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PHOTOELECTRIC SENSITIZATION OF ALKALI SURFACES BY MEANS OF ELECTRIC DISCHARGES IN WATER VAPOR

BY

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PHOTOELECTRIC SENSITIZATION OF ALKALI SURFACES BY MEANS OF ELECTRIC DISCHARGES IN WATER VAPOR*

I. Introduction

1. *Photoelectric Research at the University of Illinois Since 1909.*—Since the discovery by Elster and Geitel (1890), that layers of alkali metals in a vacuum when subjected to light release negative electricity more abundantly than metals of other groups, much research work has been done in developing light-sensitive tubes. Early in this development contributions were made at the University of Illinois which later led to significant developments in the direction of scientific and engineering applications of photoelectric tubes.

2. *Applications of Photoelectric Tubes for Scientific and Engineering Purposes.*—Apart from the scientific importance of photoelectric phenomena the study of which, since the early discoveries by Hertz and Hallwachs (1887), developed into a vast branch of physics, many practical applications of these phenomena were made possible as a result of the investigation of this interrelation between electricity and light. Precision photometry of light sources, automatic control of electrical apparatus and of industrial processes by means of light, transmission of pictures over distances with or without wires, sound motion pictures, and television were the direct outcome of this new knowledge. From the engineering standpoint the basic significance of photoelectricity consisted in the possibility of transforming light energy into electrical energy. A new task presented itself with the far-reaching problem of making this transformation more efficiently and on a larger scale than previously had been accomplished.

3. *Sensitization of Photoelectric Surfaces and Its Fundamental Importance.*—It is known that metals and their compounds are all more or less photosensitive, i.e., they will emit electrons under the influence of light, this phenomenon depending upon the frequency and intensity of the source. Search for photoelectrically sensitive materials did not lead to any considerable gains in the efficiency of the electron emission. It was found necessary to devise processes of treating the surfaces of these materials in order to increase their photosensitivity to any considerable extent. Such processes of "photo-sensitization"

*A brief preliminary communication was published in Phys. Rev., Vol. 57, 1940, p. 565.

have become important in the development of photoelectric tubes. These processes had always as their object the formation of a film of molecular dimensions which would so modify the surface and decrease its work function as to increase the output of electrons.

4. *Purpose of Investigation.*—The purpose of this investigation was to develop an efficient method of sensitization of surfaces of alkali metals by means of electric discharges in water vapor. This work was a continuation of long years of effort directed towards the improvement of photoelectric tubes.

5. *Acknowledgments.*—This investigation has been carried on as part of the work of the Engineering Experiment Station in cooperation with the Department of Physics under the general administrative direction of DEAN M. L. ENGER, Director of the Engineering Experiment Station, PROF. ELLERY B. PAINE, Head of the Department of Electrical Engineering of the College of Engineering, and PROF. F. W. LOOMIS, Head of the Department of Physics. For encouragement and financial aid given this investigation acknowledgment is due DEAN R. D. CARMICHAEL of the Graduate School and PROF. JOEL STEBBINS, Director of the Washburn Observatory, Madison, Wisconsin. Acknowledgment is also made of the able service rendered by L. R. BLOOM, Research Assistant, and R. N. WAGGENER in the final stage of the investigation.

II. ATOMIC HYDROGEN AS A FACTOR IN SENSITIZATION

6. *The Effect of Discharges in Molecular Hydrogen.*—One of the well-known methods of sensitizing alkali surfaces was devised by Elster and Geitel* and further improved by Kunz and Stebbins,† and others. It consists in depositing within an evacuated glass bulb, part of which is coated with a conductive film of silver, a layer of pure alkali metal, and introducing molecular hydrogen at a pressure of 2 to 3 mm. Hg. No reaction takes place between the gas and the alkali surface until a potential of about 300 volts is applied with the alkali layer as one electrode and a loop of silver wire as the other (+). Due to the discharge which is produced the surface of the alkali layer is modified. This change in the surface is usually accompanied by an increase in sensitivity depending upon the duration and current density of the discharge. The nature of the modification taking place is not well known. It is assumed that a layer of alkali hydride is

*J. Elster and H. Geitel, Phys. Zeits., Vol. 11, 1910, p. 260.
†Jakob Kunz and Joel Stebbins, Phys. Rev., Vol. 7, 1916, pp. 62-65.

formed, and that alkali metal in an extremely subdivided colloidal form is imbedded on the surface of the alkali hydride. The appearance of irridescent coloring of the newly-formed surface is regarded as a proof that an alkali colloid is present.

7. *The Effect of Purifying Molecular Hydrogen.*—Many of the attempts which were made to increase the photosensitivity of alkali surfaces were centered about the purification of the materials which were applied as sensitive layers and of the gas used for sensitizing. While the purification of the alkali metals by repeated distillation gave positive results, the results obtained by the purification of hydrogen were uncertain. No definite increase in sensitivity was obtained by trying extreme purification of hydrogen. However, when the purification consisted in drying the hydrogen the sensitivities were always reduced. The discharge changed in appearance, becoming gray in color.

8. *The Production of Atomic Hydrogen by Electric Discharges in Water Vapor.*—In the course of these researches the experiments with dry hydrogen coincided with an investigation of means of producing beams of atomic hydrogen. It was found, in agreement with Wood's observation,* that discharges in extremely dry hydrogen when observed through a spectroscope gave only slight indications of the three principal Balmer lines characteristic of atomic hydrogen. Only by adding considerable amounts of water vapor could the concentration of atomic hydrogen, as indicated by the intensity of the Balmer spectrum, be increased. By inference it appeared probable that the main source of atomic hydrogen was the dissociation of water vapor by electrical discharges. Further, it was concluded that it was the atomic hydrogen which was of chief importance in the process of photosensitizing the alkali surfaces. Consequently a series of experiments was made with the object of sensitizing photoelectric tubes by means of mixtures of H_2 and H_2O vapor.

9. *Sensitization of Potassium Layers by Means of Discharges in Mixtures of H_2 and H_2O Vapor.*†—In Fig. 1 is shown the apparatus which was used for the sensitization of potassium photoelectric tubes. The photoelectric tube A, whose silvered part B was covered with a thin layer of potassium, was connected either to the hydrogen source D by means of stopcocks C, E, and F, or to the water source contained in a trap G through stopcocks H. A discharge tube I connected to a

*R. W. Wood, Proc. Royal Soc., A97, 1920, p. 470.

†A brief preliminary communication was published in the J.O.S.A., Vol. 27, 1937, pp. 224 and 354.

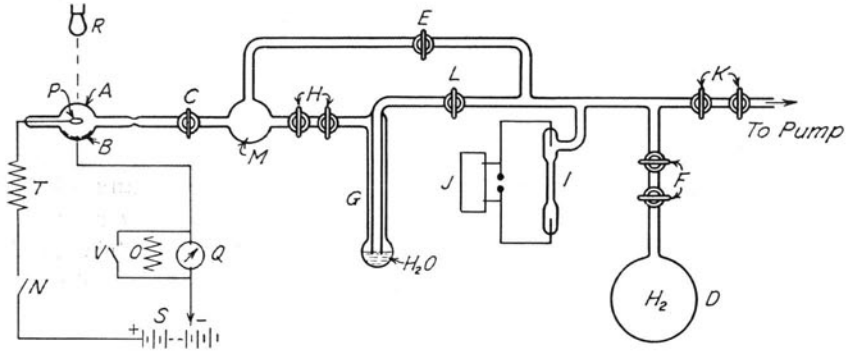

FIG. 1. APPARATUS FOR SENSITIZATION OF POTASSIUM LAYERS WITH DISCHARGES IN MIXTURES OF H_2 AND H_2O VAPOR

spark coil J served to indicate the character of the discharge and also the degree of vacuum. The entire glass system was connected to a mercury diffusion pump through stopcocks K. The water in trap G was frozen to the temperature of liquid air and the system evacuated by opening all stopcocks excepting F. All stopcocks were then closed and a small portion of H_2 was introduced into the trap G by allowing the gas to enter through stopcocks F and L and to bubble through the water, which had been allowed to return to room temperature. This mixture was passed through stopcock H into reservoir M. By closing H and L and opening E the pressure of the mixture of H_2O vapor and H_2 could be reduced so that a potential of 600 volts would be necessary to break it down. As soon as the stopcock C was opened to introduce the mixture into the cell A, the switches N and V were closed; a pinkish discharge then occurred between the electrodes B and P. This discharge was continued for 10 seconds. The stopcocks C, E, and K were next opened to the pump and the cell was evacuated. The sensitivity was then measured with the galvanometer Q by permitting light from a source R to enter into the cell, opening the shunting switch V, and adjusting the battery S to 90 volts. A 20 000-ohm ballast resistor T served to limit the current of the discharge. The procedure was repeated two or three times until a maximum sensitivity was obtained.

10. *Photoelectric Tubes Sensitized by Discharges in Mixtures of H_2 and H_2O Vapor.*—Photoelectric tubes prepared by sensitizing potassium layers with mixtures of H_2 and H_2O vapors showed increases in sensitivity of from eight to ten times the sensitivity of photoelectric tubes prepared by the usual procedure of discharges in dry hydrogen. However, the sensitivity decayed gradually, approaching after a few

weeks a value which was still about three times the sensitivity of tubes made by the usual methods.

11. *The Role of H_2 in Mixtures of H_2 and H_2O Vapor.*—A study of discharges in mixtures of H_2 and H_2O vapor has shown that the Balmer lines became more intense with a decrease of the partial pressure of H_2. The question then arose as to the role of H_2 in the discharge of the mixture. It surely did little to contribute to the production of atomic hydrogen. It was shown that the breakdown potential depended to a marked extent upon the amount of hydrogen present. The increase of breakdown potential with the decrease in H_2 content in the mixture became considerably greater when the H_2 was reduced to an almost immeasurable pressure. The idea suggested itself that H_2 must have acted as a neutral gas in the photoelectric tube, which acted only to reduce the breakdown voltage. In order to test this idea it was necessary to carry out experiments with H_2O mixed with a neutral gas so inert that in no way could a reaction take place between the potassium and the gas.

12. *Photoelectric Tubes Sensitized by Discharges in Mixtures of Helium and H_2O Vapor.*—With the purpose mentioned in the concluding sentence of the previous paragraph in view the arrangement of apparatus in Fig. 1 was used, with the exception that the bulb *D* of hydrogen was replaced by a similar bulb filled with helium. Exactly the same procedure as was described in Section 9 was followed in sensitizing a potassium photoelectric tube with discharges in mixtures of helium gas and water vapor. Increases in sensitivity were observed similar to those that had been previously obtained using H_2 instead of helium. Observations of the tubes over a period of a few weeks showed similar characteristics in rates of decline, maximum sensitivities, etc. This experiment proved that the presence of molecular hydrogen in the sensitizing discharge was not an essential factor in the process of formation of a photosensitive surface upon the potassium layer. Moreover, it appeared certain that it was the dissociation products of water vapor that were essential in the sensitization process.

III. Sensitization by Means of Beams Resulting from the Dissociation of Water Vapor

13. *Method of Producing Atomic Hydrogen by Electric Discharges in Pure Water Vapor.*—Treating alkali surfaces by discharges in an atmosphere of water vapor, as described in the previous chapter, had

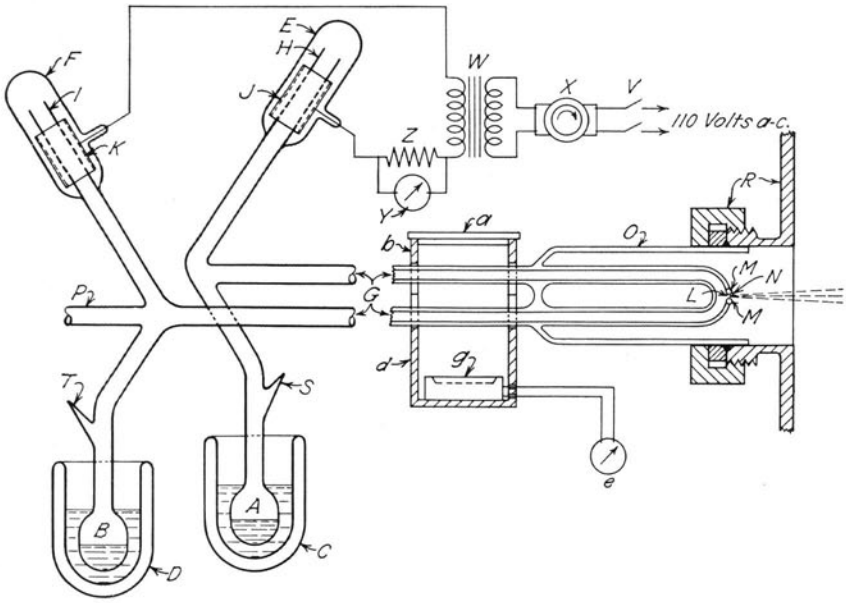

FIG. 2. APPARATUS FOR PRODUCTION OF BEAMS OF DISSOCIATED WATER VAPOR AND FOR MEASUREMENT OF RELATIVE CONCENTRATION OF ATOMIC HYDROGEN

the disadvantage that within the short time of less than a minute the process of sensitization was completed. This time was too short for proper observation and measurements. The method of causing beams of dissociated water vapor to impinge upon potassium surfaces was therefore applied, so that gradual changes of sensitivity could be observed during longer periods of time and a better control could be maintained over the discharge. The entire apparatus involved consisted of three parts, a source of beams of dissociated water vapor, a high vacuum pump, and a beam receiving and distributing apparatus.

14. *Source of Beams of Dissociated Water Vapor.*—The glass system which served as a source of the beams is shown in Fig. 2. Pure distilled water, introduced into the appendices *A* and *B* through side tubes *S* and *T* and outgassed by distillation, was kept at a constant temperature below the freezing point by an alcohol bath contained in Dewar flasks *C* and *D*. The temperature of the bath was controlled by addition of liquid air or warm alcohol. This made it possible to produce within the system an atmosphere of water vapor of any desired constant pressure. The ice in the appendices supplied the

water vapor to the discharge tube proper, which consisted of two electrode chambers *E* and *F* and the adjacent U-shaped discharge tube *G*. Each electrode chamber had a tube, *H* and *I*, protruding through cylindrical aluminum electrodes, *J* and *K*, in such a way that the disintegration products of the metal electrodes would be deposited on the glass walls of the electrode chambers and never reach the main discharge tube *G*. In this way also the recombination of atomic hydrogen near the electrodes was greatly decreased. The U-shaped discharge tube *G*, whose inner diameter was 0.8 cm. and whose total length was 70 cm., had an opening *L* at the bend into which a pair of glass rods *M* were cemented so as to form a slit *N*, 3 mm. in height and 0.03 mm. in width. The glass cylinder *O* was sealed on one side to the outer wall of the U-shaped discharge tube, and opened at the other side to fit the outlet *R* of the high vacuum pump. For initial evacuation a connecting tube *P* was provided leading to the forepump. The potential applied to the discharge electrodes *J* and *K* was controlled by means of a high voltage transformer *W* whose primary was regulated by means of a Variac type of voltage regulator *X*, so that any voltage from 0 to 15 000 could be obtained from the secondary by gradually changing the voltage input of the primary from 0 to 110. The current through the discharge tube was measured by means of a copper oxide a.c.-type voltmeter *Y* connected across a resistor *Z* in series with the discharge electrodes *J* and *K*. The maximum current (24 ma.) at which this discharge tube was operated corresponded to a current density of 30 ma. per sq. cm. For current densities above 15 ma. per sq. cm. air cooling from a fan was applied.

A more powerful type of discharge tube for the production of beams of dissociated water vapor was also constructed and investigated. It was designed for high frequency excitation by a quenched multiple spark oscillator at 500 kilocycles per second. In order to avoid recombination of atomic hydrogen at the metallic surfaces the electrodes *K* and *J* (Fig. 1) were removed from the discharge chamber. They were inserted in water-cooled jackets surrounding the chambers *F* and *E*. The U tube *G* also was enclosed in water-cooled glass tubing sealed to the discharge tube. Discharge currents up to 80 ma. corresponding to a current density of 100 ma. per sq. cm. could thus be obtained. The high frequency discharges of a deep rose color showed intense Balmer lines on a black background—evidence of large atomic hydrogen concentration. For quantitative measurements, however, the operation of the air-cooled discharge tube energized by 60 cycles a.c. proved simpler and more reliable.

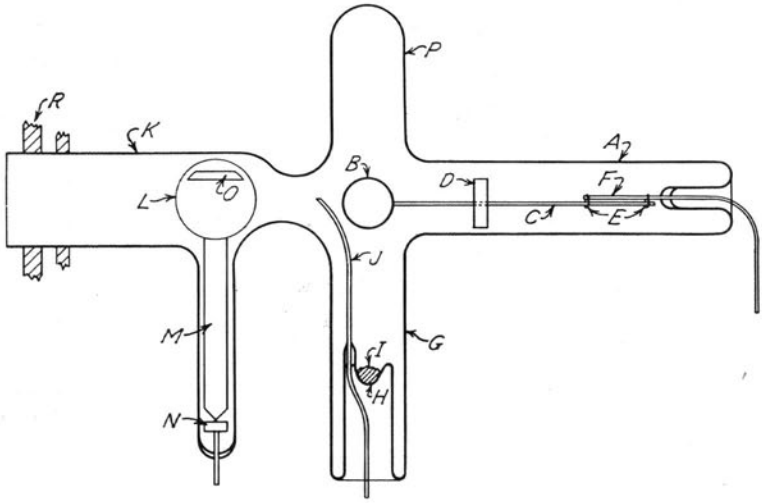

FIG. 3. BEAM RECEIVING APPARATUS

15. *Beam Receiving Apparatus.*—For the purpose of studying the effect of beams of dissociated water vapor an apparatus was constructed as shown in Fig. 3. It was designed to fit into the outlet R of the high vacuum pump opposite to and in line with the source of beams of dissociated water vapor. It was in the form of a T-shaped tube, one of whose arms A carried a circular silver disk B and was set at an angle 120 deg. with that of inlet tube K. The disk was welded to a wire C which carried an iron rod D and fitted into two eyelets E welded to the lead F. This permitted the disk to be set by means of a magnet to any angle desired. The vertical tube G had a cup H sealed into its lower end carrying a piece of potassium I inserted through the top of tube P. A lead J in the form of a nickel wire was sealed through one side of the cup. This lead acted as an anode, while the silver disk B acted as a cathode of a photoelectric cell as soon as the potassium I was heated and deposited onto the disk B. The tube K could be opened or closed by means of a butterfly valve L. The valve was made up of a copper disk carried by a supporting rod M which was pointed at the base and was free to turn on a smooth horizontal base N. The disk L could also be set into any position by means of an iron rod O soldered to one face of the disk and actuated by a magnet. Either side of the disk B could be coated with a thin potassium layer; for this purpose the disk B had to face the potassium cup H. By turning the disk through 90 deg. the potassium layer was subjected to a

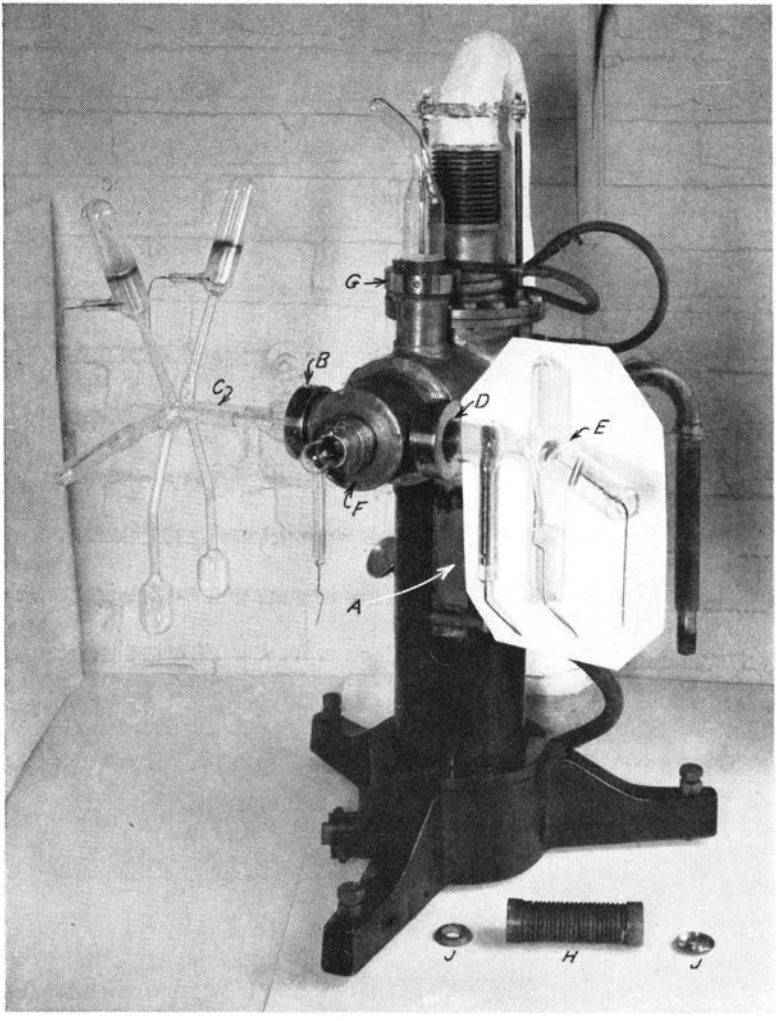

FIG. 4. ALL-METAL DIFFUSION PUMP WITH BEAM SOURCE AND RECEIVER OF BEAMS

beam of dissociated water vapor emerging from the slit of the beam source and impinging upon the surface of B whenever the valve L was opened.

16. *The Vacuum System.*—For the success of the investigation it was important that the speed of the pump be as high as possible and the vacuum obtainable should be at least 10^{-5} mm. Hg. For this purpose the principle of a rational design of nozzle as given by Phipps* was

*Copley, Simpson, Tennay, and Phipps, Rev. of Sc. Instr., Vol. 6, 1935, pp. 265-267.

adopted. A metal pump was designed and constructed to which glass or metal tubing could be attached by using special stuffing boxes in the outlets as described by Garner.* Apiezon B oil was used as the diffusion liquid. Figure 4 illustrates the pump A with its various outlets. Outlet B served as the stuffing box for the beam source C. Outlet D, which was of similar construction to B, was used to connect the beam receiving apparatus E to the pump. Outlets F and G were reserved as auxiliary outlets for testing the vacuum; G was used for an ionization gauge, and F for a discharge testing tube. A mechanical oil forepump with a capacity of 30 liters per minute in free air was used for obtaining the fore-vacuum. It was capable of reducing the pressure to 8×10^{-4} mm. Hg. The oil diffusion pump further decreased the pressure to 10^{-6} mm. Hg.

17. *Method of Measuring Relative Concentration of Atomic Hydrogen.*—Electric discharges in water vapor, when observed through a spectroscope, were seen to be accompanied by characteristic spectra which sometimes were very complex. It was found that with increase of current density, and at definite pressures, the appearance of the spectrum became simpler, and was finally reduced to the three principal Balmer lines which grew more intense with current density. The method of determining the optimum pressure was as follows. In Fig. 2 is shown a barrier-type photoelectric cell g, particularly sensitive in the red part of the spectrum, inserted in a bakelite cylindrical box consisting of two sections b and d closed by a cover a. This box enclosed a part of the U-shaped glass tube G used for the production of atomic beams, as described in Section 14. The photoelectric cell was connected to a galvanometer e which measured the intensity of the light radiated by the portion of the U-shaped discharge tube enclosed in the box. The sensitive surface of the cell was parallel to the U-shaped tube, but for the sake of clarity the U-shaped tube is shown in Fig. 2 perpendicular to the cell. The spectrum due to the by-products of dissociation O_2 or OH was relatively of such slight intensity that it could be regarded as negligible as compared to that of the principal lines $H\alpha$, $H\beta$, $H\gamma$ of atomic hydrogen. Of these lines, $H\alpha$ was the predominant one in brightness, and produced the greater part of the photoelectric effect in the cell g. The results of measuring the photoelectric current I_s as a function of discharge current I_d for constant water vapor pressure were plotted as a family of fourteen curves, shown in Fig. 5. Each of the curves was obtained for a definite temperature of the ice supplying water vapor to the discharge apparatus.

*Garner, Rev. of Sc. Instr., Vol. 8, 1937, pp. 329-332.

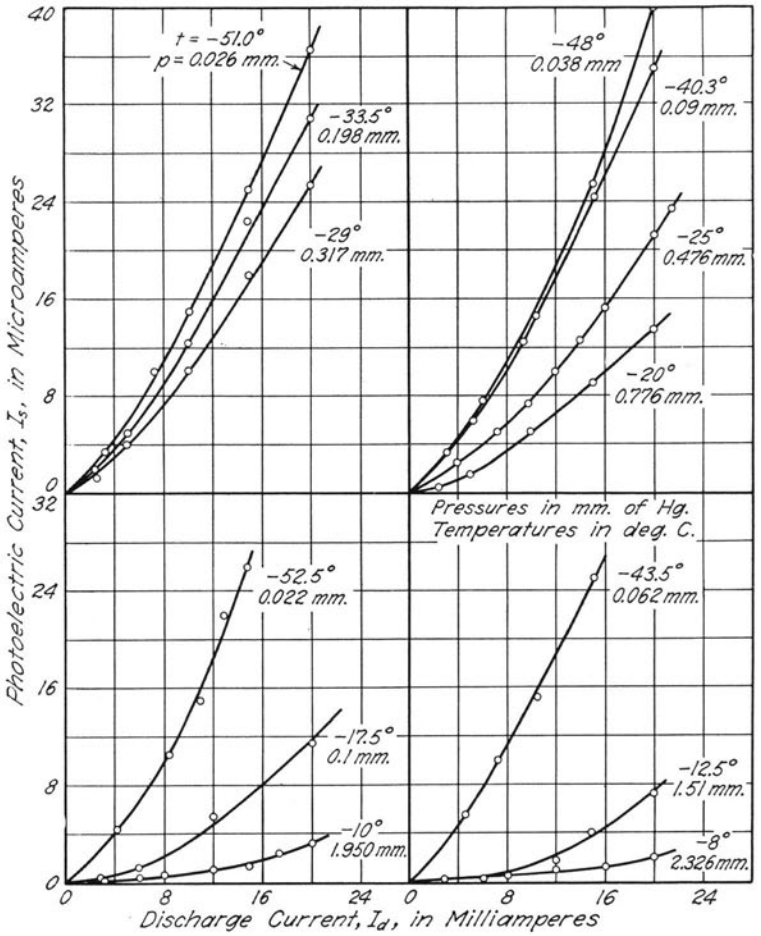

FIG. 5. RELATION BETWEEN DISCHARGE CURRENT AND ATOMIC HYDROGEN CONCENTRATION

The temperatures indicated at the top of each curve served to determine from known tables the corresponding vapor pressures. From these curves the relation between photoelectric current I_s and water vapor pressure p was found for constant discharge current I_d. The results, as represented in Fig. 6, show that there is a definite pressure within the range of 0.04-0.06 mm. Hg. for each current density which produces maximum concentrations of atomic hydrogen. It can also be deduced from the curves in Fig. 5 that for the higher values of discharge currents the atomic concentrations as indicated by the photoelectric current are approximately proportional to current density.

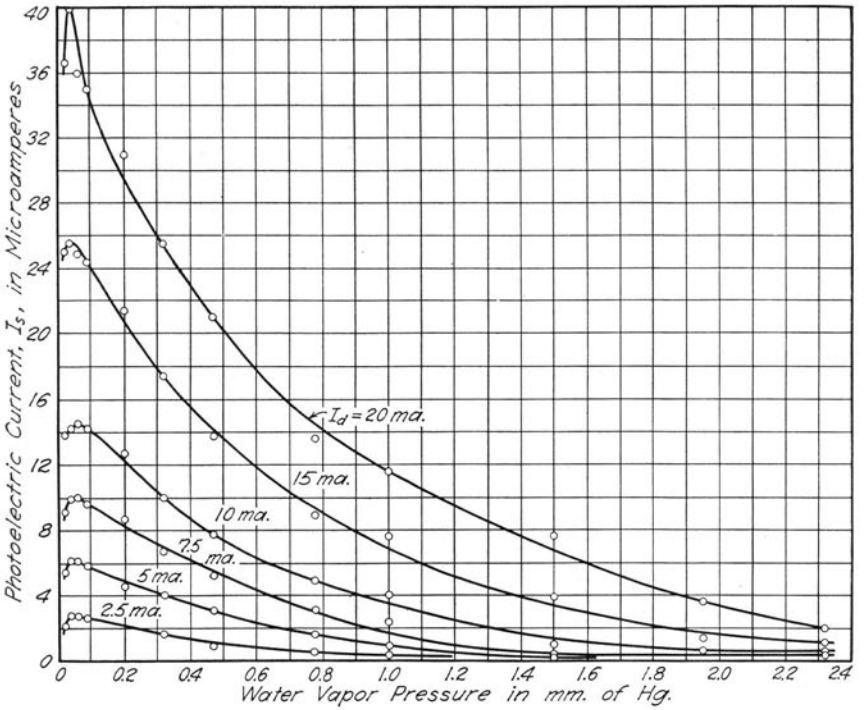

FIG. 6. RELATION BETWEEN ATOMIC HYDROGEN CONCENTRATION AND WATER VAPOR PRESSURE

By means of the method just described it was found that the atomic hydrogen concentration as indicated by the intensity of the Balmer lines remained constant as long as a continuous flow of water vapor was passing the discharge tube *G*. This condition was sustained by steadily removing, by means of the diffusion pump, the products of dissociation which emerged from the slit *N* in form of a beam. As soon as the pump was closed the intensity of the Balmer lines started to decrease rapidly and numerous bands appeared, increasing in intensity due to the accumulation of the products of dissociation.

18. *Application of Beams of Dissociated Water Vapor to Potassium Photoelectric Surfaces.*—The main object of this experimentation was to determine whether a beam of dissociated water vapor emerging from the outlet of the vacuum pump *R*, as shown in Fig. 3, and impinging upon a potassium layer deposited on the silver electrode *B*, would increase the photoelectric sensitivity of the potassium surface. The first experiments showed that even before the voltage was

applied to the discharge tube acting as a source of water vapor beams, the original sensitivity of the potassium surface decreased gradually without any apparent reason and reached a steady value after a period of about 5 minutes. A potential of about 3000 volts was then applied to the beam source, so that 15 ma. passed through the U tube. The discharge was of a deep rose color, and showed the Balmer lines very clearly. The sensitivity began to increase immediately after the water vapor beam was applied to the surface. It reached a maximum of sensitivity after 9 minutes; then it gradually decreased. The decrease continued regardless of whether or not the beam was interrupted by the butterfly valve. These experiments suggested that there were at least two factors which affected the photoelectric sensitivity of the potassium surfaces. Presumably, the factor that increased the sensitivity of the potassium surfaces was the action of the products of water vapor dissociation, while the factor decreasing the sensitivity was a thin film of oil originating from the outlet of the pump.

In order to check this assumption a baffle *H* made up of copper rings *J* was introduced into the pump, as shown in the lower portion of Fig. 4. This baffle protected the beam from oil all along the axis between the slit of the beam source and the inlet into the receiving apparatus. With this arrangement it was found that the original sensitivity of fresh potassium layers remained constant from the moment of deposition, and began to increase immediately upon the application of the beam of dissociated water vapor. The sensitivity reached a maximum, however, after about 10-12 minutes, and then began to decrease, gradually reaching a steady value. A series of such experiments served to show that even traces of oil are detrimental to the photosensitive surfaces. It was also shown that, although the dissociated beam of water vapor increased the sensitivity considerably, an upper limit would be reached, depending on the time of application and the density of the beam.

IV. Sensitization by Means of Electric Discharges in Pure Water Vapor

19. *Inferences from Water Vapor Beam Experiments.*—The beam experiments supplied the proof that the products of the dissociation of water vapor, in which atomic hydrogen predominated, could serve the purpose of sensitizing potassium layers. They also indicated that the maximum sensitivity was dependent upon the deposition of a definite number of hydrogen atoms, probably with additions of some oxygen

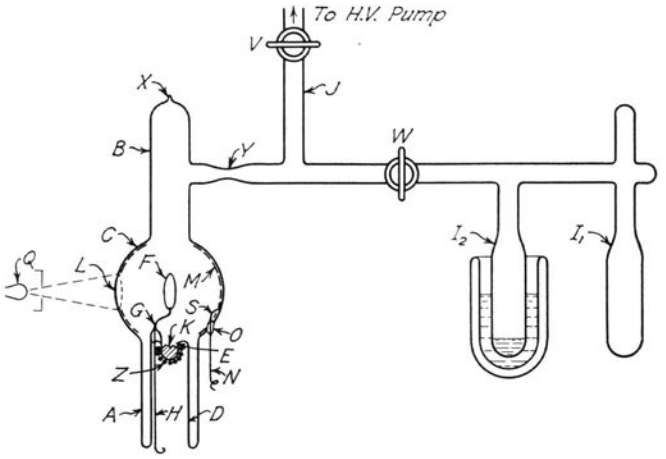

FIG. 7. ARRANGEMENT FOR SENSITIZING PHOTOELECTRIC TUBES BY MEANS OF DISCHARGES IN WATER VAPOR

or other molecules. The practical purpose of this investigation required a more direct method of activating alkali surfaces within a photoelectric tube. The experiments were, therefore, extended to the preparation and sensitization of such tubes, so that optimum conditions could be determined.

20. *Apparatus for Sensitization of Photoelectric Tubes by Means of Discharges in Water Vapor.*—The first experiments in sensitizing photoelectric tubes were made with an arrangement shown in Fig. 7. The tube C was blown from a bulb 65 mm. in diameter, into which two stems A and B were sealed. Stem A carried an inner tube D with a cavity E in the upper part, and a nickel ring anode F, 20 mm. in diameter, supported on a tungsten seal G connected to a flexible copper lead H. The cathode M consisted of a thick potassium layer covering the inner wall of the bulb except for a space about 3 cm. in diameter, which was clear, and served as a window L. The connection of the cathode with the lead N was made by means of a narrow platinum ribbon S whose one end was welded to the tungsten seal O, and the other end sealed to the glass wall. The stem B was connected to the freezing chambers I_1 and I_2 through the constriction Y and a stopcock W. A tube J supplied with a stopcock V connected the photoelectric tube C to the high-vacuum oil diffusion pump.

Comparative measurements of photoelectric sensitivity were made, using a hundred-watt nitrogen-filled lamp Q as a source of light, and

a standard Kunz potassium photoelectric tube sensitized with molecular hydrogen, and well evacuated, as described in Section 3. The sensitivity of the latter tube was considered as the average for that type of treated surface.

21. *Procedure of Sensitization.*—The procedure of sensitization was as follows: Before the cell was sealed to the system the distilled water in chamber I_1 was boiled, and the gases removed by opening the stopcocks W and V. For the purpose of further purification the stopcocks were closed and the water distilled over from chamber I_1 to I_2, the latter being immersed in liquid air. After the water in chamber I_1 froze to ice, purification continued by sublimation until the ice had all been transferred to I_2. During the process of sublimation the stopcocks were occasionally opened to remove nitrogen, oxygen, carbon dioxide, and other gases which might have been released from the ice. The cell was then sealed onto the system. A piece of potassium K was introduced through the upper stem B, and the opening X was sealed off. The cell was now evacuated with the mechanical forepump through the stopcock V. When the pressure was reduced to 0.1 mm. Hg., the high-vacuum pump was joined to the system through the same stopcock V. A vigorous torching of the entire cell with a bunsen flame followed. This continued for several minutes to rid the glass walls of gases. An electric heater Z was introduced into the lower stem to heat the cavity and the potassium. After the gas absorbed in the potassium was liberated the cell walls were cooled with wet cloths while the heating of the cavity continued. As soon as a sufficiently thick layer of potassium was deposited to assure positive contact with the platinum electrode S, the lower stem heater was removed, and a circular window L, 30 mm. in diameter, was cleared of potassium by heating this area with a bunsen flame. The cell was pumped for several minutes until all parts were cooled to room temperature. The initial sensitivity of the pure potassium layer was so small that it was difficult to measure its photo current using a light source at which the standard cell gave a deflection of 6×10^{-8} amperes. The necessary high degree of evacuation of the cell was tested by ascertaining that no discharge could be obtained with an a.c. potential of 15 000 volts supplied by a high voltage transformer. Liquid air was then removed from the appendix I_2, the stopcock V was closed, W was opened, and the ice permitted to rise in temperature until the vapor pressure in C increased sufficiently for a discharge of about 3000 volts to take place for a period of a few seconds. The stopcock W was now closed, and, by opening the pump stopcock V, the products of dissociation

TABLE 1
RELATION BETWEEN TIME OF DISCHARGE AND SENSITIVITY FOR TWO DIFFERENT POTASSIUM LAYERS

Film *a*	Sequence of discharge	0	1	2	3	4	5	6
	Duration of discharge, in seconds	0	20.5	25.5	20	25	50	40
	Total time, in seconds	0	20.5	46.0	66	91	141	181
	Sensitivity, amps $\times 10^{-8}$	0	6	10.5	15	19.5	21	7.5
Film *b*	Sequence of discharge	0	1	2	3	4	5	6
	Duration of discharge, in seconds	0	20	20	20	20	20	20
	Total time, in seconds	0	20	40	60	80	100	120
	Sensitivity, amps $\times 10^{-8}$	6.0	9	12	15	12	3	3

were then removed. The sensitivity of the cell by this one treatment was increased to 9×10^{-8} amperes, which was 50 per cent greater than the sensitivity of the standard cell. This process was repeated a few times until a maximum of sensitivity of 36×10^{-8} amperes was obtained. The current during each discharge fluctuated somewhat. The average discharge current, as measured by means of a rectifier type of milliammeter, was 3 to 5 ma. Comparing the sensitivity of the water-treated cell with that of the Kunz standard cell, the sensitivity was now six times as great as that of the standard cell. Further increase of time of discharge gradually reduced the sensitivity. When the sensitivity was reduced to half its maximum value a new potassium film was deposited by again heating the potassium container.

With a fresh crystalline potassium layer a new series of observations was then made. This time, however, the stopcock V was allowed to remain open and the stopcock W was adjusted until a uniform discharge in C was obtained. A continuous flow of water vapor was thus established, I_2 supplying fresh water vapor at all times and the high-vacuum pump removing water vapor together with the by-products of dissociation. The duration of each discharge was measured with a watch. This experiment was repeated with another layer deposited by distillation on the previous one. The results obtained with the two layers are given in Table 1 and plotted in Fig. 8. The two curves *a* and *b*, although showing distinct maxima, differed in shape. In the case of curve *a*, the duration of the discharge necessary to reach the maximum was longer, and the rate of increase in sensitivity was greater than that needed for curve *b*. While the maximum

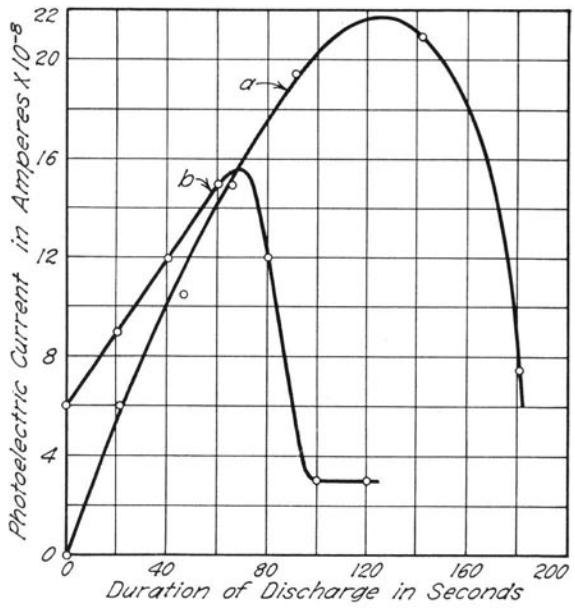

FIG. 8. RELATION BETWEEN DURATION OF DISCHARGE AND PHOTOELECTRIC SENSITIVITY

in the case of curve *a* was reached in 120 seconds, only 70 seconds were required to reach the sensitivity peak in the case of curve *b*.

The character of the two curves may be interpreted in the light of observations which were made on the variation of atomic hydrogen concentration within a discharge tube as a function of time (see Section 17). Curve *a* corresponds to a condition in which the H concentration was gradually decreasing during each period of discharge. More time was, therefore, required to produce the optimum number of H atoms than in the case represented by curve *b*, when the concentration remained constant during each discharge period. Considering the small quantity of H_2O vapor consumed in the process of sensitization, it follows that the total number of dissociated H atoms did not exceed that necessary for the formation of a monomolecular layer.

Results such as these, similar in character, but divergent in absolute values and rate of change of sensitivity, suggested the need for a better control of factors which influence the sensitivity.

22. *Example of Sensitization of a Potassium Photoelectric Tube.*— The application of a high voltage to the cell during the interval before

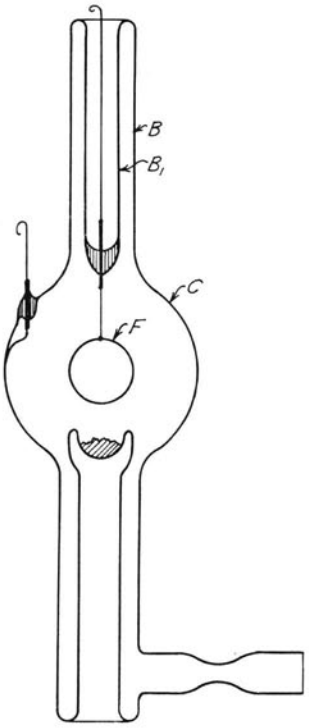

FIG. 9. CONSTRUCTION OF PHOTOELECTRIC TUBES

a discharge could take place had the disadvantage of allowing the water vapor to react with the potassium before dissociation could take place. Further, during the first stage of the discharge, long visible streamers reached out from the anode to distinct points on the cathode surface, thus concentrating the discharge on very small areas and disintegrating them. Another disadvantage consisted in violent fluctuations in the current before the electric discharge became uniform. A marked improvement was obtained by modifying the procedure as follows.

Instead of applying liquid air to the appendix I_2, as shown in Fig. 8, which reduced the temperature of the ice to approximately —190 deg. C., a Dewar flask containing alcohol at a temperature of —40 to —50 deg. C. was used as a cooling fluid to keep the ice at the prescribed temperature. When the temperature of the ice was stabilized, it was possible, by opening the stopcock W and closing the stopcock V, to establish a water vapor pressure at which an immediate discharge could occur. This modification in the procedure almost completely

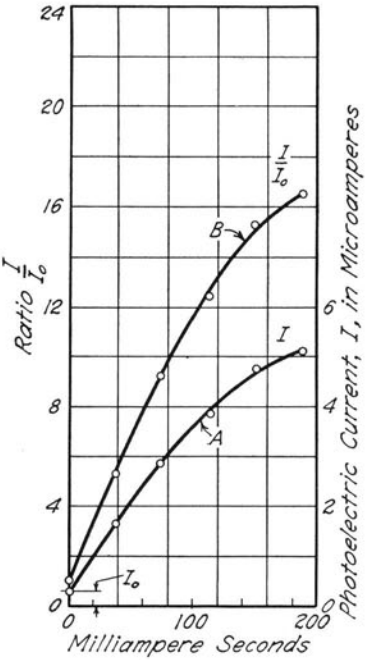

FIG. 10. CURVE SHOWING EFFECT OF TREATMENT OF A POTASSIUM PHOTOELECTRIC TUBE WITH DISCHARGES IN WATER VAPOR

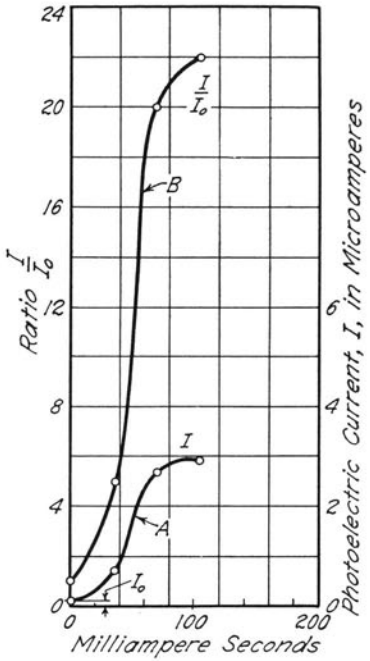

FIG. 11. CURVE SHOWING EFFECT OF TREATMENT OF A SODIUM PHOTOELECTRIC TUBE WITH DISCHARGES IN WATER VAPOR

did away with the disadvantages mentioned in the previous paragraph.

The type of construction of the cell which was used in investigating the methods of sensitization by means of discharges in water vapor is shown in Fig. 9. It differed from the cell shown in Fig. 8 in that the nickel electrode F was attached to a separate supporting tube B, which could be inserted into the cell C through the stem B.

Of the many potassium surfaces which have been investigated a typical example has been chosen to show the relation between the dissociating discharge currents passing through the cell and the gradual increase of photoelectric sensitivity. The photosensitive layer was deposited in the usual manner, by electrically heating and evaporating a piece of potassium. By cooling the cell a uniform metallic surface glittering with tiny crystals was obtained. The photosensitivity of the surface was measured by observing the current produced by a 100-watt nitrogen-filled frosted tungsten lamp fixed at a distance of 26.5 cm. In Fig. 10 the sensitivity curve A is plotted. The abscissa represents the milliampere-seconds expended during the periods of

TABLE 2

SENSITIZATION DATA FOR POTASSIUM AND SODIUM PHOTOELECTRIC TUBES

Steps in Process of Sensitization	Potassium						Sodium					
	Photocurrent I_0 μa.	Discharge Current I_d ma.	Duration of Discharge t sec.	Coulombs $\times 10^{-3}$ ma. sec.	Photocurrent I μa.	Ratio I/I_0	Photocurrent I_0 μa.	Discharge Current I_d ma.	Duration of Discharge t sec.	Coulombs $\times 10^{-3}$ ma. sec.	Photocurrent I μa.	Ratio I/I_0
1. Photocurrent measured before treatment	0.31						0.135					
2. First treatment: Water vapor admitted, Discharge in water vapor, Water vapor removed, Photocurrent measured		7.5	5	37.5	1.65	5.3		7	5	35	0.71	5.2
3. Second treatment: Water vapor admitted, Discharge in water vapor, Water vapor removed, Photocurrent measured		7.5	5	37.5	2.05	9.2		7	5	35	2.7	20
4. Third treatment: Water vapor admitted, Discharge in water vapor, Water vapor removed, Photocurrent measured		7.5	5	37.5	3.85	12.4		7	5	35	2.95	22
5. Fourth treatment: Water vapor admitted, Discharge in water vapor, Water vapor removed, Photocurrent measured		7.5	5	37.5	4.75	15.3						
6. Fifth treatment: Water vapor admitted, Discharge in water vapor, Water vapor removed, Photocurrent measured		7.5	5	37.5	5.1	16.5						
Conditions before each treatment: Temperature of ice, deg. C. / Water vapor pressure, mm. Hg. / A-c. potential, volts	−55 deg. C. 0.015 7000–7400						−55 deg. C. 0.015 5500–6500					

water vapor dissociation, while the ordinates give in microamperes the photoelectric output current I of the cell after each such treatment. Previous experiments have shown that the process of sensitization is critical. Beyond a certain number of coulombs expended during the discharges through water vapor the increasing photoelectric output of the surface, having passed through a maximum, begins to decrease rapidly. No attempt has been made in this case to reach the maximum. Curve B shows the same relation, but with ordinates I/I_0 representing the ratio of photoelectric output currents I after each treatment to the original photoelectric current I_0 of the untreated cell. In this particular case a maximum increase in sensitivity was obtained, which exceeded about 17 times the sensitivity of the untreated tube.

23. *Example of Sensitization of a Sodium Photoelectric Tube.*— When the construction of the tube and the conditions of treatment were left unchanged, but sodium was used as the photosensitive layer instead of potassium, similar results were obtained. In Fig. 11 the curve for the photoelectric current I as a function of the electrical quantity milliampere-seconds served to show that the sensitivity was close to a maximum at 100 ma. sec. Comparisons made with corresponding curves for potassium revealed that, in order to reach a maximum of sensitivity, a quantity of electricity was required for potassium which was nearly twice that necessary for the sensitization of sodium. Also the absolute values of sensitivity obtained for potassium were usually greater than those for sodium.

The curves which represent the ratios I/I_0 in Figs. 10 and 11 were plotted for the purpose of showing the relative increases of sensitivity following each treatment of the alkali surfaces. The ratios for maximum sensitivities were 17 and 22, respectively. They cannot be regarded as typical increases for potassium and sodium over that of the initial sensitivities I_0, because the sensitivity I_0 for an untreated surface varies from tube to tube. For the same alkali metal the values of I_0 depend upon initial surface conditions of the metal. The latter are difficult to control. For two successive untreated surfaces the initial sensitivities may differ greatly (from 1.5 to 3 times) from each other.

Table 2 contains further data in connection with the process of sensitizing sodium and potassium photoelectric tubes.

Greater sensitivities were obtained than shown in the examples mentioned. By a modified treatment supplemented by electron bombardment sensitization factors I/I_0 of 50 times and greater have been obtained whenever optimum conditions were more closely approached.

However, a multiplicity of factors which enter into the process of sensitization make optimum conditions difficult to realize. These factors will be discussed in a later publication.

24. *Sensitization of Lithium, Rubidium, and Caesium Photoelectric Tubes.*—Tubes made by depositing a lithium, rubidium, or caesium layer, and treated by discharges in water vapor gave similar results.

The technique required for the preparation of such tubes was even more exacting than in the case of potassium and sodium. Precautions were taken to exclude complications due to probable formation of oil films, and to avoid other possible contaminations of the photoelectric surface layers investigated. The deposition of lithium layers was made by evaporation of an oblong piece of the metal in a vacuum. For this purpose the metal was previously thoroughly cleaned and inserted into the helix of a tungsten filament which was then electrically heated to incandescence. Pure caesium was deposited by thermally reducing caesium chloride salt in the presence of calcium filings. High-frequency currents were used to heat a nickel cylinder containing the mixture. This cylinder was enclosed in a glass appendix sealed to the photoelectric tube.

The construction of the photoelectric rubidium tube was similar to that shown in Figs. 7 and 9. The lithium tube, however, differed by the addition of a quartz window attached above the top of a pyrex cylinder 2.5 cm. in diameter and 3 cm. long. The latter was sealed to the bulb at the opening L (Fig. 7) so placed that ultraviolet light from a quartz mercury arc could illuminate the lithium surface layer. Also, for the purpose of avoiding oil contaminations, the all-metal oil diffusion pump was replaced by a glass mercury diffusion pump supplied with an efficient liquid air trap.

Whichever of the three alkali metals Li, Rb, or Cs was used for the formation of a photoelectric layer, the sensitivity of the surface depended upon the reaction of water vapor dissociated by the application of electric discharges. When the discharge current was kept constant the sensitivity first increased almost linearly with the duration of the discharge and then slowed down. Once the peak was reached the sensitivity dropped rapidly, and then at a decreasing rate to a value which, however, was greater than the sensitivity of the original untreated surface.

25. *Sensitivity of Photoelectric Tubes Treated with Dissociated Water Vapor.*—A great number of factors influence the sensitivity of the new photoelectric tubes. Some of the factors have not been suffi-

ciently investigated. Others are barely known. It is, therefore, impossible to give definite values of the photoelectric output for each of the surfaces in the alkali group treated by electric discharges in water vapor. However, it may be inferred from the experimental data that the average increase in output, as compared with the output of the untreated surface, is characteristic of each of the alkali metals.

The increase of the output as expressed by the ratio I/I_0 may be represented by the series K, Na, Li, Rb, Cs arranged in the order of diminishing efficiency. Thus, potassium shows the greatest relative increase in sensitivity and caesium the least. In all cases white light from a standard 115-volt Mazda tungsten bulb was used to obtain the ratios.

The effect of discharges in water vapor could be more easily studied on potassium surfaces. Therefore, more data are available for this metal than for any other of the alkali group. The output of potassium photoelectric tubes, thus treated and thoroughly evacuated, varied within wide limits. An output of about 10 microamperes per lumen may be regarded as an average value. Compared with the average sensitivity of 0.2 microamperes per lumen for the usual hydrogenated potassium cell,* the new potassium cells are roughly 50 times more sensitive.

V. Résumé of Investigation

26. *Summary.*—Photoelectric sensitivities of several alkali surfaces obtained by discharges in purified molecular hydrogen were compared with sensitivities produced by discharges in mixtures of molecular hydrogen and water vapor and also in mixtures of helium and water vapor. Spectroscopic observations revealed that increased sensitivities followed whenever intense Balmer lines predominated in the spectrum of the discharge, thereby indicating the presence of atomic hydrogen. Unless mixtures of water vapor were used in the discharge intense Balmer lines did not appear. It was realized then that dissociated water vapor might be the source of atomic hydrogen and the main factor in the process of sensitization. In order to test the correctness of this hypothesis, beams of dissociated water vapor were produced in a high vacuum and used for bombarding potassium surfaces. A gradual increase of photoelectric sensitivity followed by a rapid decrease suggested the formation of a monoatomic gas layer, which, by interaction with the alkali surface atoms, set the condition for maxi-

*V. K. Zworykin and E. D. Wilson, "Photoelectric Cells and Their Application." Second Edition, p. 88.

mum sensitivity. Electric discharges in pure water vapor were then applied for the sensitization of Li, Na, K, Rb, and Ce photoelectric tubes. Examples of the sensitization of a potassium and of a sodium tube, with data, have been given to illustrate the operation of the new method.

27. *Results and Conclusions.*—The results obtained in, and the conclusions drawn from, this investigation may be stated as follows:

(1) Photoelectric sensitization of certain alkali surfaces by means of electric discharges in molecular hydrogen mixed with water vapor produced more sensitive surfaces than discharges in purified dry H_2.

(2) The main role of water vapor in a mixture with molecular hydrogen is to establish conditions of discharge favorable to the production of atomic hydrogen.

(3) Experiments with discharges in mixtures of neutral gases (helium) and water vapor gave photoelectric sensitivities similar to those which were obtained with discharges in mixtures of hydrogen and water vapor.

(4) The role of gases such as hydrogen and helium mixed with water vapor is to control the gas pressure and the breakdown potential of the discharge.

(5) A reliable criterion for gas mixtures which are effective in sensitization is the intensity of Balmer lines. They serve to indicate spectroscopically the abundance of atomic hydrogen produced by the discharge.

(6) A method developed for the determination of relative concentration of atomic hydrogen in dissociated water vapor is given. It consists in the measurement of the photoelectric current from a red-sensitive photocell irradiated by the discharge.

(7) When a pure potassium surface is subjected to a beam of dissociated water vapor the photosensitivity increases gradually, reaches a maximum, and then decreases rapidly, due to the continuous application of the beam.

(8) A similar phenomenon of increasing and decreasing sensitivity is observed on alkali surfaces subjected to a number of successive discharges of a definite voltage and current density.

(9) The results mentioned in (7) and (8) strengthen the view that the increase in the sensitivity is due to the formation of a thin film of gas of molecular dimensions interacting with the alkali surface.

(10) The sensitivities of potassium or sodium photoelectric tubes sensitized by dissociated water vapor exceed greatly the sensitivities of tubes treated with molecular hydrogen.

(11) The new method makes it possible to increase about 50 times the photosensitivity of an untreated alkali surface.

(12) The maximum of sensitivity of a surface is reached when a definite quantity of electricity is consumed in dissociating the water vapor. The quantity consumed is nearly twice as great for sensitizing a potassium surface as for sensitizing a sodium surface.

28. *Expansion of the Investigation.*—At the very outset of the investigation related problems presented themselves for solution, increasing in number as the work continued. Some of the problems had to be attacked at once, others could be left for subsequent stages of development. Consequently two plans were developed. The first was a general plan embracing a vast field of photoelectric surface phenomena requiring long years of research. The other was limited to what could be realized under the prevailing circumstances, and might possibly be applied for engineering purposes. The latter plan contained the following seven parallel branches of experimental investigation:

(a) Photoelectric sensitization of alkali surfaces with electric discharges in water vapor.

(b) Improvements in high vacuum technique connected with photoelectric work.

(c) Photoelectric sensitization of alkali surfaces by thermal dissociation of H_2 into atomic hydrogen, and by electronic bombardment.

(d) Photoelectric sensitization of alkali surfaces with electric discharges in deuterium oxide (heavy water).

(e) Determining factors in photoelectric sensitization of alkali surfaces.

(f) Spectral sensitivity of new photoelectric cells.

(g) Characteristics of electric discharges in water vapor and hydrogen.

Much work has been done in each of these directions during the last three years. A brief communication on (d), the effect of heavy water, was recently published.*

*J. T. Tykociner and L. R. Bloom, Phys. Rev., Vol. 57, 1940, p. 571.

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COLLEGE OF FINE AND APPLIED ARTS.—Curricula in architecture, art, landscape architecture, music, and music education.

COLLEGE OF LAW.—Professional curriculum in law.

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LIBRARY SCHOOL.—Curriculum in library science.

GRADUATE SCHOOL.—Advanced study and research.

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University Extension Division.—Courses taught by correspondence, extramural courses, science aids service, speech aids service, and visual aids service.

Colleges in Chicago

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COLLEGE OF MEDICINE.—Professional curriculum in medicine.

COLLEGE OF PHARMACY.—Professional curriculum in pharmacy.

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EXTENSION SERVICE IN AGRICULTURE AND HOME ECONOMICS
RADIO STATION (WILL)
BUREAU OF BUSINESS RESEARCH
BUREAU OF COMMUNITY PLANNING
BUREAU OF EDUCATIONAL RESEARCH
BUREAU OF INSTITUTIONAL RESEARCH
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State Scientific Surveys and Other Divisions at Urbana

STATE GEOLOGICAL SURVEY
STATE NATURAL HISTORY SURVEY
STATE WATER SURVEY
STATE DIAGNOSTIC LABORATORY (for Animal Pathology)
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