centers of catalytic activity, is a crystal nucleus of chromium oxide. Each crystal nucleus is, on the average, three oxide ions thick. The nuclei are spread very far apart, most of the surface being exposed alumina. As the concentration of chromium increases, these crystal nuclei tend to grow until they finally overlap, but this does not occur until the chromium oxide layer is many atoms thick. As the concentration of chromium is decreased, the crystal nuclei shrink until they consist, at the limit, of a true two-dimensional atomic dispersion of chromium ions. A diagrammatic representation of the catalyst surface, as at point *l*, is shown in Fig. 5.

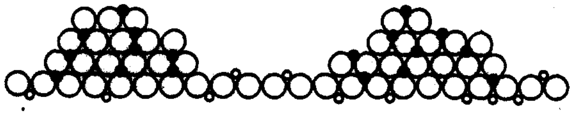

Fig. 5.—Possible structure of supported chromic oxide on aluminum oxide: O, O^{-2}; o, Al^{+3}; ●, Cr^{+3}.

In presenting Fig. 5 we do not imply that the alumina surface is flat. The representation is meant to be diagrammatic rather than pictorial. But the relationship shown of "nitrogen" area to chromium oxide is, we believe, a reasonable interpretation of the magnetic data. A second possible picture of the surface of the catalyst would have a large part of the "nitrogen" area in regions, such as pores, inaccessible to the chromium. We might, for instance, have the crystal nuclei of Fig. 5 actually touching or overlapping, with large fractions of the alumina surface free from chromium but concealed in "caves" and "pores." But, in any event, the thickness of the chromium oxide layer remains at about three oxide ions, as at point *l*. We see no reason for identifying point *l* with a monolayer of chromium oxide. Further experiments are being done to determine which picture of the surface is more nearly correct.

There is an alternative explanation for the susceptibility–composition isotherm. γ-Alumina has the structure of a spinel, with vacant places in the lattice corresponding to the missing ions. A possible structure has 21.3 aluminum ions present for every 24 possible positions for metal ions in the unit cell. The unit cell could, therefore, accommodate 2.7 chromic ions, which are only very slightly larger than aluminum ions. It might be thought that point *l* in the susceptibility–composition isotherm represented filling of all these vacant positions. It is, however, difficult to see how the isotherm would undergo anything but a very gradual change as the vacant positions became filled, and, furthermore, the positions are all filled at 9% chromium rather than at 6%, which is the actual position of point *l* in the system studied.

Acknowledgment.—It is a pleasure to acknowledge the support of the Sinclair Refining Company in connection with this work.

Summary

Magnetic susceptibilities have been measured for a series of catalysts of varying composition, but all containing chromium oxide supported on alumina. Variations in the susceptibility of the chromium in these catalysts is used to derive possible structures for the catalyst surface. The relation between magnetic susceptibility and concentration is named the susceptibility–composition isotherm.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY, THE OHIO STATE UNIVERSITY]

The Photovoltaic Effect. The Spectral Sensitivities of Cadmium, Zinc and Silver Electrodes; the Effect of *p*H and Oxygen

BY JOHN M. BLOCHER, JR., AND A. B. GARRETT

The present data extend to cadmium and zinc electrodes, the work[1] of Clark and Garrett on the spectral sensitivities of copper, silver, and gold electrodes in solutions of various electrolytes. Data are also presented for several silver and silver–silver chloride cells, for the effect of *p*H on certain silver cells and the effect of dissolved gases on various cells. The presence of dissolved oxygen is here shown to have a profound influence on the photopotentials of some cells, in certain cases to the extent of reversing the sign of the photopotential.

Experimental Procedure

The apparatus and procedure in the determination of the spectral sensitivities were essentially those used by Clark and Garrett,[1] with the exception that correction was made for the infrared transmission of the light filters.[2]

The electrodes were annealed in only a few cases since a comparison of the photopotentials developed by annealed and unannealed electrodes of silver, cadmium and zinc, indicated no differences which could be attributed to the presence or absence of annealing.

The metal and silver–silver halide electrodes were prepared as previously described.[1] Cu/"CuO" electrodes were prepared by heating cop-

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(1) P. E. Clark and A. B. Garrett, THIS JOURNAL, **61**, 1805 (1939).

(2) This has the effect of raising the points at λ = 4916 and 4358 Å. resulting in an increased sensitivity toward the ultraviolet generally without inflection.

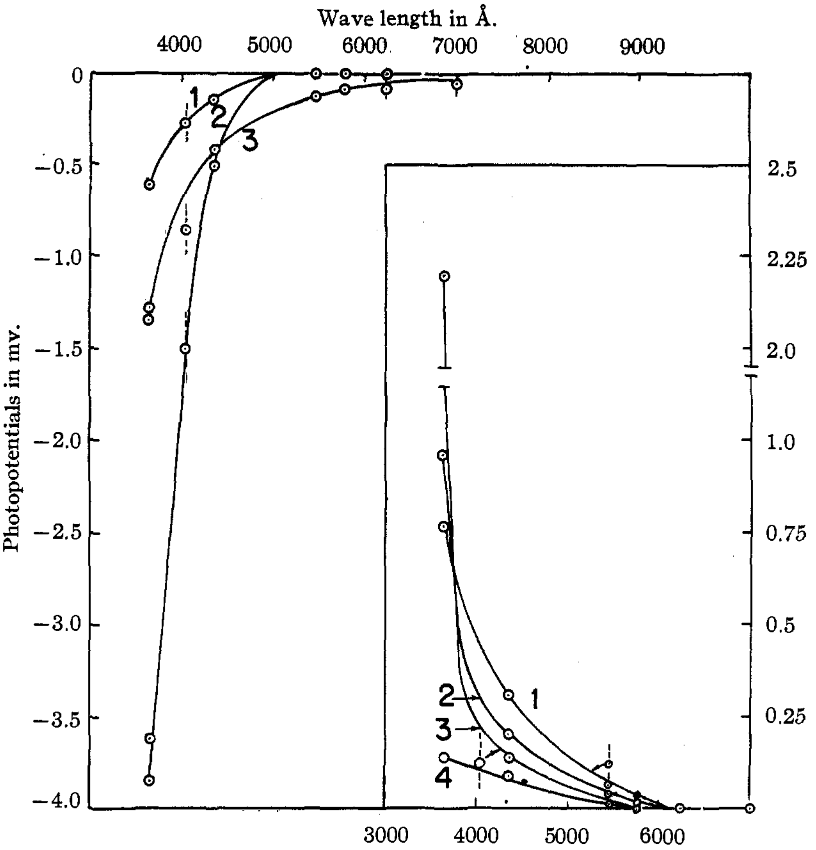

Fig. 1. Fig. 2.

Fig. 1.—Curve 1: Ag in H_2O; intensity = 36 × 10^{-6} cal./sec./sq. cm. Curve 2: Ag in 90% $C_2H_4(OH)_2$ – 10% H_2O; intensity = 57 × 10^{-6} cal./sec./sq. cm. Curve 3: Ag in 0.1 *N* NaOH; intensity = 57 × 10^{-6} cal./sec./sq. cm.

Fig. 2.—Curve 1: Zn in 90% $C_2H_4(OH)_2$, 10% H_2O, 0.001 *M* in HCl; intensity = 65 × 10^{-6} cal./sec./sq. cm. Curve 2: Ag in 0.1 *N* HCl; intensity = 20 × 10^{-6} cal./sec./sq. cm. Curve 3: Ag/AgCl in 0.1 *N* HCl; intensity = 20 × 10^{-6} cal./sec./sq. cm. Curve 4: Cd in 0.001 *M* $CdCl_2$; intensity = 65 × 10^{-6} cal./sec./sq. cm.

per electrodes to redness in a flame and allowing them to cool in air. Cu/"Cu_2O" electrodes were prepared by the method of Garrison.[3] Cd/CdO electrodes were prepared by heating cadmium electrodes in an atmosphere of oxygen maintained at 300°. This resulted in a thin oxide coat of metallic luster. In the present work, the photopotential magnitudes of metal electrodes that had undergone presumably the same treatment showed wide variations (from 20 to 100% of maximum in extreme cases). Coated electrodes showed less variation. The presence of unrecognized variables is indicated. Although quantitative comparisons of magnitudes of photopotentials between cells are not justified, the behavior with respect to the qualitative effect of dissolved gases, the shapes of the spectral sensitivity curves and their threshold positions were reproducible and a number of generalizations can be made.

Most investigators have been reticent with respect to their difficulties in obtaining photovoltaic cells of reproducible sensitivity. However, fair reproducibility in coated electrodes has been obtained by some workers.[4,5]

The procedure used to determine the effect of gases was to measure the photopotential of a cell before and after bubbling the gas through the electrolyte and around the photoelectrode contained in one leg of the H-type cell. Tank oxygen was purified by passing it through soda-lime, and through potassium iodide–sodium thiosulfate solution to remove possible traces of ozone. Tank nitrogen was passed through soda-lime, Fieser's solution,[6] and saturated lead acetate.

For some cells, a duplicate of the photoelectrode served as reference. Electrode pairs showing dark potentials greater than 10 mv. were discarded. In other cells a saturated calomel electrode was employed, relative to which were recorded the changes in dark potential of the photoelectrode due to the gas bubbling.

In all cases the dark potentials of the cells were balanced out by a potentiometer in series with the reference leg of the cell, so that the range of grid voltage applied to the FP-54 electrometer during photopotential measurements was between zero and ± 40 mv. throughout; this gave a linear galvanometer response.

In general, the exposure time was limited to either thirty or sixty seconds and the photopotential attained during that interval arbitrarily chosen as an indication of the cell sensitivity. It was deemed advisable to keep the time of illumination to a minimum since the cells generally showed a light "fatigue" and a permanent change of dark potential on prolonged illumination. Although the silver, cadmium and zinc cells giving positive effects attained a maximum photopotential within one minute, the silver cells showing negative effects required three to five minutes for the levelling off of the photopotential. The

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(3) A. D. Garrison, *J. Phys. Chem.*, **27**, 601 (1923).

(4) W. Vanselow and J. E. Sheppard, *ibid.*, **33**, 331–353 (1929).

(5) N. Hayami, *Rev. Phys. Chem. Japan*, **11**, 166 (1937).

(6) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, p. 393.

negative photopotentials of Cu/"Cu_2O" electrodes are recorded as the maximum negative surge occurring during the first five to ten seconds of exposure. This negative surge was followed by a positive trend as noted by Garrison.[3]

Experimental Results

Spectral Sensitivity.—Figures 1 and 2 give the spectral sensitivities of cadmium, zinc and silver cells showing positive and negative photopotentials. The estimated errors in the values of the standardized photopotentials due either to uncertainty in the low intensity and spectral content of the incident radiation, instability of dark potential, or to the low measured values of the photopotentials, are indicated by dotted lines about the points. In general cadmium and zinc cells exhibited such low photopotentials that few data on spectral sensitivity could be obtained.

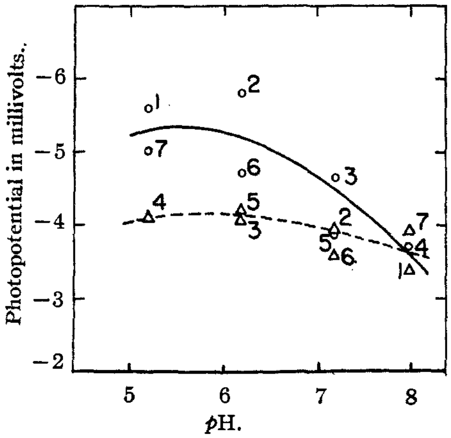

Fig. 3.—Ag in NaH_2PO_4–citric acid buffers: intensity = 860 × 10^{-6} cal./sec./cm.^{2} λ = 6234 − 3655 A. U. Circles, Run A; triangles, Run B.

Effect of *p*H and Chloride Ion.—It was noted that silver electrodes exhibited positive photopotentials in 0.01 *M* potassium chloride solutions made 0.1, 0.01 and 0.001 *M* in hydrochloric acid, and negative photopotentials in 0.01 *M* potassium chloride made 0.1, 0.01 and 0.001 *M* in potassium hydroxide. The sign of the small photopotential in the "neutral" (*p*H 5.8) 0.1 *M* potassium chloride was a function of the previous history of the electrode, *i. e.*, whether it was transferred from acid or from basic solution.

Silver electrodes were observed to give negative photopotentials in citric acid–monosodium phosphate buffer solutions[7] from *p*H 2.2 to 8.0. The data for two runs in the range *p*H 5.2 to 8.0 are given in Fig. 3. The photopotentials were determined in the order noted after one and one-half hour equilibrium of the electrode in each electrolyte using a standardized rinsing and transfer procedure between electrolytes. The data show no trend in sensitivity of the magnitude to be expected if hydrogen or hydroxyl ions were directly involved in photochemical reactions which might result in the photopotential.

Silver electrodes in buffer solution of *p*H 2.2 when made 0.1 *M* in potassium chloride gave positive photopotentials. Silver electrodes gave positive photopotentials in 0.1 *N* hydrochloric acid and negative photopotentials in conductivity water and in 0.1 *N* nitric acid. These data indicate that the positive photopotentials depend upon the presence of the chloride ion for their existence and are not a direct result of high hydrogen ion concentration.

Effect of Dissolved Gas.—The data in Table I show the effect on the photopotentials and dark

TABLE I

Intensity = 1100 × 10^{-6} cal./sec./sq. cm.; λ = 6234–3655 Å.

Time, min.	Dark potential,[a] mv.	Maximum photopotential surge,[b] mv. (usually within 5 sec. of illumination)	Photo-potential,[c] mv. (at end of 30 sec. illumination)
Cell: Cu/Cu_2O/KCl (1 *M*)/Cu_2O/Cu			
0	+ 2.3	− 3.6	−2.4
10	+ 0.5	− 4.1	−3.6
20	− 0.3	− 4.5	−4.1
N_2 bubbled, 5 min.			
30	− 9.8	+ 8.7	+6.9
40	− 8.3	+ 7.6	+5.7
50	− 8.3	+ 7.2	+5.3
O_2 bubbled, 5 min.			
60	+ 52.1	− 9.7	−5.5
70	+ 37.0	−12.5	−4.4
N_2 bubbled, 5 min.			
80	− 9.5	+ 0.2	−4.0
90	− 9.0	+ 0.2	−5.7
100	− 9.0	+ 0.3	−6.5
Cell: Cd/H_2O/Cd			
0	0	− 1.8	+4.1
10	+ 4	No surge	+5.2
20	+ 5	No surge	+5.0
N_2 bubbled, 5 min.			
30	−200	No surge	−0.1
40	−197	No surge	− .3
O_2 bubbled, 5 min.			
50	+118	No surge	+1.4
60	+140	No surge	+1.8
N_2 bubbled, 5 min.			
70	−195	No surge	+1.2
80	−199	No surge	+1.7

[a] Potential of the darkened photoelectrode relative to the dark reference electrode. [b] For cells showing a surge the derivative of photopotential with respect to time changed sign during the thirty second period of illumination. [c] Potential of the illuminated electrode (photoelectrode) at end of thirty second illumination relative to the potential of the same electrode in the dark. (Corrected for drift of dark potential.)

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(7) N. A. Lange, "Handbook of Chemistry," Handbook Publishers, Inc., Sandusky, Ohio, 5th ed., 1944, p. 1118.

TABLE II

System	Sign of air "equilibrium" photopotential	Dissolved oxygen effect on	
		Photopotential	Dark potential
Ag/H_2O[a]	−	Decrease in magnitude	Made more positive
Ag/NaOH (0.1 *N*)	−	Decrease in magnitude	Made more positive
Ag/90% $C_2H_4(OH)_2$, 10%H_2O	−	Decrease in magnitude	Made slightly more positive
Ag/HCl (0.1 *N*)	+	Slight decrease in magnitude	Made slightly more positive
Ag/AgCl/HCl (0.1 *N*)	+	Very slight decrease in magnitude	Made slightly more positive
Ag/AgBr/KBr (0.1 *M*) AgBr (satd.)	+	None	None
Cu/H_2O	+	Decrease in magnitude	Made more positive
Cu/Cu_2O/KBr (0.001 *M*)	−	Decrease in magnitude	Made more positive
Cu/"CuO"/H_2O	+	Decrease in magnitude	Made more positive
Cu/"CuO"/KCl (0.1 *M*)*	+	Decrease in magnitude	Made more positive
Cu/"Cu_2O"/KCl (0.1 *M*)	[b] +	Decrease in magnitude	Made more positive
	−	Change of sign	Made more positive
Cd/H_2O	+	Change of sign, [c]	Made much more positive
Cd/$CdCl_2$ (0.001 *M*)*	+	Change of sign, [c,d]	Made more positive
Cd/CdO/$CdCl_2$ (0.001 *M*)*	+	[c,d]	Made more positive
Zn/$ZnCl_2$ (0.001 *M*)	+	Decrease in magnitude	Made more positive

[a] Magnitude of photopotential slightly decreased by mechanical stirring. [b] Depends on thickness of Cu_2O layer. [c] Overall enhancement of positive photopotential. [d] The positive photopotential after oxygen bubbling (five minutes) is enhanced by bubbling nitrogen for short periods (thirty to sixty seconds). However, further nitrogen bubbling results in a decrease in magnitude.

potentials of bubbling nitrogen and oxygen through the electrolytes of the half-cells: Cd/H_2O and Cu/"Cu_2O"/KCl(*M*). For these particular half-cells and in the case of Cd/$CdCl_2$(0.001 *M*), the initial bubbling of nitrogen resulted in a change of sign of the photopotential. The bubbling of pure oxygen then changed the photopotential response in the direction of that which was noted when the electrode was in equilibrium with air. However, further nitrogen bubbling did not restore the conditions present after the first bubbling; this indicates that some permanent change in the electrode surface, in addition to a simple change in oxygen concentration of the electrolyte, was obtained during the oxygen bubbling. In Table II are assembled in a qualitative manner, the data for these and other cells studied in the same way. The effect of the presence of dissolved oxygen on the photopotentials and dark potentials of the electrodes is interpreted on the assumption that nitrogen is photochemically inert and its bubbling serves to displace the dissolved oxygen. The effect of stirring the solution between exposures was secondary.

Some workers[8,9,10,11] have reported that the effect of dissolved gases on the photopotentials of photovoltaic cells is small and/or secondary in the cells studied.

Additional Observations.—Cadmium electrodes in either water or 0.001 *M* cadmium chloride in "equilibrium" with air gave on first illumination (λ = 6234–3655 Å.), a sharp (5 sec.) negative surge followed by an over-all positive photopotential. The negative surge was absent on subsequent illumination. It was also absent for cells saturated with nitrogen before the initial exposure, the photopotential having been a very small (<1% air "equilibrium" value) positive effect.

Discussion

Silver.—It appears that the positive photopotentials developed by "pure" silver electrodes in halide solutions may be due in general to the presence of a photosensitive silver halide layer on the electrode surface. This is indicated by the facts that (1) the normal photopotential of silver in water is negative, (2) the dark potentials of silver electrodes in hydrochloric acid solutions approach the potential of a silver–silver chloride electrode, and (3) the spectral sensitivity curves of "pure" silver and silver–silver chloride electrodes are of the same form. Such a layer might be formed through the air-oxidation of the halide in solution(the sensitivity of such cells was observed to have increased with age), or through the formation of metastable silver halide molecules on the silver surface in the presence of silver ions from the electrode. The present data do not warrant a clear cut choice between the mechanisms proposed by Vanselow and Sheppard[12] and by Garrison[13] for the photovoltaic sensitivity of silver–silver halide electrodes, but it appears that the former is the more acceptable at present.

The effect of dissolved oxygen points to the fact that the negative photopotentials exhibited by various of the silver cells studied in the present work may arise from the presence of a layer of

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(8) T. Swensson, *Arkiv. Kemi, Mineral Geol.*, **7**, No. 19 (1919).

(9) V. Sihvonen, *Ann. Acad. Sci. Fennicae*, **A26**, No. 6 (1926).

(10) I. Lifschitz and S. B. Hooghoudt, *Z. physik. Chem.*, **141**, 52 (1929).

(11) B. Lanyi and E. Theisz, *Magyar Chem. Folyoirat*, **35**, 129–139, 145–151 (1929).

(12) Vanselow and Sheppard, *J. Phys. Chem.*, **33**, 331 (1929).

(13) A. D. Garrison, *ibid.*, **28**, 333 (1924).

silver oxide on the silver surface. Veselovsky[14] has cited the work of several investigators[15,16,17] establishing the adsorption of oxygen by silver under ordinary conditions. In order to attribute the negative effect to an oxide layer, one must allow the existence of the oxide (on the order of a monolayer) in 0.1 *N* nitric acid and in the buffer solutions of *p*H 2 to 7 where the negative photopotential is observed. Data on this point are not available.

Cadmium.—The positive photopotentials observed for cadmium electrodes in water and in 0.001 *M* cadmium chloride seem to require for their existence the presence of oxygen in the solution. A mechanism for the photopotential can be proposed based on the role of oxygen as an electron acceptor. The positive photopotential is attributed to the light accelerated process of formation of a double layer of oxide on the cadmium surface. The absence of the positive effect in nitrogen saturated solutions is attributable to the absence of oxygen. The enhancement of the positive photopotential of the oxygen saturated cell by the bubbling of small amounts of nitrogen may be attributed to the lowering of the potential barrier. The negative surge observed on the initial illumination of these electrodes does not fit into the mechanism for the positive effect. It is tentatively suggested that the negative surge is due to the presence of cadmium sub-oxide which might behave analogously to cuprous oxide.

Zinc.—The positive photopotentials observed for the zinc cells studied in this work may be principally photoelectric in origin, since photoelectric thresholds as high as $\lambda = 3760$ Å. and 4009 Å. have been observed[18] for zinc before outgassing and $\lambda = 3720$ Å. after extended outgassing. The oxygen inhibition of the photopotential then finds explanation in the raising of the potential barrier.

Copper–Copper Oxide.—The oxygen inhibition of the positive photopotentials of Cu/"CuO" electrodes is best explained on the basis of the mechanism proposed by Van Dijck,[19] where the primary process is considered to be the photodissociation, $CuO \xrightarrow{h\nu} Cu + O$, the liberated oxygen raising the potential of the "oxygen electrode." Since the photopotential is determined by the ratio of the change of oxygen concentration to the initial concentration, the photopotential would be inhibited by an increase in the oxygen concentration.

The fact that the negative photopotentials of the system Cu/"Cu_2O"/H_2O are inhibited by the presence of oxygen in the solution may be qualitatively interpreted equally well by the mechanism of Garrison[8] or by that of Van Dijck.[20,21]

General Conclusions on Effect of Oxygen.—The data of Tables I and II show that the concentration of dissolved oxygen in the electrolytes of irreversible photovoltaic cells is important in determining their characteristics. This may be due to three factors: (1) oxidation (in the dark) of the electrode surface, thus presenting an unknown surface to radiation, (2) alteration of the electrode potential resulting in a variation in potential barrier, as well as an alteration in the neighborhood of the electrode of the concentrations of other oxidized and reduced species some of which may be photosensitive or may participate in photochemical reactions, and (3) the participation of the oxygen itself in photochemical reaction.

It is evident that the complicating effects of oxygen on the behavior of photovoltaic cells with pure metal electrodes should be eliminated in future work and that the dissolved oxygen content of cells with metal–metal oxide electrodes should be controlled.

It seems worth pointing out that the presence of a labile surface film of oxygen (or oxide) on the electrode would be consistent with the conclusions that may be drawn from a comparison of the data on the shift of the threshold values of metals in solution and in various stages of outgassing in a vacuum.[22]

Summary

1. The spectral sensitivity curves have been determined for some photovoltaic cells of cadmium, zinc and silver electrodes.
2. The effect of *p*H on silver photovoltaic cells is thought to be secondary. Neither hydrogen nor hydroxyl ions seem to be directly involved in the photovoltaic mechanism. In halide solutions, however, the *p*H may be effective in determining the nature of the surface exposed to radiation.
3. Evidence has been presented indicating that the positive photovoltaic sensitivity of "pure" silver electrodes in halide solutions is due to a layer of silver halide on the electrode surface.
4. The profound effect of dissolved oxygen on the behavior of some photovoltaic cells has been established. Its effect on fifteen photovoltaic cells has been determined.
5. The data have been discussed with reference to proposed mechanisms.
6. The necessity of eliminating the complicating effects of oxygen in future work with "pure" metal electrodes has been pointed out. The desirability of controlling the dissolved oxygen content of cells with metal–metal oxide electrodes has been indicated.

COLUMBUS, OHIO RECEIVED AUGUST 10, 1946

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(16) D. L. Chapman, J. E. Ramsbottom and C. G. Trotman, *ibid.*, **A107**, 92 (1925).

(17) A. F. Benton and J. C. Elgin, THIS JOURNAL, **48**, 3027 (1926).

(18) A. L. Hughes and L. A. DuBridge, "Photoelectric Phenomena," McGraw-Hill Book Co., Inc., New York, N. Y., 1932, p. 76.

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(20) W. J. D. Van Dijck, *Z. physik. Chem.*, **127**, 249 (1927).

(21) Reduction of oxygen concentration by the reaction series: $Cu_2O \xrightarrow{h\nu} Cu + CuO$, $Cu + O \longrightarrow CuO$, $2Cu + O \longrightarrow Cu_2O$.

(22) Copeland, Black and Garrett, *Chem. Rev.*, **31**, 182 (1942).