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The Effect of Adsorbed Oxygen on the Photoelectric Emissivity of Silver

BY A. KEITH BREWER

Silver has been shown by Benton and Drake[1] to adsorb oxygen in both the "physical" and "activated" forms. The former occurs at low temperatures, the rate is rapid, and the oxygen is readily removed by evacuation. The latter occurs only at elevated temperatures, and the oxygen is not removed except by prolonged heating, but it can be burned out readily with hydrogen.

The name "activated" adsorption has been proposed by Taylor[2] since it takes place with definite heat of activation. Taylor suggests that the adsorption forces involved in this case are those commonly termed electrostatic or valence forces, while "physical" adsorption he feels is related to van der Waals' forces.

A very satisfactory conception of the electrical forces present at surfaces has been furnished by the theory for electrons in metals recently proposed by Sommerfeld. Since the photoelectric effect offers a sensitive tool for studying the electrical properties of surfaces, the present research was undertaken to see if any correlation could be made between the electron work function and the types of the adsorption as found by Benton and Drake; it is hoped that the results will furnish a clearer picture of the adsorption forces involved.

Apparatus

The apparatus was essentially the same as that described previously.[3,4] The silver (C. P.) was in the form of a ribbon 8 cm. long, 3 mm. wide and 0.03 mm. thick. The temperature was determined by a Pt-PtRh thermocouple spot-welded directly to the silver. The silver was maintained at 12 volts negative to the collector.

The silver was conditioned by glowing to near the melting point in hydrogen for one day, followed by a degassing at 800° *in vacuo*. The filament during the conditioning process was reduced to about one half the original thickness. The oxygen was liquid air dried.

Results

The values for the long wave length limit of silver as reported in the literature vary over the exceedingly wide range from 3390 to 2610 Å. The best values for outgassed silver are probably those of Winch[5] who found 2610 Å. (4.73 volts) at 20° and 2700 Å. (4.56 v.) at 600°.

The silver ribbon used in the present experiments initially gave a detectable emission for λ 3130. After the surface was cleaned in the manner described above the threshold at 20° was close to 2675 Å. and to 2725 Å. at 600°.

The effect of oxygen at room temperature is small; at 1 mm. pressure the emission current for λ 2536 was about 30% larger than for vacuum conditions, corresponding to a red shift in the threshold of about 20 Å. As the oxygen pressure was reduced below 1 mm. the photocurrent increased slightly until the pressure reached 0.15 mm.; below this point it decreased gradually until at 0.005 mm. it approached that for clean silver. The process was repeated several times without any permanent change in the silver being apparent, all the results being perfectly reproducible.

The effect of temperature on the emissivity in oxygen is quite complicated. The photocurrent at first rose and then decreased with time to some very small value. This may be seen from the following data taken for λ 2536 at 1 mm. pressure and 110°.

TABLE I

Heating time, min.	Photocurrent, amp.	Heating time	Photocurrent
0	9.5×10^{-14}	15	3.7×10^{-14}
3	75 (approx.)	30	1.6
6	46	45	1.0
10	33	90	0.67

When the temperature was raised to 200° the current fell to 2×10^{-15} amp. in two minutes and became undetectable in four minutes.

The general characteristics of the results are the same for various temperatures. An exact estimation of the effect of temperature on the rate of photoelectric fatigue could not be made since it became too fast to measure above 200°;

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[1] Benton and Drake, THIS JOURNAL, **54**, 2186 (1932); **56**, 255 (1934).

[2] H. S. Taylor, *Chem. Rev.*, **9**, 1 (1931).

[3] A. Keith Brewer, THIS JOURNAL, **54**, 1888 (1932).

[4] A. Keith Brewer, *J. Chem. Phys.*, **2**, 116 (1934).

[5] Winch, *Phys. Rev.*, **37**, 1269 (1931).

the rate evidently increases according to some exponential function of the temperature.

The final threshold taken by the silver could not be determined with certainty since no emissivity could be obtained with the light through the monochromator. The full arc, however, gave a small current; the long wave length limit, therefore, must have been in the neighborhood of 2000 Å.

The emissivity, after heating in oxygen, was not restored by lowering the temperature, or by evacuation at room temperature. It returned to the normal for clean silver, however, when the filament was heated for a few minutes in hydrogen, or after heating to 600° for about ten hours *in vacuo.*

The silver surface after heating in 1 mm. of oxygen possessed unique emissive properties upon evacuation. At room temperature the initial threshold was near 2000 Å. As the temperature was raised little change was noted below 50°; above this point, however, the long wave length limit shifted rapidly to the red, reaching a rather broad maximum between 150 and 250° with the threshold near 3150 Å. At still higher temperature the emissivity slowly decreased, the threshold at 600° lying near 2900 Å.

This shift in the threshold can be seen more easily from the change in the photocurrent for a given light frequency with respect to temperature. Typical data for λ 2653 obtained from a filament previously heated to 200° in 1 mm. of oxygen for thirty minutes are shown in Table II. These measurements were made at pressures below 10^{-6}.

TABLE II

Temp., °C.	Current, amp.	Heating time, min.	Threshold, Å.
23	0.0		2000
50	1.47×10^{-14}		
150	19.8	30	
160	55.5	35	
160	76.0	70	
160	89.5	60	
160	88.2		
260	91.0		3100
330	60.0		
410	36.0		
508	34.5		
150	88.0		
23	17.5		2900
23	1.0 (normal for clean silver)		2675

The thresholds given are only approximate.

The characteristics of the above data, namely, the sharp rise with the temperature, the broad maximum near 200° and the slow decrease for still higher temperatures, could be retraced for successive heating periods, the only changes being the absence of the creeping-up effect at 160° and the shifting of the threshold at room temperature after the first heating period *in vacuo* from 2000 to near 2900 Å. It should be mentioned that the currents for each successive heating period showed a gradual trend toward lower values, the shift increasing with the length of time the filament was held at the higher temperatures. After heating to 600° from five to ten hours the filament returned to the normal value given at the foot of the table. Heating in hydrogen rapidly destroyed this abnormally large emissivity.

An extended series of experiments was carried out to see if the sign and value of the potential applied to the silver, the presence of ultraviolet light during the heating period, and the heating temperature had any effect on the magnitude of this abnormal photosensitivity. The potential definitely had no effect. Temperatures from 200 to 600° had little effect except in the heating time required. The effect of ultraviolet light is uncertain. The data indicated a slightly greater photosensitivity after the filament had been heated in oxygen while exposed to the full arc or to λ 2536 with the monochromator open wide, but the differences were small and hence of doubtful significance.

The photosensitivity of the silver filament could be destroyed very quickly by means of a high frequency discharge in the presence of oxygen. In this case the surface became noticeably browned, indicating the presence of silver oxide formed by the ozone in the discharge. The brown coloration readily disappeared upon heating; the photosensitivity was too low to measure until the disappearance of the oxide. Upon heating *in vacuo* it was found that some of the abnormal sensitivity described above had been induced in the silver by the discharge.

Discussion of Results

The data just described show clearly that in so far as the work function is concerned, oxygen affects silver in three distinctly different ways depending on the treatment received. (1) The small enhancement in the emissivity in the presence of oxygen at room temperature, the surface immediately returning to normal upon evacuation. (2) The abnormally photosensitive surface obtained upon heating *in vacuo* after previously heating in the presence of oxygen; it is this oxygen, removable only with difficulty, that is doubtless responsible for very wide variations reported in the literature for the photoelectric threshold of silver. (3) The inactive surface found in the presence of oxygen when the silver is heated or when exposed to ozone.

The correlation between the conditions under which the three types of emissivity are obtained and the results of Benton and Drake is at once apparent. There can be little doubt but that (1) is due to the phenomenon described as "physical" adsorption, (2) to "activated" adsorption, and (3) to the presence of "surface" silver oxide. In considering this correlation it must be borne in mind that the photoelectric effect is sensitive to far smaller quantities of gas than can be detected in ordinary adsorption experiments. The data also make it clear that both types of adsorption are intimately associated with the electrical properties of the surface.

It has long been known that gases exert a profound influence on the work function of metal surfaces.[3,6,7] As early as 1904 Hallwachs suggested a distinction should be made between gases absorbed within the body of the metal and those adsorbed on the surface. He postulated that the former assist in the removal of the electrons while the latter retard the escape. This contention seems justified by the work of Rietschel[8] wherein it was shown that gas in the metal increased the photoemission even in the best tube vacuum, while gas in the phototube tended to lower the emissivity of outgassed metals. The further accumulation of a large number of facts such as the coincidental change in conductivity and work function during the outgassing process,[7] the contribution of dissolved gases to the positive current in metals detectable in certain cases,[9] the intense amount of heating necessary to eliminate the effect of gases on the photoelectric emissivity[5] and many others, support the original contention of Hallwachs that gases absorbed or at least imbedded in the surface have the most pronounced effect in lowering the work function.

The mechanism by which gases lower the work function is now believed to be through the medium of positive ions. Suhrmann[10] in an extended investigation of the effect of adsorbed hydrogen on platinum has shown that the gas contributes appreciably to the work function only when in the ionized form; also he has obtained evidence to show that hydrogen is dissociated into ions by the forces within the metal and that these ions come to the surface when the metal is annealed in a vacuum and so cause the red shift in the long wave length limit. The writer has also shown that gases affect both the photoelectric and the thermionic emissivity in a manner identical to that obtained with adsorbed alkali ions.[11]

The means by which gases become ionized at metal surfaces involved considerable uncertainty prior to the advent of the Sommerfeld theory of electrons in metals; since ordinarily the ionization potential of the gas exceeds the work function by a factor of about 3, the concentration of adsorbed ions would be expected to be exceedingly small on the basis of older theories. Sommerfeld has now shown that the work function as expressed by $e\phi$ in thermionics and as $h\nu_0$ in photoelectrics is in reality the difference between two quantities W the surface potential barrier, and μ, the kinetic energy of the electron gas within the metal. Thus $h\nu_0 = e\phi = (W - \mu)e$. The value of W for silver is about 18 electron volts while μ is close to 11.5 volts.[12] The ionization potential (I) of oxygen is 12.2 volts.[13] Thus I is but slightly larger than μ and materially smaller than W. Therefore the amount of energy (E_k) that a molecule must pick up by kinetic agitation to become ionized ($\mu + E_K = I$) is small, especially if the adsorbed molecules are highly distorted by the surface field as suggested by Suhrmann.[10] In consequence it will be seen that the fraction of the oxygen molecules that are present in the silver in the ionized form is not only high but will increase with rising temperature. A detailed discussion of the ionization of gases by metals has been presented recently by Nyrop.[14,15]

In the light of what has just been said the most probable interpretation that can be given at the

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[6] A. Keith Brewer, THIS JOURNAL, **54**, 4588 (1932).

[7] For a general discussion see Hughes and DuBridge, "Photoelectric Phenomena," and Richardson, "Emission of Electricity from Hot Bodies."

[8] O. Rietschel, *Ann. Phys.*, **80**, 71 (1926).

[9] O. Schmidt, *Chem. Rev.*, **12**, 363 (1933).

[10] R. Suhrmann, *Physik. Z.*, **30**, 939 (1929).

[11] A. Keith Brewer, *Phys. Rev.*, **44**, 1016 (1933).

[12] Rosenfeld and Witmer, *Z. Phys.*, **49**, 534 (1928).

[13] Mulliken and Stevens, *Phys. Rev.*, **44**, 720 (1933).

[14] J. E. Nyrop, *Phys. Rev.*, **39**, 967 (1932).

[15] J. E. Nyrop, "A Treatise on the Catalytic Action of Surfaces."

present time is that "physical" adsorption is a pure surface phenomenon. The effect being small it cannot be told whether the lowering of the work function is due to the presence of a few ions formed by collision with the free electrons at the surface, or to the surface being covered with a layer of molecules distorted into pronounced dipoles by the combined image and intrinsic forces of the surface. It should be mentioned in this connection that while it is theoretically possible for a layer of adsorbed dipoles to raise or lower the work function, depending on the manner in which adsorption takes place, there is as yet no experimental evidence that such changes do occur.

The results just described show definitely that "activated" adsorption is closely correlated with the condition of the gas that gives rise to the abnormal photosensitivity. It is generally accepted among those working in the field of photoelectricity "that the photoelectric properties are determined by the amount of gas actually dissolved *in* the surface" (Hughes and DuBridge, p. 77). Since ultraviolet light can only penetrate a very short distance into the surface it is probable that the gas dissolved in the first three or four atomic layers gives rise to the entire effect. On this basis "activated" adsorption is in reality a case of "surface" solution in which the gas enters the first few layers of the metal atoms. This view seems compatible with the postulate of Benton[16] "that activated adsorption is a necessary precedent to solution."

The physical state of the activatedly adsorbed oxygen is necessarily responsible for its effect on the work function. It is possible that the effective oxygen in the surface is present in the form of highly polar molecules or as positive ions. Unfortunately the action of such dipoles is unknown. The characteristics of the wave length *vs.* emission curves obtained in the present experiments are identical in every respect to those observed when alkali ions were deposited on iron and tungsten; it is reasonable to infer therefore that positive ions are also responsible for the present results. Since the effect of an adsorbed ion on the work function depends both on the nature of the ion and the base metal, it is impossible to state exactly what fraction of the surface layer is occupied by oxygen ions. Under the most favorable conditions observed the photocurrent for λ 2653 was enhanced by adsorbed oxygen from 1×10^{-14} amp. to 1.13×10^{-12} or 113 fold, while the threshold shifted from 2675 to about 3150 Å. Assuming that positive oxygen ions behave like K^+ ions and silver as tungsten, the effect is equivalent to that produced by a layer of ions covering 9% of the surface; the order of magnitude of this value is doubtless correct in the present case. It does not seem possible that any such shift in the threshold could be brought about by adsorbed dipoles.

In referring to Table II it will be seen that the emissivity rises sharply to a maximum and then slowly decreases for still higher temperatures. Since the increase in emissivity is proportional to the concentration of positive ions at the surface[11] it follows that the observed increase in the emission current with temperature represents the increase in the concentration of oxygen ions. The slow decrease, for still higher temperatures, being found only where fatigue with time was observed, is evidently due to the rate of evaporation being such that diffusion to the surface could not maintain the ion density. A similar condition has been observed by Koller,[17] for oxygen on potassium. In this case it was found that oxygen dissolving in the potassium tended to increase the photocurrent, while the presence of oxide on the surface readily destroyed the sensitivity.

It is interesting to note that adsorbed oxygen lowers the work function while combined oxygen in the form of silver oxide materially raises it over that found for clean silver. This is due to the difference in the physical state of the oxygen in the two cases. Hughes and DuBridge (Ref. 7, p. 81) show that negative adsorbed ions raise the electron work function, while positive ions shift it to lower values. In the case described where oxygen has penetrated the silver the oxygen gives up an electron to become a positive ion while the electron lost becomes one of the "free" electrons of the metal. In the case of the compound silver oxide just the opposite is true, the silver being the positive ion and oxygen the negative ion in the crystal lattice. Thus it will be seen that adsorbed oxygen being positive lowers the work function while combined oxygen being negative increases the amount of work necessary for an electron to escape.

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(16) A. F. Benton, *Trans. Faraday Soc.*, **28**, 217 (1932).

(17) L. R. Koller, *Phys. Rev.*, **29**, 902 (1927).

Summary

Oxygen is shown to have three distinct effects on the work function of clean silver, as determined by means of photoelectric emission. (1) At room temperature the presence of oxygen slightly enhances the emissivity, the effect disappearing with the removal of the oxygen. (2) After heating in oxygen the silver upon heating *in vacuo* possesses abnormally large emissive properties, the effect only disappearing after long heating. (3) Heating in oxygen or exposure to ozone destroys the emissivity.

The effects observed under (1) and (2) have been associated with "physical" and "activated" adsorption respectively while (3) is due to the presence of "surface" silver oxide.

Evidence is presented to show that the lowering of the work function by "physical" and "activated" adsorption is due to positive oxygen ions, while the increase in the work for electron emission brought about by "surface" silver oxide is due to negative oxygen ions.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Ionization of Some Weak Electrolytes in Heavy Water

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We have made some preliminary measurements of the conductivities and the ionization constants of deutacetic acid, chlorodeutacetic acid and deutammonia in heavy water. On account of the uncertainty in the measurements and the still greater uncertainty in their interpretation we should hesitate to publish the results at this time were it not for the extraordinary differences that we have observed between the deuto and the corresponding hydro compounds.

At the time that this work was done very little heavy water was available and it was necessary to use the same micro methods and apparatus used by Lewis and Doody.[1] In the study of all the other physico-chemical properties of compounds of deuterium we have found it possible to obtain accurate results with very small quantities of material. It is not possible, however, in the measurement of the conductivity of poorly conducting solutions. It is not only that the very small conductivity cell presents certain difficulties which have not yet been overcome, but that in working with fractions of a gram of heavy water we have never succeeded in obtaining a lower specific conductivity than 10^{-5}. Nevertheless, we have in each case studied under the same experimental conditions the same substances in light and heavy water and the observed differences are significant. All our measurements were made at 25°.

Deutacetic Acid,[2] CH_3COOD.—By means of a capillary buret 0.00144 g. of pure glacial acetic acid was added to 0.334 cc. of ordinary conductivity water, making the solution 0.0722 *M*. The molal conductivity was found to be 6.20. Taking Λ_0 as 391 we obtain for the ionization constant at 25°, $K = 1.84 \times 10^{-5}$, which is in accord with the best values given in the literature.

The same experiment was repeated with heavy water and the same acetic acid. The heavy water used in this and other experiments contained several per cent. of light hydrogen, but the error thus introduced is negligible compared with other errors which we shall mention. The small amount of hydrogen contained in the glacial acetic acid is also negligible. Once more the solution was 0.0722 *M*. The specific conductivity proved to be 18.3×10^{-5} while that of the heavy water was 2.2×10^{-5}. We thus find for the molal conductivity, $\Lambda = 2.53$ if no correction is made for the conductivity of the heavy water, and $\Lambda = 2.22$ if the whole conductivity of the heavy water is subtracted from that of the solution.

To the same solution another equal amount of acid was added, bringing the molality to 0.1444 *M*. Here we find $\Lambda = 1.79$ and $\Lambda = 1.63$ when no correction, and when full correction, is made for the conductivity of the solvent.

We must next consider the value of Λ_0. Lewis

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[1] Lewis and Doody, THIS JOURNAL, **55**, 3504 (1933).

[2] The results for this one electrolyte we have briefly described in an earlier communication. Lewis and Schutz, *ibid.*, **56**, 1002 (1934).