The Action of Mercury Metastable Atoms on a Tungsten Surface

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The electron emission from metal surfaces due to the action of the 2^3P_0 metastable atoms was studied under varying conditions. The metastable atoms were produced by electron impact and diffused to the surface. The sensitivity of any metal surface was found to vary markedly with the vacuum conditions in the experimental tube and the extent to which the surface had been cleaned and outgassed. After thorough outgassing and cleaning each of the metals tested acquired practically the same sensitivity, which furthermore for any metal remained very nearly constant over long periods. Heating of a surface after it had acquired this equilibrium or "normal" sensitivity always resulted in temporary changes of the sensitivity following which it returned to its normal value. Investigation of these temporary changes of the sensitivity for a tungsten surface, with different mercury vapor pressures, showed that a deposit of mercury atoms was essential for the formation of a surface sensitive to mercury metastable atoms. The nature of these changes further indicated that the residual gas (oxygen) also played an important part and that the normal value of the sensitivity was due to the establishment of a very stable, complex arrangement of mercury and oxygen atoms upon the tungsten. Carefully dried oxygen was admitted to the experimental tube, and the observations of the changes in sensitivity as this oxygen was removed by progressive outgassing confirmed the conclusions as to the part played by oxygen. Transient values of the sensitivity fifty to a hundred times larger than the normal value were observed at one stage of this outgassing process when the relative concentrations of oxygen and mercury atoms were such as to make possible the formation of monatomic films. From the values of these high sensitivities it is concluded that in the case of the normal surface not more than one or two metastable atoms out of a hundred caused the emission of an electron. The formation of the sensitive surface was found to be uninfluenced by the metastable atoms. No correlation was found between the changes of response of a surface to mercury metastable atoms and to the radiation from an external source.

INTRODUCTION

ELECTRON emission by metal surfaces as the result of impact by metastable atoms has been investigated in some detail in the case of mercury and the rare gases. Webb,[1] Messenger[2] and Coulliette,[3] have studied the action of mercury metastable atoms on nickel surfaces. Oliphant[4] found that a large emission of electrons resulted from the impact of metastable helium atoms on metals. Uyterhoeven and Harrington[5] and others have obtained large electron emissions from cold electrodes in discharges of neon, argon and helium, which they explained as due in part to the action of long lived metastable atoms. Work of similar nature in neon has been reported by Langmuir and Found.[6] On the other hand, Kenty[7] attributes a large part of this electron emission in neon to abnormal photoelectric effect or to ionization of traces of foreign gas by the metastable atoms. In the case of mercury the energy of the metastable atom is too small to produce any ionization and Messenger has shown by the use of calcite and quartz windows, which could be interposed at will between the source of the metastable mercury atoms and the metal plate used as a detector, that in the usual type of Lenard tube used to measure critical potentials the greater part of the emission from the metal plate was due to the direct action of the metastable atoms, and that the ordinary photoelectric emission due to radiation excited in the tube was only a few percent of this. This was somewhat surprising in view of the fact that the energy available in the 2^3P_0 state (which is the longer lived metastable state and therefore the more

[1] H. W. Webb, Phys. Rev. **24**, 113 (1924).
[2] H. A. Messenger, Phys. Rev. **28**, 962 (1926).
[3] H. J. Coulliette, Phys. Rev. **32**, 636 (1928).
[4] M. L. E. Oliphant, Proc. Roy. Soc. **A124**, 228 (1929).
[5] W. Uyterhoeven and M. C. Harrington, Phys. Rev. **35**, 438 (1930) and Phys. Rev. **36**, 709 (1930).
[6] C. Found, Phys. Rev. **34**, 1625 (1929); I. Langmuir and C. Found, Phys. Rev. **36**, 604 (1930); C. Found and I. Langmuir, Phys. Rev. **39**, 237 (1930).
[7] C. Kenty, Phys. Rev. **38**, 377 (1931); Phys. Rev. **43**, 181 (1933).

important) is only 4.68 electron-volts, which is very close to the work function of the metals used, while the two most important lines excited corresponded to 4.86 and 6.7 volts, respectively. This fact and the observations on the variations in the sensitivity to the action of the metastable atoms resulting from changes of temperature, of mercury vapor pressure, and of the amount of residual gas suggested the present investigation, the object of which was to determine something of the nature of the action and the factors upon which it depended.

Preliminary Tests

The experimental tubes used were four electrode tubes with an oxide coated cathode, and a grid to produce and accelerate electrons which by impact excited mercury atoms to the 2^3P_0 metastable state. These atoms diffused to the metal surface under investigation from which they caused emission of electrons which were drawn off by a second grid maintained at a suitable potential. The first significant experiments were made with a tube having no greased or waxed joints, since earlier work had shown that the vapors from such joints caused marked variations in the response of the surface both to light and to mercury metastable atoms. This tube was provided with a side arm into which the surface under test was withdrawn and thoroughly cleaned and outgassed so that the main portion of the tube where measurements were made could be kept free from contamination. The surface could be either illuminated by monochromatic light through a quartz window or subjected to the action of the metastable atoms, in order to compare these two causes of electron emission.

To determine what part of the response was due to metastable atoms and what part was due to photoelectric action of the radiation from the hot cathode and of the radiation excited by electron impact in the vapor, a sliding quartz window was moved magnetically in front of the surface screening it from metastable atoms and permitting only the radiation to reach the surface. In this way it was determined that for every metal used only one or two percent of the total response was due to such radiation.

Surfaces of tungsten, nickel, iron, platinum, molybdenum and tantalum were mounted successively in this tube and tested both for response to mercury metastable atoms and to monochromatic light from an external source. For the latter purpose $\lambda 2650$ isolated from a mercury arc by a quartz monochromator was used since the energy per quantum of this radiation is very nearly the same as the energy of the mercury 2^3P_0 state. In addition measurements of the photoelectric response to the shorter wavelengths $\lambda 2537$ from a mercury arc $\lambda 2140$ from a zinc spark were made. While the response both to light and to metastable atoms varied markedly with vacuum conditions and with previous heat treatment of the surface, no correlation whatsoever was found between the changes in response to the action of metastable atoms and changes in response to the radiation of any of the wavelengths used. For example, a twenty-fold variation in the photoelectric effect was obtained under conditions which produced no appreciable change in the response to metastable atoms; under other conditions when marked increases in the response to metastable atoms were obtained, the photoelectric response diminished.

After prolonged heat treatment and outgassing of a given surface its response to metastable atoms became very nearly constant; i.e., while large changes followed any heat treatment of the surface, its response always returned to a value which did not vary more than ten percent from day to day. Furthermore, this value was very nearly the same for all of the metal surfaces tested. This result suggested that the response of the metal surface might in every case be due to a common impurity rather than to the metal itself. Accordingly a more thorough investigation was made of the effect of the residual gas and mercury vapor upon the response of a surface to mercury metastable atoms.

Apparatus

Since the best possible vacuum conditions are essential for such investigations, large experimental tubes containing magnetically operated shutters with their inevitable large masses of metal could not be used. A smaller and much simpler tube was therefore constructed with a minimum amount of metal. This tube is shown in Fig. 1. It contains an excitation system, having as

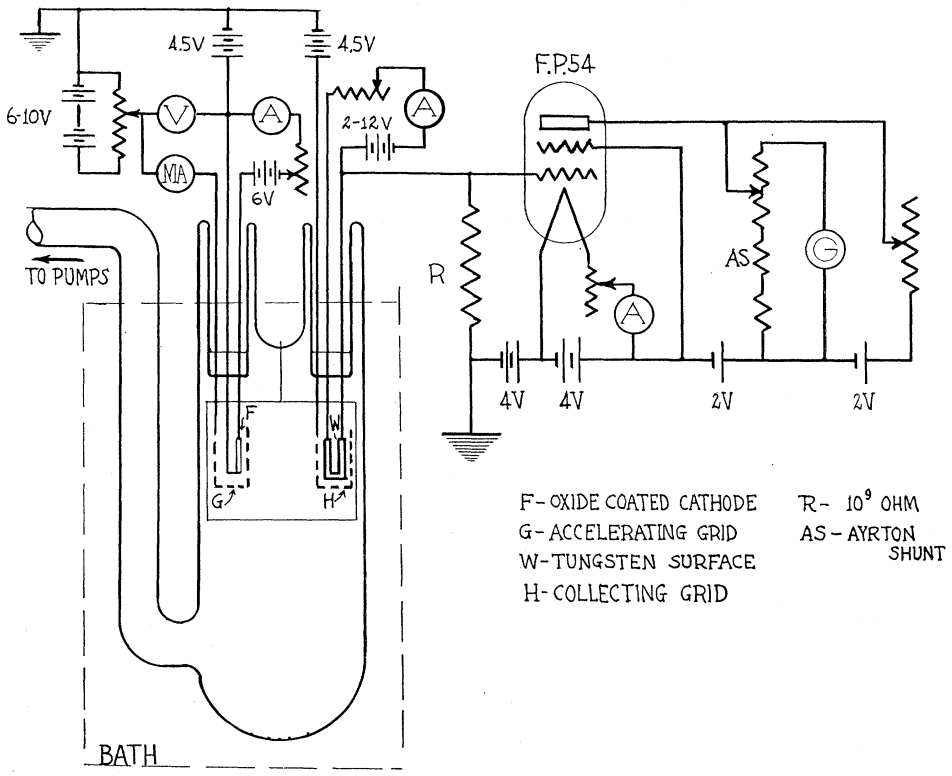

FIG. 1. Diagram of experimental tube and electrical circuits.

a source of electrons an oxide coated platinum cathode, *F*, surrounded by an accelerating grid of nickel, *G*, and a detecting system consisting of the surface studied, *W*, surrounded by a collecting nickel grid, *H*.

The surface *W* was made of tungsten foil, one mil thick in the shape of a "⊔" so that it could be heated for outgassing and subsequent heat treatment. This "⊔" was 10 mm long and 4 mm wide, the tungsten strip itself being one mm wide. A punch and die were used to cut this surface uniformly after several surfaces cut by hand had been burnt out during the outgassing process, apparently because of irregularities in the cutting.

The pumping system consisted of a mercury diffusion pump and a mechanical forepump, the residual gas pressures being measured by means of a McLeod gauge. Between the experimental tube and the pumping system was a magnetically operated mercury cut-off. To procure the best possible vacuum conditions the usual precautions of modern high vacuum technique were observed. No wax or greased joints of any kind were used, and the only stopcocks were on the fore vacuum side of the diffusion pump. Outgassed metal was used in the construction of all of the electrodes, which after fabrication were outgassed again before being put into the experimental tube. The mercury for the diffusion pump, McLeod gauge, and the cut-off was distilled into the system in as good a vacuum as possible. The tube itself was baked for many hours at about 500°C and the pumping tube flamed during this process.

The tungsten surface *W*, was heated by currents from a storage battery which was carefully insulated and shielded so that electron emission currents due to metastable atoms could be measured while the surface was being heated. This was possible up to temperatures of approximately 1000°K above which thermionic emission masked electron emission produced by the metastable atoms. The higher temperatures of the surface reached during outgassing and heat treatment

were measured by means of a disappearing filament type optical pyrometer while temperatures below the range of this instrument were measured by means of a small thermocouple welded to an identical surface in a duplicate tube.

To measure the electron currents produced by the action of metastable mercury atoms on the tungsten surface, which were of the order of 10^{-12} and 10^{-13} ampere, the surface was connected to a vacuum tube electrometer (FP–54) the changes in the plate current of which were measured by means of a galvanometer (sensitivity 10^{-10} ampere/millimeter) which was provided with a universal shunt.[8] With this method of measuring the electron current rapid changes in the response were readily followed. The circuits used are shown in Fig. 1.

The mercury vapor pressure was controlled by immersing the lower part of the tube as well as part of the pumping tube in a constant temperature bath. By occasional baking of the tube the amount of liquid mercury in it was restricted to a few small drops so that the mercury vapor pressure could be changed very rapidly. To measure the residual gas pressure the tube itself was used as an ionization manometer by using the hot-cathode and the two grids. This was calibrated against the McLeod gauge which was then sealed off. During the measurements of the residual gas pressure the tube was immersed in liquid air to remove the mercury vapor.

After the removal of the McLeod gauge the tube was again baked at 500°C for ten hours and all of the metal parts thoroughly outgassed in place by means of a high-frequency induction furnace. The vacuum attained after this procedure was of the order of 2×10^{-8} mm. The extent to which the tube had been outgassed was indicated by the amount of gas liberated when the tungsten surface was heated. If the temperature of the surface was raised to 2800°K there was no measurable increase in the pressure of the residual gas provided the walls were kept cool. If they became hot, however, the pressure rose to over 10^{-5} mm. This gas was re-adsorbed by the walls and metal parts of the tube upon cooling as evidenced by the fact that the pressure would diminish to its previous low value even though this test was carried on with the experimental tube shut off from the mercury diffusion pump by the magnetically operated cut-off.

[8] L. A. Dubridge, Phys. Rev. 37, 392 (1931).

Experimental

The response of the tungsten surface to mercury metastable atoms was determined during various stages of outgassing and the variations in this response as a result of heat treatment were carefully followed. Before discussing the variations attention must be called to two corrections which are necessary to make the various results comparable. The response of a surface depends not only upon its sensitivity but also upon the number of metastable atoms which reach it. This number depended upon the total number of mercury atoms present and upon the number of electrons emitted by the filament. Tests showed that the response of a given surface was proportional to the total number of mercury atoms present and also to the electron current from the hot cathode to the accelerating grid. In all of the following discussions all measures of comparative sensitivity have been corrected for variations in electron emission and in vapor pressure and are therefore referred to an equal number of impinging metastable atoms.

After the thorough outgassing described above the tungsten surface which had previous to outgassing been relatively insensitive to mercury metastable atoms was found to have increased in sensitivity from twenty to thirty times. Subsequent heating of the surface always resulted in marked temporary changes following which, however, the sensitivity soon returned to a value which varied on the average not more than ten percent over a period of several months, during which time the surface was subjected to numerous and varied heat treatments. This indicated that rather constant conditions had been obtained, in particular that of residual gas pressure. Under these favorable conditions, heating of the surface caused very significant changes in its response to mercury metastable atoms, which were investigated in detail by numerous tests extending over a period of many months.

The most interesting changes in the sensitivity of the surface were those following the heating of the surface to temperatures sufficiently high to

clean the tungsten surface of all surface films, that is between 1800°K and 2900°K.[9] The changes are shown in Fig. 2, which is typical of those obtained under the conditions described above. The electron currents from the surface due to the action of the metastable atoms upon it are plotted in arbitrary units as ordinates against time in minutes as abscissas.

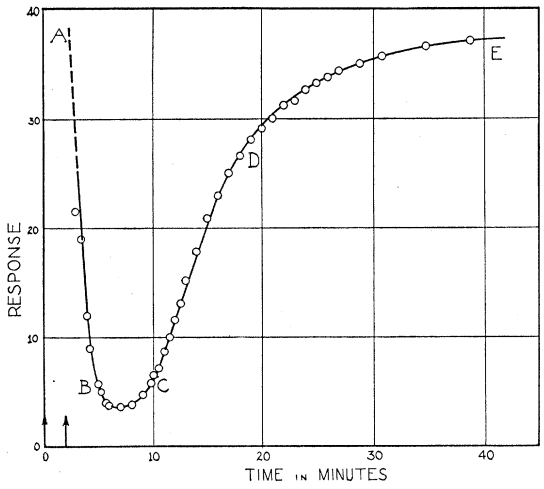

FIG. 2. Curve showing the change of response of tungsten surface with time, following cleaning by heating to 2250°K for 2 minutes. Tube temperature maintained at −5°C. Arrows show time when heating current was turned on and off.

On this curve and on succeeding curves the times at which the heating current was turned on and off are indicated by arrows. During the first three or four minutes after the surface had been cleaned by heating the sensitivity dropped sharply; portion *AB* of the curve. This drop was followed by a broad minimum, *BC*, which was followed after a few minutes by a fairly constant rise in sensitivity lasting many minutes, *CD*. The sensitivity finally reached a value, *E*, which was nearly the same in all of the repeated tests. This constant value will be referred to as the normal response of the surface. The same type of curve was obtained whenever the surface was heated to a temperature above 1800°K, whether the period of heating was a few seconds or as long as an hour.

[9] I. Langmuir and K. H. Kingdon, Phys. Rev. **34**, 129 (1929); I. Langmuir, Ind. and Eng. Chem. **22**, 390 (1930); I. Langmuir and Villars, J. A. C. S. **53**, 486 (1931); K. B. Blodgett and I. Langmuir, Phys. Rev. **40**, 78 (1932).

Furthermore, curves of the same general shape were obtained for a wide range of mercury vapor pressures. The constancy and reproducibility of this effect is indicated by the fact that fifty such tests scattered over a period of several months gave practically the same results.

The initial drop *AB* varied as to rate in the different tests made but was always too rapid to permit detailed study; consequently the conditions affecting it were not well established nor was there any clearly established evidence as to the cause of the sensitivity during this period. However, from the rate at which this drop takes place, it seems probable that immediately following the cleaning at high temperatures, the surface had relatively to the normal, a high value of sensitivity which dropped quickly to a value very much lower than this normal value.

The period *BC*, following this rapid drop in sensitivity and preceding the period of more rapid increase in the sensitivity varied considerably in duration in the different tests made. In the case illustrated in Fig. 2, the minimum value of the response during this period was ten percent of the normal value. In other tests the minimum response was only two or three percent. That this minimum value is not nearer to zero seems to be due to the overlapping of the initial process of decay of sensitivity and the process of recovery which is so marked in the stage *CD*, and to the amount of a few percent, to a feeble photoelectric effect from the radiation excited in the tube. Some of the response at this stage may also be due to the failure of the ends of the surface to receive the same heat treatment as the rest because of the cooling effect of the leads.

In the earlier part of the period *CD*, following this period of low sensitivity, the recovery of sensitivity was at an approximately constant rate. This together with the fact that this steady rise continued as a rule over a period of the order of ten minutes, permitted this portion of the curve to be studied in detail and more completely than was possible with the other portions.

RÔLE OF MERCURY IN SENSITIZATION

The well-known variations in photoelectric response with the gas content of a surface suggested that the change in response to metastable atoms described above were due to the presence

of residual gas or mercury vapor. It must be remembered in this connection that in these experiments the concentration of mercury atoms was always very much greater than that of the residual gas atoms. The residual gas pressures were of the order of 10^{-8} mm while the mercury vapor pressure was of the order of 10^{-4} mm. The part played by mercury vapor in the recovery of sensitivity of the surface was determined by varying the concentration of mercury atoms while maintaining the residual gas pressure as low as possible. While in general curves similar to that shown in Fig. 2 were obtained for various mercury vapor pressures, the slope of the rising portion of the curve, *CD*, was found to change with the vapor pressure. This indicated that the sensitive surface forming during this period was the result of a deposit of mercury atoms. That this increase in sensitivity during the period *CD* was due to such a deposit of mercury atoms was carefully checked in four ways.

(1) Observations were made of the effect of different concentrations of mercury atoms on the rate of recovery of the sensitivity of the surface as indicated by the slope of the rising portion *CD* of the curve.

(2) Observations were made of the effect of heating the surface at various stages during the recovery *CD* to temperatures at which one might expect mercury deposits to be driven off.

(3) Observations were made of the effect of removing the mercury vapor at various stages of the recovery process. This was done by immersing the lower half of the tube in a mixture of solid CO_2 and alcohol, temperature -78°C, at which temperature the mercury vapor pressure is only 3×10^{-9} mm.[10]

(4) After heating the surface at temperatures sufficiently high to clean it, observations were made of the effect of maintaining the surface at temperatures which would prevent the deposit of mercury atoms.

The tests are described below in detail:

(1) After heating the surface to some temperature between 1800°K and 2800°K in order to clean it, the changes in its sensitivity were followed for a few minutes beyond stages *AB* and *BC* until the rate of increase of sensitivity was practically constant. This rate was determined, and then the vapor pressure was quickly changed by the substitution of another constant temperature bath around the tube, and the new rate of increase determined. The results of such a test are shown in Fig. 3. The surface was first heated

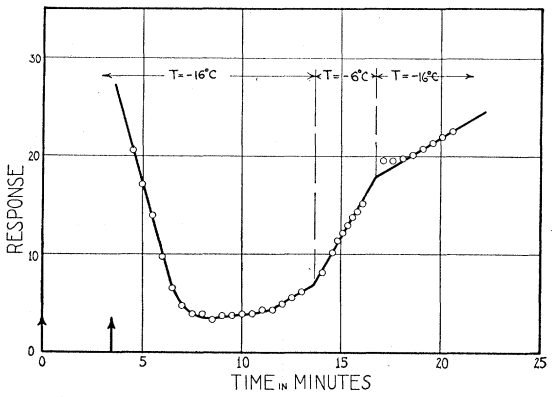

FIG. 3. Curve showing the effect of change of mercury vapor pressure upon the response curve. Surface cleaned at 2250°K for 3 minutes. Temperature of tube maintained at -16°C from $t=0$ to $t=13$ minutes, at -6°C from $t=13$ to $t=17$ minutes and at -16°C from $t=17$ minutes to $t=21$ minutes.

at 2250°K for three minutes with the temperature of the tube at -16°C. After the sensitivity had passed through the minimum, *BC*, and had begun to recover at a steady rate as indicated by the constant slope of the curve, the temperature of the tube was suddenly raised ($t=13$ minutes) to -6°C. The rate of change of sensitivity was again nearly constant but larger than before. At $t=17$ minutes when the temperature was restored to -16°C the rate of change of sensitivity returned to its earlier value. The ratio of the slopes of the curves at the two temperatures, -6°C and -16°C, is 3.0 and the ratio of the concentrations of mercury atoms present at these temperatures is 3.1. The rate of recovery of the surface was therefore proportional to the number of mercury atoms present. This test was repeated for many different changes of vapor pressure, and in all cases within the precision of the measurements the rate of recovery was found to be proportional to the number of mercury atoms present. In Fig. 3, the two points at $t=17$ and 17.5 minutes do not lie on the straight line because of a lag in the thermal equilibrium following the

[10] F. E. Poindexter, Phys. Rev. **26**, 859 (1925).

change in bath temperatures. In reducing the response to that for equal numbers of metastable atoms it was assumed that the temperature of the experimental tube changed immediately with the change of bath temperature. This lag was determined directly by using the tube as an ionization manometer to measure the varying mercury vapor pressure, and so long as the quantity of mercury was restricted to a few small drops it was of the order of one minute.

(2) A series of tests were made in which the surface was heated to temperatures between 800°K and 1400°K for a short interval during the recovery process, so as to drive off any mercury which might have deposited upon it. Fig. 4 shows

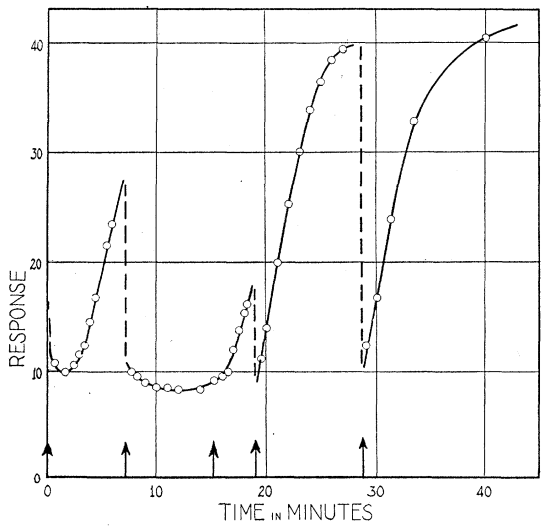

FIG. 4. Curve showing the effect of heating the surface to temperatures of 1320°K and 800°K. Surface cleaned at $t=0$ by heating to 2420°K for 10 seconds. From $t=7$ to $t=14.5$ minutes surface maintained at 800°K. At $t=19$ and at $t=28.5$ minutes, surface was heated to 1320° for 10 seconds.

a typical result. In this test the surface was first cleaned by heating at 2420°K for ten seconds, after which the usual changes in sensitivity were observed, the response dropping sharply at first, passing through a minimum, and then rising at a fairly steady rate. After this rise had proceeded for a few minutes, the temperature of the surface was raised, at $t=7$ minutes, to 800°K whereupon the sensitivity dropped and remained low as long as this temperature was maintained. The current which heated the surface was then cut off at $t=14.5$ minutes and the sensitivity was observed to rise again at a fairly constant rate. At $t=19$ minutes the surface temperature was raised to 1320°K for ten seconds and immediately thereafter the sensitivity was found to be very low, but rose again at a nearly steady rate. Repetition of this heat treatment at $t=28.5$ minutes gave the same result, an immediate loss of sensitivity followed by a steady recovery.

Fig. 5 shows another example of this phenomenon. The first three sections of the curve, (a), (b), (c), show the effect on the sensitivity of heating the surface to 1320°K for ten seconds with the mercury vapor pressure held at 2×10^{-4} mm (0°C) throughout the test. The surface had been previously cleaned at high temperature and had been allowed to recover to its normal value and was then heated to 1320°K for ten second intervals at times $t=0$, 6 and 18 minutes. The sensitivity was in each case reduced to approximately ten percent of the normal value by the heating but thereafter the sensitivity recovered at practically the same rate in each case. The sections marked (c) and (d) show repetitions of the same heat treatment, but at mercury vapor pressures of 8×10^{-5} mm and 6×10^{-5} mm, respectively, corresponding to temperatures of -8°C and -10°C. Tests of this kind were repeated many times and always showed as a result of heating the surface to temperatures in the neighborhood of 1300°K, this same sharp drop in sensitivity, which seems to be best explained as due to evaporation of a layer of mercury atoms from the surface.

Immediately after such heating the response of the surface was always a small fraction of its previous value, in Fig. 5 about one-tenth, in other cases even less. As already pointed out the failure of the ends of the surface to receive the same heat treatment as the rest of the surface, due to the cooling effect of the leads, probably accounts for the fact that the sensitivity to metastable atoms is not reduced to zero by the heating.

The rate at which the recovery took place was found in these tests, as in (1), to be approximately proportional to the mercury vapor pressure. In Fig. 5, the ratios of the slopes of the -8°C curve and the -10°C curve to the slope of the 0°C curve are 2.1 and 2.8, respectively, while the corresponding ratios of the number of mercury atoms

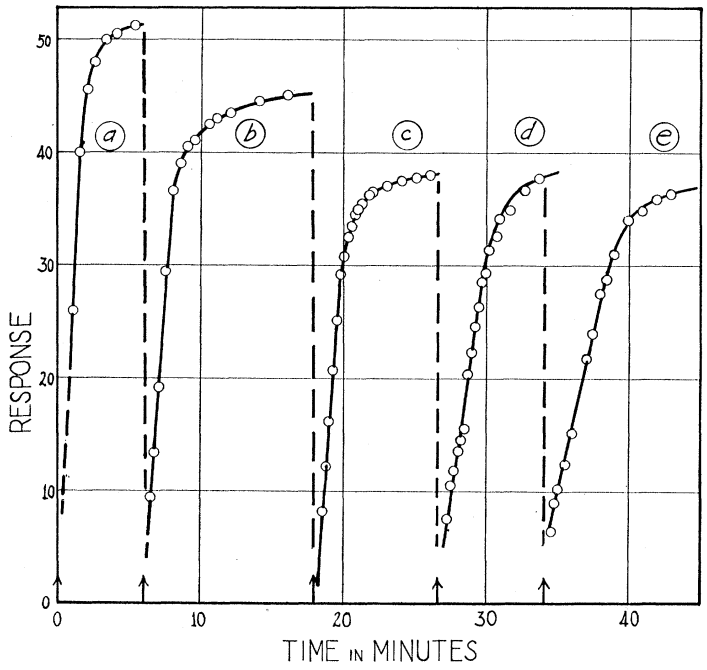

FIG. 5. Curve showing effect of heating surface to 1320°K for 10 seconds, at $t=0$, 6, 18, 26.5 and 33 minutes. Curves (a), (b) and (c) tube temperature maintained at 0°C, curves (d) and (e) tube temperature maintained at −8°C and at −10°C, respectively.

present at these temperatures to the number present at 0°C are 2.4 and 2.9, respectively.

(3) The purpose of this test was to determine the effect upon the changes in response of the surface of reducing the concentration of mercury atoms to a very small amount. This was done by immersing the lower half of the tube in a mixture of solid CO_2 and alcohol, temperature −78°C which reduced the mercury vapor pressure to 3×10^{-9} mm, approximately 0.00001 of the pressure at 0°C. The effects of such treatment is shown in Fig. 6, (a), (b), (c), (d). The surface was cleaned by heating at 2420°K and after it had almost completely recovered its normal sensitivity (curve (a)), the surface was heated at $t=14$ minutes to 1320°K for ten seconds. The sensitivity which was thus reduced to a low value recovered in the usual manner, curve (b). To compare with this we have curves (c) and (d). In these two tests the procedure was the same as for (b) except that before the surface was heated to 1320°K the mercury vapor pressure was reduced to 3×10^{-9} mm (−78°C). This value of the vapor pressure was maintained following the heating for periods of two and ten minutes in these two tests respectively, after which the vapor pressure was brought back to 2×10^{-4} mm (0°C). In each case the sensitivity then recovered in the usual manner starting from a value close to zero. We see then that in the absence of mercury atoms no appreciable recovery of sensitivity took place following the 1300°K heating, but that as soon as the mercury atoms were again present, the recovery of the surface started.

That the process of recovery stopped or was greatly retarded by the removal of mercury atoms is indicated by other tests made under somewhat different conditions. A typical curve is shown in Fig. 7. The surface was heated to 2420°K for 30 seconds and after the response had passed through the first two or three stages and the sensitivity was steadily rising, the mercury vapor pressure was reduced to 3×10^{-9} mm (−78°C). This was maintained for fifteen minutes (from $t=3.5$ to $t=18.5$ minutes) and then the pressure was raised to 2×10^{-4} mm (0°C). Although there was considerable uncertainty in the extrapolation of the curve between $t=18.5$ and

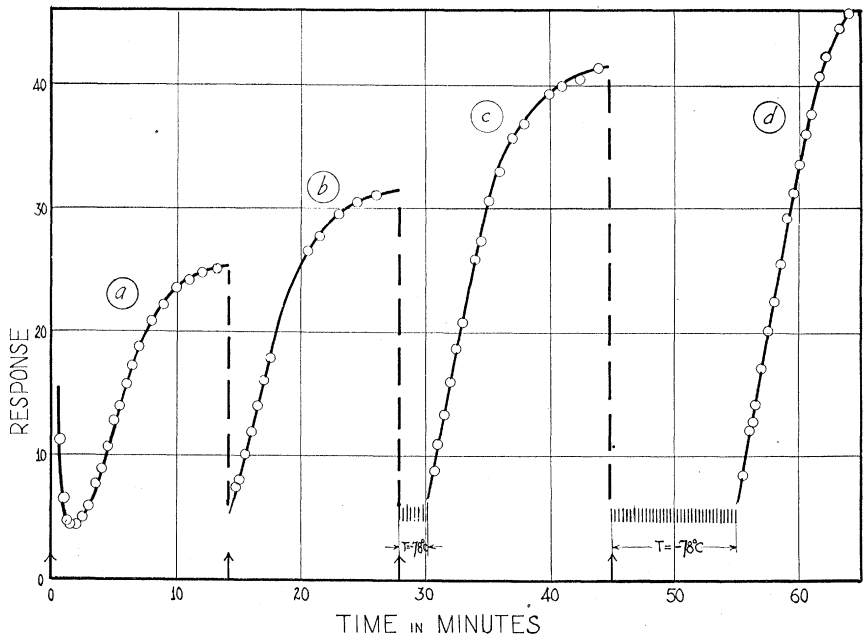

FIG. 6. Curve showing the effect of maintaining the temperature of the tube at −78°C for an interval following heating the surface to 1320°K. Surface cleaned at $t=0$ by heating to 2420°K for 10 seconds. Surface heated to 1320°K for 10 seconds at $t=14$, tube temperature 0°C. At $t=28$, surface heated to 1320° for 10 seconds, tube temperature maintained at −78°C for 2 minutes, then restored to 0°C. At $t=44$, surface heated to 1320°K for ten seconds, tube temperature maintained at −78°C for 10 minutes, then restored to 0°C.

$t=19$ minutes, made necessary by the lag in the temperature equilibrium, if we assume that the slope of the curve after the interruption was equal to or even greater than before it is seen that little or no recovery of the sensitivity took place. Tests to be described later showed that this assumption was justified.

Similar delay in the recovery process was observed when the surface was cleaned by heating to temperatures above 1800°K in the absence of mercury vapor. In such tests the recovery process was delayed many minutes until the mercury vapor pressure was restored. The curves obtained were similar to the recovery curve shown in Fig. 2, except that the initial drop AB was not observed and the rest of the curve was displaced in time by the interval during which the mercury atoms were kept from the surface by the low temperature bath.

It should be remembered that in these tests only observations taken during the first minute after replacing a −78°C bath with a 0°C bath are somewhat in error because of a lag in the establishment of a thermal equilibrium. This thermal lag is shown in curve (b) of Fig. 8, which shows the change as measured by ionization currents, in the concentration of mercury atoms following this change in the bath temperature.

(4) This test consisted in heating the surface to high temperatures to clean it of all gas films or oxides after which the temperature was reduced to about 1300°K. This latter temperature was maintained for several minutes and the surface then allowed to cool. The subsequent response showed that while the surface was kept at 1300° K the recovery process was delayed. The recovery of the surface then proceeded in a manner similar to the typical recovery curve shown in Fig. 2. The dropping portion, AB, however, was not observed and the rest of the curve was shifted in time by the interval during which the surface was maintained at 1300°K. This delay in the recovery process indicates that at these temperatures the mercury atoms either fail to condense upon the surface at all, or else do not remain in sufficiently large quantities to form

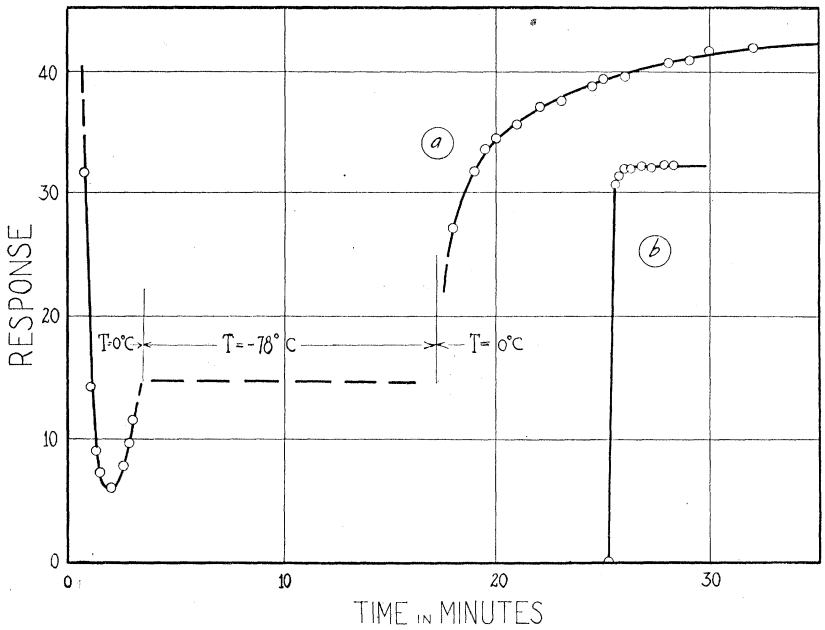

FIG. 7. Curve (a) shows the effect of reducing the tube temperature to −78°C at $t=3.5$ minutes, and maintaining this temperature to $t=18.5$ minutes. Tube temperature maintained at 0°C from $t=0$ to $t=3.5$, and from $t=18.5$ to $t=32$. Surface cleaned by heating at $t=0$ to 2420°K for 30 seconds. Curve (b), ionization currents, showing rate at which mercury vapor pressure reaches equilibrium, when the tube temperature is changed from −78°C to 0°C.

nuclei from which the growth of a surface could proceed. This is in accord with results of other observers. Wood[11] has reported the failure of atoms to condense upon a surface above a critical temperature. Again, Estermann[12] found in experiments with molecular beams of mercury and cadmium that a very narrow beam failed to produce a deposit upon a target, while a wider beam in which the concentration of the atoms was no larger did produce a deposit. This indicates that it was necessary to have some minimum number of atoms condensed upon a surface to form a nucleus for the growth of an extended surface.

The tests just described showed that the sensitivity of the metal surface, after each temporary change in sensitivity due to heat treatment returned in time to the normal value, which because of its constancy points strongly to a definite equilibrium structure of the surface. These tests further brought out that the formation of the surface involves mercury atoms as shown by the observations that the rate of recovery varied directly with the concentration of mercury atoms surrounding the surface, that the removal of

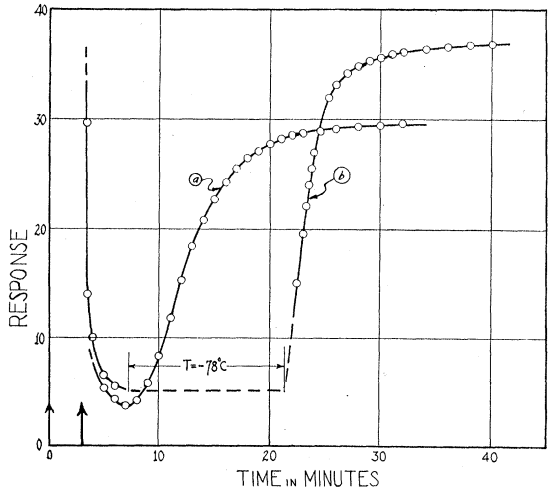

FIG. 8. Curve (a) shows the usual recovery curve, after heating the surface to 2100°K for three minutes, tube temperature 0°C throughout the test. Curve (b) shows the effect of reducing the tube temperature from $t=7$ to $t=21.5$ minutes to −78°C.

[11] R. W. Wood, Phil. Mag. **32**, 364 (1916).
[12] J. Estermann, Zeits. f. Physik **33**, 320 (1925).

mercury vapor from the tube or the prevention of a deposit of mercury on the surface by suitable heating stopped the process of recovery of sensitivity, and that heating a surface during the recovery process to a temperature presumably sufficient to drive off mercury deposits again reduced the sensitivity to a very low value. In the next section further evidence as to the nature of the sensitive surface will be discussed.

It is of interest to note that the changes observed in the sensitivity of the surface were not due to the action of the metastable atoms themselves. The same changes in sensitivity were observed whether or not the source of potential exciting the metastable atoms was cut off between readings.

Rôle of Oxygen in Sensitization

Returning again to the typical curve shown in Fig. 2 we note that between the period of quick decay of sensitivity AB, which follows the heating of the tungsten surface to a temperature sufficient to clean it of all oxide or oxygen layers, and the period of steady recovery of sensitivity CD, several minutes elapse during which time some relatively slow change takes place in the surface which appears to prepare it for the reception of mercury atoms.

The following tests seem to throw light on the nature of this change. In Fig. 8 (a) is shown the normal behavior of the surface after cleaning by heating to 2100°K for three minutes, the vapor pressure being 2×10^{-4} mm (0°C). In Fig. 8 (b) the surface was treated under the same conditions except that between $t=7$ and $t=21.5$ minutes the mercury vapor pressure was reduced to 3×10^{-9} mm (−78°C). As soon as the vapor pressure was restored to 2×10^{-4} mm (−0°C) the sensitivity started to rise, as in previous tests. However, it will be noted that the rate of rise in (b) is several times greater than in (a). In addition to the more rapid rise in sensitivity it will be noted that the response of the surface in test (b) rose to a value approximately 20 percent higher than in test (a). It is seen then that not only is the recovery of the surface delayed in the absence of mercury atoms as already noted, but that when the mercury atoms are brought back after such an interval more rapid formation of the sensitive surface follows and the sensitivity reached is somewhat greater. Subsequently the sensitivity dropped slowly back to the normal value.

Fig. 9 shows the result of keeping the mercury atoms from the surface for an extended interval by maintaining the surface at 800°K. For purposes of comparison, curve (a) shows the usual changes in sensitivity following cleaning of the surface by heating. In the test shown by curve (b) the surface was similarly cleaned by heating at 2250°K but the heating current was then reduced for about twenty minutes to a value which maintained the surface at a temperature of 800°K, after which the surface was allowed to cool. The sensitivity in this case also dropped sharply but instead of rising as in (a) the sensitivity increased but little until the surface was allowed to cool, at $t=32$ minutes, when the sensitivity rose very rapidly, at a rate several times greater than in (a), indicating that during the period when the deposit of mercury atoms was to some extent prevented, some changes were taking place which rendered the surface more susceptible to the subsequent deposit of a sensitive layer of mercury atoms.

Both of these results show that if a clean surface is kept free from deposits of mercury for some time a change takes place on the surface which accelerates the formation of the sensitive

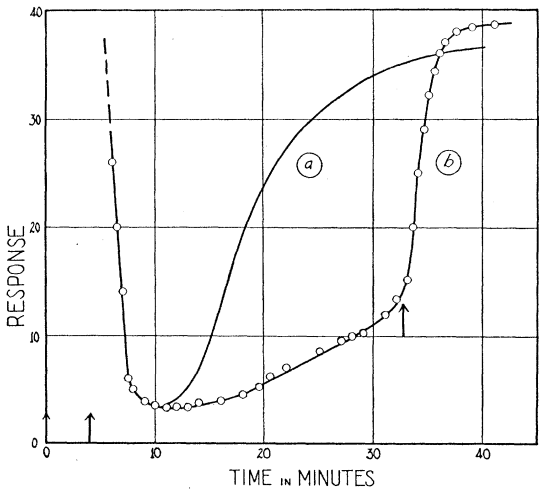

Fig. 9. Curve (b) shows the effect of maintaining the surface temperature at 800°K from $t=4$ to $t=32$ minutes following cleaning of the surface by heating to 2250°K from $t=0$ to $t=4$ minutes. Surface temperature reduced to tube temperature, at $t=32$ minutes. Curve (a) typical response curve with surface at tube temperature throughout the test.

deposit of mercury and also permits the building up of a more sensitive layer. This characteristic, as well as other results to be discussed later, indicates that the surface responding to mercury metastable atoms does not consist simply of a mercury film on the tungsten but is a more complicated surface involving gas atoms, presumably oxygen atoms. Such complex surfaces have been found in thermionic and photoelectric work to give responses which show similar variations as a result of the heat treatment. For example, surfaces consisting of barium films on platinum or of thorium films on tungsten show changes with heat treatment, which indicate that the response is determined by the fraction of the surface that is covered by such films. The changes in response following heat treatment of a surface on which there are in addition to such a metal film some gas atoms (as for example, surfaces such as Th−O−W, Cs−O−W, Ba−O−Pt and Cs−O−Ag) are found to be much more varied and complicated and dependent not only upon the fraction of the surface which is covered by the deposited metal and oxygen atoms, but also upon the order of their deposition.[13] Becker[14] has advanced the hypothesis that these layers of oxygen and barium in the case of oxide coated platinum filaments diffuse and reform as a result of thermal agitation, and that the sensitivity depends not only upon their relative amounts but also upon their relative positions. In these present experiments, the variations of the response of the tungsten surface to metastable atoms as a result of heat treatment indicate a complex surface of similar nature. It is well known that layers of oxygen form on tungsten[9] and it may be noted that the time elapsing between the cleaning of a surface at high temperatures and the beginning of its subsequent recovery, three or four minutes, is approximately the time required for the formation of such an oxygen layer. Dushman[15] has calculated from kinetic theory that at a pressure of 2×10^{-6} mm a monomolecular layer of oxygen forms on a thorium film on a tungsten surface in one second assuming as deduced by Langmuir that every atom that strikes the surface sticks to it. In the present experiments the residual gas pressure was of the order of 10^{-8} mm at which pressures the formation of such a layer would from this result require several minutes, which is the interval observed above.

In the light of the above discussion, the various stages of the curve shown in Fig. 2 may be explained as follows: Since heating the surface to 2500°K is sufficient to drive off completely any oxygen layers or oxides which form on the tungsten, we may assume that after such heat treatment the surface of the tungsten was clean, On this surface we could expect a deposit of mercury atoms and oxygen atoms, but at the concentrations obtained in these experiments a deposit of mercury atoms could have been almost instantaneous, whereas several minutes would have been required for any extended oxygen layer to form. Now, the response to metastable atoms observed immediately after cleaning of the tungsten was high but fell rapidly (see *AB*, Fig. 2). Since this response was observed within a fraction of a minute after the cleaning, the surface must have been either pure tungsten, or tungsten covered with a layer of mercury atoms. The decrease of sensitivity thereafter seems best explained as due to a deposit of oxygen upon the pure tungsten by either a displacement of the mercury layer by the oxygen layer or by a deposit of oxygen upon the mercury. We may conclude that any such surface covered with oxygen atoms would be insensitive from the fact that a large work function is found for it in thermionic and photoelectric experiments. In tests to be described later oxidized surfaces were actually found to be very insensitive to mercury metastable atoms.

That the initial decrease in sensitivity as shown by the part of the curve (*AB*) was occasioned by oxygen is also indicated by the behavior of the surface in a test previously described. In this test the surface was cleaned by heating to 2500°K in the absence of mercury vapor, (−78°C). After the lapse of several minutes the vapor pressure was raised to 2×10^{-4} mm (0°C) and the subsequent variations of sensitivity consisted only of the stages *BC* and *CD*, while the stage *AB* was not observed. Since only residual gas, presumably oxygen, was present during the

[13] Hughes and Dubridge *Photoelectric Phenomena*, pp. 171 ff.; S. Dushman, Rev. Mod. Phys. **2**, 440 (1930).
[14] J. A. Becker, Phys. Rev. **34**, 1345 (1929).
[15] S. Dushman, Rev. Mod. Phys. **2**, 447 (1930).

interval in question the failure to observe the high initial sensitivity and subsequent rapid decay may be attributed to the action of such gas atoms on the surface.

During the stage *BC*, the surface remained relatively insensitive for several minutes. During the interval, mercury atoms which reached the surface either failed to deposit upon it or the surface which they form by condensing on the oxygen layer was one which was not sensitive to mercury metastable atoms. Some further change must have taken place before the sensitive layer of mercury atoms was formed. Possibly there was some rearrangement of the oxygen and mercury atoms already on the surface during which the oxygen diffused down to the pure tungsten resulting in an oxygen on tungsten surface upon which mercury atoms deposited and formed a sensitive surface during the stage *CD*. In the stage *DE* the sensitivity gradually approached a constant value when apparently there was some kind of equilibrium established so far as the effective part of the surface was concerned. As has been pointed out this equilibrium or normal value remained very nearly constant as the surface stood and was practically the same after each heat treatment no matter how extensive. However, there is evidence that the lower layers, of this surface, which seemed to consist of a number of atomic layers, continued to change for many hours after the sensitivity had ceased to change measurably. It was found that a surface which had been left without heat treatment for several hours behaved upon being heated for a few seconds to a temperature in the neighborhood of 1300°K quite differently from a newly formed surface. As has been seen (see Fig. 7) with the latter such treatment always resulted in an almost complete loss of sensitivity. With the aged surface, on the other hand, the result was quite different. This is shown in Fig. 10, (a), (b) and (c). The surface which had been standing for many hours was heated to 1300°K for ten seconds. Instead of falling to a low value as with a newly formed surface, the sensitivity immediately after the heating was found to be five or six times greater than that of the normal surface. This sensitivity fell rapidly at first, then more slowly and gradually returned to the value observed before this heating. This was repeated (curve b) with like result and in general could be repeated three or four times in succession, but after several repetitions or if the temperature of the surface was maintained at 1300°K for a prolonged interval, this effect disappeared and reappeared only after the surface had been left again for many hours without heat treatment. This behavior seems to show that as the surface aged the atoms in the lower layers tend to diffuse and form a thin layer of mercury, possibly monatomic on a similar layer of oxygen. When this surface is heated to 1300°K for ten seconds only the outer layers of mercury and oxygen are evaporated while the thin layer of mercury is bound too tightly to the oxygen to be easily driven off, as in the case of the newly formed surface. The higher value of the sensitivity resulting from the heating seems to bear out the assumption that the normal surface has a substructure which has a more efficient disposition of the atoms forming it. The subsequent decay of sensitivity back to the normal value indicates the formation of complex layers of mercury and oxygen atoms as further deposits of oxygen take place. The prolonged or repeated heating apparently destroys the formation of this substructure either by displacing the atoms by thermal agitation or by evaporation.

To determine whether or not the decay of the sensitivity in the above test was caused or influenced by mercury atoms, this experiment was repeated with various values of mercury vapor pressures. Further the concentration of the mercury atoms was varied during the period when the sensitivity was falling by changing the mercury vapor pressure rapidly from one value to another. Neither of these tests showed any influence of the mercury vapor pressure upon the rate at which this decay of sensitivity took place. Again a repetition of the test in the absence of mercury atoms that is with the tube in a bath of temperature -78°C showed that this decay still occurred and at the same rate. Removing the mercury atoms during the progress of this decay by cooling to -78°C similarly had no effect upon this phenomenon. This last result is shown in Fig. 10 (c) which shows the effect of reducing the vapor pressure to a very small value between $t=27$ and $t=33$ minutes. Disregarding the first three points following $t=33$ minutes, which are low because of the lag in the vapor pressure, we

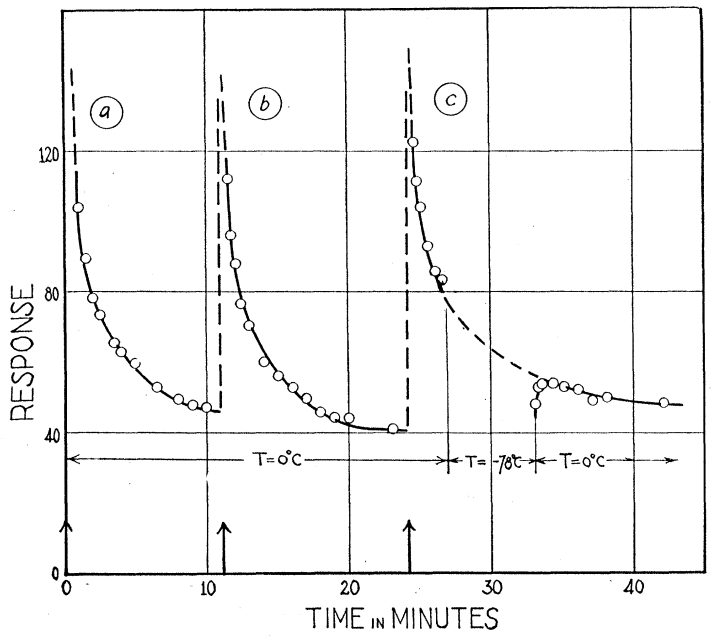

FIG. 10. Curves showing the effect of heating an aged surface to 1300°K for 10 seconds, at times $t=0$, 11 and 24 minutes. Curves (a), and (b) tube temperature = 0°C throughout, curve (c) temperature changed to −78°C from $t=27$ to $t=33$ minutes.

see, comparing the curve with 10 (a), that the falling off of sensitivity was not affected during this six minute period. It seems therefore, that this loss of sensitivity depends either upon the action of the residual gas or upon a rearrangement of the atoms on the surface by some diffusion process.

In order to study more directly the part played by oxygen in the formation of the sensitive surface, the effect of increasing the concentration of oxygen in the tube was investigated. The pumping system was filled to a pressure of one or two centimeters with oxygen from which all condensible vapors had been removed by passing the oxygen through a drier and a long narrow helix of glass submerged in liquid air. The system was then pumped out and this process repeated many times to flush out the system. Finally oxygen at a pressure of 0.02 mm was allowed to enter the experimental tube and the tungsten surface heated in this atmosphere for a few seconds at 1200°K for the formation of an oxygen layer on the tungsten, as described by Langmuir and Kingdon.[16] Following this, the surface was found to be very insensitive to the action of mercury metastable atoms, the response being approximately one-thousandth of the response of the equilibrium surface described above. This was in agreement with previous work in which oxidized surfaces were found to be quite insensitive although in the present case no oxide was visible.

The tube was then systematically outgassed and the response to metastable atoms observed as the gas content of the tube and the metal parts was reduced. The variations in sensitivity of the surface following heat treatment were also watched during this time. After repeated baking of the tube and repeated outgassing of all of the metal parts by means of the high-frequency furnace the sensitivity of the surface returned to the value it had previous to the admission of oxygen to the tube. In the final stages of the outgassing not only was the same sensitivity obtained, but the same variations in sensitivity

[16] I. Langmuir and K. H. Kingdon, Phys. Rev. **24**, 510 (1924).

following the heating of the surfaces were also observed. However, at two stages of the outgassing there were observed differences in this behavior which seemed very significant.

During the earlier stages the oxygen content of the metal surfaces was large as indicated by ionization manometer measurements taken when the tungsten surface was heated, the tube being shut off from the pumps by the magnetically operated cut-off. Pressures of the order of 10^{-5} and 10^{-6} mm were observed, but this gas was immediately readsorbed by the metal surfaces when they cooled. At this stage of the outgassing process the changes in sensitivity following the heating of the tungsten surface to clean it were significant in that immediately following heating the sensitivity instead of being high as usually observed was very low. The surface thereafter recovered its sensitivity in the usual manner, the recovery curves being similar to the typical curve shown in Fig. 2, except for the fact that the stage AB was not observed. This indicated that with relatively large amounts of oxygen present this drop in sensitivity either took place too rapidly to be observed or that the high concentration of oxygen atoms prevented the formation of a sensitive surface immediately following the cleaning.

As the outgassing proceeded another stage was reached in which the oxygen content was such that the changes in sensitivity to metastable atoms following cleaning of the surface were markedly different. The sensitivity immediately following heating of the surface was found to be very much increased, in some instances by a factor of more than fifty. This high sensitivity was very short lived and dropped very rapidly back to the value observed before the heating but did not fall below this value at any time. The rapid rate at which the sensitivity dropped in these cases, indicated that the initial sensitivity may have been even greater than recorded. From the high sensitivity obtained in photoelectric and thermionic phenomena with surfaces consisting of thin metal films on similar films of oxygen, as for example, CsO—Ag, and Cs—O—W surfaces, it seems likely that the high sensitivity observed under these conditions resulted from an analogous surface probably composed of a thin layer of mercury on a similar oxygen layer on the tungsten. The subsequent drop of sensitivity may then have been due to the deposit of more oxygen and mercury atoms forming a thicker and less sensitive surface, which, however, was very stable. This behavior of the surface following heating was observed for only a very brief period. Apparently it depended upon having the oxygen at a certain critical pressure immediately after the cleaning at high temperatures. With larger pressures too rapid deposition of the oxygen resulted, with smaller pressures the deposition was complicated by the relatively larger concentration of mercury atoms, so that this very sensitive surface could not be formed.

The marked changes in the sensitivity of the surface after oxygen had been admitted to the tube and throughout the series of tests made as the oxygen content was again gradually reduced confirm the hypothesis that oxygen is the gas which plays a fundamental rôle in the formation of the surface which responds to mercury metastable atoms.

The very high sensitivities observed during these latter tests permit an estimate to be made of the efficiency of metastable atoms in producing the emission of electrons from a metal surface. The fact that responses of some fifty to one hundred times the normal value were observed shows that with the normal surface not more than one or two metastable atoms out of a hundred were effective in causing the emission of an electron from the normal surface. This is of course an upper limit to the efficiency and is in agreement with the similar value of one in two hundred which Pike[17] has calculated for neon metastable atoms impacting upon outgassed iron. On the basis of these figures and the observed electron currents, the number of metastable atoms striking the surface per square centimeter per second in these experiments is of the order of 10^{10}, which from kinetic theory indicates a concentration of metastable atoms of 5×10^{7}.

The behavior of the tungsten surface due to heat treatment described above bears a marked similarity to the behavior of the metal probes used in mercury vapor by Webb and Sinclair.[18] In these latter experiments the contact potentials of the probes were changed to a large degree by the heating resulting from the electron current

[17] E. W. Pike, Phys. Rev. **40**, 314 (1932).

[18] H. W. Webb and D. Sinclair, Phys. Rev. **37**, 186 (1931).

and upon cooling went through a series of changes lasting in some cases several minutes. The result was that the probe characteristics did not repeat when taken first with increasing voltage and then with decreasing voltage or *vice versa*. In general, the curves obtained depended largely upon previous treatment of the probes and the rate of taking observations. It was found also that the presence of traces of oxygen in the tube caused more rapid and violent variations in the contact potentials of the probes. It seems probable that these probes had layers of mercury and oxygen atoms deposited upon them similar to those on the surface described in the present paper.

ACKNOWLEDGMENT

This investigation was undertaken at the suggestion and with the guidance and advice of Professor Harold W. Webb, to whom thanks and appreciation are herewith extended.