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BOX 7 FOLDER 34

INSTRUCTION ON THE MAKING OF POTASSIUM-HYDRIDE PHOTOELECTRIC CELLS

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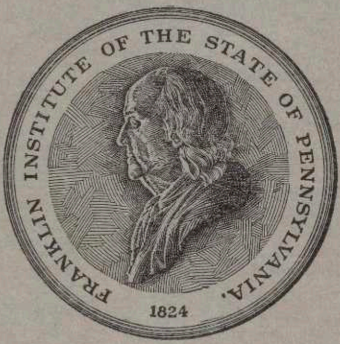

INSTRUCTION ON THE MAKING OF POTASSIUM-HYDRIDE PHOTOELECTRIC CELLS.

BY

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The photoelectric cell is fast becoming an indispensable unit in the modern laboratory, and, although there are some cells to be had on the commercial market, they may not always satisfy the particular physical or electrical requirements of special applications. In answer to just such a need, this laboratory has developed a method by which photoelectric cells of high sensitivity can be made. There is, we think, nothing unique in the method and there may be other ways which we have not thought of which are better. All that we claim for the following instruction is that it describes in detail a procedure by which photoelectric cells can be easily produced in the laboratory with a fairly high degree of certainty that the cells will turn out successfully and be reasonably uniform in their sensitivity.

In the most general terms, the method usually followed in the production of this type of photoelectric cell is as follows:

(1) The cell is designed and constructed carrying two electrodes, the "outside" electrode connecting to the light-sensitive surface, and the "central" electrode, which is the collector of the electrons.

(2) The tube is connected to a suitable vacuum system, evacuated, and baked out at high temperature.

(3) The potassium is distilled in "vacuum" through part of the system and condensed on the surface of the cell.

(4) Hydrogen is then introduced to suitable pressure and a glow discharge is operated between the "outside" and the "central" electrodes until the potassium-hydride surface so produced shows the maximum sensitivity.

(5) The hydrogen is then pumped out and argon is introduced to give maximum sensitivity.

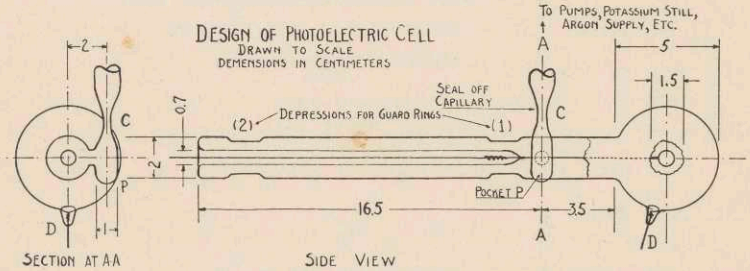
(6) The cell is then sealed off and is ready for use. All of this can be found in the literature.[1] The intention of the following instruction is simply to show one method by which these generalities can be reduced to the specific case for the benefit of those who are not specifically interested in the study of photoelectric cells as such, but are interested in using them as a laboratory instrument.

PREPARATION.

1. *Photoelectric Cell.*

The design of the cell depends on the type of work in which it is to be used, and therefore the specifications given here are to be taken simply as an example embodying many of the requirements common to all cells. The dimensions in cm. are given in the sketch in Fig. 1.

FIG. 1.



Features of the design shown here which might escape one's notice are called to attention in the following, and the reasons for their incorporation are given.

The cell should be made of Pyrex glass because it will withstand more heating in the presence of potassium without becoming brittle than other kinds. The connection (*A*) with the vacuum system and potassium still, should be made on the neck of the tube because in the distillation process it is necessary to keep the bulb cool. The "pocket" (*P*) at the entrance to the cell is provided in order to catch the liquid

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[1] H. E. Ives, *Bell System Technical Journal*, *5*, 320–335 (1926).

potassium after it passes through the capillary (*C*). The metal is heated in this pocket and passed into the cell as a vapor. If liquid metal is run directly into the hot cell, there will be the danger that it will break the glass due to the sudden chilling. If the potassium vapor instead of the liquid metal is run through the capillary, the distillation process will be found to be unnecessarily difficult as well as tedious. The space of 3.5 cm. between the pocket and the bulb is provided in order to make room for the air cooler to keep the bulb cool and to give space for the asbestos shields placed there to protect the bulb from the flames used in the distillation. See Fig. 6.

During the distillation, this part of the tube is kept at a temperature of about 300° C. by an electric heater which must be wound on before the cell is fastened to the vacuum system. The exact specifications of this heater are given below.

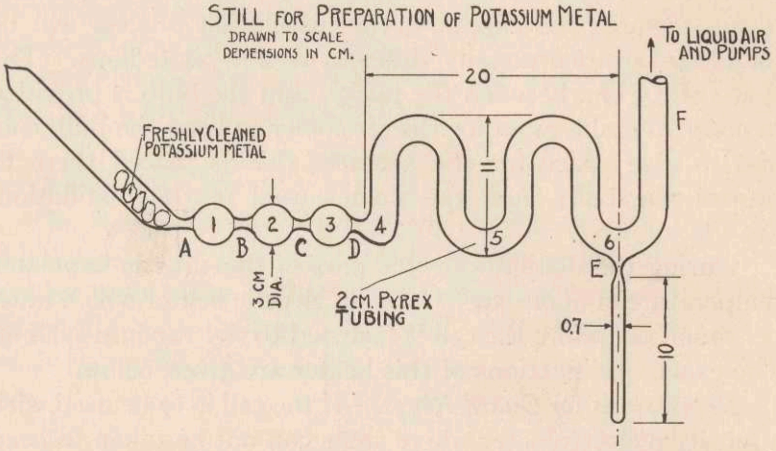
Depressions for Guard Rings.—If the cell is to be used with a sensitive electrometer where steps can not be taken to keep the cell in a very dry atmosphere, guard rings will be found necessary. Fifty to one hundred turns of No. 30 bare copper wire wound in the depressions (1) and (2), shown in Fig. 1, reduce the leakage current to a satisfactory value. The guard ring at (1) will usually be found sufficient if it is connected to "earth" along with the positive side of the battery and the shield of the electrometer. In case there is an electrometer deflection due to the potential of the voltaic cell set up between the copper ring and the tungsten seal of the central electrode over the surface of the glass, this can be greatly reduced by winding a second copper ring in depression (2) and connecting this one to the central electrode. The best way to support the cell when it is in use is by means of a band fitted around the guard ring at (1).

Location of the Outside Electrode.—The outside electrode (*D*) should be placed so that it is at the bottom of the cell when it is mounted on the system. The excess potassium will then flow around the nickel ring fastened to the tungsten seal and thus insure perfect contact between this lead and the potassium coat.

2. *Preparation of the Potassium Metal.*

A type of still in which the metal can be satisfactorily prepared is shown in Fig. 2. Two balls of potassium (1.5 cm. dia.) should be scraped clean, cut, washed in petroleum-ether or carbon-tetrachloride and carefully put into the tube as shown. (*Caution should be exercised not to allow the balls to make a hard impact with each other or with the glass because clean potassium catches fire very easily.*) The tube should be sealed as quickly as possible and the vacuum pump started. After ½ hour of pumping, the parts from "*A*" on through to "*F*" should be baked out quite thoroughly with gas burners. Then melt the potassium slowly into the first sphere (1) and seal off at "*A*." Then distill the metal into (2) and seal off at "*B*," etc. When the metal reaches (4) and "*D*" is sealed, it should exhibit a very clean appearance. Parts (5), (6) and the side tube should again be baked out with the flame. The metal can now be distilled into (5) and then into (6) where it can then be forced to flow down the side tube and sealed off at the capillary *E*.

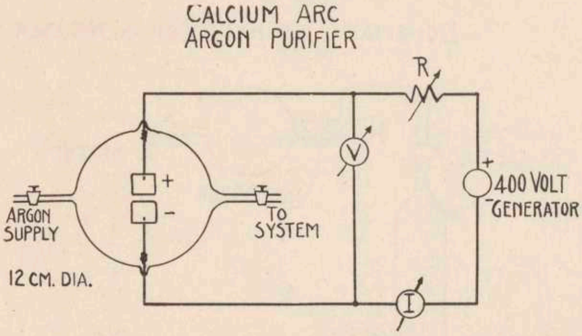
Fig. 2.



3. *Purification of the Argon.*

A calcium arc [2] purifier should be connected to the vacuum system through suitable stopcocks as shown in Fig. 5. The calcium arc argon purifier consists of two calcium blocks supported on connections and separated a distance of about 8 to 10 mm. Suitable electrical connections are shown in Fig. 3. The arc can be started after the circuit has been completed by causing the spark from a spark coil or from a Halliwell-Shelton violet ray generator to cross the gap between the electrodes. It is necessary to touch only one of the electrodes with the spark coil connection because the capacity to earth of the battery is sufficient to make the complete circuit for the spark discharge well enough to start the calcium arc. After the arc is started the pressure can be increased from the starting value of one mm. or so to any desired value without danger of putting out the arc. A high driving voltage (400 volts) and a high series resistance (450 ohms) are desirable for a strong and stable arc discharge. With a current of about 0.7 amp. the voltage across the arc should be about 80 volts. Six to eight hours running should "clean up" the argon. Mount the electrodes in the vertical position. A low pressure discharge tube (*G*) should be connected to the system as shown in Fig. 5, so that the argon can be introduced,

FIG. 3.



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[2] The "Misch Metal" arc is thought to be superior to the calcium arc by some experimenters.

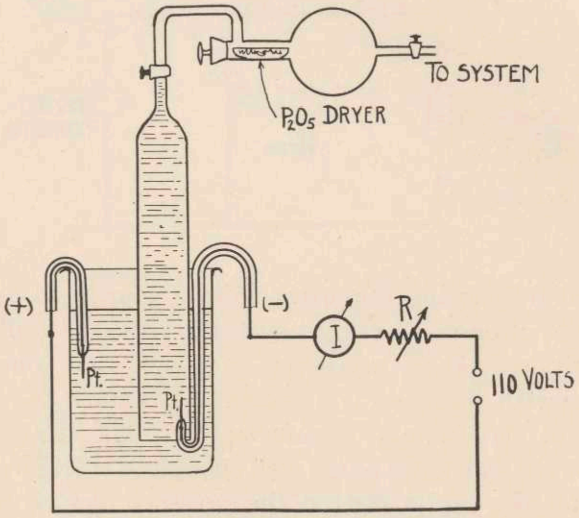
a discharge started, and impurities such as nitrogen be detected by direct vision spectroscopic observation.

4. *Production of the Hydrogen.*

Electrolytic hydrogen[3] produced as shown in Fig. 4 has been found to be suitable for the forming of the hydride. Three liters of freshly boiled distilled water to which has been added 50 gm. of phosphorous pentoxide makes a satisfactory electrolyte. With a suitable resistance *R* the current can be taken from a 110-volt source and adjusted to 0.5 amp. There is some danger of a little oxygen being carried into the hydrogen side if the generation is too rapid.

FIG. 4.

SCHEMATIC OF HYDROGEN GENERATOR



HEATERS FOR BAKING OUT AND DISTILLATION.

1. *Heater on Neck of Photo-cell.*

Before the cell is connected to the system two electric heating coils should be wound on the neck of the cell as shown

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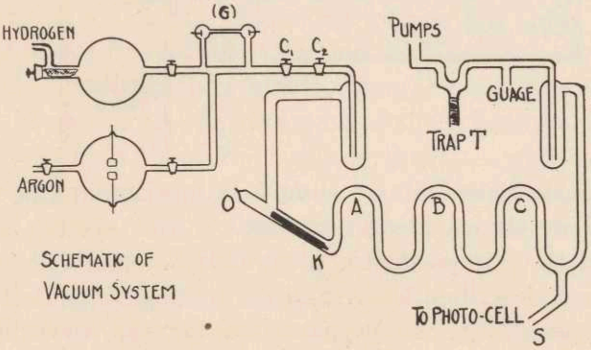
[3] Commercial hydrogen introduced through a palladium valve has been tried in other laboratories and thought to be superior to electrolytic hydrogen.

by H_1 and H_2 in Fig. 6. To make these heaters, wind on three layers of wet asbestos tape. Then wind two meters of No. 20 B. & S. nichrome wire held at each end by two turns of No. 18 copper wire. Three leads should be brought out, one for each end and one at the mid point. Three layers of asbestos tape (width 1.0 in.; thickness 0.015 in.), again wound on wet, will serve as an insulation to protect the outside of the heater. A heating current of 4.0 amps. for each coil can be furnished from a 12-volt battery and adjusted by means of a series resistance in each circuit.

FIG. 5.



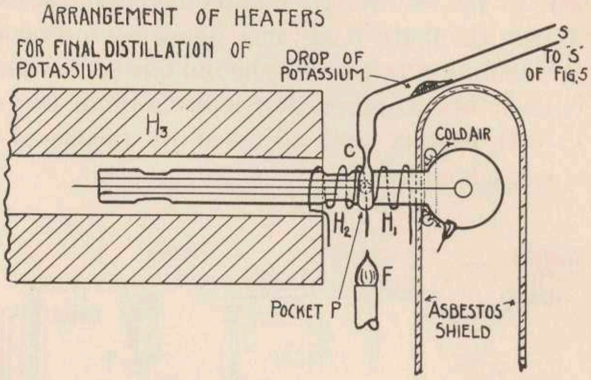
2. *Large Baking-out Oven.*

The connection *C–S* (shown in Fig. 6) to the vacuum system must be made to permit the enclosing of the entire cell in an oven in order to bake it out. A baking-out oven 17 inches long and 10 inches in diameter has been found to be perfectly satisfactory for this purpose. A temperature of 420° C. ± 10° should be maintained for a period of at least three hours, after which a temperature of about 340° C. should be held for at least one hour.

3. *Heater to Keep the Neck of the Photo-cell Clear.*

In order to prevent the condensation of potassium in the neck of the cell during the distillation process, a small oven (H_3) of Fig. 6 must be maintained at a temperature of 340° C. ± 10°. Temperature in excess of this value may drive out impurities from the glass which might contaminate the potassium surface while a lower temperature might allow enough potassium to condense in the neck to give an objectionable "dark current." The capsule of potassium prepared as described above should be broken at one end and inserted as shown at (*K*) in Fig. 5; the system sealed at (*O*), and the pumps started as quickly as possible. After the baking out described above and the baking of parts *A*, *B*, etc., with a gas flame, the preparations for the final distillation should be made. The heater (H_3) and the two auxiliary electric heaters should be started and allowed to come up to equilibrium temperature as specified above. Also the air blast coolers should be placed in position so as to keep the bulb cool at all times. (The air blast coolers consist of two perforated glass "half moons" formed so as to fit closely around the neck of the tube as shown.)

FIG. 6.

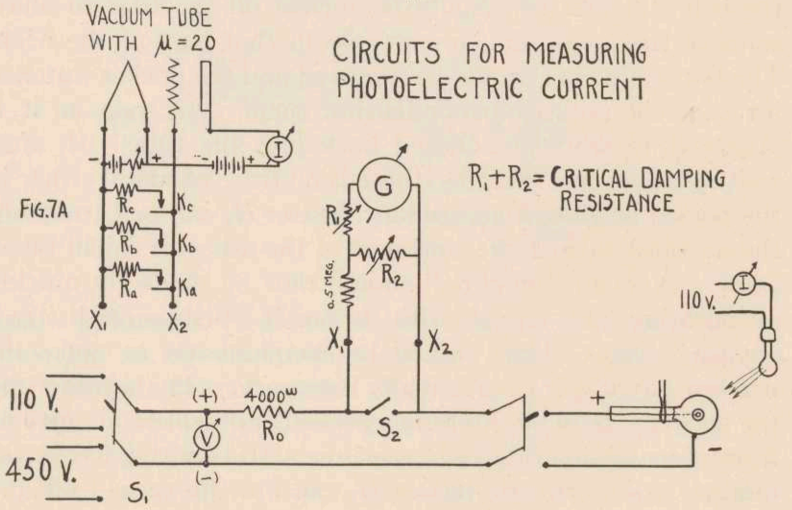


Melt the potassium and distill some of it over "*A*," "*B*" and "*C*," and force one drop at a time to roll down the side tube to the cell through the capillary and into the pocket *P*. One drop will fill the pocket if made the size shown in Fig. 1. The bunsen burner (*F*) shown in Fig. 6 should be adjusted to keep the pocket warm but not hot enough to cause rapid distillation. As soon as the drop has been driven into the pocket, additional heat from a small "gas-air" flame of a hand torch will quickly vaporize the metal, drive it through the opening in the neck where the electric heaters will keep it vaporized until it has condensed on the wall of the cool bulb. After three drops have been introduced in this way, the metal left in "A," "B" and "C" should be heated just enough to coat the inside of these tubes completely. This coat will help remove any impurities contained in either the argon or the hydrogen, which might otherwise contaminate the surface of the cell. Heater H_1 should be turned off in order to allow some of the potassium to condense in that part of the neck. The bunsen burner should be removed and the pocket watched for signs of potassium condensing there. As soon as it is observed, it should be chased back into the tube. If, after waiting about five minutes, there is no trace of metal either in the pocket or along the capillary, heater H_2 can be turned off; the air blast turned off; and part of the asbestos shield taken away. A small "window" should now be made by quickly evaporating the metal with a small, well-pointed "gas-oxygen" flame. Care should be exercised not to make the window any larger than is really necessary. The window and the pocket should be carefully watched and kept clean until no trace of metal deposit can be seen even after waiting five or ten minutes. The electric heater H_3 can now be turned off and removed.

CIRCUITS FOR MEASURING PHOTOELECTRIC CURRENT.

Two circuits for measuring the photoelectric current are shown in Fig. 7. The direct measurement method shown in the figure requires the use of a sensitive galvanometer such as the Leeds-Northrup 600-ohm instrument with a sensitivity of 13,000 megs. With this circuit it is easier to obtain quantitative results than with the circuit 7*a*. Circuit 7*a*, which can be inserted in Fig. 7 at x_1–x_2, has the following definite advantages: (1) Response is almost instantaneous; (2) during the time that the gas is being introduced into the cell continuous measurements of the photoelectric sensitivity can be made without the danger of overloading the measuring instrument in case a glow unexpectedly starts within the cell. The circuit shown in Fig. 7*a* should be set up with the vacuum tube (with $\mu = 20$ to 30), the resistances (R_a, R_b and R_c) and the keys (K_a, K_b and K_c) in a tight box with a dryer such as phosphorous pentoxide. Resistances R_a, R_b, R_c, etc., should be made in the usual way by drawing a long heavy line [4] with india ink in the form of a grid to give approximately the following resistances: $R_a = 300$ megs; $R_b = 40$ megs; $R_c = 6$ megs and $R_d = 1.0$ meg. If these resistances are mounted in glass tubes with connecting electrodes and evacuated, they will be found to be very free from "galvanic e.m.f.," and polarization, and remain constant indefinitely. The keys (K) should be designed after the manner of electrometer keys and be operated by strings as in the usual electrometer set up. With K_a operated and no current flowing through the cell, the grid of the tube will be at the potential of the negative side of the filament.[5] When a current flows through the cell and the resistance R_a, the grid becomes negative with respect

FIG. 7.



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[4] A line 1.0 mm. wide has a resistance of approximately 1.0 meg per cm. and one 0.4 mm. wide has a resistance of about 3 megs per cm. For most applications the mounting of the resistances in vacuum is not necessary.

[5] If the filament is not burned too brightly, the filament to grid current flowing through the 300-meg resistance will be less than $2(10)^{-9}$ and will introduce a small error only while the photoelectric current is small.

to the filament by the amount $V = R_a i$ and the plate current I of the tube will *decrease.* From the "grid voltage, plate current" characteristic of the tube, the V corresponding to the observed value of I will be known. Curves can be plotted (one for each value of R), which relate the plate current I and the photoelectric current i and thus make measurements with this circuit almost as quantitative as the more direct galvanometer method. The advantages of this method of measurement from the standpoint of safety and speed are obvious. In case a glow discharge or a short circuit takes place in the photo-cell or in its circuit connection, the current I drops to zero and no harm is done.

FORMATION OF THE HYDRIDE.

One of the measuring circuits drawn in schematic in Fig. 7 should be set up to measure the photoelectric sensitivity using a 75-watt lamp (equivalent to about 100 c.p.) as a source of light at a distance of one meter. With an applied voltage[6] of 110 v. the current should be about 5×10^{-9} amp. The system should be cut off from the pumps by means of a mercury trap T of Fig. 5, and hydrogen introduced by means of the double stopcock trap C_1 and C_2 of Fig. 5, while the photoelectric current is being watched continuously. At a pressure of about 0.1 mm. of Hg. the maximum sensitivity will be reached. The current should now be in the neighborhood of 25×10^{-9} amp. After the galvanometer has been short-circuited by switch S_2 of Fig. 7, the application of 450 volts at S_1 should start a glow discharge or "flash" within the cell. Cut off the discharge after it has run 0.2 to 0.3 sec. and again measure the sensitivity. It should show a large increase. In case the discharge does not start spontaneously, it can be started with the spark coil. After six to ten flashes of this kind a maximum in sensitivity should be reached with a current of about 400×10^{-9} amp. The system must now be pumped out and "flushed" with argon four or five times and then pumped down for one-half hour or more. Under the

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[6] If circuit 7*a* is used, a voltage nearer the critical voltage can be safely used. If one of the electrical restrictions placed on the problem is the operating voltage, then that required voltage should be used here instead of 110 volts.

vacuum condition the photoelectric current should be 80 $\times 10^{-9}$ amp. The introduction of argon to a pressure of about 0.1 mm. should bring the cell up to its maximum of sensitivity with a current of about 600 $\times 10^{-9}$ amp.

DETERMINATION OF THE CRITICAL VOLTAGE.

With the galvanometer well protected by shunt and series resistances (R_1 and R_2), gradually increase the voltage until a rather sudden increase in current shows up which does not depend on the presence of the light source. Cut off the potential and again bring it up slowly to within about 10 volts of the critical voltage just found and make sure that the current falls to zero when the light is out. The current flowing with this voltage ($180 - 10 = 170$ volts for the cell described here) should now be about 3500 $\times 10^{-9}$ amp. Seal off the cell heating the capillary at *C* as quickly as possible and check the reading, supporting it in about the same position as before. Again check this final reading after 48 hours. If no change can be detected within that time this cell can be considered satisfactory and if not misused will remain quite constant in its response for a long time.

TABLE OF PHOTO-CURRENT AT EACH STEP.

Vacuum	5 $\times 10^{-9}$ amp.
Hydrogen to max	25
Flash to max	400
Vacuum	80
Argon to max	600
Critical voltage—10 v.	3500

To Dr. W. F. G. Swann, under whose direction this work was carried out, I am indebted for many valuable suggestions.

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