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The Photovoltaic Effect for Sodium

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Attempts to produce a photovoltaic effect with reversible electrodes made of an active metal photoelectrically sensitive to visible light, such as sodium, and dipping into a solution containing ions of the metal, met with no success provided the solvent and salt which formed the electrolyte were carefully dried before preparing the cells. Slight photovoltaic effects of the order of 0.5 mv or smaller were observed in the case of two cells known to contain traces of water, but these effects were probably due either to the water present or to the compound electrode Na/Na₂O rather than to the pure metal. It is concluded that the energy supplied to the electrons by the visible light is not sufficient to bring about the transition of the electron from the metal to the solution.

CONVENTIONS AND DEFINITIONS

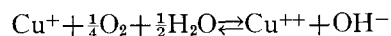
HUGHES and DuBridge¹ use the term "photovoltaic effect" to include "phenomena associated with the production of an electromotive force in a cell consisting of two similar electrodes, separated by a suitable electrolyte or other substance, when the electrodes are unsymmetrically illuminated." We shall define the photovoltaic potential as being positive when the potential of the illuminated electrode becomes more positive on illumination irrespective of the sign of the electrode potential in the dark. We believe that the use of the terms anode and cathode in the case of cells generating an e.m.f. is inadvisable and confusing if not entirely incorrect. The values and sign of the e.m.f. of the cells as given in this paper will always be the potential of the electrode which is illuminated or about to be illuminated in reference to the potential of the other electrode kept continually in the dark.

By *external* photoelectric effect we mean, as usual, the ejection of electrons from a metal to a vacuum by light. By *internal* photoelectric effect we signify the ejection of electrons by the light from one solid phase to another solid phase, the ejection of electrons from a layer of cuprous oxide to the underlying copper, for example.

INTRODUCTION

The interesting question regarding the extent to which light may affect the potential of a

metal or metal coated with an insoluble salt in contact with an electrolyte has been investigated by a number of workers from the original discovery of Becquerel² in 1839 to the present day. Hughes and DuBridge³ summarize papers published through 1929 while Audubert⁴ and Athanasiu⁵ have recently published extensive reviews. Photovoltaic potentials have been observed for a number of compound electrodes such as Ag|AgI, Cu|Cu₂O, etc., dipping into aqueous solutions, but these photopotentials largely disappear when the electrodes are carefully dried and then dipped into electrically conducting nonaqueous solutions, the photopotential of a cuprous oxide electrode, for example, drops from 120 mv to 3 mv on elimination of water from the system. Audubert explains the photovoltaic effects in the case of aqueous solutions by postulating that the light "photolyzes" water molecules which are adsorbed on the surface of the electrodes to form either hydrogen or oxygen which then enter into equilibria involving ions of the metal, thereby affecting the potential of the electrode. Consider, for example, the Cu|Cu₂O electrode whose potential becomes more positive on illumination;⁶ for this electrode the reaction



is applicable. The incident light photolyzes the water, increasing the concentration of the oxygen and forcing the above equilibrium to the right.

² E. Becquerel, *Comptes rendus* **9**, 144, 561 (1839).

³ Reference 1, Chap. IX.

⁴ R. Audubert, *J. de phys. et rad.* (7) **5**, 486 (1934).

⁵ G. Athanasiu, *Ann. de physique* (11) **4**, 377 (1935).

⁶ At least in the case of cuprous oxide made in the dry way.

¹ A. L. Hughes and L. A. DuBridge, *Photoelectric Phenomena* (McGraw-Hill Book Co., New York, 1932), p. 352.

The resulting increase in the concentration of the cupric ion produces the positive photopotential. In support of this hypothesis may be cited the fact that in the case of the $\text{Cu}|\text{Cu}_2\text{O}$ electrode its positive photopotential is increased in reducing solutions and reduced in oxidizing solutions, is reduced by increased concentration of cupric ions and is reduced by increase of $p\text{H}$.

Athanasu⁵ has studied the influence of $p\text{H}$, temperature and wave-length on the photovoltaic effect. His results may be summarized as follows; decrease of $p\text{H}$ favors the positive photoeffect, increase of temperature lowers the photopotential markedly, increase of wave-length of the incident radiation decreases the positive photopotential and may produce a negative photopotential. In the case of $\text{Ag}|\text{AgI}$ electrode immersed in a neutral solution of KCl after a basic treatment the positive photopotential shows a maximum at 4200Å and the negative photopotential a maximum at 4400Å. The maximum of the spectral absorption coefficient of silver iodide, the maximum of its photoconductivity and the maximum of the photovoltaic effect all occur in the same wave-length range, about 4200Å, but the threshold of the *external* photoelectric effect is below 4070Å. Athanasu concludes that the photovoltaic effect begins with an *internal* photoelectric effect of the light sensitive salt or oxide layer, followed by photochemical reactions in which the electrolyte may take part. In addition to a photochemical reaction there must also be a possibly reverse thermal reaction in order to account for the pronounced temperature coefficient of the photovoltaic effect.

The photopotential of pure metals has been investigated in the case of noble metals which may be assumed to be free of oxide coating than more active metals like copper or zinc, although the presence of adsorbed layers of gases makes it impossible to assert that a pure metal surface has ever been studied for its photovoltaic effect. The photopotentials of the noble metals are much smaller than those discussed above and rather difficult to measure because of the instability of the electrode potentials in the dark; the electrodes probably acting as oxygen electrodes.

Audubert and Roulleau⁷ studied the photovoltaic effect for selenium on platinum and found large photopotentials even in the absence of water. They used solutions of potassium iodide dissolved in a number of organic solvents, and found in contrast to the $\text{Cu}|\text{Cu}_2\text{O}$ electrode that the observed positive photopotentials were increased in oxidizing solutions. Very few experimental details were given, so that the purity of the selenium surface is open to question; the authors believe that a true photoelectric effect was concerned and that electrons were ejected into the solution by the action of the light.

In all previous work on the photovoltaic effect no investigations have been made to our knowledge on metals having low work functions like sodium. It would seem that if a true photoelectric effect existed, for the boundary metal|solution, it would be much more pronounced for active metals than for the relatively inert metals having high work functions. Accordingly we decided to investigate the photovoltaic effect for pure sodium surfaces in contact with a solution containing sodium ions. We hoped in this way to be dealing with electrodes giving reversible and stable potentials in the dark and with metal surfaces as clean as they could be when in contact with a liquid electrolyte. Sodium electrodes also have the advantage that there is no photosensitive oxide or insoluble salt layer which would make possible an internal photoelectric effect or photochemical reactions with the electrolyte.

EXPERIMENTAL

The general method of investigating the photovoltaic effect for sodium consisted in preparing a dry nonaqueous solvent, dissolving dry sodium iodide in it, pouring the solution onto sodium electrodes and finally measuring the e.m.f. between the two electrodes before and after the illumination of one of the electrodes. The cell used was $\text{Na}|\text{NaI}$ in $\text{C}_5\text{H}_{11}\text{NH}_2|\text{Na}$.

Sharples Solvent Company technical grade monoamylamine was selected as the solvent because it is conveniently a liquid at room temperature. It was dried by refluxing over liquid sodium-potassium alloy for three hours

⁷ R. Audubert and J. Roulleau, *Comptes rendus* **198**, 1489 (1934).

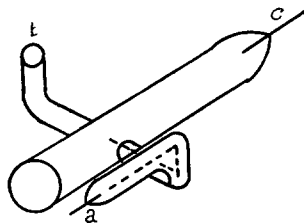


FIG. 1.

followed by repeated distillations in vacuum into flasks containing sodium mirrors until the solvent was so dry that a thin sodium mirror would no longer be removed. Connections between flasks were opened by breaking an inner bulb with a magnetic hammer; a large bulb was broken rather than a capillary tip in order to expedite the distillation of the solvent and later on the pouring of the solution from one flask to another. The iron magnetic hammer was encased in glass in order that iron rust would not catalyze the reaction between sodium and the amine to form hydrogen and an amide.⁸ Various methods were tried in an attempt to dry sodium iodide recrystallized from water by fusion, but invariably a saturated aqueous solution of the resulting fused iodide was alkaline to phenolphthalein so that the drying was usually done by heating the salt at a pressure of 1 micron from room temperature to 100°C and then at 300°C at a pressure of 0.1 micron for ten hours. This process gave a neutral salt which on solution in dry amyl amine contained insufficient water to remove a thin sodium mirror. The solutions were made by distilling the solvent onto the salt, followed by shaking. The concentrations of the solutions were estimated roughly by evaporating the solvent from a weighed quantity of the solution and weighing the dry residue or by adding a known volume of liquid to a known weight of salt. A saturated solution of the salt contains approximately 27 percent of sodium iodide by weight.

The sodium for the electrodes and mirrors was melted in vacuum, filtered through a capillary tube to remove oxide and finally pushed by means of hydrogen or allowed to run by gravity through a second capillary tube into a flask or

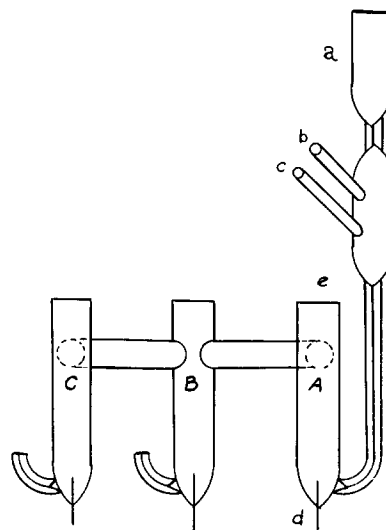


FIG. 2.

cell. The side arms containing the sodium reservoir and capillary tubes were removed after the sodium mirror had been formed. The cells, described below, were at first maintained at constant temperature, 25°, in an air bath; but later it was found that the actual temperature of the experiment was of no apparent importance so that the air in the bath was merely stirred vigorously, the essential precaution being that the two sodium electrodes be at the same temperature. An e.m.f. of 0.5 mv or higher could be produced by touching one side of a cell with the hand. The e.m.f. was measured usually to 0.01 mv with a type K-2 Leeds and Northrup potentiometer using a Leeds and Northrup type R galvanometer (sensitivity 5×10^{-10} amp. per mm scale deflection).

A 200-watt tungsten filament lamp with a liter flask filled with water or saturated copper sulfate solution as a condensing lens and heat filter was used in the first experiments, but later a mercury arc without any filter giving more intense light was constructed and used. The arc was enclosed in Pyrex glass so that light of wave-length below 3000Å was cut off. The monoamylamine also begins to absorb strongly in the ultraviolet region below 3000Å.⁹

The cells illustrated in Figs. 1 and 2 were of two types. Type A, Fig. 1, contained one sodium

⁸ T. H. Vaughn, R. R. Vogt and J. A. Nieuwland, *J. Am. Chem. Soc.* **56**, 2120 (1934), have discovered that ferric nitrate dissolved in liquid ammonia catalyzes the amide-forming reaction between sodium and ammonia.

⁹ See J. Bielecki and V. Henri, *Comptes rendus* **156**, 1860 (1913).

electrode which could be illuminated while type *B*, Fig. 2, contained three sodium electrodes capable of illumination. In Fig. 1 at *a* and *c* are two tungsten electrodes sealed through the Pyrex glass, both of which were covered with sodium metal which was admitted through a capillary not shown in the figure. A sodium mirror was deposited on the inside walls of the cell around the electrode *c* by gently heating the sodium at *c*. Light entered through a thin Pyrex window of the type described by Sonkin,¹⁰ at *d* while solution was poured into the cell at *b*. After the filling of the cell the side arm at *b* was sealed off. In Fig. 2 is illustrated a cell of type *B* and the auxiliary capillary tube for admitting the sodium is also pictured. In some cells of this type no sodium mirror was formed, the sodium electrodes simply consisting of a pool of sodium metal at the bottom of each arm of the cell.

The results of the investigation are collected in Table I which is self-explanatory but to which the following remarks should be appended. In all the cells except No. B-1 the electrodes were mirror electrodes, the electrodes of cell B-1 were formed of sodium in the bulk. After a zero photopotential had been observed for all the electrodes of cells B-1 and B-2 sodium was deposited electrolytically in the form of shiny white needles on one electrode of each of the cells, but no photopotential resulted. The electrical resistance of cells B-1, A-1, A-5, A-6, and A-7 was rather high due to the dimension of the cells or to the low concentration of the

solution, preventing measurements to be made to 0.01 mv. Water was purposely added to cell A-8 causing gas evolution at the electrodes and producing an erratic e.m.f. but after the water present had combined with the sodium leaving a thick layer of hydroxide on the electrode surface an e.m.f. could be measured, however, no photopotential was observed. No photopotential was observed in the case of pure solvent in contact with the sodium electrode, cell No. A-6, but here the measurements were not very accurate due to the high internal resistance of the cell. Cell No. A-3 was deliberately opened to the air after preparation, a small photopotential was indicated by a slight motion of the galvanometer on illumination but it was not definite enough to measure. In the case of cell No. A-5 air was purposely admitted to the cell after the sodium mirror had been formed and before the solution was poured in, thereby making it probable that a thin layer of sodium oxide covered the mirror. No photopotential was observed, possibly because of the insensitivity of the measurements or because of the thickness of the oxide layer.

The only cell which showed a definite photovoltaic effect was cell No. A-2, but this cell contained some water since on standing the sodium covering one of the tungsten wires disappeared bringing the tungsten into direct contact with the solution and causing the dark e.m.f. to rise to 0.9 v. Before this happened, the e.m.f. of the cell in the dark changed gradually

TABLE I.

Cell No.	Concn. of Soln. in wt. percent	Light Source	No. of illuminated electrodes	Dark e.m.f. of electrode to be illuminated in reference to other electrode, millivolts	Photo e.m.f. millivolts
A-1	3.9	lamp	1	8	0
A-2	18.2	lamp	1	25.10–16.5	+0.5±0.05
B-1	27	arc	3	<i>B-A</i> 76.1 <i>C-A</i> 16.0 <i>B-C</i> 61.3	<i>A</i> 0±0.1 <i>B</i> 0 <i>C</i> 0
B-2	27	arc	2	<i>B-A</i> 0.20	<i>A</i> 0±0.01 <i>B</i> 0
A-3	27	arc, lamp	1	–0.45	trace ±0.01
A-4	27	arc, lamp	1	–0.18	0±0.01
A-5	5	arc, lamp	1	–5.5	0±0.2
A-6	0	arc, lamp	1	±0.1 v	0±0.1 v
A-7	1	arc, lamp	1	26	0±1
A-8	27	arc, lamp	1	37	0

¹⁰ S. Sonkin, J. Opt. Soc. Am. **19**, 65 (1929).

from $+0.025$ v to -0.0165 v while the photopotential amounted to 0.5 mv irrespective of the dark e.m.f., the illuminated electrode becoming more positive. This photovoltaic production of an e.m.f. occurred instantaneously on illumination as far as could be told, but it was probably due to a layer of oxide or hydroxide on the surface of the sodium since no photovoltaic effect was ever observed for a perfectly dry cell in which the sodium surface was apparently clean. $\text{Cu}|\text{Cu}_2\text{O}$ electrodes in the presence of water exhibit a large photovoltaic effect so it is reasonable to suppose that a $\text{Na}|\text{Na}_2\text{O}$ electrode would act similarly. Sodium iodide dried by fusion was used in the case of cells A-1, A-2 and A-7 and sodium iodide dried in a vacuum at 300° in the case of the remaining cells.

In summarizing the experimental results we can say that no measurable photovoltaic effect exists for a clean surface of sodium in equilibrium with an anhydrous solution of sodium iodide in monoamylamine. Sodium surfaces formed by electrolysis, by condensation from the vapor state and by solidification of the liquid metal behaved alike. Changing the concentration of the solution and the source of the illumination likewise produced no photovoltaic effect. We do not believe, therefore, that a pure metal in equilibrium with a solution of its ions and of such a nature that no photochemical reaction can occur will show a photovoltaic effect analogous to the photoelectric effect exhibited by metals in contact with a gas or evacuated phase.

DISCUSSION

Having come to the conclusion that no observable photovoltaic effect exists for sodium, it is next of interest to consider what theoretical implications are inherent in this conclusion. In order to measure the e.m.f. to 0.01 mv a current

of the order of magnitude 10^{-8} amp. must flow through the galvanometer; the galvanometer, however, is sensitive to currents of 5×10^{-10} amps. Currents measured usually in photoelectric experiments vary from 10^{-11} to 10^{-15} amp., but may become as great as 10^{-3} amp.,¹¹ depending on the conditions, intensity of light, activity and dimensions of metal surface, presence of gas, etc. In our case we can conclude that if a photovoltaic current was produced it must have been smaller than 10^{-9} amp.

The probable reasons for the absence of a photovoltaic effect are; first, the absence of any chemical reaction which might take place under the influence of light such as the photolysis of water postulated by Audubert and second, unfavorable energy relationships. When visible light, or light of shorter wave-length, falls on a sodium surface exposed to a vacuum, electrons are ejected into the vacuum because the energy of the light added to the energy of the electron in the metal produces electrons having high enough energy to escape into the vacuum. In our case it may be that the stable energy level, if indeed such a level exists, of an electron in monoamylamine solution is so high that electrons in the metal activated by the energy of the visible light are unable to make the transition metal to solution. The presence of the positive sodium ions in the solution complicates matters, however, since the energy relations of the electrons may be modified by sodium ion transitions between the metal and the solution; for this reason quantitative calculations are at present impossible, but it is evident that the presence of the sodium ions does not change the energy relationships sufficiently to produce a photovoltaic effect.

¹¹ Reference 1, p. 435.