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THERMIONIC AND ADSORPTION CHARACTERISTICS OF CAESIUM ON TUNGSTEN AND OXIDIZED TUNGSTEN

By Joseph A. Becker

Abstract

Electron emission—Curves showing the logarithm of the electron current per cm^2 from tungsten and oxidized tungsten over a wide range of filament temperatures are given for several vapor pressures of caesium. At high temperatures the tungsten is covered only to a slight extent with adsorbed caesium. As the filament temperature is lowered more caesium is adsorbed. This lowers the electron work function and increases the emission many thousandfold. The process continues until a temperature is reached at which the tungsten is just covered with a monatomic layer when the work function has a minimum value. At still lower temperatures the surface is more than completely covered, the work function increases again, and the emission decreases rapidly.

The positive ion emission is constant while the temperature decreases from a high value to a low critical temperature. Here the ion emission drops suddenly while some caesium sticks to the filament. Further decreases in temperature are followed by increased adsorption and decreased ion emission. If the temperature is then increased in steps the ion current retraces its path. At an upper critical temperature, about 50° higher than the lower critical temperature, the filament cleans itself spontaneously, the caesium comes off as ions and registers as a sudden rush of current. At higher temperatures the ion current has its initial constant value which is limited by the arrival rate of caesium atoms. The critical temperatures are raised by an increase in the vapor pressure or by a decrease in the plate potential.

A method of determining the amount of adsorbed caesium is developed. At a sufficiently high filament temperature the surface is clean. At a sufficiently low temperature every atom that strikes the filament sticks to it, at least until the optimum activity is reached. The product of the arrival rate, which is given by the steady positive ion current, and the time to attain the optimum activity gives the number of caesium atoms at the optimum activity. At an intermediate temperature the surface is only partly covered. If the temperature is suddenly dropped, to a low value, it takes a shorter time to reach the optimum activity. From these times the amount of adsorbed caesium at various temperatures, plate potentials, and vapor pressures can be determined. At the *optimum activity* there are 3.7×10^{14} atoms of caesium on a cm^2 of tungsten. This is very nearly the same as the number of caesium atoms that could be packed in a single layer, but is considerably smaller than the number of caesium ions in such a layer.

The adsorption or evaporation characteristics are illustrated by curves. Caesium can evaporate either as ions or as atoms. The atomic rate depends only on the temperature and on θ, the fraction of the surface covered with caesium. For a given temperature it *increases* very rapidly with θ. The ions can permanently escape from the filament only if the potential is in the right direction. A typical isothermal ion rate curve increases rapidly with θ, comes to a maximum when θ is about .01, then *decreases* continuously for larger θ. These curves explain all the observed phenomena of these adsorbed films. They show that while the *ion work function* increases as θ increases, the *work to remove an atom* decreases with θ. The ion work function for a given θ can be decreased by increasing the potential gradient at the filament.

THE work of Davisson and Pidgeon,[1] Langmuir,[2] Langmuir and Kingdon,[3,4,5] and of Ives, [6,7,8] has shown that small amounts of electropositive materials adsorbed on tungsten may furnish thermionic and photoelectric currents which are many thousand times as large as those from clean tungsten. It was felt that a further study of these so-called "thin films" would shed more light on the nature of adsorption phenomena, surface forces, cohesive forces between atoms, contact potential, catalysis, and work functions for electrons, ions, and atoms. The present paper confirms Langmuir and Kingdon's results for the electron emission from caesium films on tungsten and oxidized tungsten. It gives new phenomena in connection with positive ion emission. Experiments will be described which confirm in a striking manner the conclusion that the electron emission has an optimum value when a definite amount of caesium has been adsorbed. A method will then be described by which it is possible to measure the fraction of the surface covered with caesium at various filament temperatures and vapor pressures. This leads at once to a method of determining the rates of evaporation for caesium atoms and ions as a function of the fraction of the surface covered and of the filament temperature. It also allows us to correlate the electron and ion emission with the adsorption characteristics. The emission and evaporation curves make it possible to determine the work necessary to remove an electron, a positive caesium ion, or a caesium atom for surfaces covered to various extents. The results show that as more and more caesium is adsorbed, the electron work function decreases until the tungsten is covered with a single layer of closely packed caesium; then this work function increases as a second layer is adsorbed. For clean tungsten the work necessary to remove a positive ion is less than that necessary to remove an atom so that practically all the caesium evaporates as ions. As more caesium is adsorbed the work necessary to remove an ion increases while the work necessary to remove an atom decreases; when the surface is about 15 percent covered, caesium

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[1] Davisson and Pidgeon, Phys. Rev. **15**, 553 (1920).

[2] Langmuir, Phys. Rev. **22**, 357 (1923).

[3] Langmuir and Kingdon, Science **57**, 58 (1923).

[4] Langmuir and Kingdon, Phys. Rev. **21**, 380 (1923).

[5] Langmuir and Kingdon, Proc. Roy. Soc. **107A**, 61 (1925).

[6] Ives, Phys. Rev. **21**, 385 (1923).

[7] Ives, Astrophys. J. **60**, 209 (1924).

[8] Ives, J. Franklin Inst. **201**, 47 (1926).

atoms evaporate as readily as caesium ions and beyond this point practically all the caesium comes off as atoms.

EXPERIMENTAL ARRANGEMENT

Most of the data to be described have been obtained with a simple tube containing a molybdenum plate, and two thoriated tungsten filaments each 4.5 cm long and .0076 cm in diameter. The plate was supported on a long glass stem and a guard ring was provided to minimize the electrical leak produced by the caesium adsorbed on the glass. A side tube contained a capsule partly filled with caesium. The tube was thoroughly baked and both filaments glowed at 2800°K so as to clean the surfaces. Air was then allowed to enter in order to produce a film of oxygen on one of the tungsten filaments. The tube was rebaked and all metal parts excepting one filament were again glowed thoroughly. The tube was then sealed from the pumps, and the clean tungsten filament glowed for some time to clean up any remaining gases. This treatment was successful since complete thorium emission could be obtained from the filament by appropriate heat treatment and the activity could be maintained constant over many hours at 1400°K.

After these preliminary tests the capsule containing the caesium was broken open by allowing a glass rod to fall on it, and the caesium vapor was allowed to diffuse into the main tube. This diffusion took a surprisingly long time. Even after several months, during which time the side tube was heated to 80°C for several hours, the pressure in the main tube was still only 1/1000 of the equilibrium pressure. The reason for this slow diffusion is not known with certainty.

The filament temperature and temperature distribution along the filament were obtained by measuring the heating current and using the relations and end corrections given by Forsythe and Worthing.[9] These were supplemented by measuring the lengths of the filament that are just barely visible at various heating currents. While no great accuracy was sought in these temperature measurements, they were sufficiently accurate for the purposes in hand.

ELECTRON EMISSION CHARACTERISTICS

The various types of temperature-emission relations which were observed for the tungsten filament in different conditions are shown in a single diagram, Fig. 1. The coordinates are $\log_{10} i$ and $1/T$ where i represents thermionic current per cm^2 and T the temperature of the filament in °K. A filament whose electron work function φ_e is independent of the

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[9] Forsythe and Worthing, Astrophys. J. **61**, 146 (1925).

temperature should give a straight line whose negative slope is nearly proportional to φ_e. This is illustrated by the electron emission lines for tungsten (*W*) and fully activated thoriated tungsten (*Th-W*) which were obtained before the caesium capsule was broken. After the caesium entered the main tube and produced a constant small vapor pressure, the characteristics of the tungsten filament were changed to those indicated by the curve *ABCD* marked *Cs-W*.

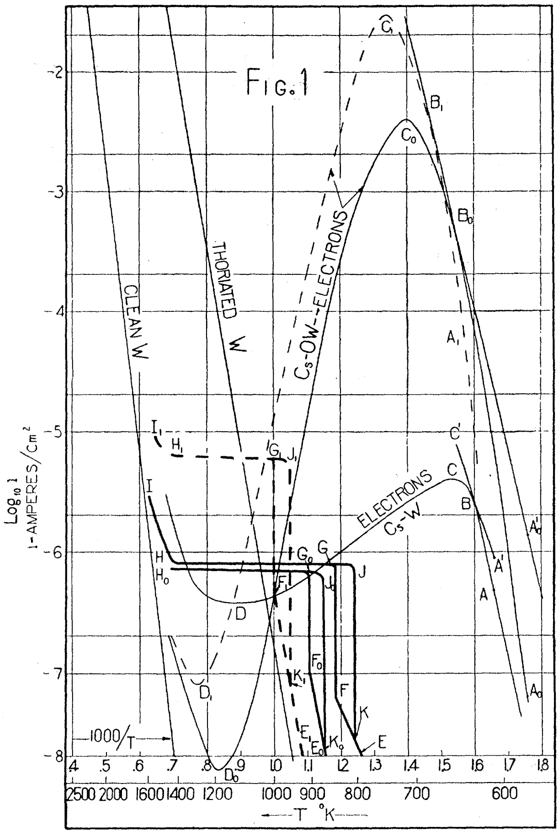

Fig. 1. $\text{Log}_{10}i$ vs. $1000/T$ where i is the thermionic current per cm^2 and T is in °K· *ABCD* represents electron emission from a tungsten filament in caesium vapor; $A_0B_0C_0D_0$ from an oxidized tungsten filament; $A_1B_1C_1D_1$ the same at a vapor pressure 10 times as great. *EFGHIJK*, $E_0 \ldots K_0$, and $E_1 \ldots K_1$ represent the corresponding positive ion emissions.

This latter curve exhibits the following features: Beginning at the extreme right with the lowest filament temperature *T*, the emission rises very rapidly with *T* over a range that terminates at *B*; beyond *B* the emission increases less rapidly to a maximum at C; from C to D an increase in T actually causes a decrease in the equilibrium value of i. Beyond D, i again increases with T and the curve approaches that for clean tungsten. At the same vapor pressure the tungsten filament which was oxidized showed practically no electron emission until it had been heated to 1550°K for about five minutes. Subsequent to this treatment its activity as represented by $A_0\,B_0\,C_0\,D_0$ exceeds that of *Cs-W* at the lower temperatures. Furthermore it retains its activity up to higher temperatures. Beyond C_0 the curve declines more rapidly than CD and part of it actually is below CD. The indications are that beyond D_0 the activity would actually be less than that of clean tungsten. This filament will be designated as Cs on OW. It was never heated beyond 1550°K so as not to evaporate the oxygen. The amount of adsorbed oxygen is unknown but is probably not more than one layer deep.

If the vapor pressure of the caesium is increased approximately tenfold by increasing the bulb temperature, the resultant curve for Cs-OW is given by $A_1\,B_1\,C_1\,D_1$. Near A_0 the activity has decreased whereas near C_0 and D_0 it has increased. For Cs-W the effect is qualitatively the same. The family of such curves for a series of vapor pressures has as its envelope a straight line as was shown by data other than that represented here. This is illustrated by the lines $A_0'\,B_0\,B_1$ for Cs-OW and $A'\,B\,C'$ for Cs-W. It is also very well illustrated by the line AB in Fig. 1 of Langmuir and Kingdon's article.[5]

The unusual temperature emission characteristics of caesium on tungsten may be accounted for by the way in which the thermionic work function, φ_e, varies with the filament temperature T. φ_e depends only upon the number of caesium atoms or ions adsorbed per cm^2. This in turn is determined by an equilibrium between the rate of condensation of atoms from the vapor and the rate of evaporation of adsorbed atoms and ions. Let us represent by N_1 the number of caesium atoms required to cover completely one square cm, and by θ the ratio N/N_1, where N is the actual number of atoms per cm^2. θ then represents the fraction of surface covered. We may anticipate the deductions from experiments to be described later in order to correlate θ and φ_e with the $i-T$ relation of Fig. 1. At the low temperature corresponding to the point A, θ is greater than unity. As the filament temperature, T, is raised θ decreases and reaches the value unity at a point such as B. For still higher temperatures, θ is less than unity and at very high temperatures it approaches zero.

Whenever θ changes, φ_e and i change. In the region from A to B, i increases not only because T increases but also because φ decreases. Thus if T is suddenly changed from its value at A to its value at B, i increases suddenly at first; then it keeps on increasing even after T is constant, while θ and φ decrease until equilibrium is established. In the region B to C, i tends to increase because of an increase in T but tends to decrease because of an increase in φ. Thus if we suddenly change T from B to C, i suddenly assumes the value C' and then gradually decreases until it reaches its equilibrium value at C. Between C and D, i again tends to increase because of an increase in T, but now this increase is more than counterbalanced by a decrease in i caused by an increase in φ. Thus if T is suddenly changed from C to D, i actually rises to a value higher than that at C and then as θ decreases, i drops to a value below that at C.

If we now suddenly change T from D to A, i at first is immeasurably small, then it increases exponentially with time, comes to a maximum at A' which may be very large compared to its final equilibrium value at A. As θ builds up at T_A, the activity passes through an optimum value probably because φ passes through a minimum. In other words, as the caesium is adsorbed it aids the activity until an optimum amount is adsorbed. When still more caesium is adsorbed, the activity decreases. According to this view if we now increase T from T_A to T_C, i should again pass through a maximum at C' as θ passes through its optimum value. This is actually confirmed by trial. The experimental results can be generalized as follows: Whenever T is suddenly changed from a value less than T_B to one greater than T_B or vice versa, the thermionic current always passes through a maximum and these maxima fall on the straight line $A'BC'$. If the vapor pressure is increased, point B is shifted along the line toward higher temperatures but the line itself is not moved. This line is evidently the Richardson line for the optimum θ. Later experiments will indicate that this optimum θ is unity.

This interpretation of the time changes as changes in φ receives weighty support from Ives' studies of the photoelectric properties of thin films.[7] In the case of sodium depositing on clean platinum, it takes 10 hours for the activity to reach its optimum value and 60 to 70 hours to become steady. This allows plenty of time to follow changes in the long wavelength limit, λ_0. Starting with clean platinum, λ_0 continuously shifts toward the red as more sodium is adsorbed until the optimum activity is reached; then as still more sodium sticks, λ_0 moves back toward the violet. Since φ varies directly with $1/\lambda_0$ it follows that the work function of such films decreases, passes through a minimum, and increases again as more sodium is adsorbed.

POSITIVE ION CHARACTERISTICS

Let us now direct our attention to the positive ion characteristics. If we apply a negative potential to the plate and increase T in gradual steps we find that positive ions leave the filament. Curve *EFGHIJK* in Fig. 1 gives the equilibrium values of the logarithm of this positive ion current per cm^2 (i_p) for various values of $1/T$ or T. Note that when T reaches a critical temperature, T_{c_2}, of 850°K the values of i_p rise abruptly. This is followed by a flat region *GH*, and then by a steep region *HI*. As T is decreased, i_p remains constant down to a lower critical temperature T_{c_1} of 800°K, and then drops suddenly to the line *EF*. This hysteresis loop *FGJK* is real and is not due to a lag in T. The rise *HI* at higher temperatures is caused by a flow of photo and thermal electrons from the plate to the filament. Dr. Ives[8] has shown that these can be suppressed by means of a magnetic field parallel to the filament, and that then the flat portion *GH* can be extended to higher temperatures. At still higher temperatures i_p again rises and can no longer be suppressed. This increase is probably due to ionization of caesium vapor by the light from the filament.[10]

It is from the flat region *GH* that Langmuir and Kingdon[3] conclude that every atom that strikes the filament leaves it as an ion. They also state that from space charge characteristics the e/m for these ions has the value corresponding to caesium atoms which have lost one electron. Ives finds that this is true only if the bulb temperature is above 60°C and that at lower bulb temperatures the carriers consist of clusters of atoms. Both Langmuir and Kingdon and Ives used saturated vapor. With unsaturated vapor such as was used in the present experiments, the indications are that every atom that strikes leaves as a singly charged ion.

The positive ion characteristics for Cs-OW at very nearly the same vapor pressure are shown by the curve $E_0F_0G_0H_0J_0K_0$. This curve is similar to that for the tungsten filament, the chief difference being a displacement towards higher temperatures. If the vapor pressure is increased approximately tenfold, Cs-OW gives the curve $E_1F_1G_1H_1I_1J_1K_1$ The portion *EF* is lengthened and shifted to the left; the hysteresis loop is also displaced towards higher temperatures; and the ion current corresponding to the flat portion *GH* is increased in direct proportion to the increase in the vapor pressure. By dividing the current corresponding to this flat region *GH* by *e*, the charge on the electron, we obtain the number of caesium atoms that strike per square cm per second. This number together with the following method enables us to determine the number of atoms per cm^2 at the optimum activity.

[10] Foote and Mohler, Phys. Rev. **25**, 195 (1925).

THE NUMBER OF ATOMS PER CM^2 AT THE OPTIMUM ACTIVITY

Suppose we are drawing positive ions at $T = 1040°K$ for Cs-OW then suddenly change T to 570°K (see Fig. 1), reverse the plate voltage so as to draw electrons, and plot log i vs. time after the change in T. The resulting curve is shown in Fig. 2 marked 570°. If we again draw positives at 1040°K but this time drop to 610°K, the entire curve is higher; the maximum occurs at the same time; the peak is less pronounced; and the emission approaches its steady value sooner. These same remarks apply to the curve for $T = 625°$. If the lower temperature is above 650°K (point B_0 in Fig. 1) the emission no longer passes through a maximum but approaches its steady value rather more suddenly than one might expect. The arrows in Fig. 2 indicate the time necessary for sufficient caesium to have struck the surface to form an amount that is actually on the surface when equilibrium prevails. The method of determining this time will be explained later. For Cs on W the results are similar to those in Fig. 2.

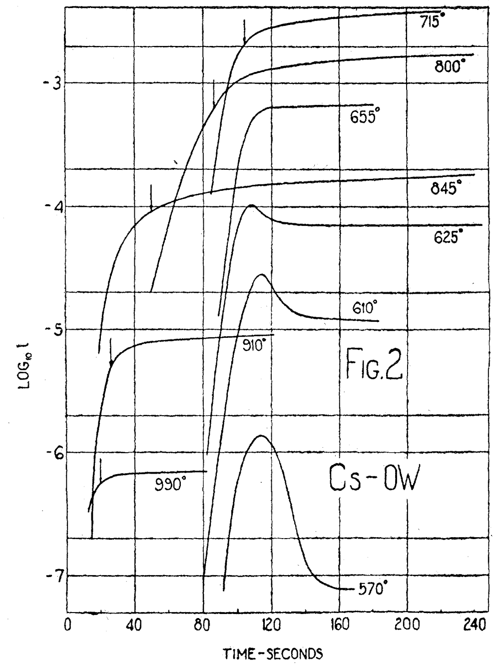

Fig. 2. The Cs-OW filament is heated to 1040°K and positive ions are drawn. This removes practically all the adsorbed caesium. At time 0 the temperature is suddenly changed to the value indicated on each curve, the plate potential is reversed, and the log$_{10}$ of the electron emission observed as time progresses. The time to reach the maximum at the three lower temperatures is called t_m.

The important point to note in Fig. 2, is that t_m, the time required to reach the maximum, is independent of T so long as $T<650$°K. This suggests that below 650°K every atom that strikes the filament sticks to it until enough are adsorbed to give the optimum activity. This view is strongly confirmed by an experiment which shows that t_m is not shortened even if the filament is kept cool for the first 80 seconds. This must mean that the fraction of the atoms that stick is the same at 570°K as it is when the filament is cool. It would be odd indeed if this fraction were anything but unity.

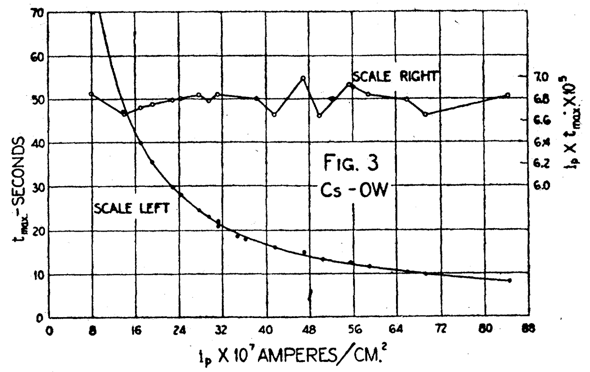

Fig. 3. If the bulb temperature is raised, the vapor pressure as measured by the saturation positive ion current per cm^2, i_p, increases while t_m decreases. The product $i_p \cdot t_m$ stays constant.

The results exhibited in Fig. 2 were obtained by lowering the filament temperature from the initial value 1040°K. The same results are obtained, however, except for slight differences due to end effects, when the initial temperature has any other value greater than T_{C_2}, the critical temperature at which the ion current rises abruptly in Fig. 1. In particular t_m is not increased by a high initial temperature. This can only mean that within the limits of experimental error the tungsten or oxidized tungsten is just as clean at its critical temperature as it is at any higher temperature; that is, perfectly clean.

It is now a simple matter to compute N_0 the number of adsorbed atoms per cm^2 at the optimum activity. As explained above, the positive ion current for the region GH tells us how many atoms strike per cm^2 per second. We saw that for $T<650$°K every atom that strikes sticks at least until the optimum is reached. To compute N_0, the number at the optimum, we have simply to multiply the rate of arrival by t_m as given by the maxima in Fig. 2. Furthermore if the above reasoning is correct, t_m should be inversely proportional to the rate of arrival of atoms. If i_p is the positive ion current per cm^2, $i_p t_m$ should be a constant independent of i_p or the vapor pressure. How nearly this expectation is fulfilled by experiment is illustrated by Fig. 3, which gives t_m vs. i_p and $i_p t_m$ vs. i_p for Cs on OW. i_p was changed by heating the bulb, thus increasing the vapor pressure and the rate of arrival of atoms at the filament. Note that while the positive current increases tenfold the product $i_p \cdot t_m$ deviates not more than 3 percent from its mean value, and in particular shows no trend downward or upward.*

From an extensive series of trials N_0 for Cs on W is computed to be 3.9×10^{14} atoms/cm^2. This is probably correct to within 5 percent. This figure is based on the assumption that the filament surface is smooth whereas actually it is probably etched because of evaporation of some of the crystal surfaces. Langmuir[2] has shown that the effect of this etching is to increase the effective adsorbing area 6 percent. If we apply this correction $N_0 = 3.7 \times 10^{14}$ to within 5 percent.

It is interesting to compare this value of N_0 with N_1 the maximum number of atoms that can be packed in a monomolecular layer. To do this we need to know the mode of packing and d, the distance of closest approach in such films. The most likely mode of packing seems to be hexagonal close packing. Then if d has the same value in the film as in a metallic crystal, we are still confronted with two possibilities depending on whether the caesium crystal is face-centered or body-centered. The first alternative together with 1.87 gms/cm^3 for the density of caesium gives a value of N_1 equal to 3.8×10^{14} atoms/cm^2 while the second gives 4.0×10^{14}. On the other hand, if the adsorbed caesium is ionized and the ions have the same diameter as in CsCl crystals then N_1 should have the value 4.85×10^{14} according to Wyckoff's figures or 7.20×10^{14} according to Davey's figures. Thus these various possibilities give values of N_1 equal to 3.8, 4.0, 4.85, and 7.20×10^{14} compared with an observed number at the optimum activity equal to 3.7×10^{14} atoms/cm^2. These figures strongly suggest that *for the optimum activity, the caesium is closely packed on the surface one layer deep and has its atomic rather than its ionic diameter.*

At the same vapor pressure t_m for Cs on OW is always found to be about 10 percent greater than t_m for Cs on W. The computed value of N_0 for Cs on OW is consequently 10 percent greater than for Cs on W, or 4.1×10^{14} atoms/cm^2. This suggests that the caesium on OW may be partially ionized and that as a result of the smaller diameter the number forming a monatomic layer is 10 percent greater.

(* The fact that this product does not vary with bulb temperature shows that at the bulb temperatures used (20 to 50°C) the particles in the vapor are single atoms or ions and not clusters. Ives, experiments show that when clusters are present, the average number of atoms in a cluster decreases rapidly as the bulb temperature increases. In that case the product $i_p \cdot t_m$ should increase considerably.)

EQUILIBRIUM θ AS A FUNCTION OF T

We have seen that if we draw positive ions at T near 1040°K, the filament is clean and that it takes t_m seconds for enough atoms to strike the filament to form a complete layer at a temperature below 650°K. For T between 1040° and 650° the fraction of the surface covered, i.e., θ, should have values between zero and one. Hence the time required to reach the optimum activity should be less than t_m. This is actually found to be the case if we draw electrons and from the times we can determine values of θ for various filament temperatures.

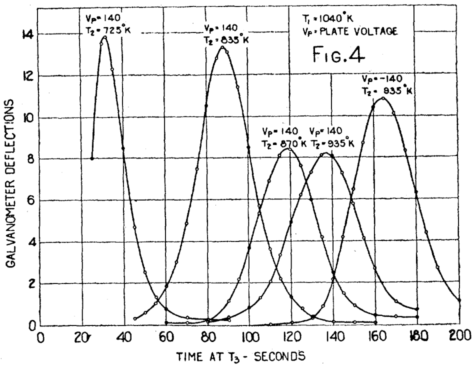

Fig. 4. The Cs-OW filament is heated at T_1 while positive ions are drawn to clean the surface. The temperature is lowered to the T_2 values indicated on each curve, and kept there until equilibrium is established. At time 0, the temperature is again dropped to a low T_3 value, of 550°K and the electron emission as measured by the galvanometer deflection is observed as time progresses. The time to reach the peak of the curve is called t_3. If the filament is clean at T_2, $t_3 = t_m$ or 165 seconds in this case.

We will find it convenient to standardize our procedure as follows. Heat the filament at $T = T_1$ for t_1 seconds to attain a known initial state. Change T to T_2 for t_2 seconds. Finally decrease T to T_3 and observe t_3 the additional seconds required to reach the optimum activity. Fig. 4 shows the galvanometer deflections against the time at T_3 for a series of T_2 values. In each case $T_1 = 1040$°K and the plate voltage V_p is -140 volts with respect to the filament. This treatment removes practically all the adsorbed caesium. For each curve T_2 is maintained until equilibrium is attained. For the curve on the extreme right, positive ions are drawn at 935°K, at this temperature the surface remains practically clean since t_3 has the same value as t_m. For the next curve T_2 is again 935°K but this time electrons are drawn from the filament. The curve is practically a repetition of the previous one but each point occurs 30 seconds sooner.*

(* The difference in the deflection is due to slight, accidental differences in T_1).

Hence, we must conclude that at 935° the surface is clean if we draw positive ions but is partly covered if we draw electrons. For the remaining curves in Fig. 4, V_p is always +140 volts. They show that the equilibrium θ becomes larger as T decreases. In this figure t_3 is the time corresponding to the maximum deflection. It is quite apparent that t_3/t_m represents the fraction of the surface being covered at T_3 while $1-t_3/t_m=\theta$ the fraction which was covered at T_2. Hence from a series of curves similar to Fig. 4 we can determine the equilibrium values of θ for various filament temperatures.

Fig. 5 shows plots of θ vs. T_2 for Cs-W and Cs-OW. The lettering is analogous to that in Fig. 1. Thus point B represents the condition at the optimum activity at which θ has the value unity; point F is at T_{C_2}. The subscript o refers to the Cs-OW filament. The vapor pressure is the same for the two curves in Fig. 5.[+] For the curve BCD for which electrons are drawn at T_2 it makes no difference what the treatment at T_1 was. For the curve $FGHJK$ for which positive ions are drawn at T_2, it does make a decided difference what the treatment at T_1 was provided that the value of T_2 lies between T_{C_1} and T_{C_2}. If the filament was clean previous to being put at a temperature in this region it stays clean; if previously it was heavily coated, it comes to nearly the same equilibrium θ as when electrons are drawn. Note that below T_{C_1} it makes no appreciable difference whether we draw electrons or positives at T_2 or what the immediate previous treatment of the filament has been. Note also

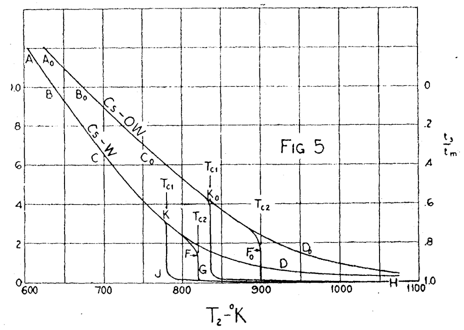

Fig. 5. θ, the fraction of the surface covered when equilibrium prevails as a function of T_2, the temperature of the filament. For the curve $ABCD$ electrons are drawn at T_2; for $ABCFGH$ positive ions are drawn at T_2, and the filament was heavily coated previous to being brought to T_2; for $HJKCBA$ positive ions are drawn at T_2, and the filament was clean previous to being brought to T_2. The subscript o refers to Cs-OW filament. $t_m=136$ seconds.

(+ This vapor pressure is less than that which prevailed for curves E—K and E_0—K_0 in Fig. 1. This is why the critical temperatures T_{C_1} and T_{C_2} in Fig. 5 are lower than the corresponding ones in Fig 1.)

that if we draw positives when T_2 is greater than T_{c_2}, θ is always very nearly zero. Evidently the caesium can evaporate from the surface either as atoms or as ions. The atoms escape irrespective of plate potential, but the ions can permanently escape only if the plate potential is negative.

Note that the Cs on OW is qualitatively like Cs on W. For the same T_2, however, its equilibrium θ is larger than for W, and its hysteresis region comes at higher temperatures. This means that caesium is held more firmly by the oxide on tungsten than by clean tungsten.

EVAPORATION CHARACTERISTICS

The curves in Fig. 5 exhibit θ as a function of T for a particular vapor pressure and therefore for a particular rate of arrival of caesium atoms at the filament. Let A represent this arrival rate. Now since each point in the diagram represents a state of equilibrium, this A must be equal to E, the total rate of evaporation of caesium from the filament. E will in general be made up of E_a and E_p the rates of evaporation of atoms and of positive ions respectively. Fortunately we can determine each of these separately, for if the plate is positive no ions can permanently escape and the equilibrium is maintained by the evaporation of atoms only. For Cs-OW, Fig. 5 shows that at 800° the rate of evaporation of atoms from tungsten whose surface is 54 percent covered with caesium is equal to the rate of arrival, which we can determine by measuring the saturation i_p as previously described. This gives us a single point on an E-θ diagram for $T=800$. For many purposes such a diagram will be found most useful. The dashed lines which decrease towards the left in Fig. 6 show how the rate of evaporation of caesium atoms, E_a, varies with θ for a series of temperatures in the case of the Cs-OW filament. The heavy horizontal line marked A gives the arrival rate or vapor pressure that prevailed for the Cs-OW curve in Fig. 5. Hence the curve $B_0C_0D_0$ in Fig. 5 gives the intersection points of the various temperature lines in Fig. 6 with this A line. By varying the vapor pressure we can similarly determine the intersections of the same temperature lines with new A lines and thus complete the E_a or dashed curves.

The light continuous curves which rise rapidly at the origin and later decrease toward the right in Fig. 6 represent the rate of evaporation of positive ions, E_p, as a function of θ for a series of filament temperatures. These curves may be obtained as follows. Starting with a cold filament, raise the temperature until the positive ion current has an appreciable value such as given by any point on the line $E_0K_0F_0$ in Fig. 1. The equilibrium is now maintained by the arrival of A atoms per cm^2 per second and by the evaporation of E_a atoms and E_p positive ions per cm^2

per second. If each ion is a single atom which has lost one electron $E_p = i_p/e$. θ can be obtained from a $\theta - T$ curve like Fig. 5. Hence in this condition E_p, θ, and T are known. This method can be used for all points on the $E_0K_0F_0$ line in Fig. 1. It will give only one point on each temperature line in Fig. 6. To get more points, we may change the vapor pressure and repeat the procedure.

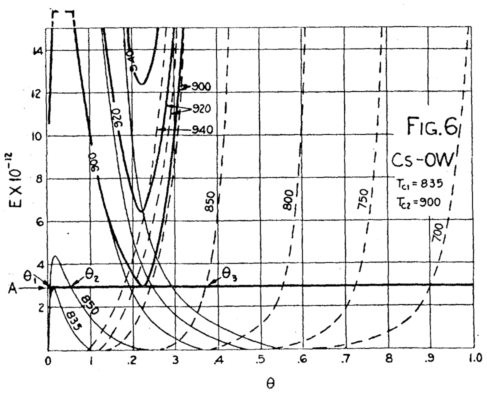

Fig. 6. The rate of evaporation, E, expressed in atoms or ions per cm^2 per sec. as θ increases. The caesium can evaporate either as ions or as atoms. The dashed curves show the atom-rate at the temperatures indicated; the light continuous curves are isothermals for the ion rate; the heavy continuous curves show a few isothermals for the total evaporation rate. The heavy horizontal A line represents the constant rate of arrival that prevailed for the curves in Fig. 5.

Another independent method of determining E_a for various values of θ and T is to proceed as follows: Clean the surface by drawing positives at T_1; suddenly reduce T to T_2 and draw electrons for t_2 seconds; then drop to a low testing temperature T_3 and observe t_3, the time it takes to get to the optimum. Repeat this procedure but vary t_2. It is evident that if $t_2 = 0$, i.e., if we drop directly from T_1 to T_3, the particular value of t_3 will be equal to t_m which depends only on the vapor pressure and the nature of the surface. It has also been shown above that $t_3/t_m = 1 - \theta$. The points in Fig. 7 show a plot of this quantity against t_2/t_m for the various values of T_2 indicated for the Cs-W filament. Note that at first t_3/t_m decreases by the amount t_2/t_m irrespective of the value of T_2. For $T_2 = 795°$, t_3/t_m is constant after t_2/t_m of about .40. The lower the value of T_2, the longer t_3/t_m decreases proportional to t_2. This must mean that E_a at $T = T_2$ has very small values as long as θ is appreciably less than its equilibrium value. In other words every atom that strikes sticks until θ builds up almost to its equilibrium value. Then for a short time only a fraction stick until equilibrium is reached when as many evaporate as strike. Also the lower the value of T_2 the longer it takes to reach equilibrium.

The slope of the curve in Fig. 7 is sufficient to determine numerical values of E. To show this, we have that

$$t_3/t_m = 1-\theta \quad \text{or} \quad y = 1 - N/N_0$$

since $\theta = N/N_1$ by definition, and $N_1 = N_0$. Also $t_2/t_m = x$ or $t_2 = t_m \cdot x$
The slope

$$= \frac{dy}{dx} = -\frac{1}{N_0}\frac{dN}{dx} = -\frac{1}{N_0}\frac{dN}{dt_2}\frac{dt_2}{dx} = -\frac{1}{N_0}(A-E)t_m = -\frac{At_m}{N_0}\left(1-\frac{E}{A}\right)$$
$$= E/A - 1$$

since $dN/dt_2 = A\text{-}E$, $dt_2/dx = t_m$, and $At_m = N_0$.
Hence if we take any point in Fig. 7, $1-y$ gives us θ and the slope tells us $E/A - 1$ and hence E.

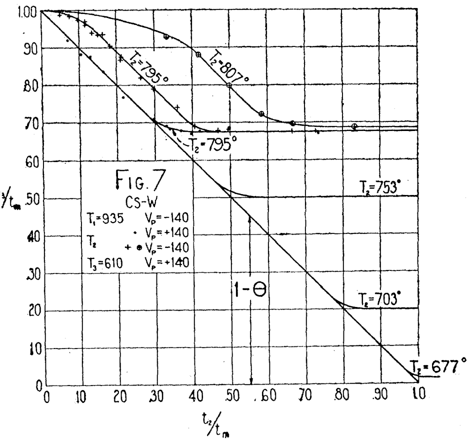

Fig. 7. The surface is first cleaned at T_1. The temperature is reduced to T_2, and kept constant for t_2 seconds when it is again reduced to T_3 and t_3, the time at which the maximum occurs, is observed. t_3 and t_2 are divided by t_m to take account of small variations in t_m during the course of the experiment. For the dots at $T_2 = 795$°K electrons are drawn; for the crosses (+) at $T_2 = 795$ and the circles at $T_2 = 807$ positive ions are drawn. $t_m = 80$ sec.

This same method slightly modified can be used to determine E_p also. If we draw positives instead of electrons when $T = T_2 = 795$°K, we obtain the + curve in Fig. 7. This curve starts out nearly horizontally, then bends downward. Next follows a straight region with a $-45°$ slope. This changes rather abruptly into a horizontal straight line. This means that at first θ increases very slowly from 0, then more and more rapidly until its rate is limited by the vapor pressure. This continues until θ reaches the same equilibrium value as before at 795°. In other words, only a small percentage of the striking atoms stick to clean tungsten, but after a few are adsorbed the rest stick more and more readily, until they all stick. However, as soon as θ reaches its equilibrium the evaporation rate is equal to the arrival rate. These same characteristics are shown even more markedly for the curve marked $T_2=807°$. By varying the vapor pressure we can get a series of E_p curves.

Having once found E_a and E_p for various values of T and θ the results may be exhibited by a family of curves such as is sketched in Fig. 6. From an accurate plot similar to this sketch and the Clausius-Clapeyron equation, the work necessary to remove either an atom or an ion can be determined for all values of θ. To do this accurately would require more precise values of filament temperature and effective filament lengths than the present tube furnishes. It would also require many more points than were taken thus far. These deficiencies could be overcome in a tube with a long filament and several collectors. For these reasons Fig. 6 is to be considered a sketch rather than a plot. From it one can, however, deduce with certainty that *the work necessary to remove an atom decreases as θ increases; while the work necessary to remove an ion increases with θ.* This last fact was at first somewhat surprising. It is not so surprising when one reflects that the adsorbed caesium decreases the work function for negatively charged particles, and that hence they might reasonably increase the work to remove a positive ion. In fact this is precisely what one would predict if some of the adsorbed caesium were ionized. These surface ions would produce local fields of very great potential gradients in such a direction as to help electrons escape from the surface, but hinder positives. In a separate paper the author hopes to produce further evidence for this physical picture.

If in Fig. 6 we add E_a and E_p we obtain the series of heavy lines representing E, the total rate of evaporation when the plate is negative. These curves all show a minimum for some value of θ. To appreciate the significance of this minimum let us increase the filament temperature in steps but keep the vapor pressure constant. The horizontal line is to indicate this constant rate of arrival, A, of caesium on the filament. At a low temperature, θ will have a large value. If we suddenly increase the temperature E will greatly exceed A. Hence θ will decrease to a smaller equilibrium value when E again equals A. This process is repeated until we get to a critical temperature T_{c_2} whose E curve is just tangent to the A line. If we then raise the temperature, E again exceeds A, and θ again decreases. Now, however, a decrease in θ is accompanied by a rise in E so that E always exceeds A and θ decreases more and more rapidly until it practically reaches zero. In other words for $T > T_{C_2}$ the filament cleans itself spontaneously. This accounts for the sudden rise at T_{C_2} in Figs. 1 and 5. While the filament is thus cleaning itself off spontaneously most of the caesium comes off as ions. This sudden rush of ions should register as a ballistic throw in the galvanometer. The magnitude of this throw should be approximately independent of the vapor pressure while the steady deflection is proportional to the pressure. These phenomena were actually observed in every detail before their explanation in terms of the evaporation characteristics were understood. With saturated vapor at any temperature above 0°C, the steady deflection is so great that it completely masks this ballistic throw. The ballistic throw can be most clearly shown if the vapor pressure is so low that t_m is about 15 minutes. The throw on our galvanometer in that case was 140 mm while the steady deflection was only 4 mm. In fact this ballistic throw can be used to detect and roughly measure the caesium vapor pressure long before the steady positive current is large enough to sensibly deflect the galvanometer. Another way of obtaining this ballistic throw is to suddenly reverse the plate potential from a positive to a negative value when the vapor pressure is low and $T > T_{C_2}$. This result was first predicted from a study of Figs. 5 and 6.

These figures show that the evaporation characteristics depend to large extent on the polarity of the plate. The curves therein shown are for potentials sufficient to saturate the electron and ion currents. For smaller negative plate potentials, E_p for a given T and θ are less than in Fig. 6, and T_c in Fig. 5 is shifted more and more to higher T values. Hence there exists a complete set of curves similar to Fig. 6 for each value of the negative plate potential. While the experimental results are still very meager, they indicate that the work necessary to remove a positive ion can be appreciably decreased by applying large negative potential gradients. In other words, even though T and θ remain constant i_p can be appreciably increased by increasing the negative plate potential. This effect is similar to the Schottky effect for electron emission.[11]

This dependence of E_p on plate potential must be taken into account in determining e/m for the caesium ions from the slope of the $i^{2/3}$ vs. V curve. In using this slope it is customary to tacitly assume that the contact potential between the filament and plate remains constant. Our experiments show that E_p and therefore θ and φ vary with the applied voltage over the range in which the positive ion current is limited by space charge. Hence the contact potential varies from point to point.

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[11] Schottky, Zeits. f. Physik **14,** 63 (1923).

This sometimes introduces appreciable errors in the calculated values of e/m.

DETAILS OF HYSTERESIS PHENOMENA

There is another interesting consequence of the evaporation characteristics which shows itself when the filament temperature lies inside of the hysteresis region. Suppose we again clean the Cs-OW filament by drawing positives at 1040°K; then choose T_2 such that it is only slightly higher than T_{C_1} and keep T_2 fixed for t_2 seconds; finally drop to the testing temperature T_3, reverse the plate potential, and observe the electron current as time progresses. Fig. 8 shows a plot of this current vs. time for the various values of t_2 indicated on the curves. Instead of getting a single maximum as heretofore we now observe two distinct maxima. With increasing t_2, the first maximum grows while the second decreases in height. The sum of the two heights stays approximately constant. If we draw electrons at T_2 until equilibrium is reached and then drop to T_3 we observe a single peak at the time of the first set of maxima in Fig. 8. Whereas if we drop directly from T_1 to T_3 we observe a single peak at the time of the second set. Evidently the filament must be rather sharply divided into two regions at T_2. The central region which produces the second maxima is clean but gets progressively smaller. The two end regions which are responsible for the first maxima get progressively larger. As long as there is still a clean central portion, we can reverse the direction of travel of the dividing line by raising T_2 near to T_{C_2}.

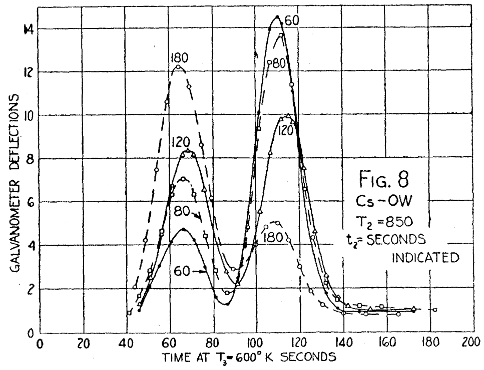

Fig. 8. The surface of the filament is cleaned at T_1. The temperature is reduced to $T_2 = 850°K$, a value about 20° higher than T_{C_1}, and kept there for the time indicated on each curve while positive ions are drawn; then the temperature is again reduced to T_3 and the electron emission observed as time progresses.

This peculiar phenomenon also can be readily interpreted in terms of the evaporation curve Fig. 6. For any temperature T_2 between T_{C_1} and

T_{c_2} such as, for example, 850° in the case of Fig. 6 the isothermal curve crosses the A line in three places, θ_1, θ_2, and θ_3. While θ_1 and θ_3 are points of stable equilibrium, θ_2 is a point of unstable equilibrium. Since there are two stable equilibrium values for the same filament temperature and vapor pressure, the surface can exist either practically clean at θ_1 or covered to an extent equal to θ_3. There must, of course, be a dividing edge separating these two regions. Fig. 8 shows that this dividing edge must be rather sharp when measured in cm. Still it may constitute a transition region many atomic diameters in width. It is known that adsorbed atoms can move over distances of the order of 1×10^{-3} cm on the surface.[12,13] There must therefore be a considerable dividing region whose θ values range from θ_1 to θ_2 and θ_2 to θ_3. For the first of these sections $E>A$ while for the second $A>E$. For temperatures near T_{c_1} the second section will be more effective than the first, with the net result for the whole region that more atoms will strike than evaporate. Consequently the covered part of the filament will grow at the expense of the clean part. For T_2 near T_{c_2} the reverse will be true.

RÉSUMÉ AND DISCUSSION OF RESULTS

This paper describes a new method for determining quantitatively how the concentration of adsorbed atoms is affected by surface temperature, surface potential gradient, and rate of arrival of atoms. The application of this method to various cases of adsorption ought to throw a good deal of light on the nature of the forces which cause one atom to stick to another. At the same time, this study also reveals the nature of the correlation between the thermionic characteristics of a surface and the state of its adsorbed layer. Thus the study of caesium adsorbed on tungsten has led to the following picture. The first few caesium atoms that strike a clean tungsten surface are ionized. If the filament temperature is above a critical value, T_{c_2}, and the plate is sufficiently negative every atom that strikes the filament comes off as an ion and it stays practically clean. If the temperature equals or is less than a lower critical value, T_{c_1}, a few of the striking atoms fail to evaporate but are adsorbed on the tungsten surface as ions. The strong local fields produced by these ions increase the work function for positive ions so that a smaller percentage of the atoms that strike come off. Soon every atom that strikes sticks. When θ reaches a certain value as much caesium evaporates as strikes. By now the adsorbed caesium can no longer all be ionized and the particles that come off are nearly all atoms and not ions. If the temperature is lowered, more atoms stick until a new equilibrium θ is

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[12] Volmer and Esterman, Zeits. f. Physik **7,** 13 (1921).

[13] Esterman, Zeits. f. Physik **33,** 320 (1925).

reached. If the plate is positive during adsorption every atom that strikes the filament sticks until the equilibrium θ is reached. At a given vapor pressure, there is a temperature such that the surface is just covered one layer deep with caesium. At this stage the caesium is packed as closely as possible on the surface and it has its atomic rather than its ionic diameter. For still lower temperatures the surface is covered more than one layer deep.

The shape of the curves which give the relation between rate of evaporation of caesium and θ, a sketch of which is shown in Fig. 6, satisfactorily accounts for the observed critical temperatures and hysteresis effects for positive ions. These curves also explain why the filament cleans itself spontaneously when we approach the higher of these critical temperatures, and why this process is accompanied by a momentary rush of positive ions from the filament.

The adsorbed caesium greatly modifies φ_e, the work function for electrons. For clean tungsten this has the value 4.52 volts. As θ increases, φ_e decreases rapidly at first, then progressively less rapidly. When $\theta = 1.00$ φ_e has a minimum value of 1.36 volts. This value is computed by putting the present interpretation on Langmuir and Kingdon's line *AB* in Fig. 1 of their article.[5] When the second layer is formed, φ_e increases again.

On the whole this picture has much in common with the one Langmuir and Kingdon[5] have arrived at from considerations which are in part entirely different than the ones presented here. There are three essential differences however. They seem to assume that adsorbed surfaces cannot be more than one layer deep, and they conclude that $\theta = .90$ at the optimum activity, i.e., for points on the line *AB* referred to above. The simple straightforward observations herein described point to a $\theta = 1.0$ for this condition, and Fig. 2 indicates that for sufficiently low filament temperatures enough atoms are adsorbed to form much more than a single layer even if $\theta = .90$ at the optimum activity.

The second difference is that according to Langmuir and Kingdon the electron work function decreases linearly as θ increases; while the experiments herein described and Ives' photo-electric experiments point to a non-linear decrease in φ_e which is followed by an increase in φ_e when θ attains its optimum value.

In the third place Langmuir and Kingdon believe they have shown "that in the adsorbed film no distinction can be drawn between atoms and ions," while the writer believes that the experimental facts can be much more readily interpreted from the viewpoint that there is a real difference between adsorbed atoms and ions. If the valence electron no longer revolves about the adsorbed nucleus the caesium exists as an ion. This will be the case if the surface work function, φ_e, is considerably larger than the ionization potential of the caesium atom in free space. It will then take a definite amount of work to transfer an electron from the surface to the adsorbed ion and at least momentarily convert it to an adsorbed atom. At high surface temperatures there will be an appreciable number of electrons endowed with sufficient energy to convert ions to atoms and hence the ratio of adsorbed ions to atoms will decrease as the temperature increases and θ is kept constant. This ratio will be governed by Boltzman's equation. Conversely if φ_e is considerably smaller than the free ionization potential most of the caesium will be adsorbed as atoms and an increase in surface temperature for a given θ will result in an increase in the ion concentration. The state in which a caesium particle evaporates depends on whether it was an adsorbed ion or an atom at the instant at which it received an appropriate thermal impulse.

Langmuir and Kingdon also find evidence for two distinct phases existing at the same filament temperature and separated by a sharp dividing line which can be made to move along the filament. The present method not only detects these phases but gives the concentration of each. Langmuir and Kingdon from their viewpoint evidently expected to find evidence for two such phases even when the plate is positive. Their failure to do so is explained by the evaporation curves which show that with the plate positive only the concentrated phase exists. They do not mention the hysteresis phenomenon for positive ions, nor the momentary rush of positive ions at T_{c2}.

Estermann[13] finds that when a vapor such as cadmium strikes a surface such as copper at a given rate A, a deposit will be formed only if the temperature of the surface is below a critical temperature, T_c. From the variation of T_c with A he computes the heat of adsorption. This critical T_c is evidently the same as T_{c1} in the present paper and the explanation of his phenomenon is given by the evaporation curves. He also finds indisputable evidence that adsorbed atoms can travel over comparatively large distances on the surface. Chariton and Semenoff[14] find similar evidence for critical temperatures. All this goes to show that evaporation curves for caesium on tungsten have their counterparts in many other cases of adsorption.

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April 2, 1926.

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[14] Chariton and Semenoff, Zeits. f. Physik **25**, 287 (1924).