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A STUDY OF THE PHOTOELECTRIC PROPERTIES OF SOLUTIONS  
OF POTASSIUM IN LIQUID AMMONIA

Adam S. Kowalczyk

A thesis submitted in partial fulfillment of  
the requirements for the degree of Master of  
Science at Loyola University, Chicago, Ill.

August, 1940

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I wish to express at this time my wholehearted appreciation and thanks to Dr. George M. Schmeing for his encouragement, advice, and guidance which were invaluable at all times during the course of this work. I want also to thank Dr. Ardith P. Davis and other members of the department of Chemistry for their kind help and advice in connection with this problem.

## Introduction

Earlier investigations concerning the photoelectric properties of ammonia solutions of alkali metals began with the work of Kraus<sup>1</sup>

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<sup>1</sup> J. Amer. Chem. Soc. 43, 749, (1921)

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who studied a solution of lithium in liquid ammonia. Kraus' work was qualitative and reported some evidence of a photoelectric effect. He introduced 0.25 grams of lithium into a tube with a platinum wire sealed in at the bottom to make contact with the solution. An aluminum wire, fixed about 3.5 cm. above the metallic solution, was connected to an electrometer which was discharged to ground through the photocell. When the metal dissolved in the ammonia and the surface of the solution was irradiated with light from a 16 candle-power lamp held about one foot above the solution, a photoelectric current was immediately observed.

Chittum and Hunt<sup>2</sup> reported that a solution of

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<sup>2</sup> J. Phys. Chem. 40, 581, (1936)

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sodium in liquid ammonia gave no photoelectric response. They studied the photoelectric properties of

a sodium solution in a closed cell at a low temperature, so that the ammonia vapor pressure was only 1 to 5 mm.. The electrodes were of platinum, and the anode was about 6 cm. above the solution. No current was detectable in a sensitive galvanometer even when a 220 volt driving force was applied. Experiments carried out under different light intensities gave the same negative result. Pure metallic sodium, however, exhibited photoelectric properties under the same experimental conditions.

Crapple<sup>3</sup> finally demonstrated that a solution of

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<sup>3</sup> Unpublished dissertation, University of Chicago,  
March (1933)

sodium in liquid ammonia produces a photoelectric effect when irradiated. Crapple used a cell in which the surface of the solution was not readily renewable. He obtained photocurrents, measured by a galvanometer, with light from a tungsten-filament, gas filled lamp held close to the cell. Currents as large as  $2 \times 10^{-7}$  amperes were observed.

George M. Schmeing<sup>4</sup> later studied the spectral

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<sup>4</sup> Published dissertation, University of Chicago,  
June (1939)

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photoelectric response of solutions of sodium in liquid

ammonia at various temperatures and concentrations. The photocurrents were measured by an electrometer, and the relative flux of the light was found with a thermopile-galvanometer. Light from a quartz mercury arc was passed through a monochromator, and a cell was designed to permit ready renewal of the surface of the solution. The quotient, electrometer reading, galvanometer reading, was plotted as ordinate against the wavelength of the radiation incident upon the surface of the solution. A maximum current of  $26.6 \times 10^{-13}$  amp. was obtained with light of wavelength  $3650 \text{ \AA}$ , and a minimum of  $4.84 \times 10^{-13}$  amp. at  $5790 \text{ \AA}$ .

In this work solutions of potassium in liquid ammonia were irradiated with light from a 75 watt-115 volt G.E. Mazda bulb held about one meter above the photocell. The photoelectric current was measured by an electrometer which was previously calibrated. It was planned in the earlier part of this work to determine whether solutions of sodium in amines produce a photoelectric current when irradiated with an intense light source. However, it was found that sodium is insoluble in diethyl amine and aniline, the two selected because they are liquids at room temperature and are easily obtainable in pure form. In determining whether or not the metal was soluble, a small

cube of sodium was cut, immediately dropped into the amine, and the container shaken. In the case of diethyl amine an evolution of a gas was observed in a few minutes. The container was allowed to stand undisturbed for a few days at room temperature. By that time a white amorphous solid had formed, which turned to a deep brown color upon exposure to air for a few hours. There was no evidence of a reaction between sodium and diethyl amine near the freezing point of the amine ( $-50.0^{\circ}$  C.). The same procedure was followed to determine whether sodium is soluble in aniline. Altho the container was shaken from time to time, no change was observed after a week of standing at room temperature.

#### Apparatus

The photocell (shown in detail in figures 1 and 2) is the same one that Dr. G. M. Schmeing used in his work on the spectral photoelectric response of solutions of sodium in liquid ammonia. The ring to collect photoelectrons was of platinum, electrically welded to a tungsten wire sealed into the glass. The light source used was a 75 watt-115 volt G.E. Mazda bulb. Figure 4 shows the cell in its circuit. Two heavy duty, 45 volt "B" batteries, V (fig. 4), supplied voltage for the cell. Two similar batteries were used in the calibration circuit.

as a source for the potential on the electrometer needle. A brass tube fitted with paraffined cork stoppers into which was inserted pyrex tubing coated with paraffin, served as the shield for the wire connecting the photocell to a Dolezalec electrometer. The wire for this connection was double cotton covered copper wire impregnated with paraffin. Contact with the wire leading from the electrometer to the photocell was made through mercury in tubes G and H (fig. 1 and 2) by means of nickel tipped copper wires.

The Dolezalec electrometer is essentially made up of three parts: two fixed conductors, called quadrants and a suspended conductor, called the needle. The quadrants consist of a brass chamber split into four parts. Opposite quadrants are connected together with wires, each pair serving as a fixed conductor. One set of quadrants is grounded, and the other is raised to the potential being measured, the final deflection of the needle being a measure of the difference of potential between the quadrants. When in use, the needle is charged to a high potential (90 volts) supplied by two 45 volt "B" batteries. It is made of aluminum, flat, and shaped in the form of a figure eight. It is suspended by means of a gold-sputtered quartz fibre. The needle and quadrants are supported



on amber blocks to prevent any electrical leak when extremely small currents are being measured. The apparatus is surrounded by a grounded metal case to cut off air currents, and to serve as a shield against stray electrostatic and magnetic charges. The deflection of the needle is observed with a telescope focused on a small mirror fastened to the quartz fibre suspension. The mirror reflects a scale about 2.5 meter away.

The electrometer connections are shown in figure 3. The needle N is kept at a fixed potential of 90 volts by battery B. One pair of quadrants is connected to the ground and the other to the platinum ring in the photocell as previously described.  $R_4$  is a protective resistance of 40,000 ohms used to prevent burning out the battery and suspension in case the needle should accidentally touch one of the quadrants. The electrometer is again shielded by a grounded metal box, lined internally with cotton to prevent sudden changes in the temperature of the air surrounding the electrometer. The metal box is fitted with a tower filled with anhydrous calcium chloride to maintain constant humidity. The entire apparatus rests upon a firm, heavy base to minimize drifts of the electrometer needle due to external vibration in the room and vicinity.

The electrometer calibration circuit is also shown

in figure 3. A dry cell, C, (1.6 volts) is connected across the resistances  $R_1$  and  $R_2$ .  $R_1$  is a high resistance of 10,000 ohms.  $R_2$  is a Leeds and Northrup resistance box capable of measuring up to 9,999 ohms.  $R_3$  is a resistance  $10^{10}$  ohms.

Calibration of the electrometer was carried as follows. 90 volts was applied to the needle by means of switch  $S_1$ . If the needle was deflected at this time, the instrument had to be leveled by means of leveling screws, so that the needle will remain in a symmetrical position between the quadrants. If no deflection was observed when the voltage was applied to the needle, the electrometer was at a mechanical and an electrical zero.  $R_2$  was then set at a definite value and the electrometer grounding switch  $S_2$  opened. The deflections at definite resistances were recorded. These values were plotted, giving a straight line curve. From this curve the voltage producing a definite deflection is easily obtained, and the current can be calculated from Ohm's law.

A diagram of the vacuum line is given in figure 5. It consists of a manifold one meter long and 2.5 cm. in diameter to which six stopcocks were sealed as shown. Two manometers, one a closed end and the other an open end, were sealed into the line. Stopcock A opened to a

three-stage mercury condensation pump and a Cenco Hi-Vac oil pump. The ammonia was drawn from the line by means of a Chapman pump through stopcock B, and then through standard sulfuric acid. A test tube, containing a small piece of potassium and a glass ampule with a long capillary neck placed in an inverted position over the potassium, was connected to stopcock C through a two-hole rubber stopper. The test tube was evacuated and the potassium melted by means of a stearic acid bath. Air, passed through anhydrous calcium chloride and phosphorous pentoxide, was then admitted into the test tube driving the molten potassium into the glass ampule. The ampule was weighed and placed in the photocell clamped in a horizontal position. A glass weight broke the ampule when the cell was turned to a vertical position. Two 3 liter bulbs, F, which served as storage bulbs for ammonia vapor were also sealed to the manifold. D led to a tank of ammonia, E to the photocell.

### Procedure

A small piece of potassium, which was stored in oil, was cut and placed in the photocell. The system was evacuated until no current leak across the cell was observed. The pumps were shut off, and the line filled to atmospheric pressure with ammonia from a storage tank containing sodium ribbon. An acetone-dry ice bath prepared in a silvered dewar was then slowly raised about the lower part of the cell. A deeply colored solution formed within a few minutes. This solution was stirred by motion of the cell and decanted over a barrier B (fig. 1 and 2), into the photocell proper. The solution was then exposed to light from a 75 watt-115 volt GE. Mazda bulb held at a distance of one meter from the cell. The electrometer deflection was recorded.

When the measurements were completed, the ammonia was drawn off through a measured amount of standard sulfuric acid and the excess acid titrated with standard sodium hydroxide. The potassium residue was removed by dissolving it in a 50-50 mixture of petroleum ether and 95% ethyl alcohol. Aliquot parts of this were titrated with standard sulfuric acid to determine the amount of potassium used.

Data

Barometric pressure	754.6 mm. (uncorrected)
Room temperature	23°C.
Temperature of cooling bath	-62° c.
Volume of photocell	395 ml.
Normality of base	1.910      0.005
Normality of acid	1.889      0.005

Quantity of potassium determined by titration:

Indicator used	Weight of potassium
phenolphthalein	0.2259 grams
Methyl Orange (in xylene cyanol)	0.1408 grams

Note: The discrepancy in the values for the amount of potassium used may in part be explained when the volume of acid required to neutralize 25 cc. of the solution of potassium in the 50-50 mixture is compared.

Indicator	Volume of standard acid	
	#1	#2
Phenolphthalein	0.30 cc.	0.31 cc.
Methyl Orange	0.20cc.	0.18 cc.

Color of solution      deep blue with a mettalic  
(potassium in liquid ammonia) luster

The electrometer was read with the photocell disconnected from the battery and at room temperature.

These readings ranged from 2.5 to 0.5 cm. from the mechanical and electrical zero of the instrument.

When light from a 75 watt-115 volt G.E. Mazda bulb was permitted to fall upon the surface of the solution from a distance of about one meter, the electrometer needle was deflected off the scale. The bulb and photocell were shielded with a sheet of copper which was grounded. Because the photocurrent produced under the conditions of the experiment was too large, no readings were obtainable to calculate the magnitude of photocurrent.

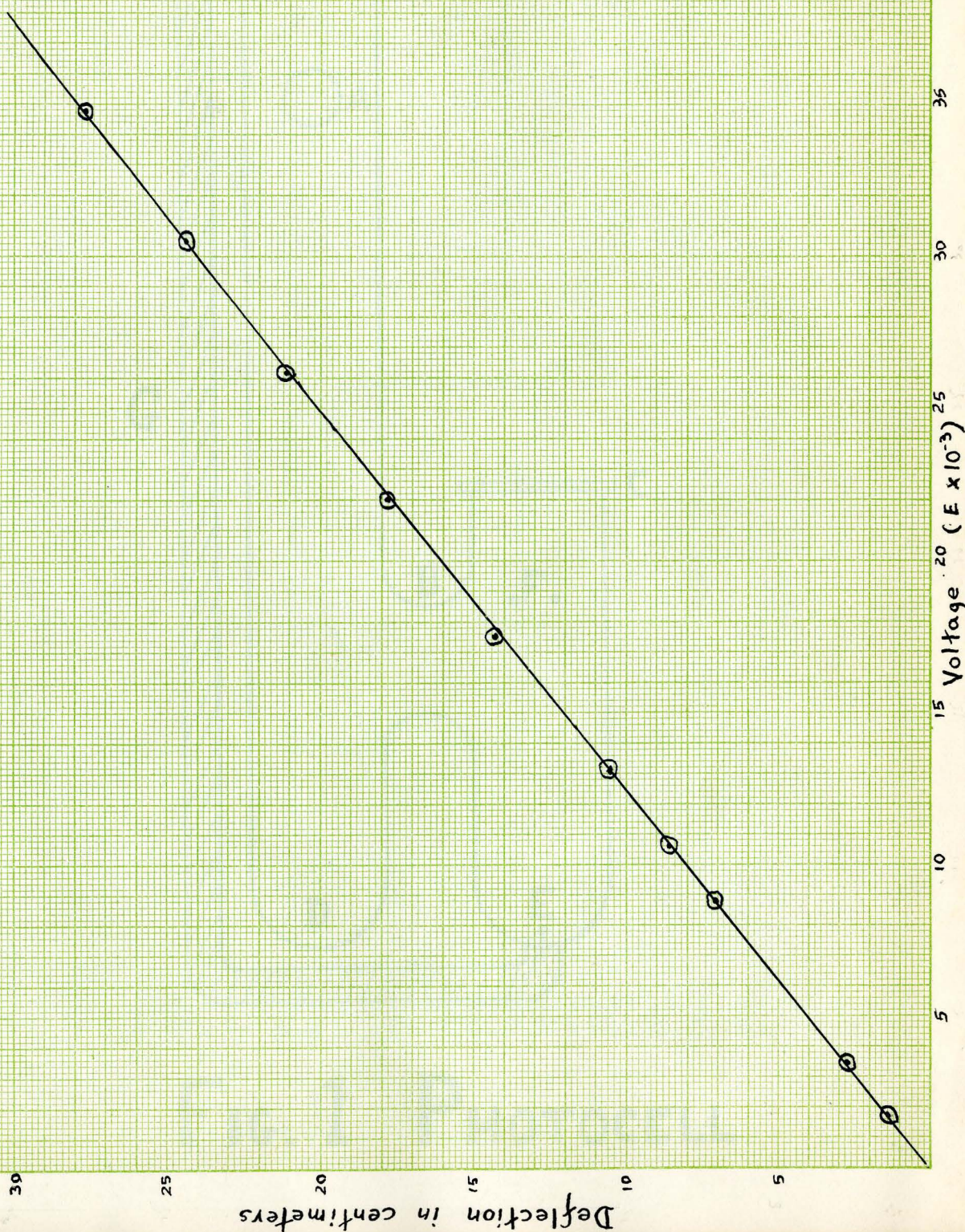
#### Summary

When light from an ordinary electric light bulb struck the surface of a solution of potassium in liquid ammonia, a photoelectric current was produced. The current was not measureable under the conditions under which the experiment was carried out.

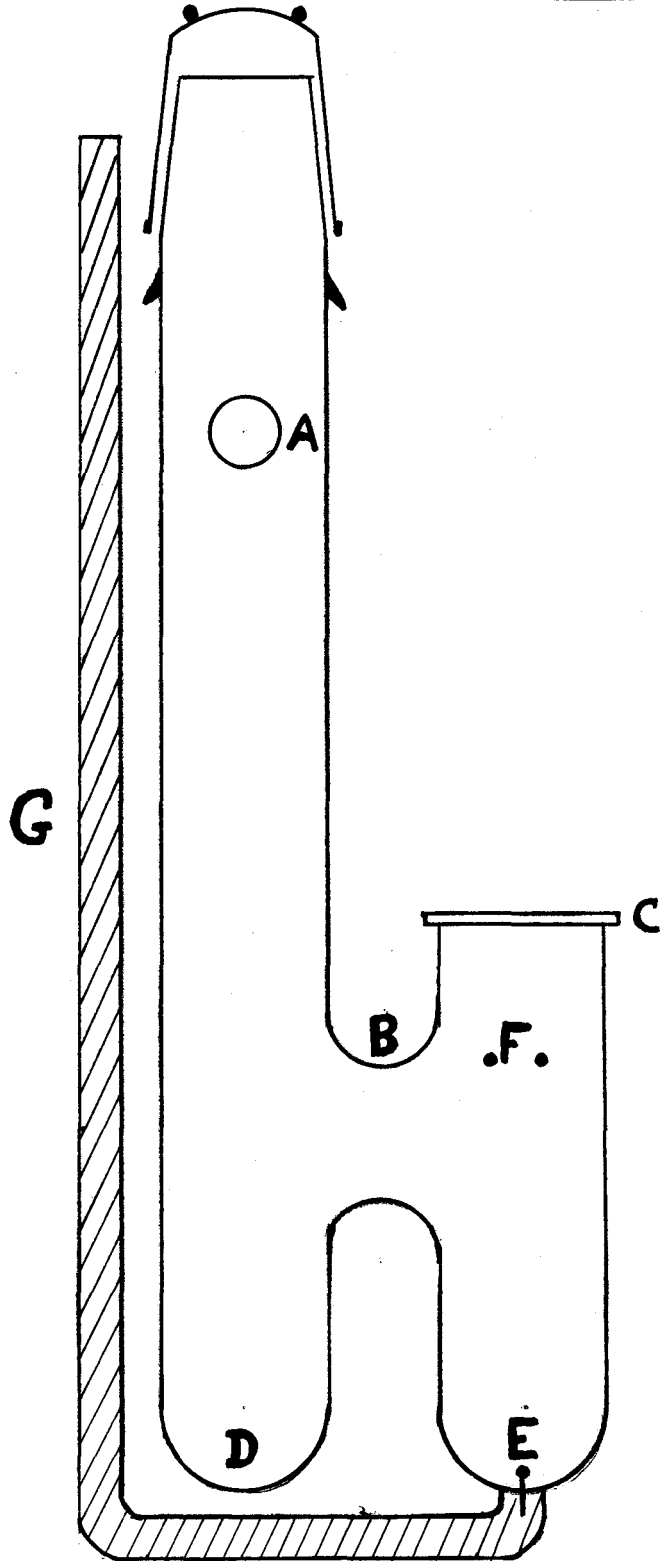
Electrometer Calibration Data

$R_1$	Zero reading	Final reading	Difference	$E \times 10^{-3}$
10	19.1	20.3	1.2	1.77
20	19.1	21.7	2.6	3.54
50	19.1	26.1	7.0	8.84
60	19.0	27.5	8.5	10.6
75	19.1	29.5	10.4	13.2
100	19.0	33.2	14.2	17.6
125	19.0	36.7	17.7	21.9
150	19.0	40.2	21.1	26.2
175	19.1	43.4	24.3	30.5
200	19.1	46.8	27.6	34.8

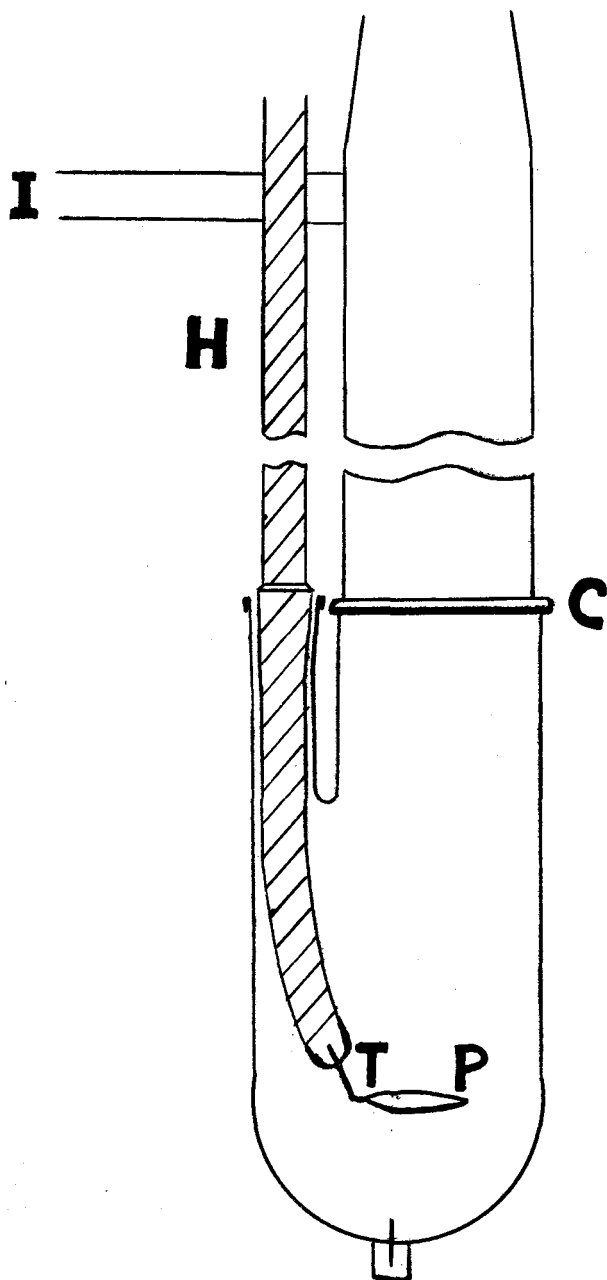
The sensitivity of the electrometer was such that 1 cm. deflection was produced by  $1.26 \times 10^{-13}$  amperes.



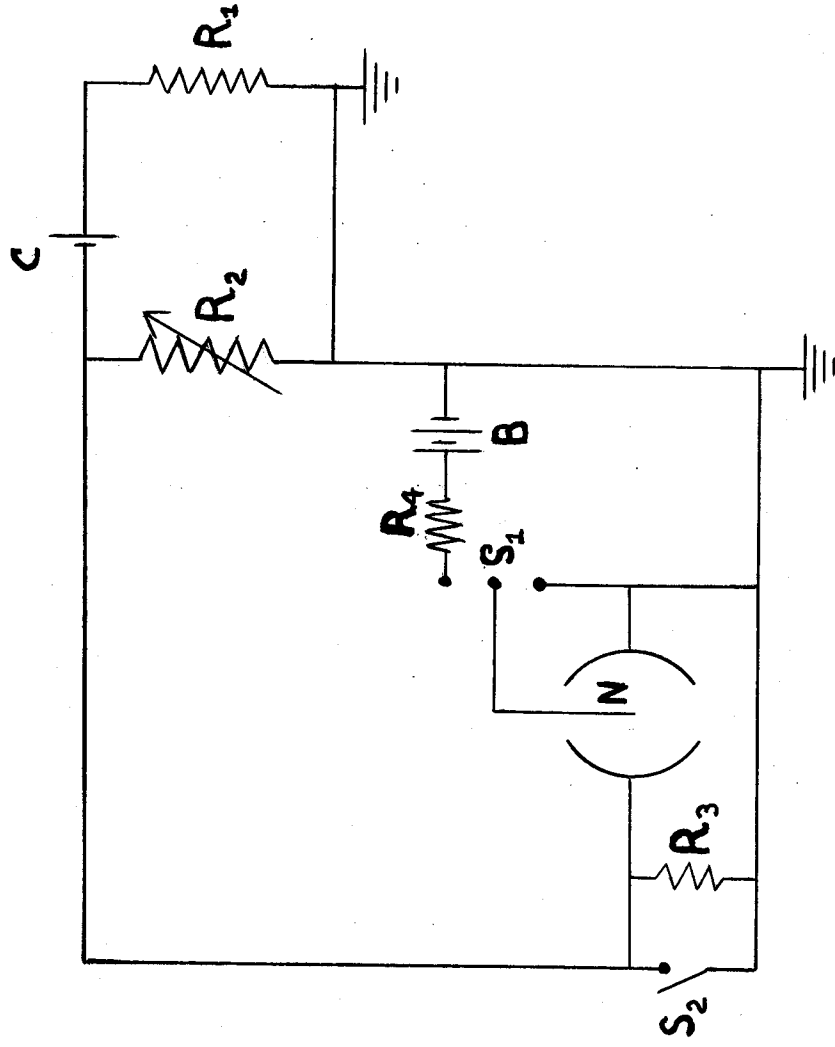




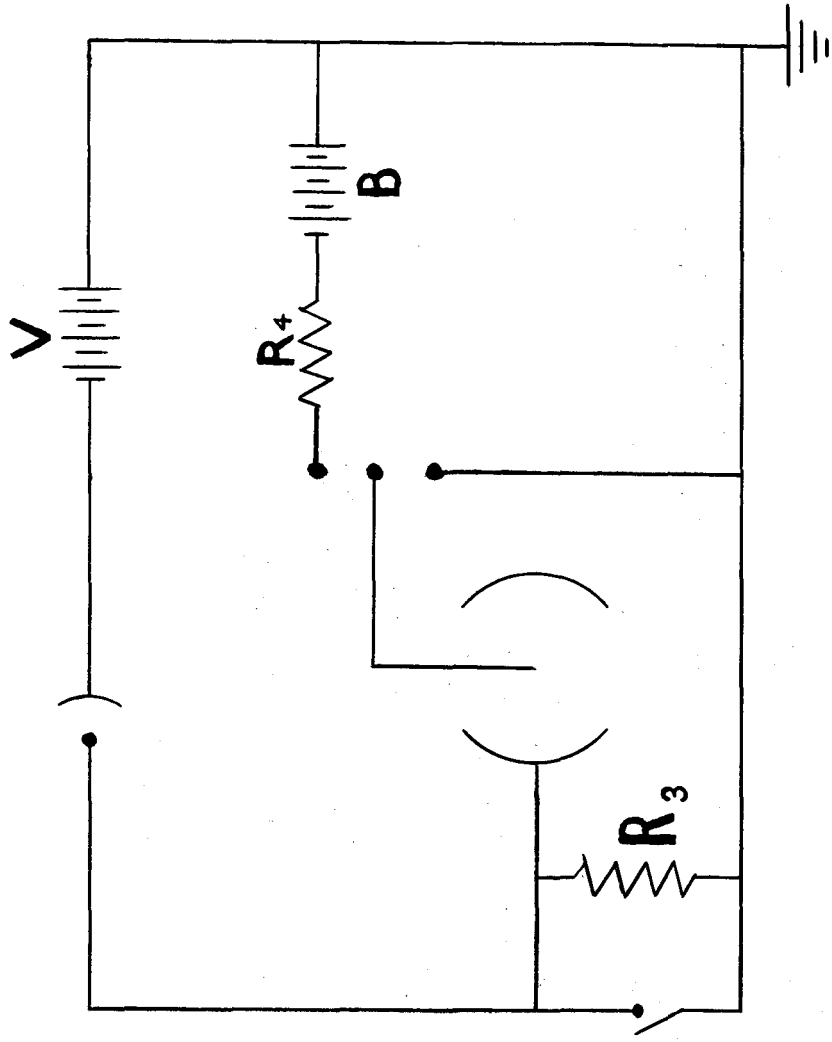
**FIG. 1 PHOTOCCELL**



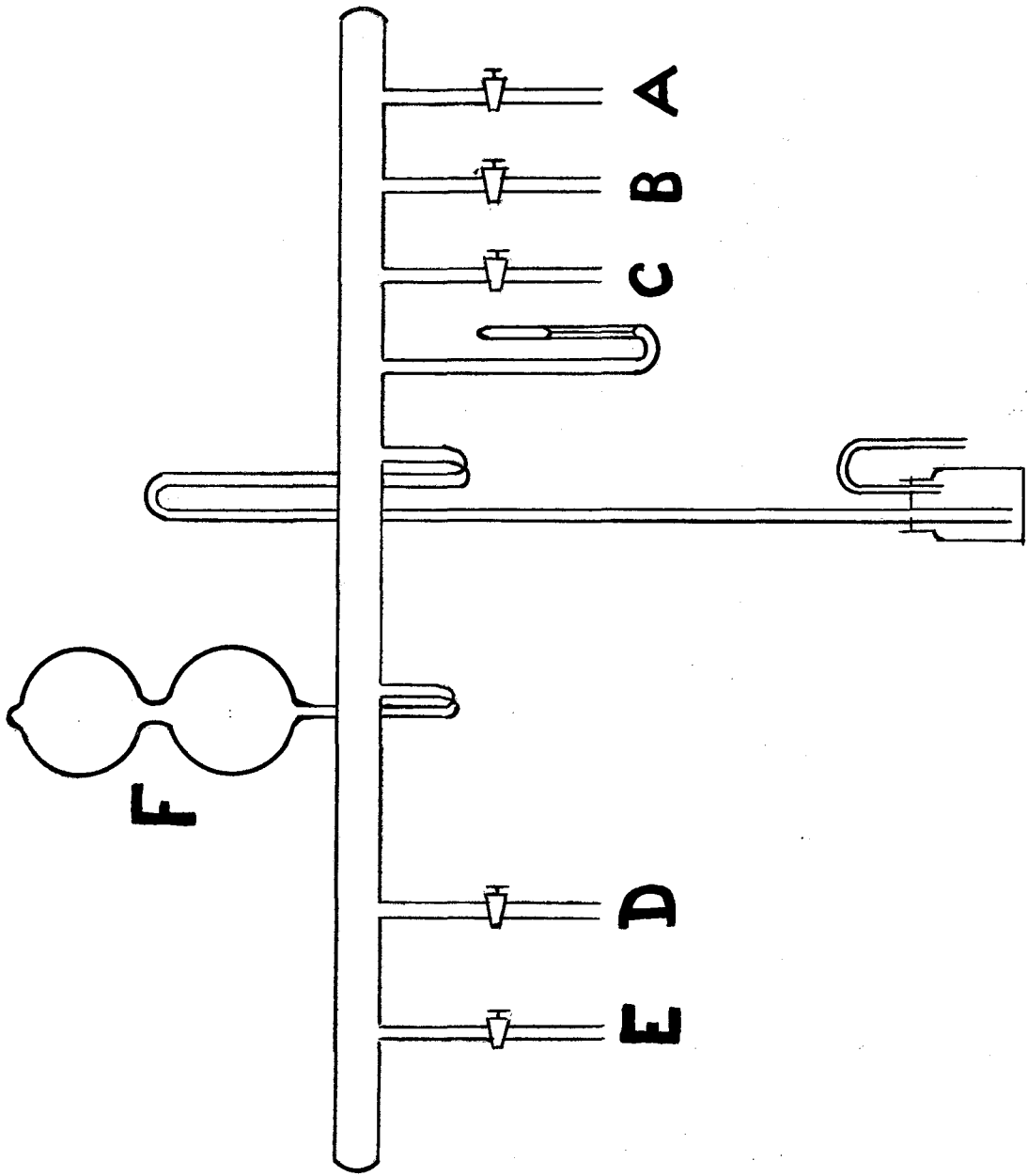
**FIG. 2 PHOTOCCELL**  
**Side View**



**FIG. 3 ELECTROMETER CALIBRATION  
CIRCUIT**



**FIG. 4 ELECTROMETER <sup>P<sub>4</sub></sup> PHOTOCELL  
CIRCUIT**



**FIG. 5 VACUUM LINE**

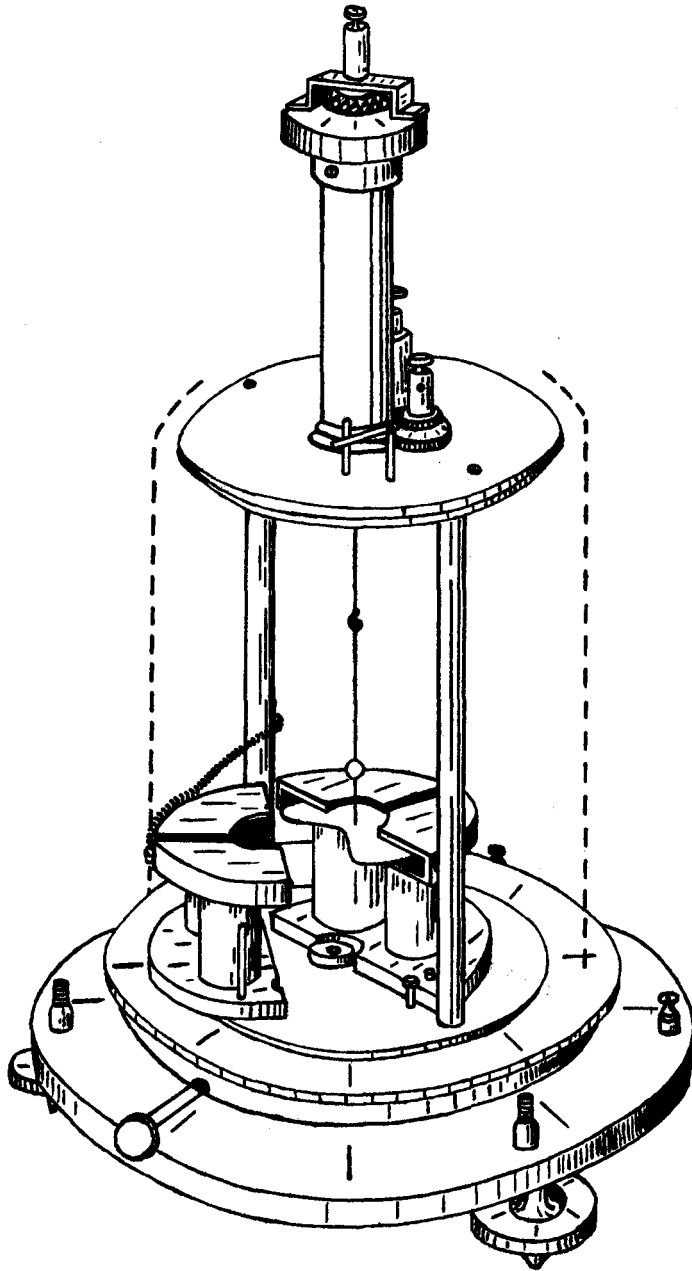
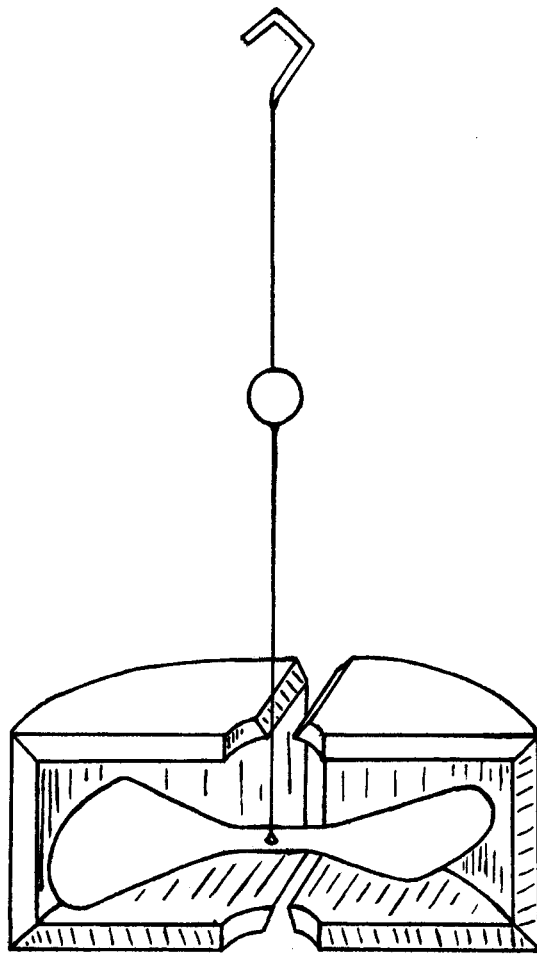
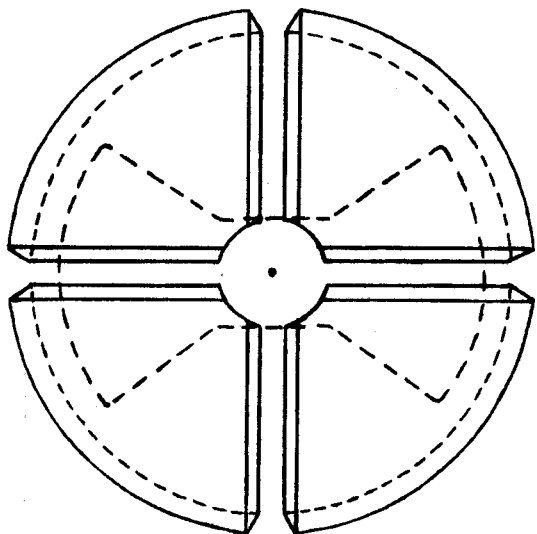


Figure 6, Electrometer with metal case removed



Side view



Top view

Figure 7. Electrometer quadrants

The thesis, "A Study of the Photoelectric Properties of Solutions of Potassium in Liquid Ammonia", written by Adam S. Kowalczyk, has been accepted by the Graduate School with reference to form, and by the readers whose names appear below, with reference to content. It is, therefore, accepted in partial fulfillment of the requirements for the degree of Master of Science.

Dr. George Schmeing

June 4, 1940

Dr. Joseph Parent

June 7, 1940