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THE EFFECT OF ADSORBED K^+ IONS ON THE PHOTOELECTRIC THRESHOLD OF IRON

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Abstract

The photoelectric emissivity of a pure iron filament, which has just previously been used as a cathode for K^+ ions, is increased directly proportional to the positive ion current, for all surfaces where the computed fraction of the surface covered is $\theta \leqq 0.03$. For larger values of θ the emissivity for λ3022 and λ3132 increases rapidly with θ while λ2804 remains proportional to θ until the fraction of the iron covered with potassium exceeds 0.08. The solution of potassium in the iron beginning above $\theta \leqq 0.03$, as well as the vaporization of potassium by the ion bombardment prevent the formation of a surface for which θ exceeds 0.10. The data have been interpreted as indicating that for $\theta \leqq 0.03$ every K^+ ion striking the iron remains on the surface as an ion, while for larger values of θ both potassium atoms and ions are present. The increase in the photoelectric current is due both to the lowering of the work function by the presence of the positive ions and to the emissivity from the adsorbed atoms.

A STUDY of the photoelectric properties of several ammonia catalysts[1] which have been used as a source of positive ions[2] has shown that it is not possible to build up anything comparable to a monomolecular layer of potassium on the surface. The threshold for most catalysts lies below 3600A, while the maximum long wave-length limit ever obtained showed a just detectable emission for λ4359. The photoelectric properties of platinum plated glass filaments[3] in which potassion ions were electrolyzed through the glass into platinum were similar in nature in that it was never possible more than just to detect emission at λ4047.

The present research was undertaken to obtain an estimation of fraction of the surface covered with potassium under conditions similar to those mentioned above, especially where potassium was deposited on the surface in the form of ions. The method employed was to study the shift in the photoelectric threshold when a known quantity of K^+ ions, as given by a measured positive ion current, was deposited on a pure iron surface.

Apparatus

The apparatus is illustrated in Fig. 1. It is essentially the same as that described in the previous papers.

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[1] A. K. Brewer, J. Am. Chem. Soc. **53**, 74 (1931).

[2] C. H. Kunsman, J. Franklin Inst. **204**, 635 (1927).

[3] A. K. Brewer, Phys. Rev. **35**, 1360 (1930).

The iron filament studied was 10 cm long and 3.0 mm wide. The K^+ ion emitter was a platinum wire coated with catalyst 922 containing 0.26 percent K_2O. The filament was placed edgewise to the emitter, and with its surface perpendicular to the path of the ultraviolet light.

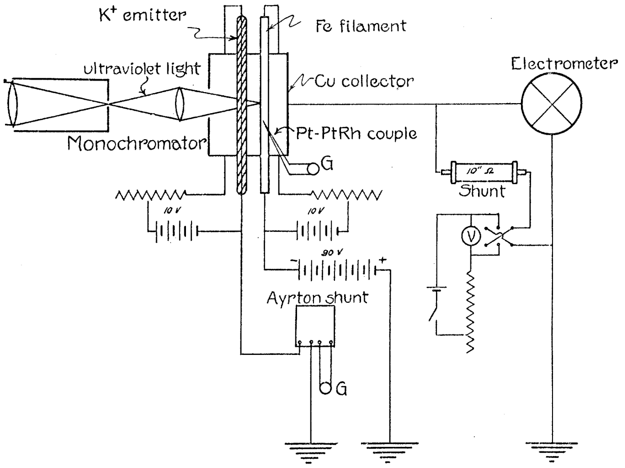

Fig. 1. Diagram of apparatus.

METHOD OF PROCEDURE

The iron filament was outgassed at 800°C until upon being cooled it showed a just detectable emission for λ2536, threshold being about 2575A. The potassium was deposited in the form of positive ions from the emitter, the amount of potassium being determined from the magnitude of the ion current and the time of flowing. The photoelectric emission from the filament was then read as quickly as possible. The first reading was usually taken in 30 seconds after the positive ion current was turned off; readings were taken thereafter at regular intervals until the emissivity became constant.

The emitter and the collector were maintained at zero potential at all times. The null method was used for the electrometer, the voltage necessary to be applied to the shunt to keep the electrometer at zero being read.

After the threshold had been determined the filament was glowed until the long wave-length limit again returned to 2575A. For small deposits of potassium this required about 10 minutes at 800°, but for the larger deposits it required from 30 to 40 minutes. The time could be cut in half by placing a positive potential on the filament.

RESULTS

In using a method of this type it was first necessary to determine the amount of potassium that passed from the emitter to the filament in the form of neutral atoms. This was accomplished by heating the emitter to the highest temperatures used for a period of 10 minutes with +45 volts on the filament. The increase in the photoelectric emissivity of the iron after this treatment was less than 1 percent of that which would have been observed had positive ions been drawn to the filament. The distillation of neutral atoms from the emitter to the filament, therefore, can be neglected.

The effect of the accelerating potential on the adsorption of positive ions was tested by running a known positive ion current for a given period of time with voltage on the filament varying from -22.5 to -270. The photoelectric emissivity for λ2653 was measured after each deposition of ions. No appreciable difference could be detected for voltages under 225 volts, although the ions deposited at 270 volts appeared to give a slightly lower emissivity.

The photoelectric emissivity from the potassium on iron surfaces for λ-2653 was measured at different voltages up to 225 volts. The voltage-current curve did not show complete saturation; a 30 percent uniform increase was observed between 22.5 and 135 volts; the surface was 2 percent covered with K^+ ions.

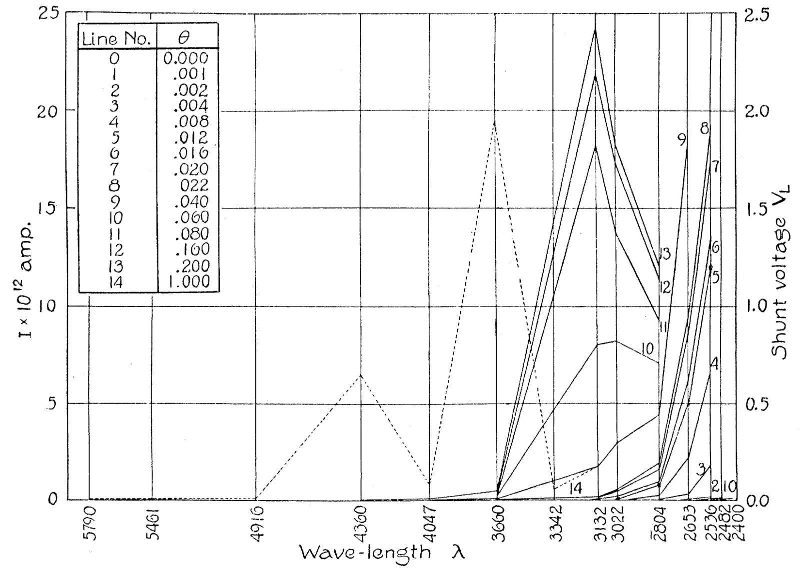

Fig. 2. The observed photoelectric current at different light frequencies for various fractions of the iron surface covered with potassium.

The effect of the positive ion density on the adsorption of potassium was determined by varying both the size and the duration of the positive ion current. Identical values, to within the limits of experimental error, were obtained when the current was increased ten fold and the time cut to a tenth. Thus the rate of deposition of ions had no appreciable effect on the photoelectric emissivity.

The photoelectric emissivity for the different surfaces formed by the deposition of varying amounts of potassium ions is shown in Fig. 2. In these experiments the potential of the filament was maintained at -90 volts with respect to the collector and the emitter. The temperature of the filament was kept at 150°C. For the sake of clearness the emissivity for the different mercury lines is plotted directly, irrespective of the intensity of the line, the observed points for a given surface being connected by straight lines to show continuity.

The column θ gives the fraction of the iron surfaces covered by potassium as computed from the positive ion current. The diameter of the K^+ ion is taken as 1.33×10^{-8} cm. Close packing of the ions is not assumed.

The results, for the most part, were very reproducible, especially for the low values of θ. This is illustrated in line 5, in which two sets of points are shown. For values of θ above 0.1, some fluctuations were observed.

A distinct difference was noted in the effect of aging on the deposits above and below $\theta = 0.04$. Below this point the emissivity increased for 5 or 10 minutes, after which it remained constant for long periods of time. For the higher values the opposite effect was observed, namely, the emissivity decreased with time, finally reaching a constant value; this is illustrated by line 13, in which the emissivity for λ2804 dropped the amount shown in 12 minutes. For ion deposits in which the computed value for θ was above 0.2, the drop in emissivity was too rapid to be measured for several minutes after turning off the positive ion current.

The fatiguing effect for the heavier deposits made it seemingly impossible to build up anything like a molecular layer on the surface. In fact a quantity of ions that should have formed two molecular layers showed but slightly greater emissivity than did a quantity capable of forming only 0.2 of a layer.

The emissivity showed an increase with temperature for all values of θ, the effect being very pronounced for those deposits showing a fatigue with time. To illustrate, a filament similar to line 10 fatigued 20 percent in 40 minutes at room temperature. When the temperature was raised to 150°C the emissivity was but 15 percent under the original, at 260° it was 3 percent under, and at 320° it was about 10 percent above. At this temperature a decreased emissivity due to evaporation from the surface set in, the emissivity decreasing slowly with time. At 400°C the photo-current fell to 40 percent of the original value in 8 minutes. The effect of temperature on the emissivity decreased with the amount of potassium on the surface; line 5, for instance, showed only a small increase below the temperature at which evaporation became appreciable.

The emissivity of pure potassium, for matter of comparison, is shown by the dotted lines. The current ordinate is 500 times that for the potassium on iron surfaces. The pure potassium surface was prepared by vaporizing metallic potassium onto a silver plate until the surface was completely covered. The tube was made entirely of Pyrex, no quartz window being used.

The long wave-length limit found for potassium was in the neighborhood of 6000A, while the maximum obtainable from the deposition of K^+ ions was about 4400A. The difference in emissivity of the two surfaces for the longer wave-length is very pronounced. This may be seen in Fig. 2 for λ3660 and for λ4360, where the emissivity for potassium is some 20,000 times that for the potassium on iron surfaces.

The effect of the fraction of the surface covered (θ) on the emissivity is shown in Fig. 3.

It will be observed that for the Hg lines λ2804, 2653, and 2536, the emissivity is proportional to the computed fraction of the surface covered under 0.08 of a molecular layer. Above this point the emissivity falls off rapidly, reaching a constant value for a surface about 0.2 covered. For the lines λ3022 and 3132, however, the emissivity increase is abnormally large. The emissivity for λ3660 was so weak at all times that the shape of the curve could not be determined.

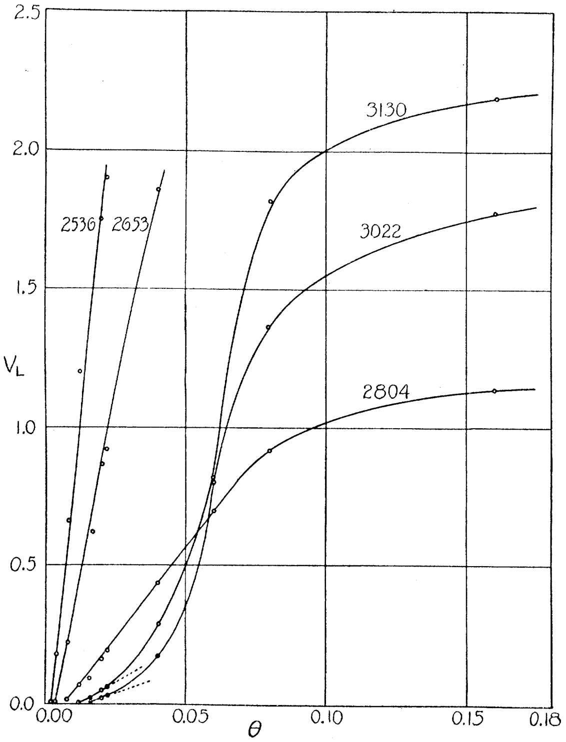

Fig. 3. The effect of the fraction of the surface covered with potassium on the photoelectric emissivity for various light frequencies. V_L = shunt voltage.

Experiments similar to those described above were made with platinum and with nickel as the filament metal. The results obtained were very unsatisfactory, except in so far as they showed clearly why so much difficulty has been experienced in the past in obtaining the work function of platinum.

Platinum was exceptionally bad in that it was exceedingly difficult to get the filament to show no shift in threshold upon further heating. After the K^+ ions were deposited on a well glowed filament the photoelectric emissivity decreased so rapidly with time that only approximate readings could be taken. Heating for hours at 1000°C failed to restore the threshold to its original value.

The results obtained with nickel were similar to those of platinum only much less pronounced. For small values of θ nickel checked iron fairly well, although it was much more difficult to remove the potassium from the surface by heat. The threshold could not be measured for the heavy deposits due to the fatiguing effect with time.

Discussion of Results

The effect of sodium vapor on the photoelectric threshold of platinum has been investigated by Ives.[4] The results show that the long wave-length limit shifts towards red as sodium is deposited on the platinum, passes through a maximum, and finally becomes constant at the threshold for pure sodium.

Becker[5] has shown that for small quantities of barium adsorbed on tungsten the ratio of adions to adatoms is large, but decreases with the amount of barium adsorbed until for a monomolecular layer only about one out of ten atoms is ionized.

These results presented in Figs. 2 and 3 are similar to those obtained by Ives in that the threshold is shifted toward the red as the amount of potassium on the surface is increased. Further, they are in accord with the postulates of Becker in that both potassium atoms and ions appear to exist on the surface.

It will be recalled that for values of $\theta \leqq 0.03$ the emissivity increased with time to a constant final value, after the positive ion current was turned off. This is evidently due to a migration of K^+ ions over the surface until a uniform distribution is established. The fact that the emissivity reached a constant value indicates that for values of θ under 0.03 the potassium is not lost to the surface either by evaporation or solution.

Line 9 of Fig. 2 is the first to show a decrease in emissivity with time; likewise it is the first to show an abnormal emissivity for λ3022 and 3132. The most probable interpretation of these facts is that for $\theta \overset{=}{>} 0.04$ part of the K^+ ions striking the surface go over to neutral atoms in which condition they are soluble in the iron. The decrease in emissivity is not due to the evaporation of potassium since the original threshold can be restored by raising the temperature of the filament.

The effect of K^+ adions on the emissivity is shown by Fig. 3 to be proportional to the positive ion current. This indicates that for $\theta \leqq 0.03$, every ion striking the surface sticks, and that the increase in emissivity is due solely to the lowering of the work function by the adsorbed ions.

The enhancement in the emissivity for λ3022 and 3132 shown by lines 9 to 13 in Fig. 2 where $\theta \overset{=}{>} 0.04$ must be due to some cause different from that mentioned above. The simplest interpretation of these results is that above $\theta \overset{=}{>} 0.04$ the increased emissivity is due not only to a lowering of the work function by the adions, but also to a photoelectric emission from the neutral potassium atoms adsorbed on the surface.

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[4] Ives, Astrophys. J. **60,** 209 (1920).

[5] J. A. Becker, Proc. Am. Electrochem. Soc. **55,** 153 (1929).

The failure to build up anything like a monomolecular layer of potassium by the deposition of K^+ ions is due to several causes. The dissolving of the adatoms in the iron has been mentioned. An equally important cause appears to be that while a bombarding K^+ ion hasn't sufficient energy to remove an adion, it is capable of removing an adatom. A state of equilibrium appears to be established for $\theta \overset{=}{>} 0.08$, wherein neutral atoms are removed from the filament as fast as ions arrive.

The work function for the various ammonia catalysts is usually far above that of an iron surface 0.03 covered with potassium. It follows, therefore, that under ordinary operating conditions all potassium at the surface is ionized. The presence of potassium ions and the absence of potassium atoms is doubtless the determining factor in making these substances such excellent positive ion emitters.

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