

## XXII. A note on the photoelectric properties of potassium-sodium alloy

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the presence of helium was detected in a cylinder of tinfoil exposed for a few hours over the emanation-tube.

These experiments show that the helium does not escape at once from the lead, but there is on the average a period of retardation of several hours and possibly longer.

The detection of helium in the lead and tin foil, as well as in the glass, removes a possible objection that the helium might have been in some way present in the glass initially, and was liberated as a consequence of its bombardment by the  $\alpha$  particles.

The use of such thin glass tubes containing emanation affords a simple and convenient method of examining the effect on substances of an intense  $\alpha$  radiation quite independently of the radioactive material contained in the tube.

We can conclude with certainty from these experiments that the  $\alpha$  particle after losing its charge is a helium atom. Other evidence indicates that the charge is twice the unit charge carried by the hydrogen atom set free in the electrolysis of water.

University of Manchester,  
Nov. 13, 1908.

XXII. *A Note on the Photoelectric Properties of Potassium-Sodium Alloy.* By J. A. FLEMING, M.A., D.Sc., F.R.S., Professor of Electrical Engineering in University College, London \*.

IN connexion with further researches on my oscillation valve or glow-lamp radiotelegraphic wave-detector, I was led to examine instances of electronic emission other than that due to the incandescence of metals or carbon *in vacuo*, to ascertain how far rectifying effects with high frequency currents could be obtained by them†. It is well known that under the action of ordinary and ultra-violet light the electropositive metals lose a negative charge of electricity, and it was shown by Elster and Geitel that this photoelectric effect is most pronounced in the case of rubidium, potassium, and the liquid alloy of potassium and sodium.

With the object of examining this effect, experiments were

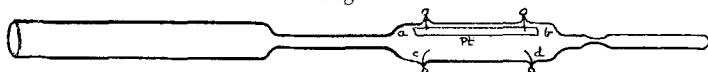
\* Communicated by the Physical Society : read November 13th, 1908.

† See J. A. Fleming, "On the Conversion of Electric Oscillations into Continuous Currents by means of a Vacuum Valve," *Proc. Roy. Soc. Lond.* vol. lxxiv. p. 476 (1905). Also "The Construction and Use of Oscillation Valves for rectifying High Frequency Currents," *Phil. Mag.* May 1906, p. 659.

made with various forms of apparatus, and, as the outcome of these, it was found that a convenient mode of preparing a suitable specimen of highly photoelectric metal was as follows :—

A tube of lead glass about 50 cms. long, and 1·5 to 2 cms. internal diameter has a constriction made at one place, and on one side of this a couple of platinum wires are sealed through the glass which are welded to a slip of platinum foil *a, b*, about 5 cms. long and 1 cm. wide (see fig. 1). This foil is

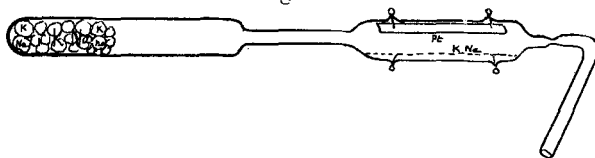
Fig. 1.



fixed close to the inside surface of the tube and opposite to it two other platinum wires *c d* are sealed through the tube. The end of this part of the tube is then drawn off and sealed to a length of smaller tube with a constriction in it by which the tube can ultimately be closed. A quantity of metallic potassium and sodium is then cut up into small cubes under naphtha, so as to give a number of clean morsels of the metal.

The operation of filling the glass tube is then as follows :—The fine quill tube at one end is first bent over at an angle of about  $75^\circ$  (see fig. 2), and by means of an indiarubber tube, coal-gas, which has been dried by bubbling through strong sulphuric acid, is led into it. The glass tube as a whole must have previously been well cleansed and carefully dried. When all the air is expelled, the fragments of sodium and potassium are dropped in at the wide open end of the tube, and about equal volumes of the two metals introduced. The open end is then loosely stopped with a plug of asbestos, and the glass tube heated in the blowpipe, and the open end so plugged is melted and sealed. If this is done skilfully, the tube can be sealed off with a rounded end by utilizing the gas-pressure to blow out the softened glass.

Fig. 2.



When cool, the lumps of metallic potassium and sodium are tilted over and should fill up about 10 to 15 cms. of the length of the so sealed off tube (see fig. 2). The tube is

then attached to a mercury pump for the purpose of making a high vacuum in it, and should be supported in a slanting position on a sheet of asbestos cardboard and covered by an iron trough. The tube should then be exhausted, and at the same time the metallic potassium and sodium heated so as to melt the lumps into a mass of liquid alloy which, however, will be covered with crusts of oxide.

When a good vacuum has been produced, the whole tube being hot and dry, the constriction in the quill tube may be melted with the blowpipe and the glass tube sealed off from the pump. If this is properly done, the part of the tube having in it the platinum plate will remain quite clean, and the molten metal or liquid alloy will be contained in the other portion of the tube. It is then easy to tilt the tube and transfer the clean mercury-like alloy of K and Na into the part of the tube containing the platinum plate, so as to make a pool of liquid alloy on the bottom of the tube having an electrical connexion with the outside by means of the platinum wires sealed through the tube, and having over it, and not far from its surface, a platinum plate also in connexion with the outside by sealed-in wires. In so doing, care should be taken that the liquid alloy is not splashed upon the platinum plate, but that the latter is kept quite clean and free from adherent drops of potassium-sodium.

It is better not to attempt to seal off that part of the tube in which the alloy is melted from that part to which it is decanted over, because the glass nearly always cracks and spoils the apparatus in so doing if there is the slightest particle of alloy smeared on it at the part heated in the flame.

A tube so prepared should be carefully handled, as if it is broken the liquid K and Na alloy is spontaneously inflammable and deflagrates violently on coming in contact with moisture. It is convenient to mount it on a wooden stand, which should be placed in an iron tray in case of an accidental breakage. By the aid of such a specimen of photoelectric alloy we can show many interesting experiments. If the tube is supported in a horizontal position, an electric arc contained in a projection lantern, equipped with the ordinary condenser-lens, can be so placed and tilted downwards as to converge on to the brilliant mercury-like surface of the pool of alloy a very concentrated beam of light. If, then, we connect the platinum plate and the alloy by means of wires with a sensitive mirror galvanometer, we find that the impact of the light upon the surface of the alloy not merely facilitates the escape of negative electricity from

it, but actually creates an electromotive force and current in the galvanometer circuit, which is in such a direction as to indicate that negative electricity is caused to move, by the action of the light, through the vacuum from the surface of the alloy to the platinum plate\*.

It has been pointed out by Professor Sir J. J. Thomson in his book 'The Discharge of Electricity through Gases' (see p. 73) that air traversed by ultra-violet light behaves like an electrolyte; and it is also stated that Stoletow has shown by direct experiment that two different metals immersed in such illuminated air are brought down to the same potential just as when they are immersed in a liquid electrolyte. Again, it is said that when plates of two different metals are opposed to each other and ultra-violet light allowed to fall on one of them, whilst the terminals of a battery of electromotive force  $E$  are connected to them so as to force a current across the space between them, the total E.M.F. in the circuit is not  $E$  but is  $E + M/M'$ , where  $M/M'$  is the contact difference of potential between the metals. There is, however, here an unexplained discrepancy. If metallic potassium or sodium were placed with a platinum plate in a liquid aqueous electrolyte, and the two metals connected by a wire outside so as to construct a voltaic cell, the current through the cell, that is the movement of positive electricity, would be from the potassium or sodium to the platinum through the electrolyte, and therefore the movements of negative electricity would be in the opposite direction. In the case of the photoelectric cell, the movement of negative electricity in the cell is from the K-Na alloy to the platinum. Hence the physical operation of the photoelectric cell is not identical with that of an ordinary voltaic cell. Stoletow has described (*Physikalische Revue*, i. p. 765, 1892) experiments in which two plates of different metals, one perforated with holes, were placed parallel and at a little distance from each other, and ultra-violet light allowed to fall through the openings of the perforated plate on to the other plate. The plates, when connected together, were found to produce a current of electricity in the connecting circuit. Prof. Sir J. J. Thomson, however, remarks (*loc. cit.* p. 73) that for this to happen in accordance with voltaic principles, the perforated plate must be made of the more electropositive metal, for then only

\* In the case of one tube of alloy prepared as above, my assistant, Mr. G. B. Dyke, noticed that the galvanometer deflexion was largely increased for a time by tilting the tube so as to make momentary contact between the alloy and the platinum, but the increased effect is not permanent.

would the negative electricity move towards it across the interspace between the plates. As a matter of fact, the best photoelectric metals are the most electropositive metals. Accordingly, if we imagine a sheet of potassium opposed to a sheet of zinc, then to make the photoelectric current agree in direction with the volta-electric current, we should have to illuminate the zinc plate with ultraviolet light, but keep the potassium plate in the dark. In the present case, the photoelectric current is in the opposite direction to the volta-electric current, assuming the ionized gas replaced by an aqueous electrolyte.

It seems therefore that in the case considered there are two separate sources of electromotive force, viz.: the volta contact-difference of potential of the metals in the cell and a photoelectromotive force due to the illumination; and to these may be added an external electromotive force due to any battery inserted in the circuit. In two tubes, made as above, I found that the electromotive force produced by the incident light was equal to 0.45 volt in one, and in the other tube to 0.6 volt. This E.M.F. was measured by the counter E.M.F. (produced by a shunted cell) which had to be introduced into the photoelectric cell circuit to reduce the galvanometer deflexion to zero. These differences are no doubt due to small differences in composition of the alloy in the two cases, to differences in the intensity of the light used at the time of making the measurements, or to differences in the pressure of the residual gas in the tube. The current produced by the tube of E.M.F. equal to 0.6 volt through a galvanometer of resistance 180 ohms, was found to be 5.4 microamperes. This indicates that the equivalent resistance of the tube is 74,000 ohms on the assumption that the effective E.M.F. is the same when the circuit is open and closed. The current increases very rapidly at first with the intensity of the incident light, but the author has not yet been able to find time to make measurements of the relation between the illumination per square cm. of the surface and the E.M.F. created in the circuit.

By the use of two such cells placed in series, I have found that the separate photoelectromotive forces are additive, and that if such photoelectric cells are joined in series like voltaic cells and separately illuminated, the individual E.M.F.'s are added together in an external circuit connecting the first and last plate. In the case of the two tubes mentioned above, giving separately 0.45 and 0.6 volt E.M.F., the E.M.F. when in series was found to be 1.0 volt.

At one time I contemplated constructing a photoelectric

battery of such cells which should give a high E.M.F. by the mere impact of light upon its most electropositive elements.

With the above described cells we can also verify easily a number of interesting observations made by previous experimentalists.

As regards the nature of the radiation which is chiefly effective, we find that for potassium alone, or for the potassium-sodium alloy, the effective rays are the most refrangible ones of the visible spectrum. The ultra-violet light in the arc is considerably filtered out, if not altogether stopped, by the thick glass condenser-lens, and by the glass walls of the tube. We can, however, effect a further separation of visible rays by screens of coloured glass, or solutions or stained gelatine films.

If we interpose in the path of the incident light a very thin film of gelatine stained with a yellow dye or a sheet of ordinary yellow glass, the deflexion of the galvanometer drops almost to zero. The same reduction is effected by a sheet of ruby glass or gelatine film stained red. A green glass cuts off a good deal of the deflexion, but a sheet of cobalt glass reduced it only to about two-thirds, showing that the blue glass is fairly transparent to those rays which can produce this electromotive force.

The galvanometer deflexions increase very rapidly with the intensity of the incident light, and unless an extremely sensitive galvanometer is used it is necessary to throw a very intense beam of light upon the surface of the metal to obtain any marked evidence of the production of electromotive force by the mere action of light upon the surface of the alloy. If the energy required to produce this photoelectric current comes from the incident light, then the latter must in some degree be absorbed, and the active rays must therefore be those which are absorbed by the photoelectric metal or conversely emitted by it when it is heated. We know well that the light due to the violet line in the flame spectrum of potassium salts passes easily through cobalt glass. Hence the fact that light which has passed through cobalt glass is still exceedingly active in producing the photoelectric effect with potassium, may indicate that it is this ray which is absorbed in its production. In the case of rubidium, Elster and Geitel showed that the yellow and orange rays were relatively more active in the production of the photoelectric effect, and a glance at the flame spectrum of rubidium salts shows that the lines are most numerous in the red, yellow, and green region.

Also, we can confirm easily another observation of the

effect of the plane of polarization of the incident light. If we polarize the incident light by a Nicol's prism, and connect the metals of the photoelectric cell with a galvanometer either with or without a battery of 1 or 2 secondary cells inserted in the circuit, then we find at once that the galvanometer deflexion is much greater when the plane of polarization is at right angles to the plane of incidence, than when these planes coincide.

On the electromagnetic theory of light, this may be stated by saying that the effect is a maximum when the electric vector of the plane-polarized light is normal to the surface of the photoelectric metal, and a minimum when it is parallel to it. The theory that fits in best with the above facts, is that the light facilitates or causes an escape of negative corpuscles or electrons from the surface of the photoelectric metal, and to do this it must of course impart to them energy sufficient to give them a velocity enough to carry them beyond the range of attraction of the positive charge which remains behind on the metal.

Since the electropositive metals are those which most easily lose electrons from their atoms, this is in accordance with the observed fact that the most electropositive metals are the most highly photoelectric substances. Again, if there is an emission under the action of light of electrons from the surface, we have an explanation of another fact easily proved with these tubes, viz. that the formation of a magnetic field parallel to the surface of the alloy greatly reduces the photoelectric current. We can show this easily by the great reduction which occurs in the galvanometer deflexion when even an ordinary horseshoe magnet is placed with its poles across the tube. Again, we can explain on this hypothesis the unilateral conductivity of the vacuous space over the illuminated alloy surface. If we connect the negative pole of a secondary cell to the external terminal of the alloy and the positive to the platinum plate, and insert a galvanometer as usual in the circuit, we greatly increase the galvanometer deflexion, which occurs when no cell is inserted. On the other hand, if the cell is reversed, then, provided the platinum is quite free from splashes of alloy, we cannot reverse the deflexion of the galvanometer.

It is obvious that if a magnetic field is created parallel to the surface of the alloy, a force will be exerted on the negative ion as it moves normally away from the surface, deflecting it from its path, and this will reduce the number of ions which in any time reach the platinum plate, and therefore will diminish the current. Again, the negative electrification



of the photoelectric metal will increase the force of propulsion on the ion, and hence increase the emission per unit of time, and therefore increase the observed current.

It is obvious, then, that the ionized gas over the illuminated alloy has a unilateral conductivity, and will conduct the current from a voltaic cell in one direction, but not in the opposite. Negative electricity can be conveyed from the alloy to the platinum across the rarefied air-space, but not in the opposite direction. Hence, an alternating current whether of low or of high frequency, can be rectified, and by interposing such a light-cell in the circuit of a galvanometer, in which circuit high-frequency oscillations are also created by the inductive action of a discharging condenser, I have been able to rectify these oscillations. The action, however, proved to be much more feeble and irregular than the similar rectifying effect which can be produced by a glow-lamp, and as at that time I had succeeded in finding a far more efficient glow-lamp rectifier or oscillation detector, the experiment with the rectifying effects of potassium-sodium alloy were not continued.

The interesting question, however, still remains as to the source and nature of this photoelectromotive force which is produced by the absorption of light by the surface of highly electropositive metals.

It is much affected by temperature, being increased by heating the alloy and by exposing it to powerful radiation for some time. If a galvanometer is used as described to detect the photoelectric effect, the current is found to be dependent upon the pressure and nature of the residual gas in the tube.

This was confirmed as follows:—A tube was prepared as above described with potassium-sodium alloy. Before sealing it off the pump, dry hydrogen gas was admitted and pumped out and then admitted again, and the tube exhausted to a pressure of about 0.01 mm. This tube was compared with others, in which the residual gas was air, but the exhaustion carried below 0.001 mm. The former tube exhibited only the very smallest evidence of photoelectric effect as measured by the galvanometer current, whereas the highly vacuous tube with residual air under very small pressure exhibited the effects well. The case of other tubes made as described, in which water vapour was accidentally present, which in a short time liberated hydrogen under the action of the metal; these after an interval ceased to give any current, even under the action of the strongest illumination, when the platinum plate was connected with the potassium-sodium

alloy through a galvanometer. These experiments and others show that to obtain the effect well a very high vacuum is necessary. In the process of preparing the tube the potassium and sodium should be melted, and the alloy and tube well heated for some time whilst the pump is going to drive off all traces of water vapour, also of hydrocarbon derived from the naphtha in which the metallic potassium is commonly preserved, and especially to drive off the hydrogen which seems to be occluded in considerable quantity by the alkaline metals, no doubt derived from the decomposition of water vapour.

The effect of variation of pressure of the gas upon the photoelectric effect was first investigated by Stoletow, and an account of his researches is given in Prof. Sir J. J. Thomson's treatise on the "Conduction of Electricity through Gases" (p. 224). He found that the current increased rapidly as the pressure diminished, which continued until the current reached a maximum value, after which it began to decline, but had a finite value at the lowest attainable pressures.

Stoletow's experiments appear to have been made with zinc plates and ultra-violet light. Owing to the greater manipulative difficulty when dealing with the more oxidisable and electropositive metals no attempt has been made to push these investigations with potassium-sodium alloy very far. The primary object in view in conducting them was to ascertain if the photoelectric effects could be utilized as an oscillation detector in radiotelegraphy; but as a type of glow-lamp detector has now been found by the writer far more efficient than that originally proposed by him, involving the employment of a carbon filament, these photoelectric experiments have not been pursued. They are put on record here merely for the sake of aiding any who may wish to show them as interesting lecture or class experiments, or pursue the purely physical investigation of the effect itself still further.

The question of photoelectric effects is not without interest in connexion with long distance radiotelegraphy. It has been shown that perfectly dust-free air is not ionized by ultra-violet light. If, therefore, the absorption of long radiotelegraphic electric waves which is found to exist when they pass through considerable distances of sunlit air is due to the presence of free ions in the air, these may arise from the photoelectric action of the light upon the dust particles. This suggests the question whether these particles may not be the same that create the blue colour of the sky. We know that whenever photoelectric effects take place, light must be

absorbed, and light of the same kind as that emitted by the photoelectric substance if it radiates. Thus zinc is rendered photoelectric under the action of ultra-violet light, but zinc when heated, whether by being used as spark-balls for an electric spark or as arc terminals for an electric arc, radiates much ultra-violet light.

In the same manner, the photoelectric effect of potassium appears to be due to the absorption of that violet ray which potassium itself emits if heated. If, then, these atmospheric particles absorb ultra-violet light, that would account for the relatively small percentage of ultra-violet light found in sunlight at the earth's surface, and also for the ionization found to exist in the atmosphere. This suggests the need for further observation on the number of ions present in the terrestrial atmosphere at various heights above the sea-level.

In conclusion, I have pleasure in mentioning the aid rendered in these experiments by my assistant, Mr. G. B. Dyke.

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XXIII. *On Variations in the Conductivity of Air enclosed in Metallic Receivers.* By C. S. WRIGHT, B.A., Exhibition Scholar, University of Toronto, and Wollaston Student, Gonville and Caius College, Cambridge\*.

[Plates IV. & V.]

## 1. INTRODUCTION.

IN a paper in the Phil. Mag. of December 1907, Professor McLennan records some observations made on the ionization of air enclosed in cylindrical receivers of lead, zinc, and aluminium. For " $q$ ," the number of ions generated per c.c. per sec. in these receivers he obtained the value 15, when they were made of zinc and aluminium; while with lead, values were found ranging all the way from 23 to 160 ions per c.c. per sec., depending on the sample of lead from which the cylinder was made. From these results Prof. McLennan drew the conclusion that ordinary commercial lead contained in general varying amounts of some active impurity.

From these and other experiments he pointed out also, that four possible causes must be considered as contributing to the ionization in the cylinders, viz.:—(1) penetrating radiation from the earth; (2) secondary rays excited by this

\* Communicated by Prof. J. C. McLennan, and read before the Royal Society of Canada, May 28, 1908.