

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

Photovoltaic Cells: The Spectral Sensitivities of Copper, Silver and Gold Electrodes in Solutions of Electrolytes

BY PAUL E. CLARK AND A. B. GARRETT

The spectral sensitivities of metal and coated-metal electrodes are useful data, in conjunction with other cell characteristics, for the interpretation of the mechanism involved in photovoltaic cells. Spectral sensitivities may also prove to be

valuable for the determination of the potential barrier at a metal-solution interface.¹ Moreover, information concerning the effect of light of different wave lengths upon metals commonly used for various types of electromotive force measurements should be made available. This paper reports the determination of spectral sensitivity values of copper, silver, and gold electrodes from $\lambda = 3650$ to 6908 \AA . These three metals were chosen for this work chiefly because (1) copper and silver are known to have definite photovoltaic action,^{2,3} so much so that silver electrodes must be protected from light when used in the potentiometric titration of halides and (2) copper, silver and gold are closely related due to their similar electron configuration.

voltaic cells composed of metal electrodes in solutions of electrolytes has been reported by several workers,⁴⁻⁷ but no systematic study of the spectral sensitivities is reported for this type of cell. However, Athanasiu⁸ has determined the spectral sensitivity of coated metal electrodes of Ag-AgI and Hg-Hg₂I₂ electrodes. Other reported work on spectral sensitivities of coated electrodes is less quantitative and not complete enough for the purpose outlined above.

Experimental

The Solutions.—All solutions used were prepared volumetrically from reagent quality chemicals. Conductivity water was used in all of these preparations.

The Cells.—The cell used was H-type with a chemical Pyrex⁹ window through which one electrode could be illuminated and which transmitted radiation from $\lambda = 3300$ to $25,000 \text{ \AA}$. The electrodes were stamped from sheet metal giving uniform disks approximately 8 mm. in diameter. These were fused to wire of the same metal, polished with 4/0 polishing cloth, annealed in an atmosphere of hydrogen and again cleaned and polished.

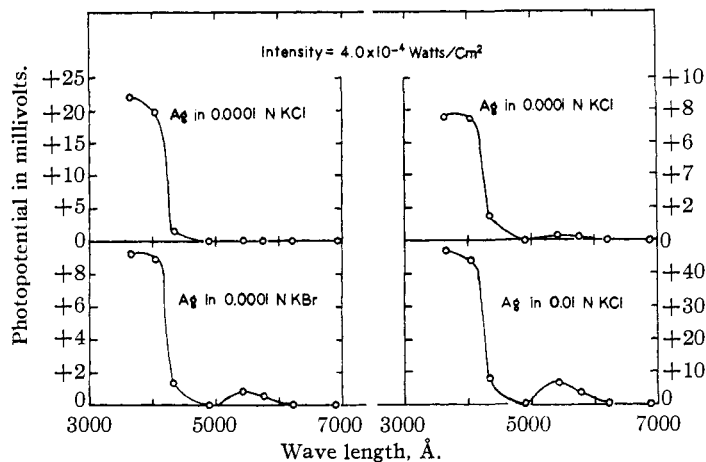


Fig. 1.

Some previous work on observations of photovoltaic cells composed of metal electrodes in solutions of electrolytes has been reported by several workers,⁴⁻⁷ but no systematic study of the spectral sensitivities is reported for this type of cell. However, Athanasiu⁸ has determined the spectral sensitivity of coated metal electrodes of Ag-AgI and Hg-Hg₂I₂ electrodes. Other reported work on spectral sensitivities of coated electrodes is less quantitative and not complete enough for the purpose outlined above.

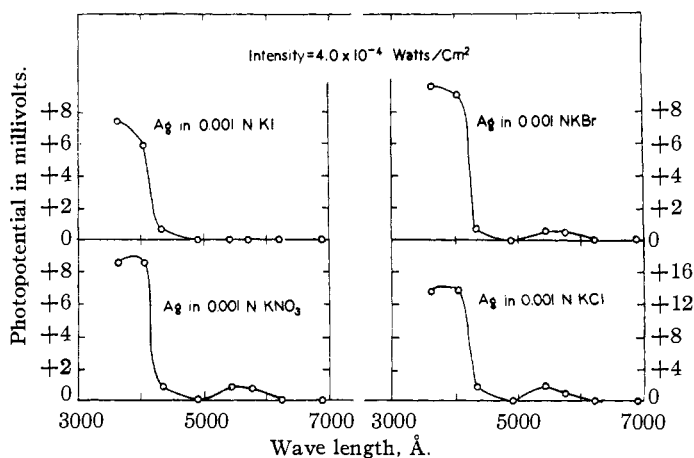


Fig. 2.

Some previous work on observations of photovoltaic cells composed of metal electrodes in solutions of electrolytes has been reported by several workers,⁴⁻⁷ but no systematic study of the spectral sensitivities is reported for this type of cell. However, Athanasiu⁸ has determined the spectral sensitivity of coated metal electrodes of Ag-AgI and Hg-Hg₂I₂ electrodes. Other reported work on spectral sensitivities of coated electrodes is less quantitative and not complete enough for the purpose outlined above.

(1) Gurney, "Ions in Solution," The University Press, Cambridge, England, 1936.

(2) Copeland, "The Photovoltaic Effect," M.S. Thesis, The Ohio State University, 1936. This gives a complete bibliography of the literature concerning Photovoltaic Cells.

(3) Hughes and DuBridge, "Photoelectric Phenomena," McGraw-Hill Book Company, Inc., New York City, N. Y., 1932, Chapter IX.

(4) Athanasiu, *Compt. rend.*, **178**, 386 (1924); **178**, 561 (1924).

(5) Sihvonen, *Ann. Acad. Sci. Fennicae*, **26A**, 3 (1926).

(6) Schlivitch, *Compt. rend.*, **182**, 891 (1926).

(7) Audubert, *ibid.*, **177**, 818 (1923); *ibid.*, **177**, 1110 (1923); **194**, 82 (1932); **189**, 800 (1929); **189**, 1295 (1929); *J. chim. phys.*, **24**, 357 (1927); *J. phys.*, **6**, 313 (1925).

(8) Athanasiu, *Compt. rend.*, **181**, 101 (1925); *Ann. phys.*, [11] **4**, 377 (1935).

(9) The Corning Glass Works, Corning, New York.

Each wire lead was then drawn through a small glass cylinder filled with paraffin, one side of the disk was coated with paraffin and the other side again polished. These were

to the cell were carried through the thermostat wall in glass cylinders filled with sulfur.

The Illumination Source.—A 100-watt mercury vapor lamp, type H-4, manufactured by the General Electric Company, was used as the source of illumination. The characteristics of this lamp are given in Table I.

Monochromatic radiation was obtained by means of a series of glass filters manufactured by the Corning Glass Company.

The Intensity Measurements.—A Moll Microthermopile was used for the measurement of the intensity of the radiation for each filter at various positions of the mercury lamp. This thermopile was calibrated by means of a standard carbon filament lamp which was standardized by the National Bureau of Standards. The calibration was extended to higher intensities than those obtained from the standard lamp at the distance specified by the National Bureau of Standards. This was done with the use of a second standard lamp working at a higher current and by the methods suggested by Leighton and Leighton,¹²

as well as by Forbes.¹³ A linear relationship of (galvanometer deflection/intensity) for the galvanometer-thermopile system was obtained up to 30 cm. deflection; this

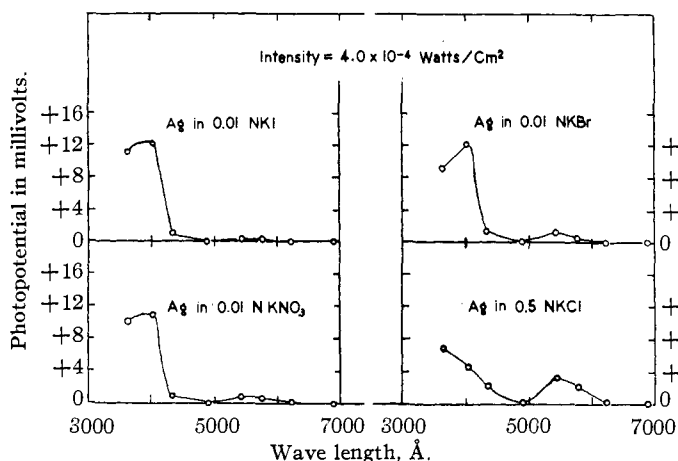


Fig. 3.

washed carefully in conductivity water and placed in the solution in which they were to be used. The silver electrodes were made of Eimer and Amend¹⁰ 999 fine silver, the gold electrodes of Eimer and Amend 24 carat gold and the copper electrodes of pure annealed sheet copper. The copper oxide coating was obtained by heating the copper electrodes in an atmosphere of oxygen. The silver bromide electrodes were obtained by electrolyzing silver electrodes in a solution of silver bromide. The bimetallic electrodes were prepared by electroplating processes recommended by Blum and Hogaboom.¹¹

The Thermostat.—The thermostat was a water-bath insulated by means of four concentric tanks of mirror tin, which were separated by wood, air and glass wool, respectively. A top for the bath was of similar construction. This insulation reduced heat transfer to a minimum and eliminated the necessity of an electrical thermostat control which might have been a source of parasitic currents to be picked up by the Plotron circuit. This type of thermostat gave very steady temperature control; any temperature change in this thermostat was of a unidirectional nature rather than of a fluctuating nature. Such a characteristic is valuable in determining accurately the dark potential drift of the cells studied if any of the potential drift is due to a thermal effect. A chemical Pyrex glass⁹ window was mounted in one side of the thermostat. A camera shutter and a glass filter holder were mounted opposite the glass window on the outside of the thermostat. The cell was placed in line with the glass window, in the thermostat, on a mounting on which could also be mounted a thermopile in the place of the cell. The wire leads

(10) Eimer and Amend, Third Avenue, New York, N. Y.

(11) Blum and Hogaboom, "Principles of Electroplating and Electroforming," 2d ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1930, p. 362 for gold on silver or platinum, p. 219 for copper on silver.

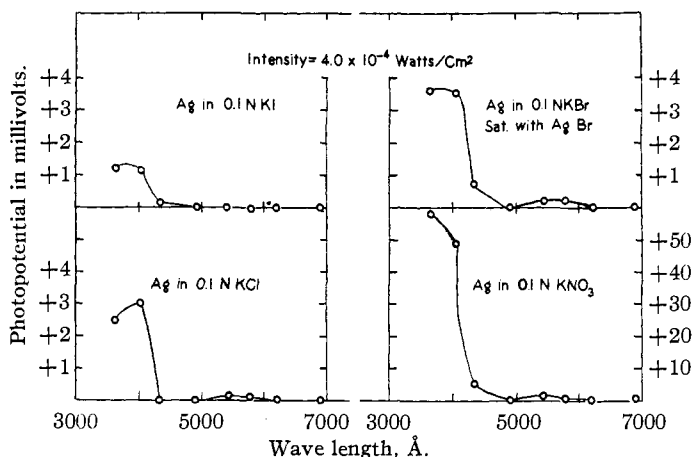


Fig. 4.

TABLE I
SPECTRAL DISTRIBUTION DATA FOR ILLUMINATION SOURCE
As given by the General Electric Vapor Lamp Co.

Wave length, Å.	Spectral intensities (micro-watts per cm. ² at one meter distance from lamp axis) developed by 100-watt, Type H-4 lamp
14,000-40,000	285
7,000-14,000	39
6,500-7,000	5
5,500-6,500	23
4,650-5,500	37
3,900-4,650	36
3,000-3,900	35

(12) Leighton and Leighton, *J. Phys. Chem.*, **36**, 1882 (1932).

(13) Forbes, *ibid.*, **32**, 490 (1928).

TABLE II
PHOTOPOTENTIALS IN MILLIVOLTS FOR IRRADIATION AT STANDARD INTENSITY OF 4×10^{-4} WATTS/SQ. CM.

Electrode	Solution		3650 Å.	4047 Å.	4358 Å.	4916 Å.	5461 Å.	5780 Å.	6234 Å.	6908 Å.
	N	Cpd.								
Ag	0.0001	KCl	+22.0	+19.7	+1.5	0.0	0.0	0.0	0.0	0.0
Ag	.001	KCl	+13.5	+13.7	+1.8	.0	+1.8	+1.0	+ .1	.0
Ag	.01	KCl	+46.8	+43.6	+7.8	+ .3	+6.7	+3.4	.0	.0
Ag	.1	KCl	+ 2.5	+ 3.0	0.0	.0	+0.1	+0.1	.0	.0
Ag	.5	KCl	+ 3.4 ^a	+ 2.3 ^a	+1.0	.0	+1.6	+1.0	.0	.0
Ag	.0001	KBr	+ 9.2	+ 8.9	+1.3	.0	+0.8	+0.5	.0	.0
Ag	.001	KBr	+ 9.5	+ 9.0	+0.7	.0	+ .5	+ .5	.0	.0
Ag	.01	KBr	+ 4.5	+ 6.0	+ .7	.0	+ .6	+ .2	.0	+ .1
Ag	.1	KBr	+ 1.0	+ 1.5	+ .4	.0	+ .3	+ .1	.0	.0
Ag	.0001	KI	+ 7.5	+ 7.4	+1.5	.0	+ .3	+ .2	.0	.0
Ag	.001	KI	+ 7.3	+ 5.9	+0.6	.0	.0	+ .1	.0	.0
Ag	.01	KI	+11.0	+12.1	+1.0	.0	+ .2	+ .2	.0	.0
Ag	.1	KI	+ 1.2	+ 1.1	+0.1	.0	.0	.0	.0	.0
Ag	.1	KBr satd. with AgBr	+ 3.6	+ 3.5	+ .7	.0	+ .2	+ .2	.0	.0
Ag	.001	KNO ₃	+ 8.5	+ 8.5	+ .8	.0	+ .8	+ .7	.0	.0
Ag	.01	KNO ₃	+10.0 ^a	+10.7 ^a	+ .9 ^a	.0	+ .9 ^a	+ .6 ^a	.0	.0
Ag	.1	KNO ₃	+58.0	+48.3	+5.2	.0	+1.3	+ .6	.0	.0
Ag	1.0	KNO ₃	- 4.3	- 1.3	-0.7	.0	-0.1	.0	.0	.0
Ag	0.001	AgNO ₃	- 1.3	- 1.2	.0	.0	.0	.0	.0	.0
Ag	.01	AgNO ₃	- 1.2	- 1.3	- .2	.0	- .6	.0	.0	.0
Ag	.001	KBr	+ 2.0 ^a	+ 2.1 ^a	+ .7 ^a	+ .1	+ .6 ^a	+ .5 ^a	+ .2	.0
Ag	.01	KNO ₃								
Ag	.001	KBr	+ 2.8	+ 2.0	+ .6	.0	+ .3	.0	.0	.0
Ag	.1	KNO ₃								
Ag	.001	KBr	+ 2.3 ^a	+ 2.0 ^a	+ .7 ^a	.0	+ .3	+ .2	.0	.0
Ag	.5	KNO ₃								
Ag	.001	KBr	+ 4.2	+ 3.9	+ .5	.0	+ .1	.0	.0	.0
Ag	.1	CCl ₃ COOH								
Ag coated with AgBr	.001	KBr	+ 5.5	+ 5.2	+3.6	+ .3	+2.8	+1.6	+ .1	+ .4
	.001	KI	+ 1.9	+ 0.7	+0.6	.0	+0.4	+0.2	.0	.0
Au	1.0	KNO ₃	- 1.4	- 1.2	- .2	.0	.0	.0	.0	.0
Au on Pt	0.001	KBr	+ 1.1	+ 1.7	.0	.0	+ .1	.0	.0	.0
Au on Ag	.001	KNO ₃	+ 3.3	+ 3.8	.0	.0	.0	.0	.0	.0
Au on Ag	.001	KBr	+22.8	+22.8	+3.0	.0	+ .8	+ .4	.0	.0
Au on Ag	.001	KI	+11.4	+10.6	+1.7	.0	+ .7	+ .4	.0	.0
Cu	.001	KBr	+ 3.1	+ 4.9	+1.0	.0	+ .3	.0	.0	.0
Cu on Ag	.001	KNO ₃	+ 1.8	+ 1.8	+0.3	.0	.0	.0	.0	.0
Cu on Ag	.001	KBr	+12.6	+10.6	+2.0	.0	.0	.0	.0	.0
Cu on Ag	.001	KI	+ 3.7	+ 5.4	+0.3	.0	+ .1	.0	.0	.0
Cu coated with CuO	.001	KBr	+41.2	+41.4	+24.0	+7.5	+30.0	+20.0	+2.0	+15.0

^a These showed an initial negative surge.

was extrapolated to 50 cm. deflection. Such an extrapolation is justified for this work since the values at these high intensities were of several filters for which the photo-responses were extremely small or nil. In the main, the working intensity was within the limit of the intensity range of calibration of the thermopile.

The Measurement of the Photopotentials.—In some cases the photopotentials were measured with a Leeds and Northrup type-K potentiometer and galvanometer whose sensitivity was 1×10^{-9} amp./mm. All leads were protected with grounded shields.

In most cases, however, the photopotentials were measured with the aid of an F. P. 54 Plotron tube in a balanced bridge type of circuit designed by Brown and DuBridge.¹⁴ The galvanometer used in this circuit was the same as the one above. The entire circuit was shielded; in addition, the main circuit was protected from humidity effects. In comparison with the potentiometer system this circuit had the advantage of eliminating effects due to polarization since the grid current was of

(14) Brown and DuBridge, *Rev. Sci. Instruments*, **4**, 532 (1933).

the magnitude of 10^{-15} amp.¹⁵ The Plotron circuit was calibrated with the aid of a voltage divider and the potentiometer circuit described above.

The Data.—The data are shown in Table II and Figs. 1–9, inclusive. These data are all transposed to the same intensity of the 4047 Å. line.

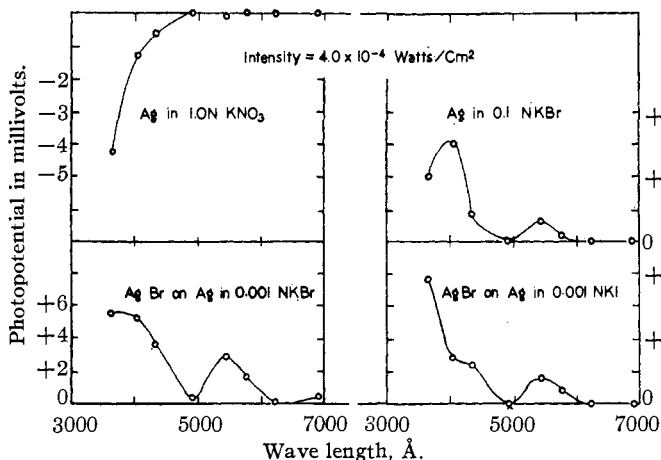


Fig. 5.

This transposition was effected by determining the change in photopotential with the change in intensity for each filter and interpolating or extrapolating the data so obtained.

The accuracy of these data can be determined from the sensitivity of the measuring instruments, the reproducibility of the measurements (relative to each other for a given cell) and the error involved in transposing the data to a standard intensity. The potentiometer circuit had a sensitivity of 1×10^{-5} volt and the vacuum tube circuit 4×10^{-5} volt; the measurements of a cell for each filter were reproducible to $\pm 5\%$ relative to those measurements with other filters of the same cell; the error involved in transposing the data to a standard intensity is not more than 5% of the value of the photopotential of the line chosen as the standard of reference.

The accuracy of the absolute values depends upon their magnitude; thus an expression of the error involved in the absolute values is difficult to formulate. However, since the major merit of the data is their comparative utility, it is safe to conclude that the maximum probable error is not more than $\pm 5\%$

(15) The authors are indebted to Dr. P. M. Harris for suggestions relative to the use of this circuit.

of the value of the photopotential of the 4047 Å. line at the standard intensity of 4.0×10^{-4} watts/sq. cm. and that in most cases it is much lower than this.

The error involved in expressing the threshold value is controlled by the distance between the lines of monochromatic radiation used. Hence it is only possible to suggest that the threshold value lies some place between $\lambda = 4358$ and 4916 Å. and more probably very near $\lambda = 4916$ Å.

In order to detect any possible effect of "activation" by short wave length, a number of cells were studied by consecutive irradiations from the long wave lengths to the short wave lengths then back to the long wave lengths again; these studies showed no "activation."

Drift in the vacuum tube circuit and drift due to slow dark potential changes were determined by a series of potential readings before and after illumination.

These drift values, together with the values of the potential on illumination, were plotted as ordinates and times were plotted as abscissas; by this method the value of the photopotential was determined graphically.

The effect of temperature reported by Athanasiu¹⁶ was investigated for a number of the cells.

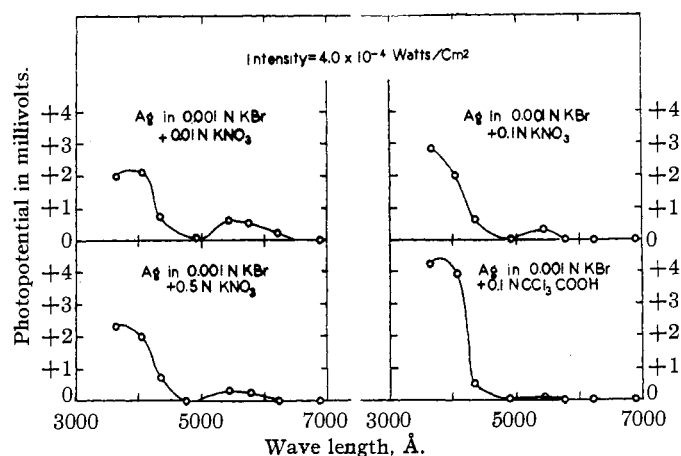


Fig. 6.

Several factors indicate that the potentials developed on illumination were not the direct result of temperature effects. Of those factors can be listed the following: (1) the long wave lengths of light are relatively ineffective in developing photo-

(16) Athanasiu, *Compt. rend.*, **180**, 587 (1925); **181**, 101 (1925)

potentials; (2) the potential response appears to be inertialess; (3) the temperature effect is negative whereas the photo-response is positive for many of the cells studied. Other unpublished work¹⁷ shows that an important factor for the reversal of the potentials of these cells is the con-

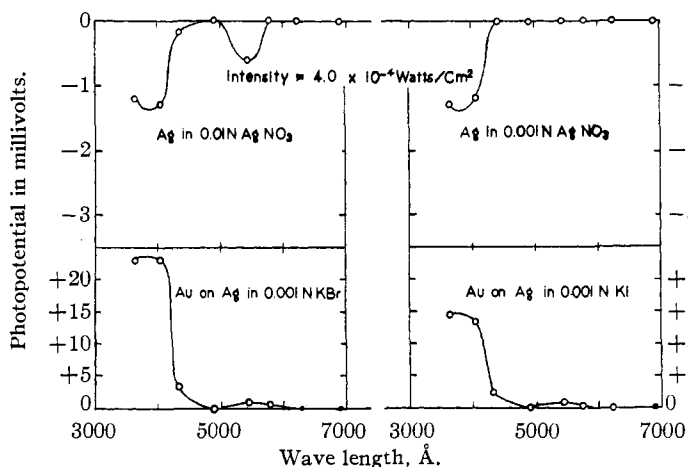


Fig. 7.

centration of the electrolyte. This is rather indicative that the photopotential may be the sum of several effects, but the effect due to temperature must certainly be only a minor one.

The photopotentials cannot be explained in terms of absorption by the solutions, particularly for the halides, since the longest wave lengths absorbed by the potassium halide solutions are given by A. K. Dutta¹⁸ as follows: KCl $\lambda = 2760 \text{ \AA.}$; KBr $\lambda = \text{---} \text{ \AA.}$, and KI $\lambda = 3600 \text{ \AA.}$ Furthermore he found no appreciable absorption for solutions more dilute than 0.1 normal in case of the chloride and iodide and no appreciable absorption above 2550 \AA. for the bromide at any concentration.

The sign of the dark potential had no observable effect on the sign of the photopotential. In general the magnitude of the photopotentials for a given line at a given intensity is characteristic of each cell.

Potential reversals with time¹⁹ were observed for cells marked (a). No general statement can

(17) This work and much of that on the effect of temperature was done by Mr. Otis Black, for whose help the authors are grateful.

(18) A. K. Dutta, *Trans. Bose Research Inst. Calcutta*, **10**, 209 (1934-35). Additional information on absorption of halide solutions is given by Getman, *J. Phys. Chem.*, **29**, 853 (1925), and by W. R. Brode, *THIS JOURNAL*, **48**, 1877 (1926). Unfortunately Brode's interesting work is not cited in Dutta's paper.

(19) Vanselow and Sheppard, *J. Phys. Chem.*, **33**, 331 (1929); Sheppard, Vanselow and Hall, *ibid.*, **33**, 1403 (1929).

be made concerning this phenomenon; the period of the galvanometer limited the observations of this reported negative surge. Further observations should be made concerning the characteristics of this phenomenon.

A number of cells show a hump in the wave length/photopotential graph indicating that the cells are not sensitive to light of $\lambda = 4916 \text{ \AA.}$ but may be sensitive to $\lambda = 5461 \text{ \AA.}$ Several cells did not show this effect. It is evident that the hump is much more pronounced in cells having a coated surface such as Cu-CuO, Ag-AgBr, etc. That observation rather suggests that those electrodes showing sensitivity at $\lambda = 5461$ probably contained a coating of oxide or halide which was responsible for such an effect.

A comparison of the photovoltaic threshold values with the photoelectric threshold values for the same metals in various stages of outgassing is interesting and is found in Table²⁰ III. The order of apparent decrease in the value of the work function is in the direction one might expect if the ease of removal of an electron depends upon the material at the interface. Furthermore, this

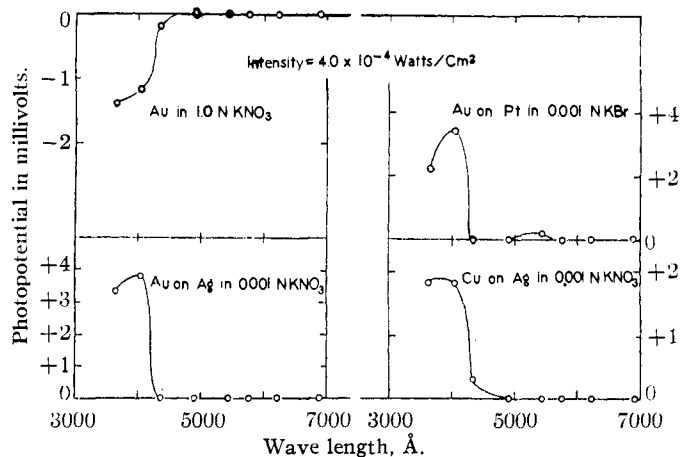


Fig. 8.

suggests a similarity between the mechanisms involved in both phenomena. Other cell characteristics are necessary before conclusions can be drawn in this regard but thus far it can be said that other unpublished observations point

(20) The threshold values for the metal-gas-vacuum system are taken from those compiled by Hughes and DuBridge, ref. 3, p. 75. The threshold values of the metal-solution system are those of this research.

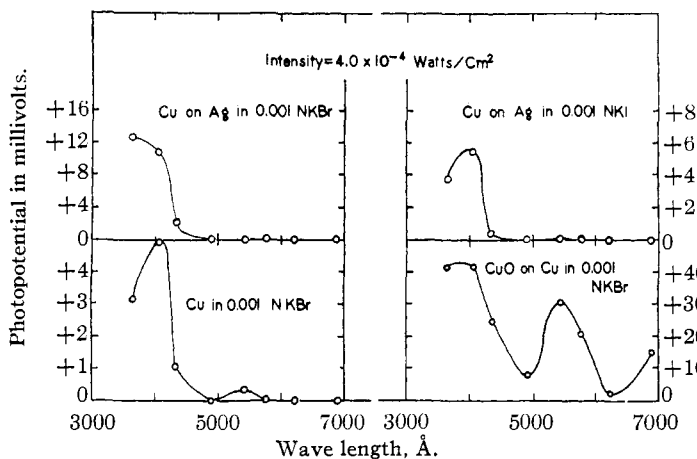


Fig. 9.

strongly to the fact that the above relationship is apparently more than a fortuitous one.

TABLE III

APPROXIMATE^a PHOTOELECTRIC THRESHOLDS OF SILVER, GOLD AND COPPER

Metal	Metal in solution	Threshold wave length, Å.		
		No outgassing	Partial outgassing	Extended outgassing
Silver	4900	3200-3400	2900-3100	2600-2700
Gold	4900	2625	2600-2800	2650-2610
Copper	4900	2700-3000	2700-3000	

^a Column 2, this research; columns 3, 4, and 5, compiled from those given by Hughes and DuBridge, ref. 3, p. 75.

Summary

The spectral sensitivities of copper, silver and gold electrodes have been determined for a number

of lines of monochromatic radiation ranging from $\lambda = 3650$ to $\lambda = 6908$ Å. The photovoltaic threshold values for these metal electrodes have been determined.

The sensitivity of coated metal electrodes and some metal electrodes at $\lambda = 5461$ Å. is attributed to the coating on the electrode.

A similarity in the mechanism of the photovoltaic and photoelectric effects is suggested from a comparison of the photoelectric threshold values of metals at various stages of outgassing and the photovoltaic threshold value.

A vacuum tube circuit employing an F.P.-54 Plotron tube is described as suitable for the measurement of photopotentials.

COLUMBUS, OHIO

RECEIVED DECEMBER 30, 1938

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF OKLAHOMA AGRICULTURAL AND MECHANICAL COLLEGE]

The Preparation and Identification of Three Alkali Molybdotellurates¹

BY S. R. WOOD AND ARTHUR CARLSON

The systematic preparation and study of salts of the complex heteropolyacids of molybdenum and tellurium are comparatively recent developments in inorganic chemistry. In 1910 Miolati² prepared a compound of apparent formula $\text{Te}_2\text{O}_{11} \cdot \text{K}_{10} \cdot 12\text{MoO}_3 \cdot 18\text{H}_2\text{O}$, or possibly $\text{TeO}_6 \cdot \text{K}_5\text{H} \cdot 6\text{MoO}_3 \cdot 8\text{H}_2\text{O}$. In 1929 Meloche and Woodstock³

(1) This is an abstract of a thesis submitted by S. R. Wood in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin in 1933, and of a thesis submitted by Arthur Carlson to the faculty of the Department of Chemistry of Oklahoma A. and M. College in partial fulfillment of the requirements for the degree of Master of Science in 1938.

(2) Miolati, *Z. physik. Chem.*, **70**, 330-334 (1910).

(3) Meloche and Woodstock, *THIS JOURNAL*, **61**, 171-174 (1929).

isolated and analyzed two ammonium molybdotellurates, which proved to have the empirical formulas $3(\text{NH}_4)_2\text{O} \cdot 2\text{TeO}_3 \cdot 6\text{MoO}_3 \cdot 10\text{H}_2\text{O}$ and $3(\text{NH}_4)_2\text{O} \cdot \text{TeO}_3 \cdot 6\text{MoO}_3 \cdot 7\text{H}_2\text{O}$. Since that time Hansen⁴ prepared and described a potassium salt, $3\text{K}_2\text{O} \cdot \text{TeO}_3 \cdot 6\text{MoO}_3 \cdot 8\text{H}_2\text{O}$; Thomsen⁵ studied a sodium molybdotellurate, $3\text{Na}_2\text{O} \cdot \text{TeO}_3 \cdot 6\text{MoO}_3 \cdot 22\text{H}_2\text{O}$; and Dyess⁶ reported the composition of the lithium salt to be $3\text{Li}_2\text{O} \cdot \text{TeO}_3 \cdot 6\text{MoO}_3 \cdot 13\text{H}_2\text{O}$. Specimens of the salts of sodium, lithium, cesium,

(4) H. F. Hansen, unpublished thesis, University of Wisconsin, 1930.

(5) Thomsen, unpublished thesis, University of Wisconsin, 1933.

(6) Dyess, unpublished thesis, Oklahoma A. and M. College, 1934.