figure 8, the selenium photoelements show the greatest departure in the short wave spectral region. If the spectral composition of all sources of radiation were the same, this departure would in general not be troublesome, it could, rather, be taken into consideration in the calibration. But this is not the case. The radiation of an incandescent lamp corresponds to a temperature of 2700° K, whereas the sun has approxi-

mately 6000° K. Accordingly about 40% of the sun's radiation lies in the visible spectrum, but for the incandescent lamp scarcely 10%. Fortunately, in spite of these very different distributions of radiation, an illumination meter with a selenium photoelement calibrated at 2840° K (International photometric standard lamp A) in comparison with solar radiation (standard lamp A with filter according to R. Davis and K. Gibson [16]) shows deviations of only a few percent. Similarly small also are the deviations for various kinds of incandescent lamps. Hence for daylight and incandescent lamp measurements the use of any sort of correction filter is saved; likewise for incandescent gaslights, since the selective radiation of the rare earth oxides is valued the same by the cell as by the human eye. The relations are different for mercury and sodium lamps and for helium and neon glow-tubes. The monochromatic radiation of these lamps causes deviations which correspond to the differences in the sensitivities of the cell and the eye for the wave-lengths present.

As H. Krefft [17] showed, a factor for every wave-length can be determined from the spectral sensitivity curve of the cell, by the use of which the photoelectrically measured values state the intensity of illumination in Hefner candle units, (see note). The mathematical procedure according to Krefft is not restricted to the visible spectrum but is likewise suitable for the ultraviolet region and can, for instance, be applied to the erythemal sensitivity of the human skin. For the visible spectrum, however, filters have already been developed which provide equivalence with the sensitivity of the eye without calculation. More than 50 years ago

Translator's Note: Lange, in common with many writers, is at times not very precise in his use of photometric terms. Illumination is measured in lux, luminous intensity or candle power in HK, that is, Hefner candles.

The reader should realize that German photometric units are based on the Hefner candle while U. S., British and French are on the International candle and that the two differ in magnitude as follows:

Hefner candles $\times 0.900 =$ International candles. All German units involving this are therefore different from our units. We use the term lux or meter candle in the International system but it is not the same as the German lux. Since photocell properties vary considerably from cell to cell, the reader can consider the units as approximately the same although he should keep the difference in mind and make a conversion where more precise comparisons are made. (E. F. K.)

C. E. Fritts [18] made his first selenium photoelements equivalent to the sensitivity of the eye, by connecting 3 cells in parallel and providing each of these cells with a particular color filter. This arrangement of the parallel connection of the filters was recently modified by A. Dresler [19] who did not use the 3 cells but placed the different filters side by side on a single cell. This arrangement of the filters beside each other offers the advantage of being able to match each cell individually by displacing them. But it is disadvantageous in that the individual parts of the cell differ in sensitivity, so that beams of radiation are measurable only if they are at least as large as the cell. It is another disadvantage that considerable deviations from the cosine law appear through reflection and polarization of the incident light, which are increased further by refraction of the light at the contact edges of the individual filters. Since, however, we can at present secure a very uniform spectral sensitivity by the use of neutral gray platinum electrodes, matching each cell individually is saved. Hence it is possible to obtain a good adjustment to the sensitivity of the eye with a homogeneous filter. As O. H. Knoll [20] shows, an almost ideal adjustment to the mean sensitivity of the eye can be secured by a liquid filter of suitable absorption. But for technical purposes a solid filter of high constancy is needed. B. Lange [21] secured very satisfactory results with a filter of two cemented color glasses of Schott and Company. An even more favorable action can be obtained by the use of a cover glass of opal glass through which a good agreement with the cosine law is secured at the same time, see Figure 9.

In estimating the correction attained it must be kept in mind that the sensitivity of the eye represents only a theoretical mean value, from which the sensitivity of individual observers deviates considerably. In Figure 10 the shaded area represents graphically the "scatter region" for the sensitivity of 200 observers of normal color response according to recent American investigations, and at the same time the values for a Dresler filter after measurements by J. Rieck [22]

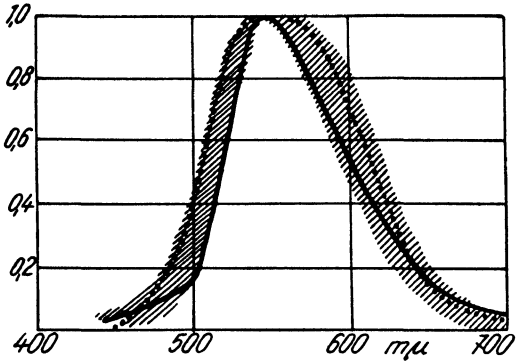


FIGURE 10.—Modification of Spectral Sensitivity by Filters.

///// "Scatter Region" of spectral brightness sensitivity of the eye

——— Spectral sensitivity of a selenium photoelement with filter according to Dresler

- - - with filter according to Lange

and the sensitivity curve of the Lange opal glass filter are given. Although noticeable deviations appear for certain wave-lengths, photoelectric measurements are nevertheless preferable to visual, since the individual observer seldom knows the deviations of his own eyes from the mean eye sensitivity and must take into account the possibility that his measurements show great deviations. It must also be kept in mind that visual heterochromatic photometry fatigues the eye greatly.

INFLUENCE OF TEMPERATURE

Since illumination measurements are frequently performed in the open it is important that the influence of temperature on the measured values remain small. In Part I, page 106, it has already been shown that favorable relations are present for selenium photoelements at low intensities of illumination and small external resistances. But with illumination meters the temperature errors of the moving coil galvanometer must also be taken into consideration. This effect, however, can be reduced by the use of temperature-constant series and shunt resistances, so that the total temperature error of a good photoelectric illumination meter is slight. Thus a Standard Model illumination meter, see page 199, shows an error of —2% for a temperature rise of 10°, and +2% for a temperature decrease of 10°.

Different Models of Photoelectric Illumination Meters

Illumination Meter for the Visible Spectrum

As we have already mentioned, a simple illumination meter consists of a photoelement connected to a needle galvanometer. The "Standard" illumination meter illustrated in Figure 11 has such a structure. For the measurement the



Figure 11.—Photoelectric Illumination Meter. "Standard" Model. According to B. Lange.

cell is held in the place where the intensity of illumination is to be measured, and the value in lux is read off directly from the deflection of the needle. Two ranges of measurement, to 100 lux and to 1000 lux are obtainable by a switch.

There are, however, difficulties in reaching smaller and higher ranges of measurement. For small intensities of illumination the photocurrents are very small, and for intensities of illumination over 1000 lux the non-linear form of the photocurrent, the fatigue phenomena, and the inconstancy are troublesome. It is natural to use filters for high intensities of illumination. Such filters, however, must satisfy various conditions. They must not absorb selectively, nor cause departures from the cosine law, they must not be heated too much by the absorbed radiation, and above all they must be constant. It was difficult to find a filter that satisfied all these requirements. H. Pettersson,[23] however, secured very favorable results with a filter that consisted of an opal glass in conjunction with a fine mesh screen. This

filter named after Pettersson was improved by Lange, who covered the coarse ground surface of the opal glass with a thin layer of platinum by cathode sputtering instead of the mesh screen. The deeper parts of the rough surface receive less platinum and act like a fine porous sieve. Through the choice of a suitable duration of sputtering the thickness of the platinum layer can be so determined that filters can be produced with an exactly defined light transmission of from 50% down to 0.1%. The favorable action of scattered light in the platinum opal glass filter was also assisted by a special housing, Figure 12. The opal glass 1, ground also on its

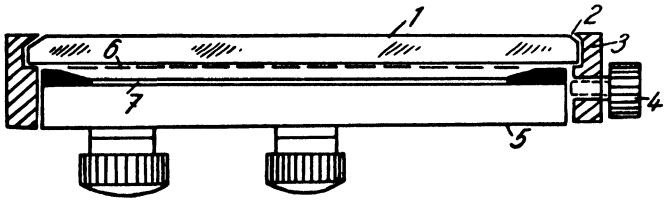


FIGURE 12.—Platinum Opal Glass Filter according to H. Pettersson (section).

upper surface, is fastened by a small facet 2 in the metal ring 3. The thumbscrew 4 holds the filter on the cell housing 5 so that the platinized side of the glass lies just in front of the cell surface. Thus the frame has practically no shadowing rim, and hence works favorably with very glancing incident light. Because the surface of the opal glass is larger than the effective cell surface a more extended agreement with the cosine law is secured. The correction filter for eye sensitivity has the same construction as the platinum opal glass filter, except that instead of the platinum layer two colored glasses are cemented to the opal disc. Hence this filter also shows a good agreement with the cosine law.

Through use of a platinum glass filter with 1% transmission the two ranges of measurement of the "Standard" lux meter are enlarged a hundred-fold, so that in this way

intensities of illumination of 100,000 lux, that is, direct sunlight, are measurable.

We come now to the extension of the range of measurement to small intensities of illumination, for which, as already mentioned, the difficulty lies in the measurement of the small photocurrents. A photoelement of 50 mm diameter delivers about 40 microamperes at 100 lux. For this the full deflection of a needle instrument with small temperature errors and aperiodic adjustment is secured. Needle instruments with higher sensitivity have indeed been built, but such instruments are sensitive to transportation and have great errors of adjustment. On these grounds another way of increasing the sensitivity is more suitable, namely, the use of multiple cells. The illumination meter illustrated in Figure 13 accordingly has seven cells in multiple on the front

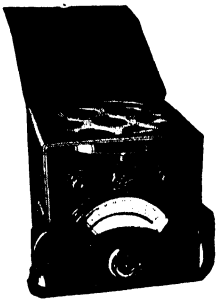


FIGURE 13.—Photoelectric Illumination Meter. Special model in portable case.
According to B. Lange.

of the carrying case. With this large cell and the use of a sufficiently stable and precise measuring instrument a sensitivity of 10 lux for the full deflection can be secured, so that intensities of illumination down to 0.1 lux are measurable on the 100 division mirror-backed scale. Such an illumination meter is particularly suitable for measuring street lighting, which frequently amounts to only a few lux, and also for the determination of the range of projectors, which according to German law[24] are to be measured at 100 meters distance.

By means of a built-in switch two further ranges of measurement are available, which can be extended to 100,000 lux by a platinum opal glass filter, so that this highly sensitive special instrument is suitable for all engineering measurements of illumination.

For astronomical measurements and for scientific work a still higher sensitivity is sometimes required, which can be attained by the use of mirror galvanometers. But mirror galvanometers require a special reading device with telescope or light pointer, for which special structures are necessary, which make transport difficult. A real simplification can be secured by the use of the "Multiflex" galvanometer, which combines the sensitivity of a mirror galvanometer with the simplicity of a needle instrument. The "Multiflex" galvanometer is a mirror galvanometer, in which the illuminating equipment, light pointer, scale and control resistance are assembled in a handy case. Through multiple reflection of the light pointer on three first-surface mirrors a light pointer 1 meter long is provided for in a case 23 cm high. As can be seen in the schematic section, Figure 14, the point fila-

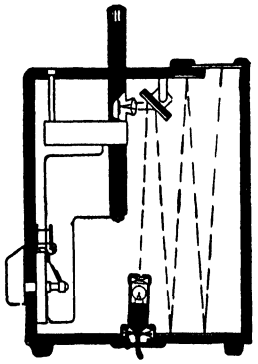


FIGURE 14.—Multiflex Galvanometer.
According to B. Lange.

ment of the lamp is focused on the galvanometer mirror, while the image of a fine line on the front of the condenser lens falls on the 200 mm long scale. Different ranges of

measurement can be secured by means of a rotating switch, besides the system can be quickly closed for transport. The lighting equipment requires a 4-volt battery or a small transformer, which is likewise built into the housing. The moving coil, stretched from both ends and suspended by springs, is quickly installed and requires no leveling device, so that measurements are also easily carried on in the open. The sensitivity of the system amounts to about 3×10^{-9} amperes at 1000 ohms resistance, so that with a selenium photoelement S 50 a sensitivity of 1/100 lux per scale division is obtainable, which can be increased to 1/1000 lux per scale division by the use of the large cell S 145. This sensitivity suffices for various astronomical and meteorological measurements. Thus R. Roch has measured the moonlight with the apparatus illustrated in Figure 15, and has investigated its

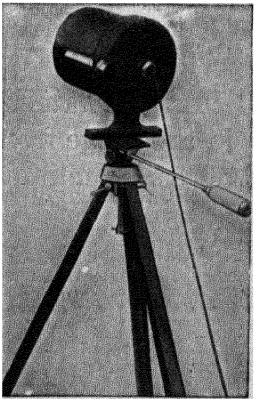


FIGURE 15.—Large Cell in Water Tight Housing and Light Protecting Tube on Tripod with Graduated Head. According to B. Lange.

influence on cloud formation and weather. The large cell is in a watertight case with a tube, upon a stand with graduated head and is connected to the "Multiflex" galvanometer by a rubber-covered cable.

With the illumination meters just described the entire range of measurement is attainable. Nevertheless there was need of a particularly simple, handy and inexpensive illumination meter. B. Lange [25] was able to secure a specially

handy structure by arranging the cell in the housing of the measuring instrument underneath the transparent scale. The pocket lux meter, Figure 16, constructed in this way, has a logarithmic scale so that a larger range of measurement of

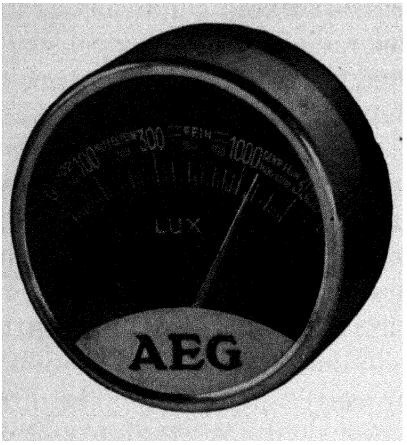


FIGURE 16.—Pocket Luxmeter. According to B. Lange.

10-3000 lux is attained. The exposure time for photographs, in the range from 1/1000 second up to a minute can be read off from the indicated intensities of illumination on a rotating table.

PHOTOMETER FOR THE ULTRAVIOLET AND X-RAY REGIONS

The most highly sensitive illumination meters with "Multiflex" galvanometer described in the preceding section are suited not only for the visible spectrum, but also for the entire range of radiation from 1000 mμ over through the ultraviolet into the short-wave x-rays. Selenium photoelements are hence suitable for measurements in the therapeutically important ultraviolet range from 200-400 mμ. The visible radiation can be screened off by the use of a black glass filter. Since, however, the different ultraviolet regions show particular effects, the possibility of determining the

intensities of individual spectral regions separately through the use of suitable filters is interesting.

Another procedure for measuring the short-wave ultraviolet was given by L. Bloch.[26] For this Bloch used a saturated alcoholic solution of the leucocyanide of crystal violet. The solution, colorless in the unradiated condition, gradually turned blue in ultraviolet radiation. The intensity of the radiation can be ascertained from the degree of discoloration. Since the coloration undergoes no change at all under the influence of visible light the discoloration can be measured simultaneously during the irradiation with ultraviolet. This procedure is suitable for the determination of the total ultraviolet radiation during a day as well as the determination of the intensities of radiation for the different hours of the day. For this it is a question of an integrating measuring process which we will discuss in detail in the next section.

A similar process for the objective measurement of ultraviolet intensities was developed by L. W. Pollak and Fr. Fuchs [26a] with the use of the bioclimatic ultraviolet dosimeter of the I. G. Farbenindustrie. Differing from the measuring device of Bloch the leucosulfide of fuchsin was used in this and the discoloration was measured with the test tube lengthwise, so that a very much higher sensitivity was secured by means of the greater thickness. According to Pollak's process the normal ultraviolet dosimeter can be supplemented by mounting on the head piece of the dosimeter a 4-volt lamp which illuminates through the test tube an ocular cell placed at the other end. The photocurrent is measured with a microammeter in such a way that the needle deflection for the un-irradiated dosimeter is adjusted to 100 by means of a built-in control resistance. The percentage absorption and from this the ultraviolet intensity is given directly by the return of the needle.

In Part I, pages 128-134, it has been shown already that selenium photoelements are also sensitive in the x-ray region. An S 50 cell delivers about 2 microamperes per Roentgen

unit. With the "Multiflex" galvanometer, accordingly, about 1/1000 r can be measured.

The radiation of the invisible part of the spectrum can also be measured by using suitable fluorescent materials. According to R. Herz (I. G. Farben., Berlin) with the use of luminous coatings (intensifying screens) the photocurrent is 40 times greater than for the direct action of the x-rays on the cell, on account of the fluorescent light. Within the range of tube currents measured there was an almost proportional increase of the photocurrent, and within the potential range an almost quadratic increase, while the absorption in metal filters showed the known exponential regularity. In all x-ray measurements, however, care must be taken that the cell and the leads to the galvanometer are in a grounded metal shield, since otherwise a charging up takes place when the x-ray tube is turned on which may lead to injury to the cell.

M. Pirani and R. Rompe [27] describe an interesting use of fluorescence for the photometry of different colored light sources. The advantage of this process lies in this, that the measurement of the different colored radiations is reduced to a comparison of intensities of light of the same color, so that the difficulties of heterochromatic photometry are surmounted.

Recording and Integrating Illumination Meters

We have already heard of an integrating apparatus for ultraviolet light in the preceding section the action of which is based upon the photochemical process of discoloration of leucocyanide. But for bioclimatic and meteorological purposes the cumulative intensity is not only important, but the momentary value of the radiation is also of interest. An apparatus that gets both these values simultaneously is the recording illumination meter illustrated in Figure 17. This consists of a depressor bar recorder and a cell on a metal stand with a ball joint. Such instruments can be made with

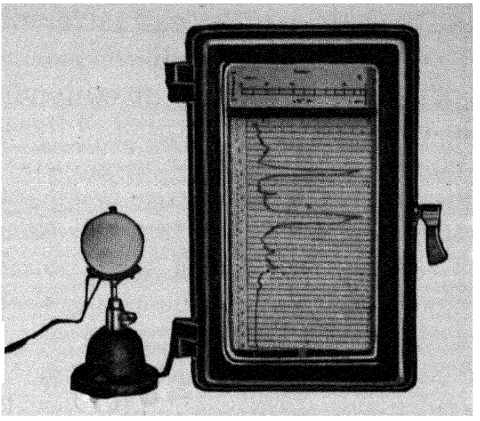


FIGURE 17.—Recording Illumination Meter. According to B. Lange.

an S 50 cell with a sensitivity of from 100 to 1000 lux for the full scale deflection. With a large S 145 cell a sensitivity 10 times greater is attainable. For measurement of daylight over 1000 lux merely an S 50 cell in combination with a platinum opal glass filter is used. The instantaneous intensity is given by the height of the curve at the time, while the enclosed area corresponds to the cumulated intensity. For control purposes signal contacts can be introduced which come into action when the illumination goes above or below predetermined intensities.

In photochemical work, bleaching experiments or photographic copying processes we are less interested in the instantaneous value of the illumination, which varies greatly, for instance, with day light or arc light, but merely in the quantity of light radiated. For this measurement all integrating ammeters can be used, as for instance, a rotating counter or an electrolytic current counter. In Figure 18 is shown an open rotating counter with a cell on a pedestal base.

In this counter* the disc armature rotates between the poles of a permanent magnet, while the conduction of the

* Such measuring instruments, which make about 3600 revolutions per hour, have in recent years aroused considerable attention in the technical and daily press, and have thus led to utopian exaggeration. Thus it was reported in a technical journal that a direct transformation of the energy of the sun into electric currents had now been accomplished with such an efficiency that a Siemens' cuprous oxide cell the size of a pfennig drove a household motor by solar radiation.

electric current takes place over sliding brushes and small collectors. The revolving armature disc drives a counter that can be calibrated in milliampere hours or in lumen hours.

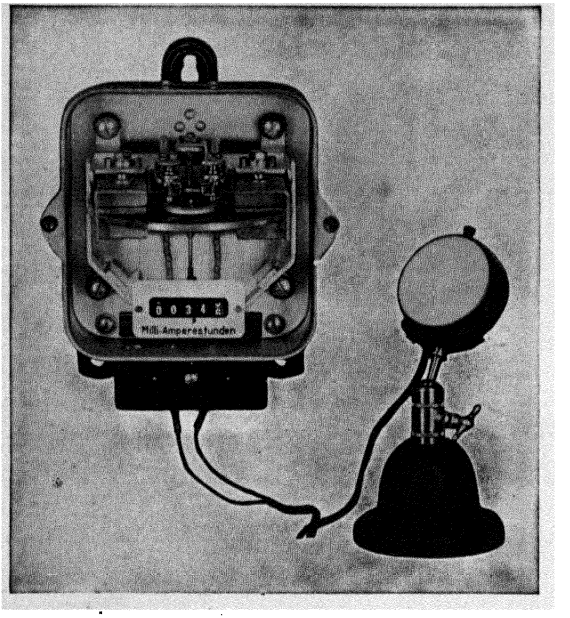


FIGURE 18.—Cell with Rotating Counter.

In Figure 19 is illustrated an equipment for determining the bleaching of color samples in sunlight, which was described in detail by H. Sommer and F. Jacoby.[28] Two cells are attached at the two ends of a board with the color samples. One cell operates the graphic recording instrument at the bottom, the other cell drives the rotating counter placed above it. If it is a question of recording photocurrents under 0.2 milliampere the use of a rotating counter offers difficulties, inasmuch as friction of the bearings is troublesome and may lead to an inaccurate reading. To eliminate this inconvenience the counter can be equipped

with a second armature on the same axle. The one armature is driven by a small auxiliary current, while the photocurrent is connected to the second armature. The quantity of irradiated light is given by the difference between the number of revolutions in the dark and in the light. In place of rotating counters electrolytic counters can be used with a higher sensitivity.

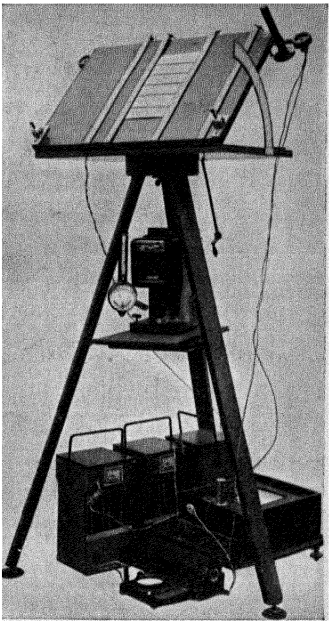


FIGURE 19.—Photoelectric Measuring Equipment for Bleaching Experiments. According to H. Sommer and F. Jacoby.

VOLUME BRIGHTNESS AND DIFFUSIVITY METERS

Whereas the intensity of illumination is measured only for a definite plane, usually horizontal, illumination engineering is also interested in the spatial light flux, which was introduced by W. Arndt [29] as the conception of volume brightness and which, as it were, measures the total brightness of all intensities of illumination arriving at a single point from

all directions in space. According to a work of B. Lange [21] an opal glass photometer with a photoelement screwed on can be used for the measurement of the volume brightness.

As Arndt [29] proved, the ideal solution would be a spherical cell, which, however, for technical reasons is not producible. According to a contribution from the Tungsram Research Laboratory [30] an approximate solution can be found by the use of a dodecahedral body which consists of 12 five-edged selenium photoelements.

Another way of characterizing the spatial illumination was described by R. Roggan. He introduced the conception of diffusivity or "scatterability of the light." If all partial light fluxes are equally strong, then ideally scattered light exhibits 100% diffusivity. For the existence of partial light fluxes all in a single direction the diffusivity would equal zero. For measuring the diffusivity Roggan suggested the use of a polyhedral cell, the surfaces of which were so connected that the photocurrents annuled each other in illumination equal from all sides. But with unsymmetrical illumination of the individual surfaces a photocurrent results which is a measure of the diffusivity of the spatial light distribution. Roggan also described an illumination meter with two cells standing at right angles to each other, which acted on a crossed coil instrument, so that with this the ratio of the horizontal to the vertical intensity of illumination was measurable.

Ulbricht's Sphere and Photometric Integrator

For rating incandescent lamps and luminous bodies, the total light flux, or the mean light intensity, measured in an Ulbricht's sphere, is of special significance. The light yielded is calculated from this value and the power consumption of the lamp. Such measurements can be performed with photoelectric illumination meters without further aids. Merely the intensity of illumination at the sphere window is mea-

sured and the average spatial light flux is calculated from the value thus secured and the diameter of the sphere. For simplification a complete apparatus has been built with a wattmeter for determining the power consumption of the lamp and an indicating instrument calibrated in lumens. For the photometry of colored lamps and luminous tubes the use of a correction filter is required and for the measurement of powerful lamps a platinum opal glass filter.

Simple special apparatus with photoelements can also be prepared for photometry of lamps of special construction. In Figure 20 is illustrated the schematic structure of

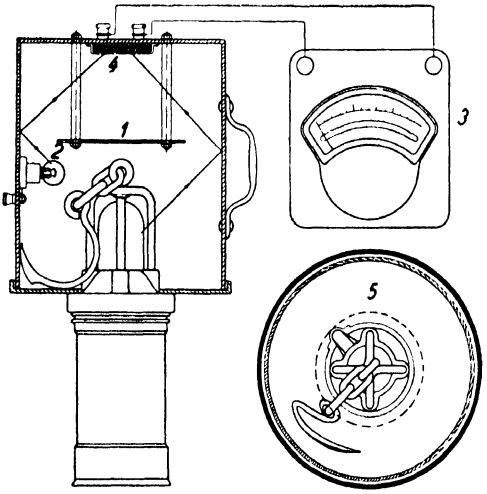


FIGURE 20.—Photometric Integrator for Miner's Lamps. According to Hiepe.

a photometric integrator according to Hiepe [31] for the determination of the spatial light flux of miner's lamps. The direct radiation from the lamp is screened off from the cell by the circular shield, so that only the radiation reflected from the whitened walls falls on the cell. A built-in auxiliary lamp serves for control measurements.

Chapter 3

Exposure Meters for Photographic Purposes

Simple Exposure Meter

The correct time of exposure is the first and most important condition for the success of a photographic picture. Hence particular interest has been directed to photoelectric exposure meters, which make an objective determination of the correct exposure time possible. In a few years photoelectric exposure meters have not only found a distribution in hundreds of thousands, but exposure meters are now beginning to be built into the cameras, and a wholly automatic control of the exposure time is proposed.

As was mentioned already on page 203, every simple luxmeter can be used for determining the exposure time. For the measurement the cell of the luxmeter is directed toward the object to be pictured and the intensity of illumination of the reflected light is determined. From this the correct exposure time can be calculated or even read off from a turntable. If we define the correct exposure time as the shortest exposure, which for normal object range leads to a negative of correct quality, whose density or blackening lies in the straight part of the plate characteristic, then an exposure time of 1 second corresponds to an intensity of illumination of 50 lux at 16/10 DIN * and *f*/9. In measuring the light reflected from the object to be pictured, however, side and top light must be screened off from the cell, perhaps by holding out the hand.

Hence for simplification of the measurement special photoelectric exposure meters were developed which are

* DIN means a German Engineering Society standard of plate speed. Note DIN on scales of Figs. 22 and 23. E. F. K.

provided with a scale marked off directly in exposure times, and which are so constructed that the illumination angle of the cell corresponds to the image angle of the camera. In Figure 21 such an exposure meter, "Ombrux," is illustrated. This instrument has a double scale for exposure times of 1/10-30 seconds and 1/500-1/10 second referred to a stop of *f*/9 and a plate sensitivity of 23° Scheiner (16/10 DIN). The cell is placed behind a glass lens in a shallow

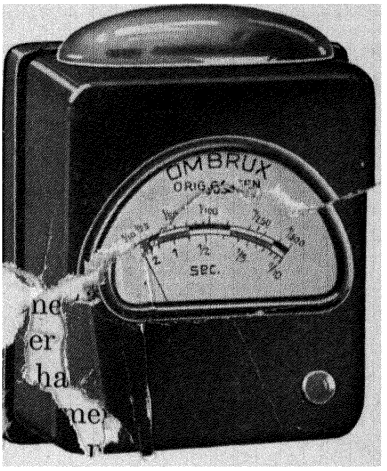


FIGURE 21.—"Ombrux" Exposure Meter.

compartment, which is divided by several diaphragms into small chambers, such that the angular opening of each chamber corresponds approximately to the image angle of the apparatus. For the measurement the lens is turned toward the object to be pictured and the correct exposure time is furnished directly by the deflection of the needle. A logarithmic scale is provided for covering a large range of measurement. The exposure time for other plate sensitivities and other stops is determined from tables.

To save all calculations, exposure meters have been constructed in which the correct exposure time for every stop and every plate sensitivity can be read directly from the

deflection of the needle. Regarding the stop various methods can be used. Thus a diaphragm can be placed in front of the cell and adjusted accordingly. But with the adjustment to a small stop the photocurrent becomes small and the needle deflection is no longer easily readable. The exposure meter, "Tempophot," illustrated in Figure 22, in which the full cell area is used, works decidedly more conveniently, and the calculation results from merely turning scales, which are shifted to the needle deflection.



FIGURE 22.—"Tempophot" Exposure Meter.

Whereas the exposure time is indicated directly in the instruments described above, we will now describe an indirect principle of measurement that resembles the optical exposure meter. In the latter instrument the image brightness is reduced to a threshold value and the time of exposure is derived from the required adjustment of a gray wedge or other device for reducing the light. In complete analogy the illumination of the cell can be so far reduced that a pre-determined photocurrent is produced. We will become acquainted with this model in the "Emig" moving picture camera. The photocurrent, however, can also be reduced to a pre-determined value by a rheostat. If the knob of the rheostat is provided with a corresponding time scale the

exposure time can be read on it. The "Helios" exposure meter illustrated in Figure 23 works on this principle; it has recently been supplied with a built-in rangefinder. Since no large needle scale is required in this instrument, it yields, as a particular advantage, a very compact structure. The measurement, however, is no longer quite as simple as with the direct indicating instruments. The exposure meter must be

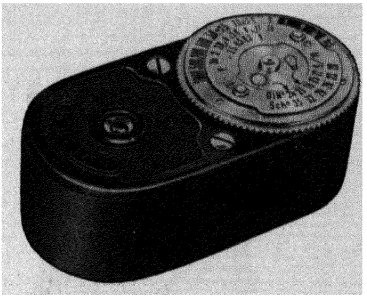


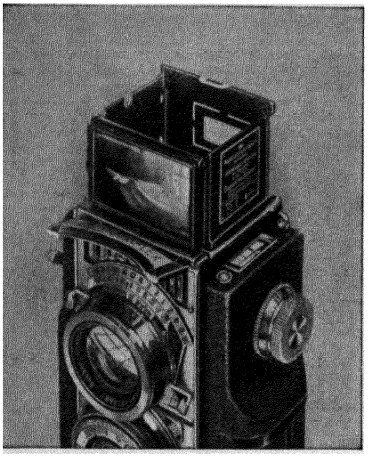
FIGURE 23.—"Helios" Exposure Meter.

held before the eye and at the same time the rheostat must be operated until the little pointer is adjusted on a line, a measuring process for which both hands are necessary. For extension of the range of measurement other adjustment marks are provided, which require multiplication of the measured values.

BUILT-IN EXPOSURE METERS

The compact structure, however, makes the "Helios" exposure meter just described particularly convenient for building-in. Hence this instrument was used for the first camera with built-in photoelectric exposure meter, the "Contaflex." As is evident from Figure 24, the cell is placed under a protective cover above the finder lens, while diaphragm, sensitivity and exposure time are adjusted on the ring scales lying above it. The small needle instrument with 3 reference lines is placed beside the light compartment.

For the measurement the ring scale connected with the resistance is adjusted until the needle stands on one of the referance lines. On the time scale the proper exposure time for each diaphragm can be read off, which must be multiplied by the factor for the adjustment mark.



'IGURE 24.—"Contaflex" with Built-in Photoelectric Exposure Meter.

In the "Helios" exposure meter and the "Contaflex" the measurement results from the adjustment of the photocurrent by means of a resistance. In the new motion picture camera of the Eumig firm, on the contrary the photocurrent is controlled by an iris diaphragm. As can be seen in Figure 25, a tube with built-in iris diaphragm and cell is located alongside the camera objective. The pointer of the measuring instrument is visible behind the cross mark of the finder. The reduction of the light results from the adjustment of the iris diaphragm, which is mechanically coupled with the objective diaphragm. In the exposure it is only necessary to take care that the pointer of the meter rests on the finder line through adjustment of the iris diaphragm. The built-in exposure meter offers, accordingly, particular advantages since it makes possible a continuous control of the diaphragm

during the exposure, while the chosen frame speed and the film sensitivity are adjusted before the exposure.

But we are no longer satisfied with the semi-automatic operation of such cameras. There are already new patents according to which a completely automatic adjustment of the diaphragm takes place. In the construction of O. Rissdör-

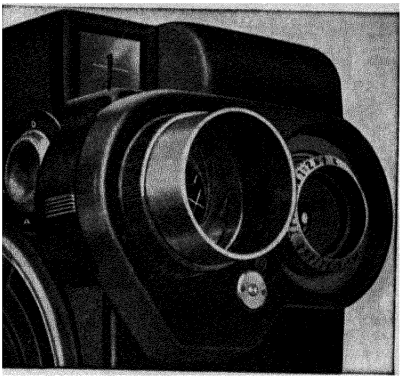


FIGURE 25.—"Eumig" Motion Picture Camera with Built-in Exposure Meter.

fer's German patent 615,177 the leaves of the diaphragm are so lightly mounted that they are operated by the moving coil system. According to German patent 614,221 of W. Zügel, the photocurrent merely accomplishes the adjustment of a controller while the motion of the diaphragm results from a built-in electric motor. However, nothing is thus far known about the practical performance of these new constructions.

EXPOSURE METERS FOR COPYING APPARATUS

The choice of the correct time of exposure in the copying process is just as important as in the exposure. Since the latitude of exposure of copying materials is much smaller than for negative materials, the copying time must be that much more carefully determined. In proper recognition of

these relations the "seeing" copiers have been developed, which are suitably equipped with photoelectric measuring devices.

In the "Mafikometer," illustrated in Figure 26, the negative is measured in the copying apparatus so that the brightness of the copying lamp is taken into account. For the

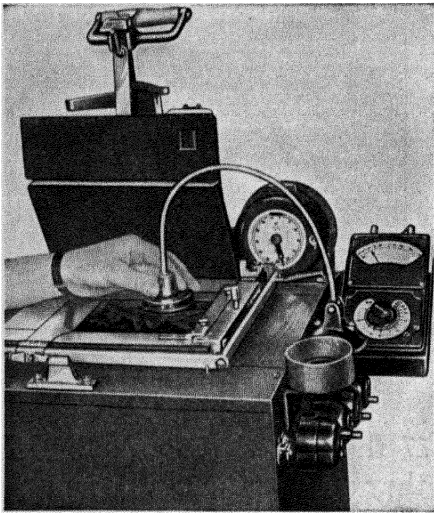


FIGURE 26.—Copying Apparatus with Photoelectric Exposure Meter. Made by Mafi.

measurement the cell is placed over a part of the negative important in the image, and the photocurrent for this is measured by the pointer instrument mounted at the side of the copier box, and calibrated directly in exposure times. Since the measured value, however, depends not only upon the image brightness but also upon the sensitivity of the paper, a variable shunt resistance is provided. This resistance controls the sensitivity of the meter so that the time scale is referred to the sensitivity of the chosen paper and the exposure time can be read directly. A drawback of the "Mafikometer," however, is the relatively large size of the cell, with which not only the important parts of the image

but also occasionally definitely brighter or darker neighboring parts are measured. This defect is avoided in the new "Seriograph," Figure 27, by the use of a point of light and a small cell. Since the sensitivity of the needle instrument no longer suffices for the measurement of the small photocurrent, an expensive light pointer instrument must be selected, the scale of which is visible in the upper part of the apparatus. It is also to be distinguished in this apparatus that the measurement does not take place on the copy surface but on a measuring plate with a pinhole screen mounted

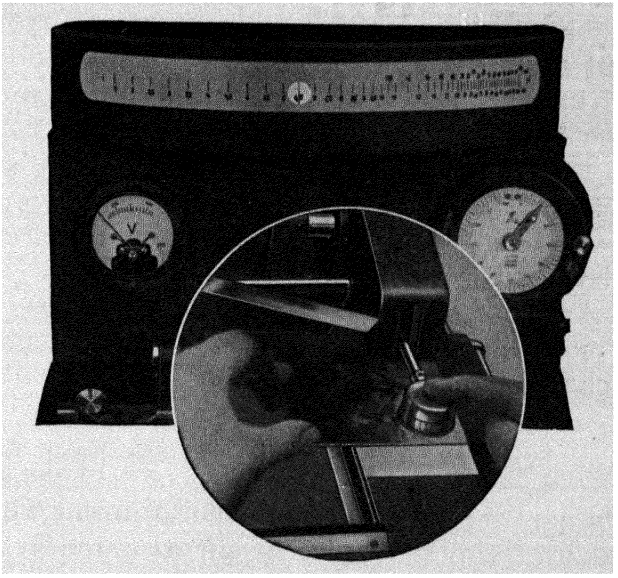


FIGURE 27.—Agfa "Seriograph" with Built-in Photoelectric Exposure Meter.

nearby. As can be seen in the round inset in Figure 27, the cell is pressed down for the measurement, and the light marker of the mirror galvanometer is switched on at the same time. Through the introduction of an iris diaphragm in the cell housing the sensitivity of various sorts of papers can be taken into account, so that with this apparatus the exposure time can be read off directly.

Exposure Meters for Photomicrographic Use

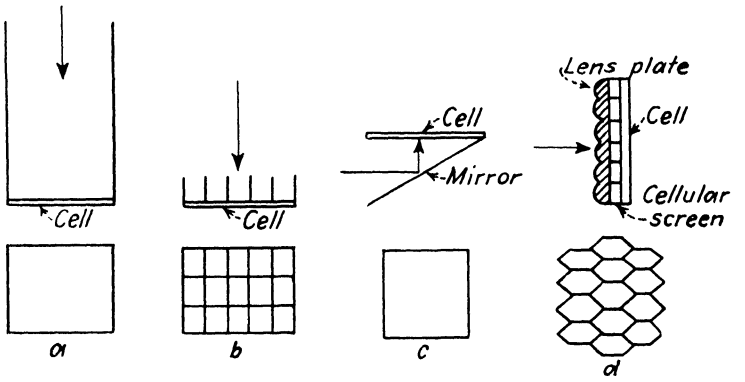
The choice of the correct time of exposure is also important in photomicrographic pictures, particularly in cinematographic pictures of living preparations, for here the possibility of determining the correct time of exposure by means of test pictures, is often lacking. Photoelements are also especially suitable for such measurements. But there exists a difficulty, inasmuch as the intensity of illumination on the ground glass of the microcamera is very small. This difficulty can, however, be overcome by the use of the "Multiflex" galvanometer already described on page 202. In order to see important parts of the image, the ocular photocell is used, mounted in a special frame with hard rubber ring. The instrument has two double scales for exposure times from 1/100 to 10 seconds which can be switched in by a pointer knob on the side, and a control resistance for different plate sensitivities. For the measurement the plate sensitivity is adjusted on the control resistance, the cell is placed upon the important part of the image, and the exposure time is read directly on the light marker indicator. For moving pictures the cell can be mounted in a side tube.

Different Styles and Their Limiting Sensitivities

In spite of the very different external forms we can distinguish two basic principles in all exposure meters: the direct indicating devices, and the exposure meters operating with a definite adjustment value, which we have compared with the optical threshold value meters. To the class of directly indicating instruments belongs the "Ombrux" exposure meter, which indicates the exposure time directly for a pre-determined diaphragm and film sensitivity. The "Tempophot" is a directly indicating instrument with a slide-rule type of circular scale. The "Mafikometer" and the photomicrographic exposure meter also belong to the directly indicating instruments.

Representatives of the second class, on the other hand, are the "Helios" exposure meter, the "Contaflex" and the "Eumig" moving picture cameras, which already operate semi-automatically, inasmuch as adjustment of the exposure meter is coupled mechanically with the diaphragm adjustment.

We have recognized the limitation of the image angle as a further essential constituent of the exposure meter. The different models are grouped schematically in Figure 28. The



a "Shaft" screen
b. Lattice screen
c Mirror screen
d. Honeycomb lens plate with cellular screen

FIGURE 28.—The Different Methods of Limiting the Image Angle.

most primitive structure *a* requires an inconveniently long tube. A considerable shortening is accomplished by the lattice screen *b* introduced by H. Tönnies, which can also be made concentrically. The cell can be protected against top light by construction in a recess with a slanting mirror *c*. The flatest structure for the greatest light intensity, however, is secured by the lens plate *d* of Tönnies. This lens plate consists of an array of honeycomb shaped lenses or prismatic glass bodies which transmit only the light incident within a definite angle, while sharply inclined incident light is totally

reflected in the glass body. A further limitation of the aperture results from a honeycomb screen lying under this.

Among the various photoelectric exposure meters there is, however, also a real difference with respect to their sensitivity. For on the sensitivity of the apparatus depends the longest exposure time, that is, the smallest intensity of illumination that is measurable. Just as the value of an objective depends upon its light intensity, the value of an exposure meter is determined by its sensitivity. The sensitivity of an exposure meter can be stated by the longest exposure time that can be read off. But this value depends upon the choice of the reference diaphragm and the film sensitivity. Hence the concept of the limiting sensitivity as the intensity of illumination measured in lux for a needle deflection of 1 mm was introduced by B. Lange.[32] For comparison the limiting sensitivities of various exposure meters are stated in the accompanying Table 4.

TABLE 4. Limiting sensitivity of various exposure meters

Type	Lux
Ombrux	4
Tempophot	10
Contaflex	1
Multiflex	0.03

In the effort to increase the limiting sensitivity attention has been turned to using larger cells. Thus in a recent model of the "Tempophot" a second cell can be put on for strengthening the photocurrent. In the micro-exposure meter a limiting sensitivity of 1/100 lux is secured with the S 50 cell.

The photoelectric exposure meters, today already the greatest field of application of the photoelements, are typical examples, therefore, of an apparatus finding an extensive entrance into practice, although, from a scientific standpoint, considerable sources of error are still present. The deter-

mination of the time of exposure of an object with very different brightness values by means of the measurement of the total light flux is wrong. To this is added also the difference in spectral sensitivities of cell and plate. On these grounds the leading photographic specialty manufacturers questioned the introduction of photoelectric exposure meters at first. On the other hand these exposure meters found an unexpectedly good reception among electric specialty firms, by whom the photographic considerations were less known. To the author this example seems instructive also for other new fields of application, and particularly worth considering if no other method exists which permits just as simple a measurement.

Chapter 4

Special Photometric Apparatus

The exposure and illumination meters described in the last two chapters could also be reckoned among photometric apparatus. In this chapter, however, we will only be concerned with those instruments in which the determination of the intensity of illumination is not the real object of measurement, but another value which is determined by photometric measurement, for instance, density or spectral absorption, is sought.

We have already become acquainted in the preceding chapter with two important photometric methods of measurement; the direct determination of the photocurrent as a measure of the intensity of illumination and the reduction of the photocurrent to a definite standard value. We will here also become acquainted with a third sensitive and accurate null-method using two cells in a differential circuit. We begin with the simple device in which the photocurrent is measured directly.

Transparency and Density Meter

The light transmission of glasses, filters, fabric, paper and other solid or fluid bodies is frequently of importance, for instance for the selection of materials of equal light transmission or for continuous control in manufacture. The density of photographic films has indeed reached an even greater importance, not only for characterizing the sensitivity but also for the great field of sound film records.

The photoelectric determination of the light transmission is particularly easy. If the photocurrent i_o corresponds

to the intensity of the incident light and i to the photocurrent with the test body introduced, then the optical transmission, or transparency, $T = i/i_o$. The values of absorption and density derived from this are calculated as follows: If I_o is the intensity of the incident light, I_a that of the absorbed light, and I the intensity of the transmitted light, then $I_a/I_o = A$ is the absorptive capacity, and $A \cdot 100$ the percentage absorption. $I/I_o = T$ is labelled the transparency or transmission. Transparency and absorption stand in the following relation: $T = 1 - A$ and $T\% = 100 - A\%$. The density D is defined as $D = \log (I_o/I)$; it stands in the following relation to the transparency and the absorption: $D = \log (1/T) = \log [1/(1 - A)]$.

For measuring the optical transmission a very simple apparatus suffices, the transparency meter illustrated in Figure 29. The cell is located in the pedestal base, and



FIGURE 29.—Transparency Meter. According to B. Lange.

mounted on it is a reflector with a flashlight bulb which illuminates the test body uniformly. The structure is so arranged that the cell and lamp are replaceable, so that the place measured can be observed visually beforehand. The

transparency is secured from the needle deflections with and without the specimen. If the deflection of the needle is adjusted at 100 for the empty apparatus by means of a control resistance built into the instrument, then the needle deflection corresponds directly to the optical transmission.

But if it is a matter of measuring the density of very small strips in spectral lines or sound film records, the simple transparency meter just described no longer suffices, since no narrow slit can be introduced, and also the displacement of the plate by hand cannot be accomplished exactly.

Microphotometer

Measuring through a line spectrum with a visual photometer, for instance, a Hartmann microphotometer, is not only very time-consuming, but it also fatigues the eyes greatly. Hence there were efforts to develop objective instruments. Among these devices only the thermoelectric instrument of Moll and the self-registering microphotometer of Zeiss, which worked with an alkali cell and an electrometer, will be mentioned. Very decided simplifications are secured by the use of photoelements. In principle it is only necessary that the spectrum to be measured shall be moved past an illuminated slit, and that the varying light flux behind the slit be measured with a photoelement. A simple arrangement of this kind with a carriage and mechanical slit on an optical bench was described by B. Lange.[33] In place of the mechanical slit an optical slit image can also be used, and instead of screening off, or aperturing, the object to be measured, the slit can be transferred to the enlarged image of the object.

The microphotometer of Fr. Goos and P. Koch [34] has this sort of arrangement, but it works with an alkali photocell. A simplified structure with selenium photoelements on an optical bench was described by H. von Oehmke [35] and was built by Zeiss as a spectrum line photometer. Such struc-

tures can, however, be much simplified by the use of an ordinary microscope stand with cross-table. Thus, as J. Lehner [36] showed, a simple optical slit which produces an optical image of a slit on the spectrum picture can be used in place of the illuminating system of the microscope.

Such measurements are made still more simply with the use of a slit ocular. The slit ocular can be used with every strong light illuminating system. It is advantageous to use a special illuminating system with a built-in miniature lamp which is mounted in place of the microscope condenser. Figure 30 shows a slit ocular of this kind. The slit ocular

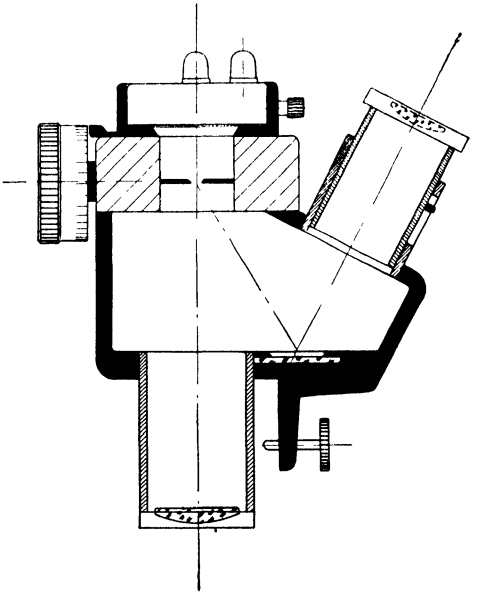


FIGURE 30.—Slit Ocular.

has a slit which is adjustable by a micrometer screw and which can be limited in length from 0-12 mm by a slide. The ocular cell is placed above the slit, while an image of the spectrum is made on the white back of the slit by the lower lens. This spectrum can be observed through the eyepiece of the side tube and can be sharply focused. Then the slit

width is adjusted with the micrometer screw. The "Multiflex" galvanometer, Figure 14, is particularly suitable for measuring the photocurrent. If the light pointer is adjusted on the end value of the scale, for clear parts of the plate, then transmission and density are readable directly.

Such microphotometric measurements are of course not limited merely to plates and films, but can be carried out also for all microscopic preparations. With colored preparations the spectral absorption can be measured by the use of a monochromator or spectral-pure filters. An instrument of this kind can be used for determining the absorption of small quantities of liquid in microbulbs.

If it is a matter of the definition of fine and coarse lines the microscopic instruments no longer satisfy all requirements. The displacement of the object to be measured by the cross-table is no longer exact enough. The microphotometer according to B. Lange [37] works by far more precisely.

The external form of the microphotometer can be seen in Figure 31, while the optical and mechanical arrangement will be described in terms of the section reproduced in Fig-

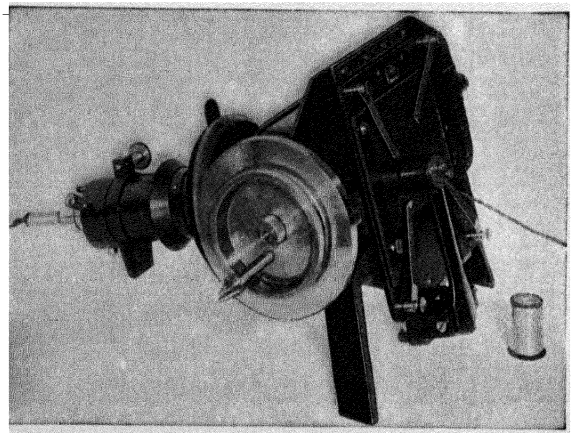


FIGURE 31.—Photoelectric Microphotometer.
According to B. Lange.

ure 32. The incandescent lamp G is centered by the thumbscrew z and displaced in the direction of the optical axis by the supporting shaft f. The slit Sp is uniformly illuminated by the condenser C and the filament of the lamp is focused in the principal plane of the objective o, so that its image fills the whole objective opening, by which the maximum brightness is secured. The objective focuses the slit, reduced,

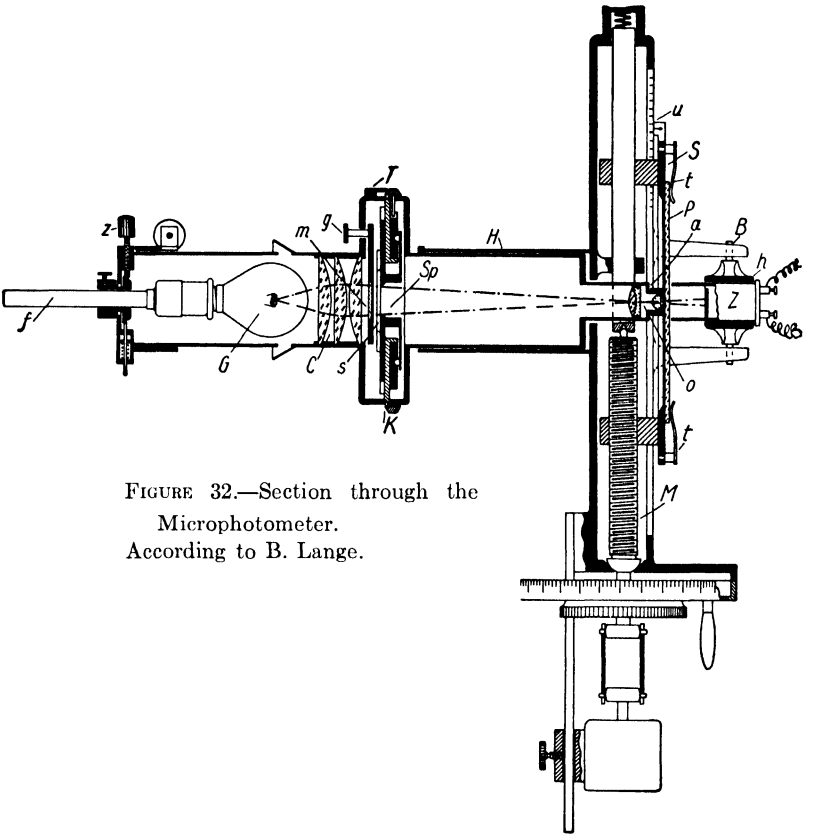


FIGURE 32.—Section through the Microphotometer. According to B. Lange.

on the plane of the carriage table, which is moved by a micrometer screw M. The adjustment of this five thread screw with a pitch of 5 mm can be read on a 500 division drum, so that one interval corresponds to a table movement

of 0.01 mm. Through the particularly precise preparation and mounting of the spindle the accuracy of adjustment amounts to about 0.001 mm. The object to be measured P is held on the carriage table with table springs t and is oriented by a movable straight-edge. Behind the plate in the collar h is mounted the photoelement Z, which is interchangeable with a magnifying glass for inspection of the object to be measured. The slit is constructed with particular care, with its width adjustable by a graduated arc from 0.1-20 mm. The adjustable widths of the optical slit reduced ten times are 1/100-2 mm, so that measurements can be made over great ranges of density, as is particularly important in the measurement of x-ray films, W. Büssem and B. Lange.[38] A ground opal glass plate can be placed on the objective o, so that densities can also be measured in diffuse light. In place of the opal glass plate a small pinhole screen can be attached, which limits the aperture to about 1°. The density depends upon the aperture of the pencil of rays. It is smaller for diffuse light than for parallel illumination. The quotient of these two values, the so-called Callier factor, according to recent work of J. Eggert and A. Küster [39] stands in a close relation to the grain size, so that from it the grain diameter and the average grain count per square centimeter can be calculated.

To make the applicability of the microphotometer still more versatile, an opal glass plate with a reference mark can be flapped over the slit and a magnifying glass can be introduced in place of the cell, so that the apparatus can be used as a comparator for measuring the line spacings. For diffuse lines the exact position of their optical center of gravity can be determined from the density curve.

The point by point evaluation of very fine line spectra, however, is time-consuming, and possesses the danger that minute details get lost through choice of too large a measuring interval. In such cases, accordingly, the use of the recording arrangement of the synchronous writer illustrated in Figure 33 is brought in. The novelty of this device is that

the record of the density takes place in an entirely separate apparatus, so that every photometer can subsequently be supplied with the recording arrangement and also the synchronous writer can be used for recording other measured quantities. The synchronous course of the measuring and recording devices is emphasized as an essential principle. This occurs through two synchronous motors driven by the same alternating current one of which controls the spindle of the photometer and the other the continuous deflection of a light ray by a mirror system, so that the record takes place on a stationary plate, whereby the highest accuracy is secured. In the synchronous writer, Figure 33, there is

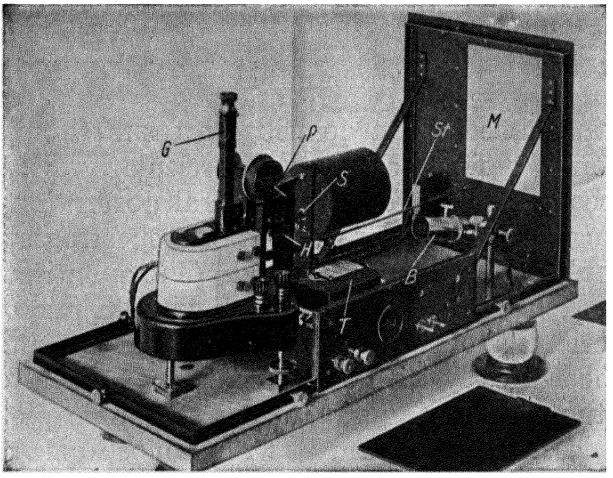


FIGURE 33.—Synchronous Writer. According to B. Lange.

a short period, torsional ribbon, mirror galvanometer and in front of it a mirror, which is driven by a synchronous motor through a lever with a tangent screw. The pin-hole diaphragm of a built-in projector is focused through the galvanometer mirror and the mirror system onto the plate as a point. For the measurement the plate in the microphotom-

eter is moved slowly past the light slit, while the light ray in the synchronous writer is moved perfectly uniformly from top to bottom over the recording plate. The coordinate perpendicular to this is given by the galvanometer deflection. By variation of the motor speed different transformation ratios from 2:1 to 1:240 can be introduced in the record, so that even very dense sets of lines, as for instance in high frequency light-sound patterns, can be very exactly reproduced.

The microphotometer is built in two sizes, for measurement distances of 12 and 25 cm.

To characterize the precision obtained it should be stated, that the recorder curve gives a measure of all fine irregularities, and that on a repetition of the recording an exact congruence of the two curves should be secured.

Spectrophotometer

The instruments just described are suited only for the evaluation of a single color, and particularly, neutral gray substances. But the form of spectral absorption is often interesting. For such investigations spectrographs with photographic attachments are used. The quantitative evaluation of such pictures can take place with the microphotometer described above. But the spectral absorption can be determined directly with a photoelement and monochromator, without detouring via the photographic picture. B. Lange [40] describes an apparatus with monochromator, ocular photocell and light source on an optical bench. In Figure 34, P is the ocular cell, M a direct vision monochromator, O_2 and O_1 two lenses for securing a parallel light beam in which the object to be measured is placed, and L the low voltage lamp whose point filament is focused by the two objectives onto the entrance slit of the monochromator. For the measurement the photocurrent is measured in the individual spectral regions with and without test specimen and the absorption is calculated from the accompanying galvanom-

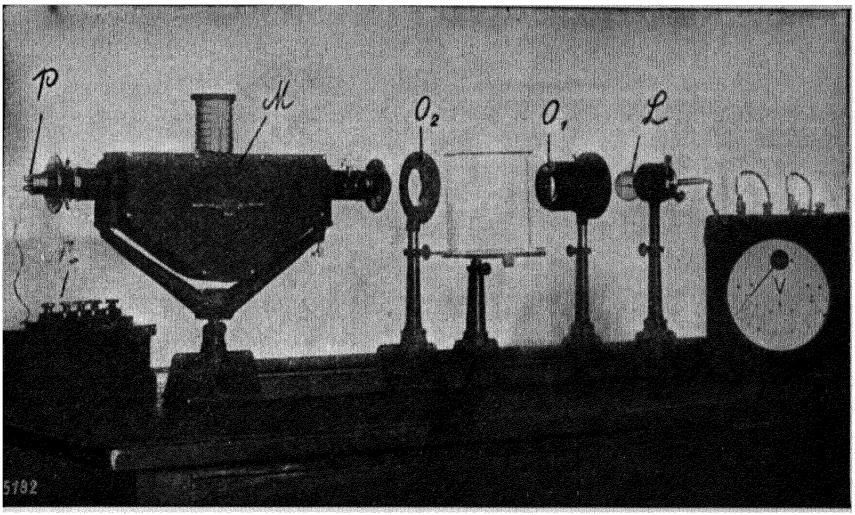


FIGURE 34.—Monochromator with Ocular Photocell and Illuminating Equipment for Determining Spectral Absorption. According to B. Lange.

eter deflections. With the arrangement just described B. Lange was able to determine the slight absorption of optical glasses in the visible spectrum.

An assumption for the precision of spectrophotometric measurements is that the photocurrent increases linearly with the intensity of illumination. As we have seen, there are noticeable departures from a linear form for intensities of illumination over 1000 lux, which can be explained theoretically. But for small intensities of illumination there are no grounds for similar deviations. Nevertheless, H. C. Hamaker and F. W. Beetzhold [41] report on such deviations and variations of the photocurrent with time. More exact investigations of H. Pfeilschiffter and B. Lange have not confirmed these deviations; nor have measurements recorded by the synchronous writer. The deviations found by Hamaker point to disturbing thermoforces, as does the statement that the cells were sensitive in the infrared region at 10 μ.

B. Lange secured high spectral purity and great precision with a Müller-Bechstein double monochromator with built-

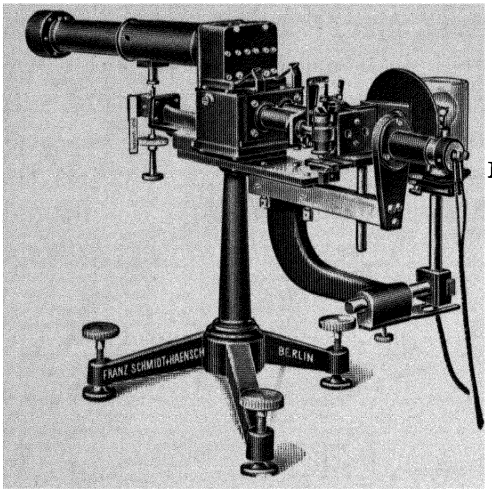


FIGURE 35.—Photoelectric Spectrophotometer with Double Monochromator, Built-in Cell and Illuminating Equipment.

According to B. Lange.

in light source and cell, Figure 35. The preparation is placed upon a sliding device so that the two measurements with and without the preparation could be carried out one after the other. With this apparatus B. Lange [40] was able to measure even the fine absorption of a neodymium glass and to determine the dependence of the absorption of a cerium glass on the temperature. C. Schusterius and B. Lange [42] have determined the absorption bands of potassium permanganate, and have also measured the absorption of pure water in the visible spectrum and have shown the difference between ordinary and distilled water. The highest precision was secured with a differential connection of two cells described by B. Lange,[43] as is represented schematically in Figure 36. Here L is the light source, O_1 an objective that focuses the light source on the entrance slit Sp_1 of the monochromator, G a small glass plate that deflects a part of the light onto the cell Z_1, J_1 an iris diaphragm for regulating the light flux falling on the cell, P_1 a prism that directs the radiation onto the entrance slit of the monochromator, P_2 a prism for the first dispersion, Sp_2 a mirror acting as a slit, P_3 the prism for the second dispersion and Sp_3 the exit slit. The monochromatic radiation reaches the measuring cell Z_2 by

way of the two objectives O_2 and O_3 and the shutter V, so that the absorption vessel A with a length up to 500 mm is placed in the parallel beam between the two objectives. In the diagram of connections Z_1 and Z_2 are the two cells placed in a differential circuit, R a control resistance and M the mirror galvanometer with a sensitivity regulator E. Through variation of the contact on the resistance R the diagonal

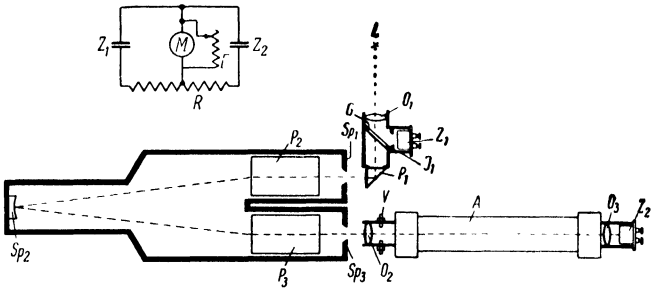


FIGURE 36.—Structure and Connections of the Photoelectric Spectrophotometer with Double Monochromator and Two Photoelements in Differential Connection. According to B. Lange.

arms of the bridge connection can be equalized so that the measuring instrument is without current. For the measurement the balance of the bridge is first adjusted, and then, with lowered sensitivity of the galvanometer, the deflection d_o is determined for darkened measuring cell, which should be made as large as possible in order to increase the precision. If d_o is the deflection with complete darkening and d the deflection with the interposed test absorption, then for the Extinction: $E = \text{Log}_e \frac{I_o}{I} = \log_e \frac{d_o}{d_o - d}$. If it is assumed that the absorption is small, that is d is small compared with d_o, then it follows, using the formula for calculating with small quantities, that: $E = \frac{d}{d_o}$

Large specimens are not always available, however, for spectrophotometric measurements. In mineralogical investigations particularly, measurements are required on very small parts of a thin slice. W. Eitel and B. Lange [44] have described an apparatus for such measurements. By using the slit ocular described in the preceding section, Figure 30, the measuring equipment can be simplified. If the place to be measured is apertured in the image plane of the ocular, then the optical arrangement for producing a slit image in the specimen is saved.

Colorimeter

Colorimetric measurements are reaching an ever greater significance for the rapid determination of the concentration of colored or turbid substances, not only for chemists but also in the fields of doctors, bacteriologists and dairymen, as well as for breweries and sugar refineries. Especially by the introduction of objective photoelectric equipment can considerable advances in these fields be accomplished, so that tedious gravimetric determinations can be carried out in a few seconds through colorimetric measurements. With the use of continuous flow colorimeters, indeed, a completely automatic control and regulation of operations is possible.

Colorimetric measurements are made just as simply as transparency and density measurements, (see page 224). For this a light source and a cell with the absorption vessel between are sufficient. Hence the transparency meter shown in Figure 29 can be used as a simple colorimeter. The photocell colorimeter of F. Hellige, illustrated in Figure 37, also operates on this principle. The solution to be measured is placed in a glass container between the lamp and the cell, while the photocurrent is measured by the built-in needle instrument. For the measurement a second container filled with the pure solvent is needed. With this the photocurrent is adjusted to a particular value, the containers are inter-

changed and the deflection read, from which the absorption is calculated. A similar single cell colorimeter with a turning device for interchanging the containers was described by Th. W. Schmidt and H. Hirschmüller.[45] Whereas the Hellige colorimeter operates with an ordinary incandescent lamp, the instrument of Schmidt and Hirschmüller is usable only with luminous tubes. The use of sodium lamps was

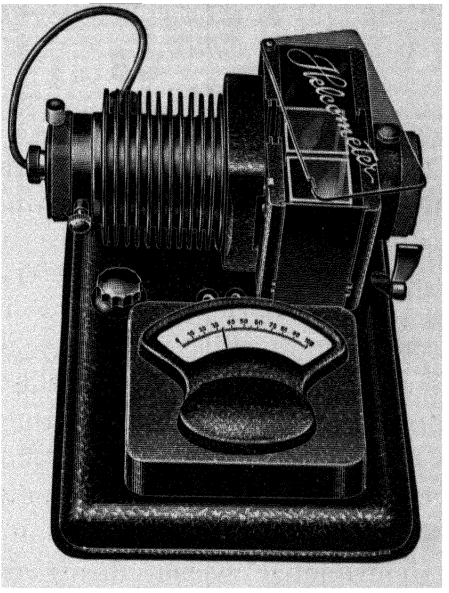


FIGURE 37.—Single Cell Colorimeter. According to F. Hellige.

shown some time ago by Hellige to be expedient in the Duboscq colorimeter, as definite absolute values are measurable with them. On account of the large aperture of illumination and the close position of the lamp in front of the container there is in the Schmidt and Hirschmüller colorimeter, however, a considerable difference between thickness of the container and the light path, which depends upon the index of refraction of the solvent, the wave-length of the light and the effective luminous surface of the sodium lamp, so that the measured values display deviations up to 80% of the absolute value of the absorption.

The single cell colorimeter exhibits two other drawbacks, namely, the dependence of the zero point adjustment on the variations of brightness of the light source, and the slight sensitivity for small absorption. If, for instance, the needle deflection is adjusted to 100 scale divisions for the pure solvent, then it changes only 5 divisions for an absorption of 5%. If the accuracy of adjustment of the measuring instrument is ½ scale division, and if the brightness of the lamp is entirely constant, then a precision of only 10% results. For smaller absorptions, those most interesting in colorimetric measurements, the error becomes so great that on the whole no usable measurements can be secured. These two weighty defects of insensitiveness and inconstancy of the zero point were avoided in the universal colorimeter with two cells connected differentially according to B. Lange,[46] which is now to be described. This connection, in which the dissimilar poles of the cells are connected, is characterized, as L. A. Wood[47] has proved, by a linear dependence of the photocurrent on the light absorption. Besides the effect of temperature and the fatigue of the cells is much less than in the connection of similar poles, as is customary with alkali cells and compensation circuits.

The colorimeter is arranged for ordinary incandescent lamps as well as for monochromatic measurements with luminous tubes. The external form of the colorimeter is shown in Figure 38, while the connections and the schematic structure are evident from Figure 39. Here 1 is the incandescent lamp, 2 and 3 are containers, 4 and 5 the two photocells, 6 and 7 are color filters which are placed in guide rails between the lamp and the containers. The right-hand cell can be completely darkened by the shutter flap 8 and the knob 9, while a partial screening of the light is possible with the iris diaphragm 13. The lamp 1 is placed at the focus of the two lenses 14 and 15 so that the containers are irradiated approximately parallel. By turning the lamp the intensity of illumination of the two cells can be so equalized that the needle of the measuring instrument stands at zero and indeed



FIGURE 38.—Photoelectric Universal Colorimeter. According to B. Lange.

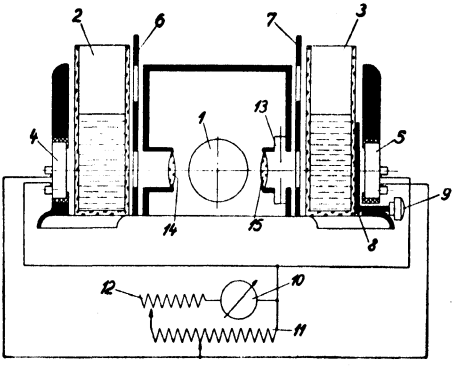


FIGURE 39.—Schematic Structure of the Two-Cell Universal Colorimeter. According to B. Lange.

is independent of the brightness of the lamp. For getting a definite sensitivity one of the cells can be completely darkened by the shutter 8. If the needle is set at a deflection of 100 for this, by adjustment of the control resistance, then this deflection corresponds to 100% absorption and 1 scale division to 1% absorption, a value which can always be adjusted exactly, independently of the sensitivity of the cell and the brightness of the lamp. Preceding from this adjustment the radiation incident upon the cell can furthermore be reduced to a pre-determined amount by closing of the iris diaphragm, 13. For example, if the incident radiation is reduced by the iris diaphragm to 10% and the needle deflection is set at 100 for this, then 1 scale division corresponds to an absorption of 0.1%, so that even very slight colorations or turbidities that are scarcely visible with the eye, become measurable. The lamp housing and the containers can be protected against stray light by light-tight covers, so that the measurements can be carried on in a brightly lighted room. A 15-watt lamp serves as light source. With a reducing socket low voltage lamps for 4-6 volts can be used, so that measurements can be made in the open without connection to a line. For many measurements a small 4-volt/4-watt lamp suffices. If the lamp is unscrewed from the colorimeter then the colorimeter can be operated with a sodium lamp or other luminous tube, by means of an auxiliary device. Also, in place of the large containers micro-containers in special holders can be used for liquid specimens of from 0.2 to 30 cubic centimeters, and by means of a special insert test tubes can be introduced, which is very convenient for investigations of purity.

For the measurement of solid bodies the reflector insert illustrated in section in Figure 40 is used, with a container for powdered bodies and with a glass plate for solid bodies, paper or cloth. In Figure 40, 1 is the lamp whose filament is at the focus of the lens 2. The parallel rays are reflected by the mirror 3 to the bottom 4 of the container and, according to the color and whiteness of the powder in the

container, are reflected by the mirror 5 into the cell 6. To distinguish fine differences of color it is expedient to work with a comparison method, so that a similar insert with a standard specimen is placed in front of the second cell. If the color of the two specimens is the same, then the photocurrent from the two cells is the same and the needle of the measuring instrument stands at zero. For the measurement of solid bodies a glass plate is introduced in the reflector, on which the material to be measured is laid.

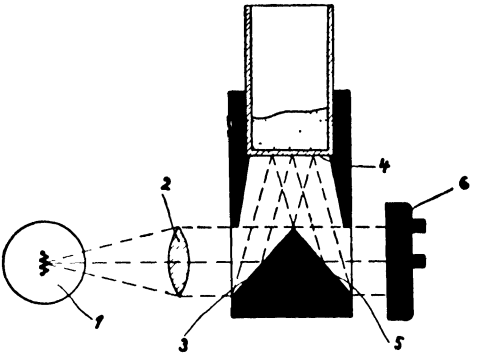


FIGURE 40.—Reflector Insert for Measuring Solid and Powdered Bodies.
According to B. Lange.

Although absorptions of 1% can be measured exactly with the colorimeter just described, in special cases a still higher sensitivity is desired, for instance in the investigation of water for the quantitative determination of scarcely noticeable turbidity or of slight quantities of iron. For such measurements a colorimeter operating on the same principle was developed with a container-tube 30 cm long and a sensitivity ten times greater. The schematic structure of this apparatus is shown in Figure 41. To reduce the dimensions the two cells are placed at right angles. Between lamp and cell are placed the tubular container 4 on its support and the shutter 5 with the knob 6. The illumination of the compensation cell 3 takes place by way of a silvered tube 7 and can be regulated by the shutter 8 which is adjusted by the knob 10 through the gearing 9. The built-in microammeter

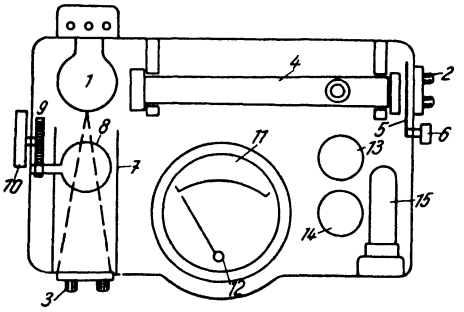


FIGURE 41.—Schematic Structure of the Large Colorimeter for Tubular Containers. According to B. Lange.

11 with the zero point corrector 12 serves for measuring the photocell current, and the two resistances 13 and 14 regulate it. A built-in iron resistance 15 holds the lamp voltage constant. The adjustment and mode of operation are similar to the small colorimeter so that the absorption can be read directly from the needle deflection. For continuous control measurements a needle instrument with movable signal contacts and a continuous flow container instead of the tubular container are provided. In case a pre-determined absorption or turbidity is exceeded signalling apparatus is set in action. A complete equipment with continuous flow container, sounder and signal lamp is illustrated in Figure 42. For many purposes, for instance, continuous filter control in waterworks, a graphic recording instrument can be connected in parallel.

Hitherto only the directly indicating deflection method has been described. But with the two cell colorimeter it is possible to work with a null-method such that the intensity of illumination of the comparison cell is so far weakened that both cells give the same photocurrent and the pointer of the measuring instrument remains at zero. The weakening of the light can result, for instance, from the addition of a comparison solution of known content to the second container or through reduction of the light flux by a measuring diaphragm

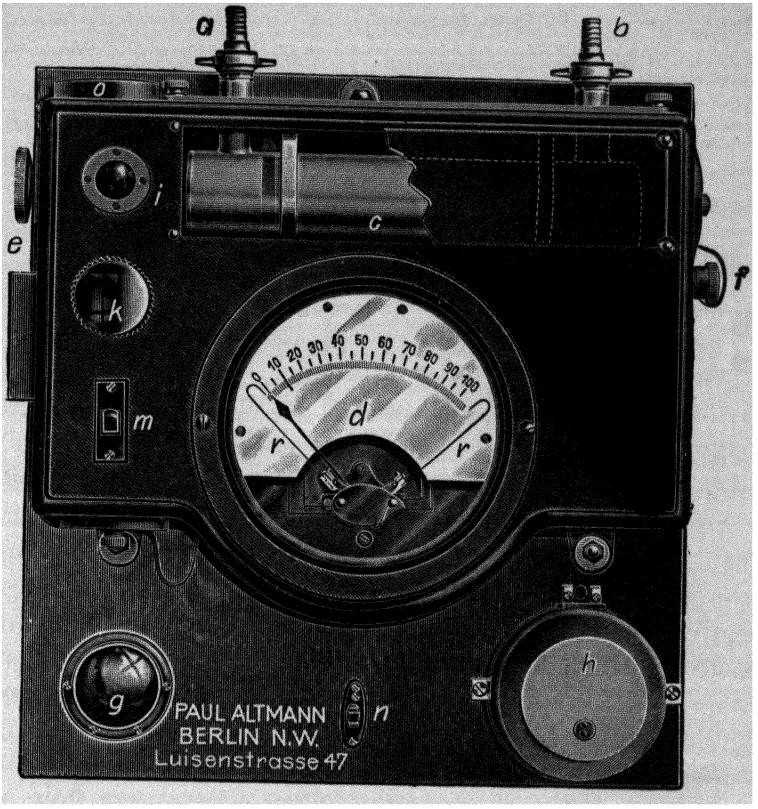


FIGURE 42.—Continuous Flow Colorimeter with Signal Equipment. According to B. Lange.

or by a measurable displacement of the lamp. Measurements by the last method with the same cell connections were carried out by G. A. Shook and B. J. Scrivener.[48] But in this there was the defect that the cell compensation depended upon the color of the solutions, so that a shift of the zero point occured, which introduced great inaccuracy. Besides, the sensitivity attainable is slight, since small absorptions require very small displacements of the lamp, which are hard to measure. The direct deflection method is simpler and has a far higher sensitivity, so that it proves to be the most practical and has found the greatest application.

The colorimeters described in the foregoing are also suitable for turbidity measurements of the kind where the turbidity is measured through its absorption. The high sensitivity of the two-cell colorimeter makes it possible to measure extremely slight turbidities, so that it saves the use of special turbidity meters.

Geffken and Richter [49] have described an assembly similar to a Strauss "Mekapion," using an alkali cell with a tube voltmeter, which is suitable for distinguishing absorption and scattering. The solution to be measured is traversed by a parallel beam and the filament of the lamp is focused on a small screening disc behind which the cell is placed, so that only the scattered light is photoelectrically active.

The turbidity meter developed by Tungsram depends upon a measurement of the Tyndall rays. In this apparatus the tube irradiated with parallel light is surrounded by a cylinder, on the inner side of which are arranged several photocells, whose currents correspond to the intensity of the scattered light. The slight intensity of the scattered radiation is, however, a disadvantage, so that very sensitive instruments are needed.

Although the zero point is independent of the brightness of the lamp in the differential connection of two cells, the deflection depends upon the intensity of the radiation. This influence can indeed be eliminated by regulating the deflection with iris diaphragms or shutters in the light path. If

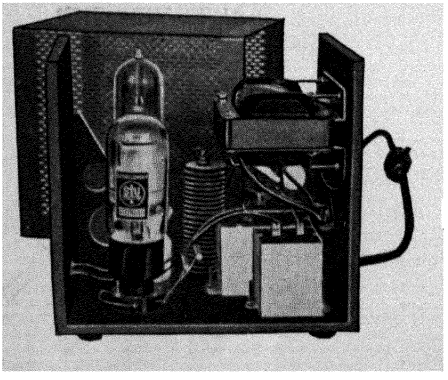


FIGURE 43.—Power-pack with Stabilizer.
According to B. Lange.

the line is very unsteady this frequently disturbs the regulation and demands the use of a uniformly burning low voltage lamp with storage battery or an iron resistance in series. The greatest exactness, however, can be attained, according to L. Körös,[50] by the use of a stabilizer with glow discharge tube. Such a complete powerpack with built-in transformer for 110-220 volt and rectifier including smoothing condensers is illustrated in Figure 43. Even with line variations of 10% the stabilizer holds the voltage constant to 0.1%.

Reflection and Gloss Meters

We have already seen that reflection measurements can also be made with the universal colorimeter using a special insert, as in Figure 40, and likewise with the slit ocular and illuminated objective. In this section we will now become acquainted with simple devices which were specially developed for reflection measurements.

Figure 44 shows the cell mounting of such a reflection meter, while Figure 45 shows the section of the cell mounting in a pedestal base. As is evident from these the device has a

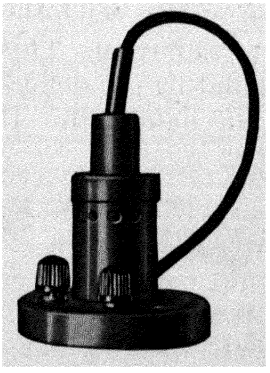


Figure 44. — Cell Mounting of the Photoelectric Reflection Meter. According to B. Lange.

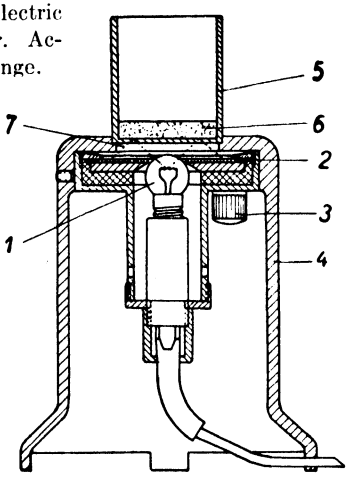


Figure 45.—Section. Cell Mounting in Pedestal Base for Powder Measurements.

According to B. Lange.

cell with a central hole through which the radiation from a built-in lamp falls upon the surface to be tested. According to the reflecting power and whiteness of the specimen the radiation is reflected back onto the cell and produces a photocurrent which is measured with a needle microammeter. The deflection of the needle for a standard white body or any other comparison substance can be adjusted to 100 by two control resistances incorporated in the measuring instrument, so that percent values can then be read off directly.

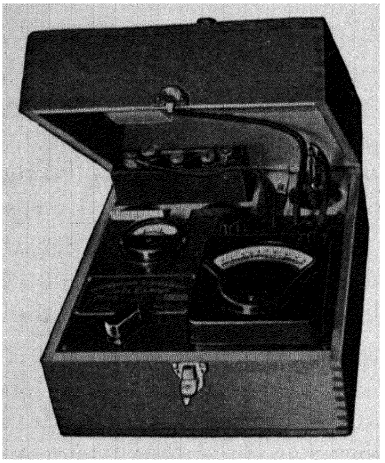


FIGURE 46.—Photoelectric Reflection Meter. Complete Apparatus. According to B. Lange.

In Figure 46 a complete equipment with cell body, microammeter, built-in source of current, voltmeter and control resistance for adjusting the lamp voltage is depicted. For powder measurements the cell mounting can be fastened in a pedestal base, as shown in Figure 45. Here 1 is the incandescent lamp, 2 the photoelectrically active layer of the cell, 3 one of the two binding posts, 4 the pedestal base, 5 the glass container, 6 the powder under investigation and 7 the path of the rays. The rays from the lamp fall on the powder through the glass bottom of the container and are reflected by this to the cell. By depositing the powder in a suitable liquid the effect of different sized grains on the reflection can be eliminated. According to measurements of H.

Harkort [51] a precipitate of barium sulfate in the container makes an appropriate reference body.

The devices just described are chiefly suitable for the measurement of powders, flours, starches and for the determination of the whiteness of paper, celluloid and textiles. According to the work of M. Mengeringhausen [52] washing processes and the efficiency of various detergents can be exactly ascertained through the measurement of the whiteness of soiled samples.

In other cases the interest lies not in the diffusely reflected radiation and the whiteness but exclusively in the gloss, that is, the radiation reflected regularly, as for instance, in the polishing of glass and marble. L. Bloch [26] and L. Bergmann [53] have described simple devices which consist of a cell and a lamp arranged in such a way that the regularly reflected light falls on a selenium photoelement. In addition to the regularly reflected rays, however, diffusely reflected rays which depend upon the color of the specimen, also reach the cell. To avoid this defect B. Lange has developed the gloss meter illustrated in Figure 47, which can be used besides for determining diffuse reflection or light transmission. The schematic structure and the path of the rays of this device are to be seen in Figure 48. Here 1 is the low voltage lamp

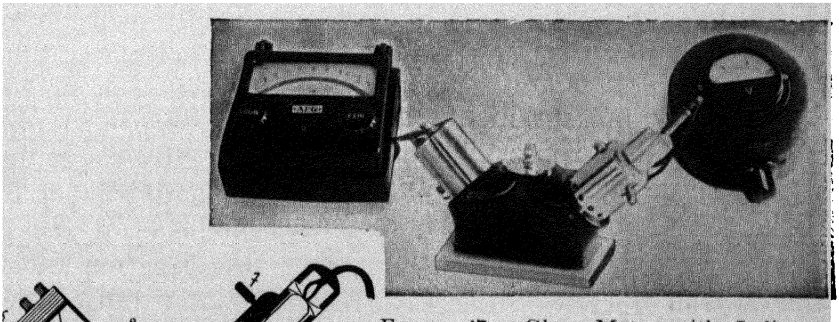


FIGURE 47.—Gloss Meter with Indicator Instrument and Potential Regulator. According to B. Lange.

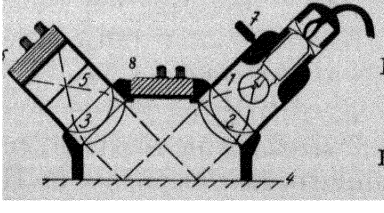


FIGURE 48.—Schematic Section of the Gloss Meter.

with pointed filament, 2 and 3 are two objectives through which the rays reflected from the specimen 4 are focused upon the pinhole diaphragm 5, 6 is the cell and 7 centering screws for the incandescent bulb. In the foregoing arrangement only a vanishingly small percentage of the diffusely reflected radiation enters the pinhole, whereas the entire regularly reflected radiation passes through and falls on the cell. If the deflection of the needle of the instrument for measuring the photocurrent is adjusted to the value corresponding to a body of definite gloss, then absolute values can be read off. But the cell 6 can also be placed in position 8, where the diffuse reflection will be determined. In the measurement of paper, two further data are also of interest; the contrast and the optical transmission. Both these values can likewise be determined with the gloss meter. For this the diffuse reflection of the paper is measured on white and black backgrounds. If w and b are the corresponding needle readings, then $w - b$ is the contrast. From this the percent transmission T is given as: $T = 10\sqrt{(w - b)}$.

In addition to the data important in paper technology, gloss, contrast and optical transmission, the whiteness of a paper sample can also be determined. Hence the density and gradation of a photopaper can be ascertained by this means.

Visibility Meters

Visibility measurements are not only important for meteorological purposes, but during recent years they have attained a particular significance for air and marine traffic. Hitherto the optical visibility meter according to Wiegand or the new visibility photometer according to F. Löhle [54] have been used. Such instruments, however, are usable only in daylight and require observers with strong vision. An objective instrument that is equipped with its own source of light and hence is usable at night was described by L. Bergmann and L. Krügel.[55] The principle of this visibility meter

is represented in Figure 49. The incandescent filament of a moving picture projector Q, of 100 watts, is focused by the condenser K_1 on the rotating perforated screen U. The pulsating light ray passes through a filter F for equalizing the cell to the sensitivity of the eye and is made parallel through two other lenses K_2 and L_1. A mirror at 20-50 meters distance reflects the light which is concentrated by the lens L_2 onto the selenium photoelement Z_2. This cell delivers a

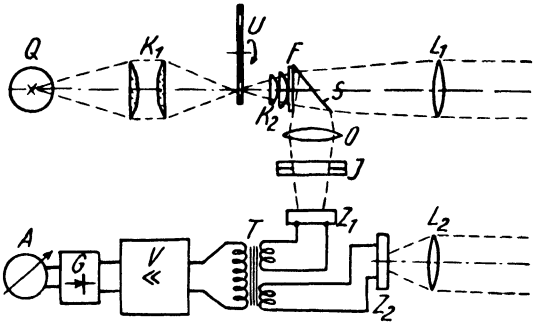


FIGURE 49.—Photoelectric Visibility Meter.
According to B. Lange.

pulsating direct current, which, however, depends upon the radiation of the lamp as well as upon the absorption of the air. To secure independent values Bergmann uses a second cell Z_1 which is illuminated from the same light source by a half-silvered mirror. Both cells are connected to the opposed primary windings of a transformer T which is connected to an amplifier V, in whose output circuit are placed a dry rectifier G and a direct current instrument A. The illumination of cell Z_1 can be weakened so much by an iris diaphragm that the pulsating photocurrents are equal and nullify each other so that the measuring instrument A stands at zero. The absorption of the air is obtained from the setting of the iris diaphragm and the light path. Since only the photocurrents made intermittent by the perforated disc are

transmitted by the transformer daylight does not influence the measurements. We here become acquainted with a technical "trick" for eliminating a continuous supplementary illumination, that was used for the first time in optical railway signalling, as we will describe in detail in Chapter 8. To be sure, F. Löhle expresses hesitation as to the validity of extrapolating to great distances the visibilities measured over a short stretch. For determining the ground visibility at airports and for measurements on shipboard, for which no large spaces for measurement are available, the apparatus is likely, however, to give valuable service.

Current Meters and Pyrometers

At high frequencies current measurements are performed with difficulty, since the frequency limit for hot-wire and thermoinstruments lies at a wave-length of 30-300 meters. For this region and for still shorter wave-lengths optical current meters have been approved. In these instruments a glower is heated by the current to be measured and its radiation is measured by an optical photometer or an incandescent filament pyrometer. The measurements are made much more simply by using a photoelement in such a way that the high frequency current is measured through the intensity of illumination at a definite distance from the radiator. A simple device according to J. Stanek [56] is illustrated in Figure 50. The glower *a* consists of a thin platinum tubelet, whose

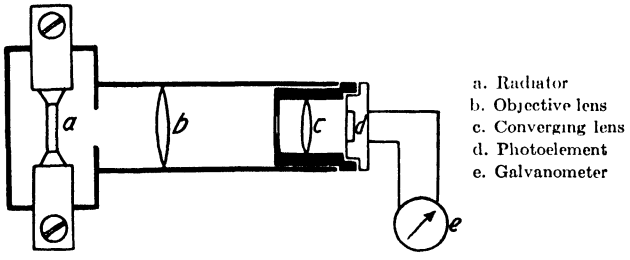


Figure 50.—Optical Current Meter. According to J. Stanek.

frequency error even to 5×10^7 hertz is smaller than 1%. For small current strengths a tungsten or carbon filament lamp suffices as glower. The calibration of the instrument is made with direct current, in such a way that for every current strength of the glower the corresponding intensity of illumination is measured.

In the apparatus just described merely the current strength is of interest, which is given by the brightness of the radiator. With this arrangement the temperature of radiators can also be measured. For this another calibration is all that is needed. However, it is to be noted that the radiator is focused upon the cell under exactly defined conditions and that the calibration is referred to the color temperature of the specimen.

Chapter 5

Long Distance Transmission of Measured Quantities

Transmission of a Circular Scale. Remote Compass and Wind Direction Indicator

In various measuring devices a mechanical transmission of the indications to a distance is not possible since the directive force of the measuring mechanism is too weak to steer mechanical feelers. These difficulties are avoidable by using light rays and photocells. As an example of the transmission of a circular scale we will describe a remote compass. In aircraft the compass cannot generally be installed in the control station since the iron parts of other instruments and machines influence the magnetic needle. Hence the compass must be mounted in a remote place and the measured value must be transmitted to a remote indicator on the control board, for instance, with the pneumatic direction indicator of the Askania Works. Such transmission to a distance is accomplished also by two photoelements in a differential connection. The "scanning" of the compass-card, as can be seen in Figure 51, is done by two light rays. Here 1 is a screening

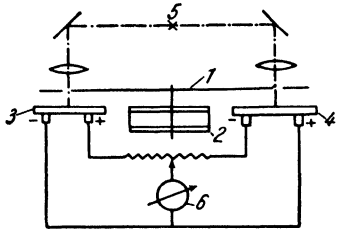


Figure 51.—Photoelectric Remote Compass.
According to B. Lange.

disc attached to the magnetic needle 2, which moves above the two photoelements 3 and 4. The radiation from lamp 5 falls on the two cells by way of the mirrors and lenses and is more or less screened off according to the position of the slotted disc. If the two cells are illuminated equally then the current difference is zero and the indication of the measuring instrument 6, incorporated as a direction indicator, corresponds. If the aircraft deviates from the direction as adjusted, the screen above the cells rotates. The intensity of illumination of the cells is altered and the differential current causes a deflection of the direction indicator. If the radiation of the lamp is constant then the photocurrent corresponds to the deviation from the course, so that the indicating instrument can be marked off in angular degrees, for which, however, the range of measurement is limited to 90° right and left from the zero point. The full scale can be transmitted by means of a circular slotted screen, for which the second cell is illuminated directly from the lamp.

Similar systems can be used for the transmission of any turning movement, thus, for instance, also for wind direction indicators.

Transmission of a Straight Scale. Water Level and Manometer Indicator

Photoelectric systems are also suitable for the transmission of straight scales, for instance, in water-level tubes and mercury manometers. In the latter case the transmission of the measured value is particularly simple, since the mercury acts as screen for a cell placed behind it and the photocurrent corresponds to the height of the mercury. According to L. Bergmann [57] for such measurements a U-tube can be used with a differential cell arranged behind the two arms.

The principle illustrated in Figure 52 is also suitable for use with colorless liquids. This method depends upon the fact that a filled glass tube acts as a cylindrical lens and

forms a brilliant image of the incandescent filament. In Figure 52, 1 is the cross-section of the elongated filament, 2 is the filled glass tube, 3 a slotted screen and 4 the cell situated behind it. The filled glass tube focuses the filament on the slotted screen, so that the radiation falls on the cell lying behind it. If the surface of the liquid goes down, the liquid lens is removed, no focusing occurs, and only a small part of the scattered light gets through the narrow slit in the screen to the cell. Hence the photocurrent corresponds to the height to which the glass tube is filled.

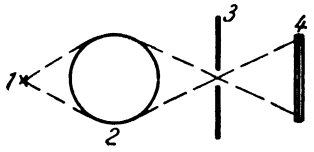


FIGURE 52.—Path of Rays in Water-level Indicator.
According to B. Lange.

Since the height of the water-gauge in technical plants can frequently vary through several inches and continuous oscillations of the control should be reduced, the use of two cells is recommended by F. Tuczek,[58] so that alternately the upper or the lower is energized. Tuczek describes a similar layout with float and screen for controlling the stop setting of the trough mechanism at the Niederfinow Dry Dock.

AUXILIARY CONTROL. PHOTOELECTRIC BALANCES

If special requirements for accuracy are set up for the transmission of measured values to a distance then the methods described in the foregoing no longer suffice, since the measured values depend upon the brightness and the constancy of the cell. But exact values can be secured with auxiliary control, the principle of which we will describe for a photoelectric balance. Photoelectric balances are known in which the indicator shaft of the measuring mechanism carries a disc with a perforated screen. An auxiliary mechanism

is operated by a motor, that turns a light source with the cell so far that the light ray falls on the cell through the hole in the screen and a relay arrangement stops the auxiliary motor. The movement of the cell and light source, however, require a complicated mechanism and a powerful driving motor. E. Busse and P. Görlich [59] were able to secure a considerable simplification, with simultaneous increase of the accuracy, by the use of a mirror system. The schematic structure of

a. Balance pointer
b_1, b_2. Mirrors
c. Illuminating equipment
d. Motor
e. Counter
f. Photocell
g. Relay
h. Contactor of relay g.

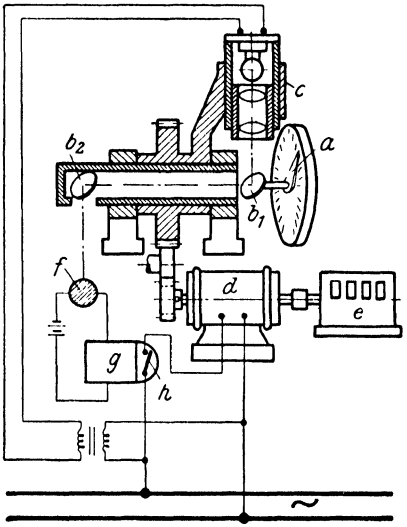


FIGURE 53.—Tilting Scale with Photoelectric Indicating Device. According to E. Busse and P. Görlich.

such a balance is illustrated in Figure 53. The mirror b_1 is attached securely to the shaft of the pointer a. The light source c is turned about the mirror b_1 perpendicularly to the pointer shaft by the motor d. If the auxiliary mechanism has reached a definite position, then the mirror b_1 reflects the light beam by way of mirror b_2 onto the photocell f. The cell operates the relay g, which stops the motor d by opening the contact h. The counter e is directly connected to the motor d. The measured value can be read off or

printed according to the stopping position of the auxiliary mechanism. The counting mechanism can also be connected electrically with the auxiliary mechanism and thus the readings can be transmitted to various places. By attaching the counter mechanism to a calculating machine freight and customs costs can be printed automatically alongside of the weight on the freight bill and the daily total of all weighings can be added.

Similarly the indications of other measuring equipment can be transmitted with an auxiliary control, not only for circular scales but also for arrangements with straight scales.

Chapter 6

Amplifying Equipment

After having occupied ourselves in the preceding chapters with the use of the photoelements for purposes of measurement, we will now become acquainted with their usefulness as technical control devices. For this, however, the photocurrent must be amplified. We begin therefore with the different possibilities for amplifying.

Auxiliary Cell Voltages

We have already seen in Part I, page 156, that just as for alkali cells so also for photoelements the photocurrent can be increased by the use of an auxiliary voltage. But we have also mentioned that constancy and stability are reduced by this. On these grounds we must be contented with small auxiliary potentials of a few volts. The simplest connection consists of a battery, a cell and a meter in series, as illustrated in Figure 54a. To get the most favorable auxiliary

A. Meter
B. Battery
P. Photoelement
R. Resistance
S. Switch

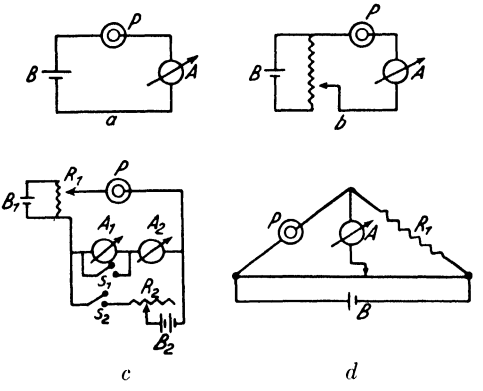


Figure 54.—Connections of Photoelements with Auxiliary Potentials.

potential it is expedient, as in Figure 54b, to regulate this by a potentiometer, since in many cases 0.5-1 volt is sufficient. For increasing the precision the compensation circuit of A. Dresler,[60] illustrated in Figure 54c has been used. The battery B_1 supplies, through a potential divider R_1, a steady current which is measured by the ammeter A_2 while the ammeter A_1 is short-circuited by the switch S_1. By means of the control resistance R_2 the deflection of the ammeter is brought to zero and the switch S_1 is opened. If the cell is now illuminated a strengthened photocurrent flows which is determined by the sensitive ammeter A_1. Using cuprous oxide frontwall cells with a dark current of 1 milliampere Dresler secured readable deflections at an intensity of illumination of 0.1 lux. To be sure it was necessary to wait about a quarter hour for a steady adjustment; besides a large temperature effect of about 1% per degree was present. With selenium photoelements the adjustment lag is still greater so that for these cells such enhancing circuits are not generally used. On this account there is also no hope that we will be able to measure intensities of illumination below 0.1 lux directly without an amplifying circuit. But if it is a question of increasing the photocurrent for the operation of relays then the use of an auxiliary potential can sometimes offer advantages. Since here in reality only the change of resistance of the cell upon illumination is utilized, the circuits known for photoresistances can be used. The author secured good results with the Wheatstone bridge circuit illustrated in Figure 54d. In place of the bridge resistance R_1 a second cell can also be used, by which a better temperature compensation and also independence of the zero point from potential fluctuations are secured.

Tube Amplifiers

We have already mentioned on page 183, that in grid control of electron tubes the potential sensitivity of the cell

is decisive, and that this is the greatest for photoresistances and alkali cells. In certain cases, where no high potential is available or where it is a question of particular sturdiness or of the spectral sensitivity of the eye photoelements still offer advantages.

A single stage tube circuit with compensated meter is illustrated in Figure 55.

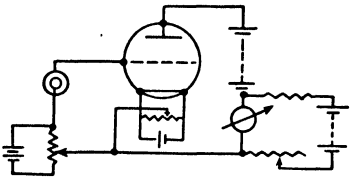


FIGURE 55.—Direct Current Amplifier for Photoelement with Compensated Meter.

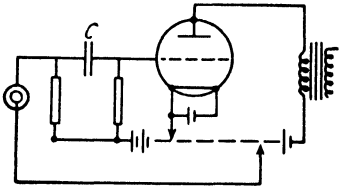


FIGURE 56.—Amplifier for Fluctuating Light.
According to H. Thirring.

A considerably higher amplification is secured, however, by the use of pulsating photocurrents. A circuit particularly suitable for this, Figure 56, was devised by H. Thirring.[61] The dark current of the cell and the sluggish changes of resistance were cut out by the condenser C, so that a continuously constant adjustment was secured. In place of the condenser C a transformer can also be used, which at the same time permits an increase of the control potential.

A measurement amplifier for pulsating light constructed with particular care, Figure 57, was described by Fr. Müller

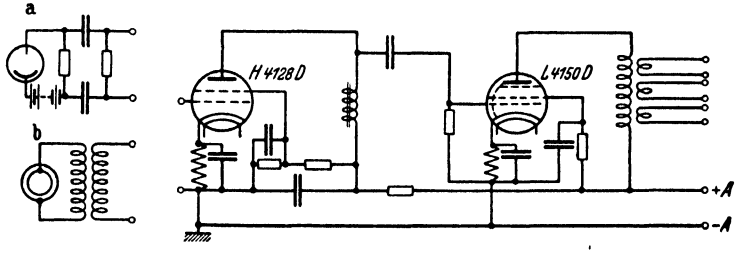


FIGURE 57.—Two-stage Amplifier with Diode Rectification. According to Fr. Müller and W. Dürichen.

and W. Dürichen.[62] In place of simple electron tubes, pentodes and hexodes are used in this, while the rectification takes place in the tube output through a duodiode with a slope of 0.1 milliampere per volt. The disturbance level of this amplifier lies at about 10^{-7} ampere.

By the use of grid controlled thermionic tubes, "Thyratrons," [63] energies of 100 amperes or more can be controlled The use of these relay tubes, which are always gaining more importance in electrical engineering as a whole, is limited to switching purposes since the full anode current sets in if the breakdown potential is exceeded regardless of the grid potential, so that periodic switching can only be carried out with alternating current. But with direct current, on this account, the possibility is presented of using very short current impulses for releasing switching operations. Thus K. Johannsen [64] describes a rolled sheet testing equipment in which extremely small holes in a rapidly moving sheet are detected by a photocell with a "Thyratron."

Relays

With electron tubes the photocurrents can, indeed, be amplified almost at will, yet for technical measurements no benefit is gained by this, since the disturbance level increases simultaneously. Hence the efforts to secure a higher amplification run parallel with the development of measuring instruments and mechanical relays of higher sensitivity, which can be operated directly by the photoelements. In the realm of measuring instruments we have already become acquainted with the "Multiflex" galvanometer specially developed for this. In this section we will now consider mechanical relays of the highest sensitivity.

The ordinary electromagnetic relays are little suited for photoelements, as even the most sensitive types require a current of 0.1-1 milliampere. Substantially greater sensitivities are secured by the use of moving coil instruments

with contact devices. Such contact galvanometers operate with a few microamperes at an input of about 10^{-7} watt. A very stable model of contact galvanometer with a load capacity of about 1 watt is shown in the continuous flow colorimeter in Figure 42. A drawback of this instrument, however, is its slight load capacity. Hence experiments have not been lacking to increase the load capacity by auxiliary devices. Thus L. Bergmann and H. Fricke [65] describe a galvanometer relay in which the needle of a moving coil galvanometer carries a small sphere on its tip, which is pressed by a spring on contacts placed beneath it. Above the spring is an electromagnet, which is rythmically excited through a clockwork and releases the needle of the measuring mechanism for the adjustment, the same as in the depressor bar recorders. But the complicated construction is disadvantageous, and also the switching which takes place only every 15 seconds, so that processes which go on rapidly are for the most part not caught. A simpler way of raising the contact pressure consists in the use of a pointer with an iron core and a magnetic contact. The "Sensitrol" relay of Weston works on this principle, where the pointer after contacting, clings to the magnet until released by hand. A promising novel relay construction was devised by O. Lühn, which causes an almost complete release of the contact in rapid procedures. The essential advances were secured through the use of a moving coherer, which lies parallel to the contacts of the moving coil instrument. During the trivial electrical oscillations set up on making the contact the coherer is so low resistance that an auxiliary relay is operated through it, which fully discharges the instrument contact and closes a powerful master relay. The coherer is placed on the relay armature, so that a decohering results through the motion of the latter. The connections of such a relay can be seen in Figure 58. The weak impulse of the contact instrument K is strengthened by the coherer, F, through this the auxiliary armature A_1 is attracted, the instrument contact, including the coherer, is short-circuited and the master armature A_2

attracted. This actuates the master contact K_1 through the escapement wheel R and at the same time interrupts the current of the relay coil through K_2 so that the non-operated position is restored. In this four-stage switching process a millionfold amplification of the photocurrent is

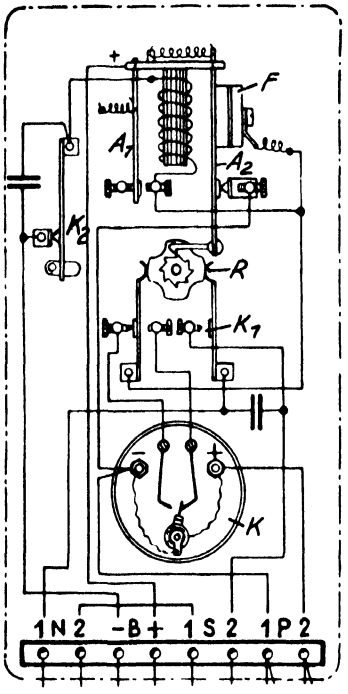


FIGURE 58.—Diagram of Connections of the Coherer Relay.

reached, with a load amplification factor of almost 10^{10}. A particular advantage of this contact release by means of the coherer is freedom from lag, so that light flashes of only 1/200 second cause a release of the relay. The rapidity of the switching is limited solely by the mobility of the contacts. The mechanical structure of the relay with built-in rectifier for alternating current connection is visible in Figure 59. We will become acquainted with the versatile application of this coherer relay in the next chapter.

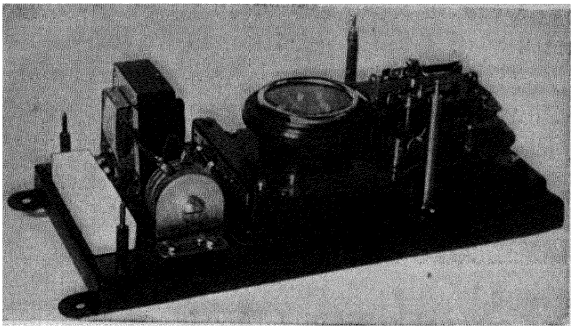


FIGURE 59.—Coherer Relay, uncovered.

GALVANOMETER AMPLIFIER

In the relay just described the switching operation is set going by the motion of a needle. A substantial increase in the sensitivity is made possible by using a light ray as switching means, the same as in the transfer from needle to mirror galvanometers, so that with this the ultimate limits of sensitivity are reached.

Among the utilizations of the heat rays of light, a thermorelay was described by W. Moll and H. Burger.[66] In this instrument the measured current actuates a primary galvanometer with a light-pointer that falls on a differential thermoelement. According to the position of the light-pointer a thermocurrent arises, which is measured by a second galvanometer.

Substantially stronger currents and an amplification factor of 10^3 were secured with the bolometer amplifier according to H. Sell.[67] This amplifier includes a small membrane bellows which blows onto two heated nickel spirals in a bolometer bridge arrangement. The needle of the controlling measuring instrument has a flag, which covers the air stream more or less. The controlled current of about 20 milliamperes suffices for operating relays or continuously writing recorders. A pneumatic amplifier operating with air

pressure and current balance was developed by Askania. The sensitivity of this apparatus, however, is not so high.

As A. V. Hill[4] showed, in the thermorelay according to Moll the thermoelement can be replaced by a differential photocell, Figure 5. Hill has measured a current of 6×10^{-12} amperes with such an arrangement, while the deflections at currents of 1×10^{-12} ampere showed fluctuations of 5 mm which were caused by the Brownian molecular movements.

L. Bergmann [68] also has used the differential cell for the measurement of small torsional movements, and has arranged a line grating in front of the cell for increasing the sensitivity, in such a way that with a slight displacement of the modified light ray a greater change of brightness is secured. Bergmann [57] furthermore describes a direct current amplifier with a moving coil galvanometer whose needle covers an illuminated slit more or less, so that the cell placed behind it is exposed accordingly. For securing a good adjustment, however, the galvanometer must be shaken constantly by a buzzer. The range of measurement of the apparatus lies between $3\text{-}30 \times 10^{-7}$ ampere and the photocurrent secured between 0.3-3 milliampere. To increase the sensitivity a sort of feedback was used such that a part of the photocurrent reacted on the moving coil system. In this range of measurement, however, needle instruments or coherer relays are usable. Amplifiers are important only for substantially smaller photocurrents. For this B. Lange has developed a photoelectric galvanometer amplifier. To secure a handy structure the principle already tried in the "Multiflex" galvanometer, the multiple reflection of the light ray, was used. Differing from the arrangement provided by Hill, two separate cells are used in the differential circuit already described, page 238. The schematic structure of this amplifier can be seen in the simplified sectional sketch, Figure 60. The point filament of a 4-volt lamp is focused, enlarged, on the mirror of a torsional ribbon galvanometer, and the rectangular aperture of the projector is focused on the two cells and a small orientation scale for adjusting the zero point,

by means of the lens placed in front of the mirror galvanometer and two mirrors. The torsional ribbon system is twisted by means of a long lever arm and a spindle drive through a knob at one side. The amplification factor can be regulated

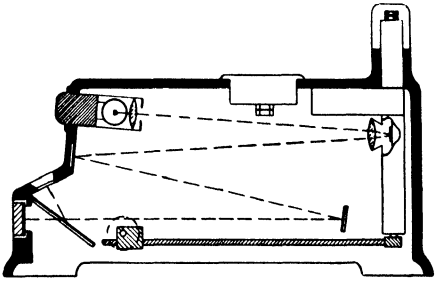


FIGURE 60.—Photoelectric Galvanometer-amplifier. According to B. Lange.

up to about 10^3 by controlling the lamp voltage with a built-in heater resistance and voltmeter, so that the theoretical limit of sensitivity can be reached by using a simple mirror galvanometer, "Multiflex" galvanometer.

Chapter 7

Photoelectric Switching and Signal Devices

As mentioned already at the beginning of the preceding chapter, the basis for the technical application of photoelements is a suitable amplification. Of the many amplifiers, however, only two have proved to be sufficiently reliable, galvanometer relays and tube amplifiers, and the latter only with the use of pulsating light. We have already become acquainted with a measuring contrivance with pulsating light radiation, the visibility meter of Bergmann and Krügel.[55] In this chapter we will describe the optical train-control likewise operating with tube amplifiers. For all other applications galvanometer relays are used exclusively, particularly the coherer relay described on page 261.

Twilight Switch

The automatic switching of illuminating equipment when the brightness falls below or rises above pre-determined values is an old problem, for the solving of which photocathodes or photoresistances have frequently been used. Nevertheless a wholly satisfactory solution of this problem has not yet been secured. That is, a high sensitivity for intensities of illumination of 1-2 lux, operating reliability and continuous constancy. Besides a greater use presupposes cheaper apparatus. In the latter respect, particularly, the twilight switches developed with alkali cells are not satisfactory. The twilight switch illustrated in Figure 61 operates with a large photoelement in a waterproof case and a coherer relay with built-in potentiometer for

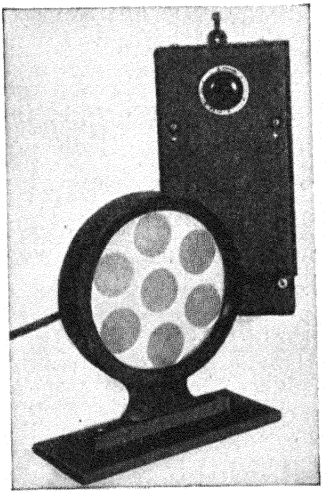


FIGURE 61.—Twilight Switch with Giant Cell and Waterproof Housing.
According to B. Lange.

adjusting the switch sensitivity. Whereas alkali cells must be in the immediate neighborhood of the switching equipment, in the foregoing apparatus the wiring between cell and relay can be almost as long as desired, so that the cell can be placed on the roof or in the street. Twilight switches have not only acquired significance for street, show-window and train lighting, but are also of particular importance for remote and inaccessible switching equipment in airport illumination, airway lighting and other light beacons.

LIGHT BARRIERS AND LIGHT RELAYS

A very great field of application of the photocells is opened by light barrier devices. They count articles of all sorts, control signal equipment, guard rooms and buildings against intruders. They are universally called on for assistance where mechanical equipment is prohibited. Such light barriers are very simple in principle. They consist merely of a projector, a cell in a lens tube, as detector, and a suitable relay. A complete switch assembly with projector, pho-

toelement and coherer relay is illustrated in Figure 62. The projector with focusing parabolic mirror is sufficient for distances of from 10 to 20 meters. For greater distances projectors with lens systems are used, and for very great distances modulated light and tube amplifiers. H. Thirring,[61] with the connections already given in Figure 56, was able to raise the range of light barriers to more than 10 miles. The light ray can be directed at will by using mirrors, so that for burglary protection, for instance, all the doors of a room can be guarded by light barriers.

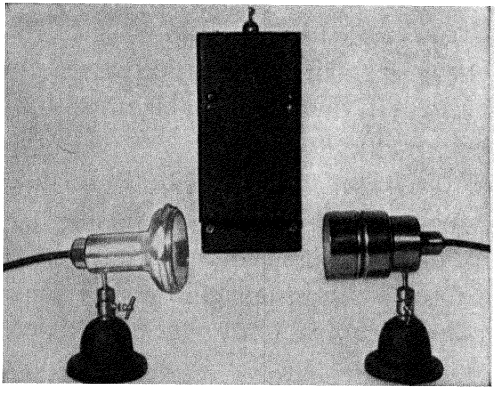


FIGURE 62.—Light Barrier Apparatus.
According to B. Lange.

From the abundance of further applications will be briefly mentioned: protection of fingers in presses and stampers, control of escalators, the switching on of show-window and advertisement lighting by passing people, the use as warning signals, the control of machine tools and packing machines, the automatic operation of doors in hotels, the opening of garage doors, the sorting of mixed products, the starting of a cutting process in the paper and film industries, the signalling of a sag in the working material between reel and manufacturing machine and protective devices in elevators. Light relays have also found an interesting application for the control of the pendulum in precision clocks,

Schuler and O. Schmücking. A light ray depending upon the position of the pendulum acts on photocells, so that the ideal case of the "free pendulum" is attained through the complete freeing of the pendulum from doing mechanical work. The application for rolled sheet inspection has already been mentioned on page 260. Light relays have also found an application in rolling mills for actuating the shears. The light radiation from the rolled material acts on the cell as soon as the material shoots over the cell and so actuates the shears.

Light barriers can also be so constructed that a complete interruption of the light ray is not necessary, but merely a weakening of the light suffices for the switching. On this is based the sorting of objects passing by, according to their color, or automatic switching of the heaters in coffee roasters. Photoelectric smoke density indicators for chimneys and furnaces work on the same principle.

The signal can be initiated not only by solid bodies, but the passage of solutions through glass tubes can also be used. Even with colorless liquids the refraction of light at the meniscus can be used for the switching. Thus A. Reinsch and U. Schmidt have constructed a photoelectrically controlled fuel measuring equipment with photoelements and coherer relay.

Light relays are suitable for the automatic control of temperature, where a mirror galvanometer is actuated by a thermoelement and its light pointer controls the furnace current photoelectrically. Using a compensation connection E. Voos and B. Lange[69] were able to get an accuracy of regulation of 1/10° at 1000° C.

In the examples cited an extensive simplification and cheapening in comparison with alkali cells and tube amplification was secured through photoelements and galvanometer relays (coherer relays). This creates the possibility of versatile use, which has been greatly limited hitherto by tube apparatus.

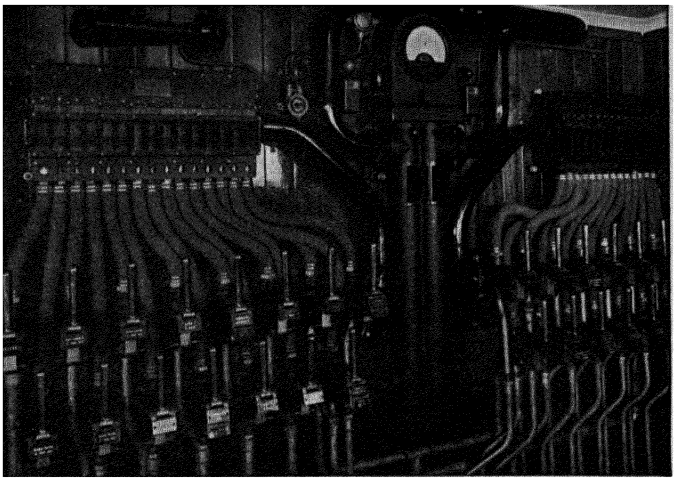


FIGURE 63.—Photoelectric Smoke Indicator with CO_2 Extinguishing Equipment of Walther & Co. Mounted on the Control Bridge of the "Scharnhorst."

SMOKE INDICATORS AND GENERATOR PROTECTION

Incipient fires, indeed, can also be signaled photoelectrically by means of the luminosity of the flame. The announcement takes place much more quickly through the formation of smoke, since frequently a slow smoldering precedes the blazing-up of the flames. Since the quickest possible discovery of the location of the fire is necessary for preventing a conflagration, it is thus expedient to use light absorption of the smoke for giving the signal. The light barriers described in the preceding section can be used for this in such a way that the light of the projector is weakened by the intervening smoke. For this, to be sure, auxiliaries are required for maintaining the lamp voltage and the illumination of the cell constant. Besides, for the protection of several rooms, a corresponding number of separate equipments are needed. For fire protection of an entire building or ship, accordingly, a centralized protective equipment with a special apparatus that is connected with the rooms to be watched over by means of conducting tubes has proved more

suitable. In this air is continually sucked out of the rooms to be protected and led through the photoelectric apparatus. The optical smoke indicator of the firm of Walther & Company, Köln-Dellbrück, operates on this principle. Carbonic acid for safely fighting the fire can be sent through the same conducting tubes by means of an ingeniously constructed valve. The structure of the complete smoke indicator installation on the control bridge of the express vessel "Scharnhorst" of the North German Lloyd is illustrated in Figure 63. An exhauster placed on the upper deck sucks the air through the apparatus from the rooms to be watched over. As can be seen the tube connections for the various rooms lead through the reversing valve to an optical indicator constructed by H. Hübner in which a display glass with lamp and lens is provided for each tube connection so that the smoke becomes visible through the Tyndall effect of the light scattered laterally. A collecting connection leads to the photoelectric apparatus, whose schematic structure is shown in Figure 64.

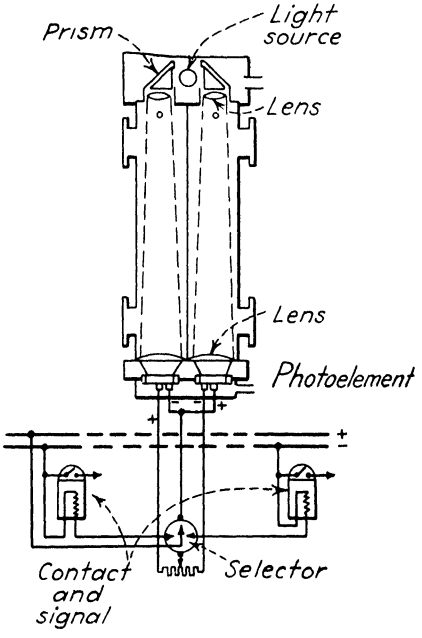


FIGURE 64.—Buchholz-Lange Smoke Indicator Apparatus. Simplified section through the generator protector.

In the head piece of the apparatus is placed an incandescent lamp with two prisms and lenses in such a way that the two parallel smoke tubes are scanned by the rays without penetrating the walls of the apparatus. The smoke tubes are closed by lenses, which concentrate the light on two photoelements. The two cells are placed in the differential circuit, already described many times, and are connected to the contact instrument. If the light absorption increases in the smoke tube, then the differential photocurrent actuates the fire-alarm equipment by means of the contact instrument. The deflection of the contact instrument corresponds to the development of smoke, so that the sensitivity of the apparatus can be adjusted by displacing the contact arms. A test pin can be shoved into the light path in one chamber, which screens off the light somewhat, through which the sensitivity of the apparatus is controllable. Through a special relay circuit even a very brief appearance of smoke turns on a continuous alarm and at the same time the contacts of the instrument are freed. To reduce the dilution of the smoke by the air from the separate rooms both test chambers of the apparatus can be connected with different groups of rooms. A further increase in sensitivity of the announcer was secured by the suction switch of M. Buchholz, which connects the different rooms one after the other. As an example of the sensitivity obtainable it should be stated that the smoke appearing when a friction match is blown out causes a release of the signal equipment.

The same photoelectric apparatus is used also in the generator protector according to Buchholz-Lange. M. Buchholz and H. Schwenkhagen [70] have proved that in transformers and likewise in generators every electrical disturbance produces a development of smoky gas from the insulating materials. In oil transformers this development of gas is used for actuating a switch mechanism by means of the rising bubbles. In the generator protector the signalling results photoelectrically through the light absorption of the smoky gas. The generator protector is specially suitable

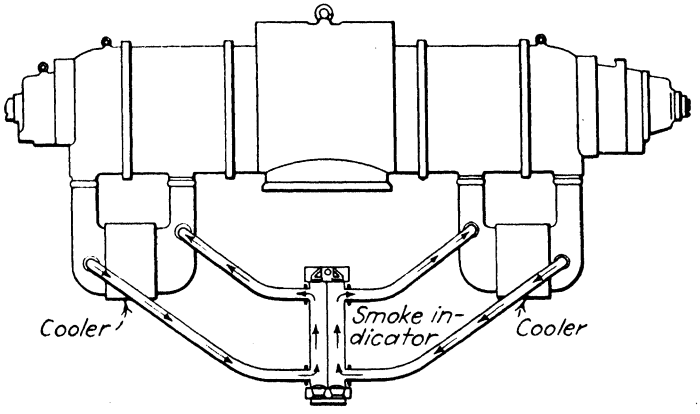


FIGURE 65.—Buchholz-Lange Protector for Ljungström Generators. Using Buchholz-Lange smoke indicator.

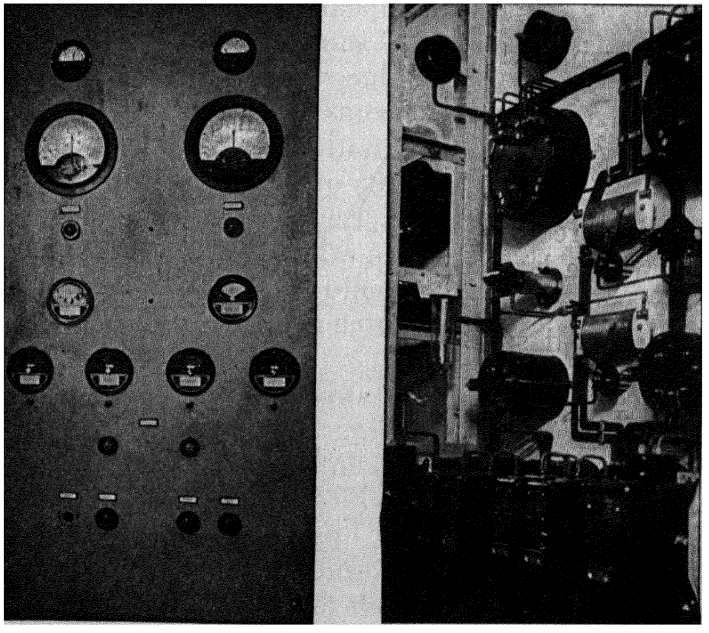


FIGURE 66.—Photoelectric Generator Protector. Front and rear views of the switchboard, Gumbinnen Power Plant. According to Buchholz-Lange.

for generators with closed circulation cooling, for here the certainty exists that the smoke will flow through the indicator equipment. The connection of the photoelectric apparatus to a Ljungström generator can be seen from Figure 65. In simple generators the protector can even be installed in the cold air chamber. The apparatus compares in the two tubes the generator air with pure air, or in the Ljungström assembly, the air of the two generator compartments. With a cloudiness of the air the intensity of illumination is changed, and the differential current actuates the contact instrument so that by means of an intermediate relay the release of the field control and the generator switch takes place. Figure 66 shows the switchboard of such a generator protection installation for a Ljungström assembly.

Optical Train Control

The examples of the use of photoelements as engineering switch mechanisms can be greatly multiplied. We will, however, in conclusion be concerned with only a single field of application, which is not only interesting for its general significance but which also presents a typical example of the successful overcoming of numerous difficulties. In the optical train control a high task, humanly speaking, is presented. The photocell assists the not infallible watchfulness of the human eye and so helps the safety of life and property. Hence the solution of this problem has been worked on by the most prominent places in the state and in industry. The most favorable results were secured with the system of the German State Railways through Dr. Bäseler in cooperation with Zeiss.

Before we describe the system of optical train control "Opsi" more fully we will discuss first the various requirements to be set up for such an installation. The solution of the problem might seem simple at first sight, something of this sort, that at the location of the stop signal a projector

is installed which sets in operation the train brakes by means of a relay placed upon the train. But it must be kept in mind that a train travelling at high speed has a braking distance of more than ½ mile. Hence auxiliary signals are required, which at threatened danger cause a slowing down of the train speed. Thus the first requirement is to provide two different photoelectric signals for the stopping and for the speed reduction. A second important requirement is that daylight or sunlight shall not produce any false action. Furthermore the difficulty often exists that the signal station on open stretches is remote from power lines and hence no current is available for operating a projector. Hence the entire signal installation must be placed on the train in such a way that the releasing is merely transmitted from the signal post by means of a mirror. In this it must be kept in mind that a small displacement of the mirror must have no effect. As the last but basic requirement we mention also certainty of action, sturdiness of the whole layout and reliability in spite of the influence of weather. We will now see how these various requirements have been met.

The influence of daylight can be eliminated by periodic light that is produced by means of a perforated disc driven by compressed air. Through a transformer or a condenser in the input of the amplifier, as in the connections illustrated on page 238, the effect of daylight is completely eliminated and at the same time a high sensitivity is secured. The use of a triple mirror for reflecting the projector light has proved furthermore of decisive significance. Such a mirror consists of a three sided glass pyramid, whose side surfaces, through triple reflection, throw back the light approximately parallel to the direction of incidence, even at rather oblique angles, so that small displacements of the signal post are without effect. With the triple mirror the transmission of different signals is also made possible. Thus through different angular positions of the mirror different detector positions can be aimed at and different signals released by means of several cells. In this simple directivity of the reflected ray through

one and the same space device lies the foundation of the unique versatility in its possibilities of use.

The arrangement of the projector on the locomotive, the mirror on the signal post, and the path of the rays, are indicated schematically in Figure 67. According to the setting of the signal and the turning of the mirror either a distance signal can be released or the train brakes can be automatically actuated.

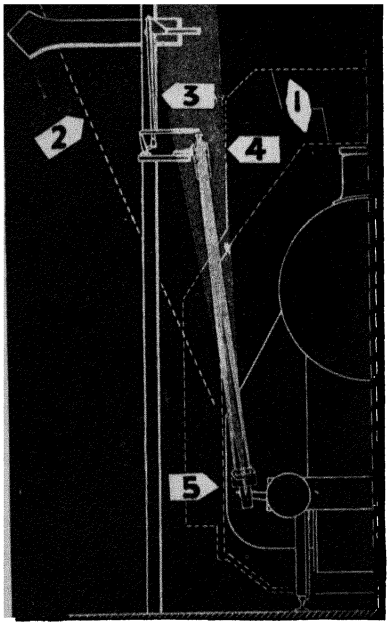


FIGURE 67.
Optical Train Control of the German State Railways.

1. Profile
2. Highest point of Sun
3. Signal rod
4. Mirror
5. Projector

For the last requirement of constancy, independence of weather influences, and sturdiness, the selenium condenser cells of H. Thirring [71] and the photoelements have proved the most suitable. It is decisive here also that the latter cell requires no high auxiliary potential, which is not available on the locomotive. The example of the optical train control seems noteworthy also in still another respect. By the use

of two agents, namely, periodic light and the triple mirror, not only were two separate actions secured, but also a whole collection of other advantages, so that the technical efficacy depends upon a power of the number of individual efficacies known in and for them.

Bäseler [72] suggested that such a photoelectric arrangement could also be used for guarding railway crossings and for controlling traffic in the streets, if the individual vehicles are equipped with triple mirrors. He also described a travelling crane installation with photoelectric equipment and projector, such that every workman can drive the crane by means of a small triple mirror. If the mirror is attached to the head with a forehead band then the movement of the crane can be guided merely by inclining the head in a definite direction without interrupting the hand work.

But at present we are still far distant from such many-sided uses of the photoelements and must learn much before dealing familiarly with photoelectric switching contrivances. But the time seems to be approaching when photoelements will become a popular experimental device as amplifying tubes and radio apparatus are now. But be it ever so far, still we have hands enough, who understand how to deal with photoelectric switching installations: still we could build, operate and maintain photoelectric apparatus easily on a large scale. Just on account of their simple and obvious mode of action the photoelements seem suited to lead us to this goal.

Chapter 8

Use in Various Fields of Activity

In the preceding chapters we have described the individual measuring and switching devices separately. In the closing chapter we will give a brief summary of the applicability of photoelectric devices for various fields of activity.

Chemistry

The principal use of the photoelements consists here in the colorimetric measurements for rapid determination of the content of a colored solution or for the control of a reaction process. Iron, manganese and titanium had already been determined earlier by optical colorimeters. M. Bendig and H. Hirschmüller [73] have reported on the performance of such determinations with the photoelectric colorimeter. Also older works of Gericke [74] are known concerning the colorimetric determination of phosphoric acid. Ch. Zinzadze [75] has devised for this a special method for the photoelectric colorimeter using a molybdenum blue reagent. With this the determination of phosphoric acid in the presence of silicon, arsenic, iron and nitrates was successful. Zinzadze used the same reagent for the determination of arsenic in phosphorus-free solutions. M. Cerny [76] reported concerning the determination of silicic acid in the presence of phosphoric acid with ammonia molybdate and citrate solution. Another method for determining phosphoric acid was devised by C. Fiske and J. Subbarow,[77] and used by F. Rothschild [78] for colorimetric measurements. R. Uzel [79] reported on the determination of mercury with Berlin blue as indicator. The question of the applicability of sodium rhodizonate as indi-

cator for the determination of sulfate ions in acid mixtures was discussed by M. N. Maruschkin.[80] Bismuth can be determined with cinchoninic iodide. Sulphurous chloride, according to a statement of A. Castiglioni,[81] gives with ammonia a violet coloration which is suitable for colorimetric determination. K. Yamamoto and M. Abe[82] reported on the determination of methylene blue, quinoline yellow and eosine red. F. H. Cohen[83] succeeded in determining a lactoflavine solution (Vitamin B) by measuring the fluorescent radiation set up with ultraviolet light. C. Griebel[84] reported on the determination of chlorogenic acid in coffee, important in food chemistry. Nitrate determinations were carried out with Nessler's reagent. K. Kramer[85] reported on such determinations in sea water. Through the addition of a protective colloid, deflocculation of the fine precipitate was prevented. According to works of E. and K. Naumann[86] the use of such a protective colloid is recommended in the determination of barium and lead. Naumann also describes the use of the photoelectric colorimeter for the determination of small quantities of iron and manganese in water and gives methods for the colorimetric determination of phenol and aluminum.[87] Detailed methods for light metal investigations on copper, manganese, silicon and iron are given in a report of the German Versuchsanstalt für Luftfahrt by H. Pauschardt and R. Bauer. A. Bruckner and Becker[88] report on the use of photoelectric colorimeters in the sugar industry. W. Kordatzki[89] mentions colorimetric methods for p_H determinations.

The photoelectric colorimeter is also suitable for the measurement of very slight turbidity. Thus A. Willer and E. Heinemann[90] were able to make investigations of suspended matter in lagoon water and through this to study their influence on lagoon sickness. For continuous supervision of drinking water and sewage the continuous flow colorimeter is useful.

Photoelectric switching devices have found application in the automatic control of manometer levels and for inde-

pendent pressure regulation. Light relays are used for counting tablets and other packed articles which pass by on moving belts, as well as for the automatic sorting of colored substances.

For celluloid factories, dye works, and textile mills photoelectric reflection measurements are important. Thus H. Freytag [91] reports on measurements in textile photochemistry. Measurements in ceramics were carried out by H. Harkort.[51] M. Mengeringhausen [52] has conducted photoelectric investigations in washing technology. Furthermore, the determination of the quantity of light with registering or counting devices is full of significance for bleaching experiments, H. Sommer and F. Jacoby,[28] or for photochemical work. B. Lange [46] has given a comprehensive description of the use of photoelectric apparatus in chemistry.

Physics

Since the spectral sensitivity of the photoelements reaches from the infrared through the ultraviolet into the region of x-rays, an applicability for all kinds of radiation measurements results. Indeed the photoelements in combination with monochromators are shown to be very suitable for the determination of spectral absorption, see page 232. The evaluation of spectrum pictures is made quite simply with a microscope and slit ocular, page 227, or with a photoelectric microphotometer, page 228. The use of the photoelements as sensitive direct current amplifiers is new.

Particularly advantageous is the use of photoelements for demonstration experiments in the teaching of physics. Thus the dependence of the intensity of illumination on the distance, the law of reflection, the cosine law, light absorption, the distribution of energy in the spectrum and many other conformities to law can be demonstrated impressively. Even complicated processes such as the vectorial dependence of reflection and absorption in the optics of metals can

be demonstrated in a large auditorium with the experimental arrangement described by L. Bergmann.[92]

Astronomy

Through the fundamental work of P. Guthnick[93] the use of photocells in astronomy gained an always greater importance in the determination of the transit of stars, for star photometry, and for the photoelectric evaluation of star pictures. Photoelements are particularly suitable for the last purpose, for instance, by using a microscope with slit ocular and the "Multiflex" galvanometer. For the photometry of stars the photoelements are useful only to a limited extent. The highest current sensitivity of the galvanometer is about 10^{-12} ampere per scale division. With this, intensities of illumination to about 10^{-6} lux are measurable. Since with alkali photocells as well as with the photographic plate continuous integrating methods are applicable, for instance the determination of the time of charging of an electrometer, much more is accomplished with them. According to K. O. Kiepenheuer[94] it is even possible to exceed the sensitivity of the eye considerably in the violet and red regions. To this is added also that the measurable difference of brightness, the threshold of distinction or gradation, is greater for photoelectric photometers than for visual, since the eye, like the photographic plate, rates the brightness logarithmically (Fechner's Law) whereas the photocurrent depends linearly upon the brightness. For the measurement of moonlight and for the determination of the light of the sky photometers with photoelements, on the other hand, are very suitable on account of their simple arrangement for measurement.

Bioclimatology and Meteorology

W. Schmidt,[95] in various works, has referred to the special importance of simple photoelectric illumination meters for

bioclimatic and meteorologic investigations. By using Pettersson filters, page 199, it is possible to measure intensities of illumination up to 100,000 lux and also to record them. Detailed experiments on the importance of the light intensity for plant growth were carried on by F. Schulz,[96] while O. H. Volk[97] has worked on the light relations in forests and vineyards.

Oceanography and Hydrography

Since 1923 the leaders in the realm of submarine light measurements have been H. H. Poole and W. R. G. Atkins[98] who based their method originally on alkali photocells and later developed it with photoelements, and who have carried on numerous measurements in the open sea. In the coastal regions of the northeastern Pacific E. A. Williams and C. A. Utterback[99] have measured the submarine daylight for different seasons of the year with photoelements and various light filters. H. Pettersson[100] and Pettersson and Landberg[23] have carried on measurements in Scandinavian coastal waters and in the Baltic Sea and have recorded the submarine daylight in a Bohusland fiord during a long time. The same authors, together with H. Höglund[101] have conducted a culture experiment on phytoplankton, in which a photoelement sunk in the water of the fiord along with the cultures served to hold the arrangement at a constant illumination during up and down movements.

In order to carry on exact measurements of the transparency and light scattering of sea water independent of varying daylight, H. Pettersson[100] has constructed special instruments which contain an electric lamp whose rays traverse a water column 2 meters long and are measured with a photoelement. Pettersson has conducted measurements with this apparatus to a maximum depth of 500 meters. Measurements at sea were carried on by O. Eckel.[102]

Medicine

In modern medicine physico-chemical methods of working have found a wide reception. The uses in chemistry mentioned in the first section have hence become important also for medical investigations. For serial experiments the use of a photoelectric colorimeter with insert for the test tubes, page 239, presents advantages. The use of photoelements, however, has led to the development of entirely new methods of investigation in medical research. Thus a procedure was developed by K. Kramer [103] for continuous measurement of the oxygen content in flowing blood in unopened vessels. According to this the light absorption in the vein is continuously recorded by a photoelement. Since the absorption, however, depends upon the number of erythrocytes and the oxygen content, the haemoglobin content must be known. Hence according to the procedure of Matthes [104] the absorption in the red and green spectrum is measured and from this the haemoglobin content and the oxygen content are deduced. H. Netter and S. L. Orskov [105] describe a procedure for recording the haemolisis with photoelements. The latter authors refer also to the use of photoelements for demonstrating the irritating action of rapidly increasing currents. If a photoelement is connected directly with the irritating electrode then the nerve muscle preparation twitches with rapid darkening of the cell. We thank L. Nicolai [106] for detailed investigations on this, who made exact data concerning the form of the light flux by using a rotating toothed disc with various notches. Recent experiments concerning the determination of the color of tooth cements with the photoelectric colorimeter were carried out by F. Schoenbeck and E. Czapp.[107]

Electrical Engineering

In recent years electrical engineering has been able to open up new fields of activity through the use of photocells

for facsimile telegraphy, television and sound films, which have aroused a general interest far beyond the circle of the special branch of science. Since a tube amplification of the small photocurrents and high freedom from lag are always requisite for these, however, alkali photocells and photoresistances have found almost exclusive use. According to the work of J. H. Rose [108] a substantial improvement of the frequency behavior can be secured by using a self-induction in the grid circuit, so that photoelements have also already found a use in sound films.

The use of photoelements for film gramophones with cellophane film according to the diazo process, which can be made particularly fine and free from grain, seems promising. Connected to a radio instrument these film gramophones give a better sound reproduction than plate instruments and make possible the reproduction of long pieces with small roll films without interruption.

The use of photoelements for illumination measurements is of signal importance. Whereas such measurements were formerly carried on by illumination engineers only with complicated optical apparatus, illumination measurements have now become so simple, as we showed in Chapter 2, that they can be made by any electrical specialist just as readily as current and voltage measurements. A new field of application of photoelectric illumination measurements has been opened by M. v. Ardenne [109] for the investigation of the light flux characteristic of Braun tubes. These tubes connected to a special amplifier according to M. v. Ardenne [110] are suitable for oscillographic investigations in the range of $0.2\text{-}3 \times 10^6$ hertz.

Photoelectric switching and signalling devices have also acquired increasing importance in electrical engineering, as has already been shown for the twilight switch, page 266, and the generator protector, page 270. Among the numerous possible applications we will mention further only the photoelectric synchronizing arrangement of Sterzel. The potentials to be synchronized act upon a revolving mirror so that

this oscillates in step with the alternating potential. A light ray is reflected from this mirror to a second which oscillates about a vertical axis. If both lines are synchronous then the reflected light ray falls on a photocell through a pinhole screen and releases the switching operation.

Photoelements as Sources of Energy

It is really astonishing that the enormous energy of the sun, which our earth receives daily is not used technically, or stated more exactly, is not transformed into other forms of energy. But it is still more astonishing that we have not changed the light, whose electromagnetic character we have known for decades and whose field strength amounts to several volts per centimeter, into useful electric energy and converted the displacement currents of the light into electrical conduction currents. The solar energy received per square meter amounts to approximately 1 horsepower and the solar energy corresponding to a surface the size of Lake Champlain would, on transformation without loss into electrical energy, cover the requirements of the whole world. Hence it is understandable, that the possibility of a direct transformation of light into an electric current by means of photoelements arouses great interest, since through this the realization of the old dream of a solar-power plant seems possible. So reports have not been lacking, in which the small counter motor, (see page 208), which operates by the exposure of the photoelement, was called a solar motor, and in which calculations as to the necessary size and cost of solar-power plants with photocells were prepared. In America, indeed, cell assemblies of great area have already been put together whose electrical output sufficed for operating small incandescent bulbs. The data concerning the output of photoelements given on page 187, however, show that, with an efficiency of only about 1%, we are still far removed from a practical utilization. At present we must be satisfied with using photoelements for measuring and switching pur-

poses. But it is not probable that with the facts mentioned here the relations between light and electricity are exhausted. Perhaps in later years just this relationship between electricity and light will be of supreme interest.

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