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ACCOMMODATION COEFFICIENT OF HYDROGEN; A SENSITIVE DETECTOR OF SURFACE FILMS

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Abstract

An equation is derived which gives the accommodation coefficient α of a gas striking a surface as the ratio of the observed heat loss from the surface to the theoretical heat loss that would be observed if all the gas molecules came to thermal equilibrium with the surface. The experiments show that at temperatures above 600°K the values of α for hydrogen (0.20 mm pressure) are greatly reduced by the presence of oxygen on the surface of the tungsten. Oxygen is inevitably produced in a tube when a tungsten filament is burned at $T > 1500$°K in hydrogen, as the atomic H thus formed dislodges oxygen from the walls even when the walls are cooled in liquid air. Hydrogen is adsorbed on tungsten at $T < 1200$°K in two different forms, both of which reduce α from its value for bare tungsten. A film of the first type, which is adsorbed at $T < 600$°K, changes over into the second type slowly at 600°K and rapidly at 1100°K. The numerical values of α range from 0.537 for bare tungsten to 0.143 for tungsten with an adsorbed hydrogen film of the second type, and 0.094 for tungsten with an adsorbed film of oxygen. At $T < 200$°K an oxygen film forms which increases α to 0.422 at 150°K, provided that a small concentration of oxygen is continually present in the gas phase.

THE heat taken up by a gas at low pressures from a hot metal surface is governed by a factor which Knudsen[1] has named the "accommodation coefficient" of the gas. This coefficient measures the extent to which a gas of known temperature striking a surface of a different temperature "accommodates" its temperature to that of the surface. Knudsen defined the accommodation coefficient α as follows

$$\alpha = (T_2 - T_1)/(T_2' - T_1) \tag{1}$$

where T_1 is the temperature of the molecules before they strike the surface, T_2 the temperature of the molecules when they leave the surface, and T_2' the temperature of the surface. Then α is less than unity when the molecules fail to reach thermal equilibrium before leaving the surface.

The definition in Eq. (1) is open to the objection that the concept of a temperature T_2 of the molecules leaving the surface has no clearly defined meaning unless the molecules leave the surface with a Maxwellian distribution of velocities. If thermal equilibrium is not reached, it is almost certain that the distribution is not Maxwellian. Therefore, in this paper α is defined in terms of the heat which the molecules carry away from the surface. The theoretical heat loss from the surface which would occur if the incident molecules reached thermal equilibrium with the surface has been calculated ac-

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[1] M. Knudsen, Ann. d. Physik **34**, 593 (1911).

cording to the kinetic theory, and α represents that fraction of the theoretical heat loss which is observed experimentally. The experimental values are obtained by subtracting from the watts consumed by a filament at a given temperature in the presence of gas, the watts consumed by the filament at the same temperature in vacuum, the resistance of the filament affording in each case a measure of the temperature.

Previous papers[2,3,4] have described the mechanism of heat conduction from small wires in a gas. When heat is conducted by a gas from a wire of diameter d and temperature T, placed in the axis of a tube of diameter b and wall-temperature T_1, there exists between the wire and the gas adjacent to the wire a temperature drop which may be a large fraction of $(T-T_1)$ when the pressure of the gas is low. Let T_a be the temperature of the gas at a distance of one mean free path λ from the wire, so that the temperature drop is $(T-T_a)$. Then T_a may be calculated[4] when W_c, the heat carried from the wire per cm of length per sec., is known, for W_c is carried from the region of temperature T_a to the walls according to the ordinary laws of heat conduction. We have

$$W_c = 2\pi(\phi_a - \phi_1)/\ln\left[b/(d+2\lambda)\right] \tag{2}$$

where

$$\phi_a - \phi_1 = \int_{T_1}^{T_a} K dT \tag{3}$$

K being the coefficient of heat conductivity of the gas. Numerical values of $(\phi_a - \phi_1)$ are given in Table I, calculated for $T_1 = 80°\text{K}$; T_1 had this value since the liquid air used in our experiments was nearly pure nitrogen. The values of K used in making the calculations were taken from measurements made by Eucken[5] at temperatures from 81.5°K to 373°K.

TABLE I. $\phi_a - \phi_1$ for hydrogen. $T_1 = 80°\text{K}$.

T_a deg. K	$\phi_a - \phi_1$ Watt deg. cm^{-2} sec.$^{-1}$
80	0.0
100	0.0126
150	0.056
200	0.114
250	0.185
300	0.270

The gas molecules which strike the filament come from the region of temperature T_a, and the number which strike the filament per cm² per sec. is[6]

$$n = p/(2\pi m k T_a)^{1/2} \tag{4}$$

where p is the pressure in dynes per cm², m the mass of a molecule, and k the Boltzmann constant (1.371×10^{-16} ergs per deg. K). The average internal

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[2] I. Langmuir, Phys. Rev. **34**, 401 (1912).
[3] I. Langmuir, J.A.C.S. **36**, 1708 (1914).
[4] I. Langmuir, J.A.C.S. **37**, 417 (1915).
[5] A. Eucken, Phys. Zeits. **12**, 1101 (1911).
[6] I. Langmuir, Phys. Rev. **2**, 329 (1913).

energy of each incident molecule is $(\beta-3/2)kT_a$ where βk is the specific heat at constant volume per molecule, expressed in ergs per deg. K. When hydrogen is cooled to low temperatures, the specific heat approaches that of an ideal monatomic gas,[7] and β has the value 3/2 at 45°K; at higher temperatures the specific heat increases to the values characteristic of diatomic gases, and $\beta=2.42$ at 273°K, and 2.68 at 1000°K. But the average kinetic energy[8] of each of the n molecules which strike a surface per cm^2 per sec. is $2kT_a$, so that the incident molecules bring a total energy of $n(\beta+1/2)kT_a$ ergs cm^{-2} sec.$^{-1}$ to the filament. If the molecules reach thermal equilibrium before leaving the filament, they carry away $n(\beta+1/2)kT$ ergs cm^{-2} sec.$^{-1}$, so that the total energy loss in ergs cm^{-2} sec.$^{-1}$ is[9]

$$W = (\beta + \tfrac{1}{2})pk(T - T_a)/(2\pi mkT_a)^{1/2}. \tag{5}$$

If the molecules do not reach thermal equilibrium, the total energy loss W_c per cm length of the filament is a fraction of $\pi d\ W$ such that

$$W_c = \alpha\pi dW \tag{6}$$

and

$$\alpha = W_c(2mkT_a/\pi)^{1/2}/[d(\beta + \tfrac{1}{2})pk(T - T_a)]. \tag{7}$$

The experiments which will be described in this paper were made with hydrogen at 0.20 mm pressure in a cylindrical tube 6.4 cm in diameter containing hairpin filaments of tungsten wire 0.00779 cm in diameter.

Expressing W_c in watts per cm, p in mm of Hg, and placing $d=0.00779$ cm, and $m=3.32\times10^{-24}$ g for hydrogen, we have

$$\alpha = 119.5W_c(T_a)^{1/2}/[(\beta + \tfrac{1}{2})p(T - T_a)]. \tag{8}$$

Evidence that Surface Films are Formed on the Filament

Preliminary measurements of the heat loss from a tungsten filament in hydrogen at constant pressure gave results that were reproducible at high filament temperatures (above 2000°K), but when the filament was operated at a dull red heat the wattage consumed at a given resistance was higher in some experiments than in others. Since such variations never occurred when the filament was in vacuum, the change in heat consumption was attributed to a change in the heat loss to the gas. It was found that the change had been occasioned by the procedure of sending a discharge of a few milliamperes at 100 volts through the gas, for a filament that had been cathode of this discharge would subsequently show a higher heat loss than a filament that had been anode or disconnected in the discharge, or that had been incandescent in the presence of hydrogen with no discharge. But a filament that had the property of showing a high heat loss would lose this property instantaneously if heated to 2000°K or more in hydrogen without a discharge.

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[7] Int. Crit. Tables, **V**, 82.

[8] O. W. Richardson "The Emission of Electricity from Hot Bodies", 2nd Ed. p. 156.

[9] This differs from the value given in 1915[4] by the addition of the term $k/2$ to the specific heat. Eq. (5) checks with the equation given by Knudsen

$$W = 43.46 \times 10^{-6}(T_1 - T_2)(c_p/c_v + 1)p/[(MT)^{1/2}(c_p/c_v - 1)]\text{g-cal.}$$

These observations led to the belief that the change in heat loss was due to some change taking place at the surface of the filament itself, and not in the main body of the gas. In other words, since the factor which controls the transfer of heat at the surface is the accommodation coefficient, whereas the factor controlling transfer in the gas is the heat conductivity, the observed changes were to be attributed to a change in the value of the accommodation coefficient. This conclusion was borne out by the test of pumping all of the hydrogen out of the tube, and replacing it with fresh pure hydrogen; whenever this was done, and whatever the heat loss of the filament might be, the loss was found to be exactly the same with fresh hydrogen as it had previously been with the old hydrogen.

Experiments were therefore planned for the purpose of learning what properties of the surface were responsible for producing changes in the accommodation coefficient. The properties of the surface to be investigated fell into two classes: the composition of the surface layer, and the temperature of the surface. The procedure for investigating heat loss consisted in measuring the current and voltage of a filament, over a range of currents, and then calculating the corresponding watts and resistance from these data and plotting them in a curve, similar to one of the curves in Fig. 1. The curves marked *A* and *B* represent the heat lost by a filament in hydrogen, and the curve marked *V* the loss from the same filament in vacuum. The vertical distance from an *A*-curve or a *B*-curve to the corresponding point on the *V*-curve is therefore a measure of the heat lost to the gas when the filament has the temperature which corresponds to the resistance at which this vertical distance was measured.

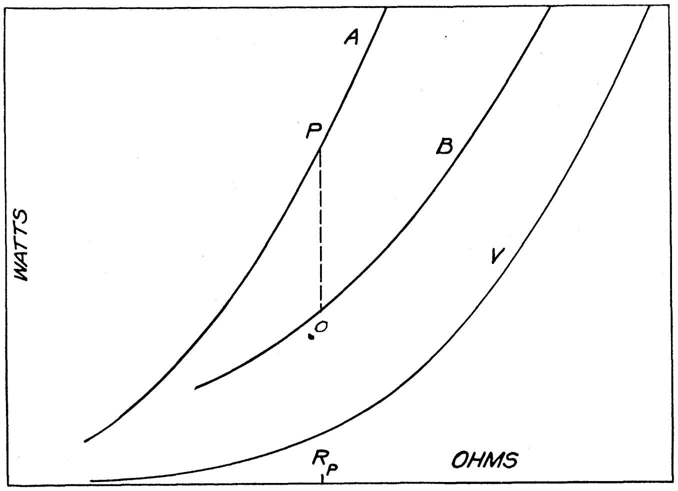

Fig. 1. Typical curves showing heat loss from tungsten filament in hydrogen, plotted against resistance of filament.

Any change which takes place in the accommodation coefficient causes the rate of loss of heat by the filament at a given temperature to be changed, so that the watts measured at any given resistance R_P are caused to vary along a line such as the line OP in the diagram, moving in the direction of P as the coefficient increases. Thus in order to study the effect which the composition of the surface layer had upon the accommodation coefficient, the surface was subjected to a variety of treatments, and after each treatment the watts were measured at a chosen resistance which was the same for every test and was called the testing resistance. When studying the effect which temperature alone might have upon the accommodation coefficient, the composition of the surface layer meanwhile remaining constant, it was found that there were certain ranges of temperature within which the temperature of the filament could be shifted up or down without altering the surface layer, and data taken in this way lay along one of a family of curves such as A or B. The first tube contained three filaments which could be operated independently of one another, making it possible to study the simultaneous effects which any process taking place within the tube had upon filaments of different temperatures and potentials.

As soon as it was known that a filament showed a higher heat loss at 1000°–1400°K in some experiments than in others, due to the treatment which the filament had received in a 100-volt discharge, an effort was made to single out the individual factors in the experimental conditions which led to this effect. As a result, methods were gradually found of widening the spread in the values of the heat loss until the spread could be made much greater than had been at first observed. As the experiments proceeded it became apparent that the values of the heat loss tended to group themselves about a maximum and a minimum value in a way that suggested that there were two distinct states in which the filament surface could exist; and that all values between the maximum and the minimum represented a surface condition intermediate between these two states. The filament states were therefore named Y, the state having the maximum heat loss to the gas W_Y, and X having the minimum heat loss W_X. The wattage consumed by the filament in vacuum will be called W_V; then W_Y and W_X each represent the difference between total wattage consumed by the filament at a given temperature in hydrogen, and the corresponding W_V for the same temperature. In the earliest observations W_X was 0.9 W_Y to 0.5 W_Y; recent experience has shown that suitable experimental technique widens the spread between W_X and W_Y so that at certain temperatures $W_X < 0.3\ W_Y$.

It was natural to try the hypothesis that one of these states represented a clean metal surface, and the other a contaminated surface. Since a very sensitive test of the purity of tungsten on the surface of a filament is readily available by measuring the electron mission in vacuum and comparing the currents with the known values of the emission from pure tungsten,[10] the tube was evacuated and baked until the filaments gave normal emission. When hydrogen was then admitted to the tube and the filament tested for W at a dull red heat, it was found to be in state Y; but at higher temperatures it immediately started to creep toward X, and only by making the filament

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[10] H. Jones and I. Langmuir, Gen. Elec. Rev. **30**, 310 (1927).

negative in a discharge could it be caused to return to *Y*, as long as there was hydrogen in the tube. If the filament was in state *X*, and the hydrogen was then pumped out of the tube and the filament tested for electron emission in vacuum, the emission was found to be far below normal, as it is when a tungsten surface has become contaminated. From these observations the conclusion was drawn that state *Y* corresponds to a clean tungsten surface, and state *X* to a surface contaminated with a substance which will be called substance *X*.

In the early experiments which were conducted with the tube in a water bath at room temperature, state *Y* proved to be very troublesome to study, because of the difficulty of maintaining the filament in this state for a time long enough to make consistent measurements. At temperatures above about 1300°K the wattage of the filament had to be lowered every minute, or half minute, in order to keep the resistance constant, which meant that the surface conditions were changing over into state *X*. At higher temperatures the change became so rapid that there was doubt whether a true state *Y* was ever attained at these temperatures. The rate at which the filament departed from *Y* was entirely erratic, and was apparently governed to a large extent by whatever processes had previously taken place in the tube.

The fact that substance *X* lowered the electron emission from tungsten suggested that this substance contained oxygen, for oxygen is known to have similar effects on the electron emission from tungsten.[11] This is in agreement with the recent experiments of Farkas[12] who found that oxygen lowered the accommodation coefficient of hydrogen in contact with tungsten at temperatures above 625°K.

Since it was known[3,4,13] that hot tungsten dissociates molecular H_2 into atomic H and that atomic H will reduce oxides to form water vapor, the experiment was tried of immersing the tube in liquid air so that any water vapor formed in the tube would be removed from the gas phase as fast as it was formed. The heat loss from the filament at any given temperature was now greater than it had been before, due to the lower temperature of the gas molecules striking the filament, but the cold walls were found to have a marked effect upon the experimental results entirely apart from this cause. It was found that the highest values of W_Y were now obtained by the treatment of flashing the filament at 2500°K or more, whereas with the walls at room temperature this treatment always left the filament in state *X*. It was no longer necessary to make use of a discharge to produce state *Y*, the state which represents clean tungsten; on the contrary, when the filament was negative in a discharge the resulting values of W_Y were never higher than those obtained by flashing, and were often lower. On the other hand, the standard method of obtaining state *X* by heating the filament was now inoperative, and the only way that the filament could be brought into state *X*

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[11] I. Langmuir, Ind. and Eng. Chem. **22,** 390 (1930); I. Langmuir and D. S. Villars, J.A.C.S. **53,** 486 (1931).

[12] A. Farkas, Zeits. f. physik. Chem. (B) **14,** 371 (1931).

[13] I. Langmuir, Gen. Elec. Rev. **29,** 153 (1926).

was by lighting a *neighboring* filament. It made no difference whether the neighboring filament were the hot cathode in a discharge, or were burning without a discharge, this procedure always left the test filament in state X (with the single exception that if the test filament were charged to -100 volts or higher negative potentials with respect to the anode during the time of a discharge, it would be brought to state Y, as stated above). Moreover, state Y was now fairly easy to maintain, and state X had become the troublesome state to study because it tended to change over into Y.

EXPERIMENTAL TECHNIQUE FOR WORKING WITH STATE Y

The experience gained in the course of trying to bring the filament to one state or the other under many sorts of conditions has shown that the state of the filament can be controlled with little difficulty, provided that certain experimental conditions are met, but that if these conditions are neglected the observed values will "creep" in a very persistent and annoying fashion.

In order to maintain a filament in state Y, it is imperative that the gas within the tube be kept free from both oxygen and water vapor. The presence of the smallest trace of either of these substances in the gas will cause the filament to depart from Y in a short space of time, i.e., in a few seconds, or at the most a few minutes. When preparing to study state Y, it is a good plan to observe, first, the pure electron emission from the filament in vacuum as a test of whether the bake-out of both tube and connecting system has been satisfactorily accomplished, for experience has shown that unless conditions in the tube are such that a filament can maintain normal saturation emission in vacuum for a long time, a filament in this tube will never be able to maintain state Y when the hydrogen is admitted. However, if the electron emission is normal, it by no means follows that state Y will always be constant, for a tube may remain free from water vapor when the filaments are operated in vacuum, but not when they are operated in hydrogen, since lighting the filaments will cause atomic H to be formed and this will react with oxides that are present on the filament leads and the walls of the tube to form water vapor.

The only experimental procedure found up to the present time which will yield consistent and reproducible data on state Y is that of keeping the tube immersed in liquid air while the experiments are in progress. Hence it appears that the tendency of the filament to become contaminated by a substance or substances which are formed by the atomic H which the filament itself produces, can be overcome only by removing these substances from the gas as fast as they are formed, and that cooling the tube in liquid air removes the greater part of them. If there is much oxide on the walls, the atomic H also produces from this oxide small quantities of oxygen or oxide in a form which does not remain condensed on the walls at liquid air temperature, but reaches the filament. Oxygen from this source is not troublesome after the oxides on the walls have been reduced.

A deposit of potassium or magnesium on the walls of the tube has not been found so satisfactory an agent for removing contaminations as the liquid air.

The failure of these substances to accomplish the complete removal of oxygen in these experiments is significant, in view of the fact that they are both highly effective agents for this purpose in vacuum tubes. For example, we know that when potassium or magnesium is vaporized on to the walls of tubes containing thoriated filaments, these filaments will maintain normal electron emission for great lengths of time, although if the same type of filament is exposed to a trace of oxygen its emission instantly falls to a minute fraction of the normal value. We attribute the failure of these agents in the case of a tube containing hydrogen dissociated by a hot filament or by a discharge, to the reaction of the atomic H with the K_2O or MgO which are formed on the walls when a deposit of K or Mg cleans up residual oxygen or water vapor. As a result of this reaction with atomic H these oxides become partly reduced, and oxygen is liberated in the gas phase as free oxygen or water vapor. In general, this oxygen or oxide will then traverse the tube only once, for it will be taken up by K or Mg wherever it makes its next impact with the wall. But it may subsequently be set free again by atomic H and the process repeated in a cycle, so that whenever there is atomic H in the tube there may also be a slight concentration of oxygen and water vapor in the gas phase.

We have already said that when the tube was cooled in liquid air without a deposit of K or Mg on the walls, oxygen ceased to be troublesome after the oxides on the walls, which in this case were oxides of tungsten, had been reduced. We therefore conclude that under these conditions the process was not repeated in a cycle. The process differs from that described in the preceding paragraph in that tungsten at the temperature of liquid air combines only very slowly with water vapor, so that oxygen which at first appears in the tube in the form of oxides of tungsten, is ultimately converted to a great extent into water vapor condensed on the walls. Tubes which had a thin deposit of tungsten on the walls, vaporized from one of the filaments, were found to give far less trouble in maintaining a clean filament than tubes with bare glass walls, so that forming such a deposit has been included in the regular practice of preparing a new tube for these experiments. The tungsten keeps atomic H away from the glass, which is composed of several different oxides, and also acts as a catalyst to cause atomic H to recombine to form molecular H_2.

The tubes used in our experiments were made of Pyrex glass and were sealed to a vacuum system. Each new tube was evacuated and baked for 1 hour at 460°C, and afterwards whenever it was opened to the air or when water vapor had access to the tube, it was thoroughly torched with a Bunsen flame while being re-exhausted. It was imperative that at least two traps cooled in liquid air come between the tube and the main vacuum system, to keep the water vapor that was baked out of the tube from diffusing back into it again; and this protection was effective only when the trap nearest the tube was baked every time that the tube was baked, for if the nearest trap were left in liquid air during the bake-out, water vapor would collect in the inch or two of cold tubing that adjoined the liquid air flask, and would diffuse back into the tube at some later time. The traps and connecting tubing were therefore made of Pyrex glass for greater convenience in torching with a Bunsen flame. Experience has shown that the sensitiveness of a filament in state Y to the presence of water vapor is so great that if one neglects the bake-out of the connecting tubing and liquid air trap, the measurements are apt to show troublesome and erratic variations which do not appear when the tubing is properly baked.

Hydrogen was admitted through a hollow platinum tube 0.15 cm in diameter and 7.0 cm in length, sealed to the system. Platinum must be sealed into soft glass and therefore had to be joined to the rest of the system through a glass seal graded from soft glass to Pyrex. When a tube of this sort is brought to red heat in a Bunsen flame the hydrogen present in the flame penetrates the platinum wall and enters the system; it took about 5 minutes to fill the system in this way with hydrogen at 0.20 mm pressure. This is known to be a method of obtaining hydrogen which is free from all impurities and has the added advantage that hydrogen can be introduced to a system without the use of stop-cocks. Our system had no stop-cocks connecting the experimental tube, traps and platinum tube, and these were shut off by a mercury trap from the rest of the system.

There is sometimes danger that traces of oxygen may be held adsorbed to the glass walls of one of the traps when the liquid air on the trap has nearly the temperature of liquid nitrogen, and this oxygen will later evaporate from the trap and diffuse into the tube as the level of the liquid air falls. We have had evidence in these experiments that oxygen is sometimes stored in this way, and therefore the measurements that will be given in this paper were all made with a charcoal U-tube, cooled in liquid air, separating the tube from the main system. A charcoal tube is not needed, however, except when making refined measurements, and its presence makes the experiments more troublesome since charcoal absorbs large volumes of hydrogen and then gives up hydrogen quite rapidly with increasing liquid air temperature, so that one must take precautions to hold the pressure constant.

Experimental results, state Y. The measurements were made in a tube containing two parallel hairpin filaments all made of pure tungsten wire 0.00779 cm in diameter. The data in Fig. 2 were taken with filament b, which was 40.7 cm long; filament a was 30.3 cm long. The curves show the watts consumed in 0.20 mm hydrogen, plotted against the resistance. The entire tube, including the leads, was immersed in liquid air. Two temperature scales are given on the graph. The upper scale, T_m, represents the maximum temperature at the center of the filament for a given resistance, and was calculated from the current[10] which brought the filament to the same resistance in vacuum. But a filament of the dimensions of filament b, running at 1000°K or less, can maintain its maximum temperature for only a part of its length at the center, the remainder of the filament being cooled by loss of heat to the leads. Calculation[14] shows that at $T_m = 1000°K$, 17.9 percent of the filament has a temperature 20 degrees or more below the temperature at the center; at $T_m = 800°K$, 26.8 percent shows a similar cooling, and at 600°K, 48.7 percent.

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[14] I. Langmuir, S. MacLane, K. Blodgett, Phys. Rev. **35**, 478 (1930).

Because of the lack of uniformity of temperature along the filament, it was necessary to choose a method of estimating an average temperature of the entire filament which would serve as an approximate value to be used in making calculations of heat loss. The lower scale, T_r, in Fig. 2 represents this average which was taken to be the temperature corresponding to the average resistance.

In the range of temperatures shown in Fig. 2 the heat loss due to dissociation of H_2 into atoms was negligible. H_2 dissociates in the presence of a hot tungsten filament at a rate which consumed approximately 0.25 watt when filament *b* was at 1600°K. At higher temperatures the heat consumed by dissociation becomes a very large factor in the heat measurements, for it increases 25-fold between 1600°K and 2000°K, and at temperatures above 2400°K constitutes the greater part of the total heat loss to the gas. But although the dissociation of H_2 below 1600°K was unimportant from the standpoint of the heat which it consumed, a small amount of dissociation nevertheless took place at considerably lower temperatures and the resulting atomic H could be detected by effects which will be described later in this paper.

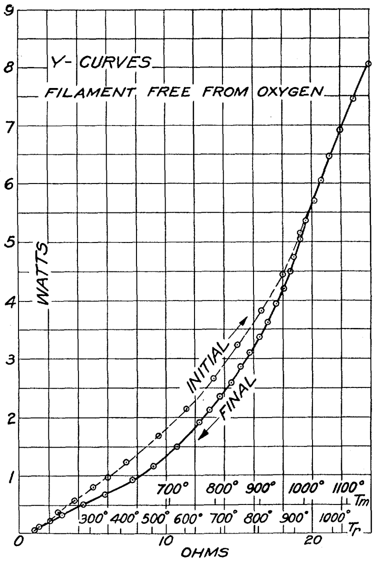

Fig. 2. Heat loss curves for filament *b* when the filament is free from oxygen. Hydrogen at 0.20 mm pressure. T_m represents maximum temperature in deg. *K* at center of filament. T_r represents average temperature, calculated from the resistance.

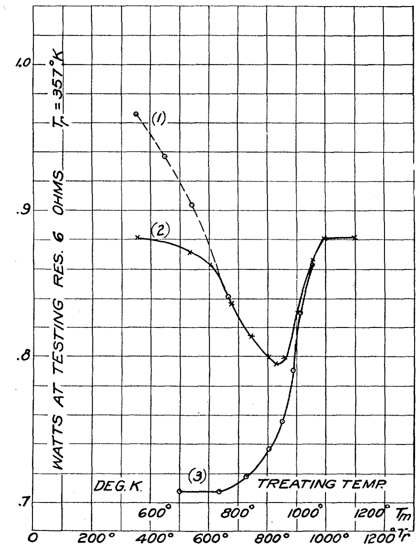

Fig. 3. Curves which gave evidence that hydrogen adheres to tungsten. Wattage of filament *b*, measured at a testing resistance of 6 ohms, after the filament had been subjected to various heat treatments.

Before taking the data plotted in Fig. 2, filament *b* was brought to state *Y*, i.e., rid of surface contaminations, by flashing it in 0.001 mm of hydrogen at 2800°K. The hydrogen residue was due to the presence of the hydrogen adsorbed in the charcoal tube. The effect was the same as that of flashing in a good vacuum, so that hereafter this treatment will be called flashing in vacuum. It was said earlier in this paper that a filament can be rid of oxygen by being flashed at 2500°K or more in hydrogen. This was true of a filament 0.0125 cm in diameter and 11.4 cm long, which had only 20 volts across the leads when it ran at 2500°K in hydrogen. Filament *b* took 47 volts at 2000°K in hydrogen, so that at higher temperatures a large fraction of the current passed from one lead to the other in a gaseous discharge, and the ends of the filament were much hotter than the center. A filament can be almost completely rid of oxygen at 2000°K in hydrogen, however, and will remain free from it when cooled to 1400°K or lower temperatures, provided that the oxides on the walls have been previously reduced, or have been covered by a fresh layer of tungsten evaporated from the filament; there was another reason why it was important to flash the filament *in vacuum* which will appear presently.

After the vacuum flashing, hydrogen was admitted to the tube while the filament was at 80°K. The dotted curve in Fig. 2 represents the heat loss from the filament as the temperature was raised from 80°K; the solid curve the heat loss as the temperature was then slowly lowered from 1100°K, the temperature remaining for at least one minute at each of the points that mark the descending curve. Upon again raising the temperature it was found that the ascending curve exactly retraced the solid curve. If the filament was allowed to cool rapidly from 1100°K to 80°K by switching off the filament current, and the heat loss then measured at about 400°K, it was found to have a value intermediate between those of the two curves, and never returned to the high value of the initial curve until the filament was again flashed in vacuum. We interpret these results to mean that hydrogen attaches itself to tungsten in a stable film which forms more rapidly at 600°–1000°K than at 80°K, and that in the neighborhood of 1000°K the process takes place so rapidly that whenever a filament is cooled suddenly from temperatures above 1000°K to low temperatures, it always becomes partly coated with hydrogen as it passes through this temperature range.

Fig. 3 represents a more detailed analysis of this effect. The experimental procedure used in the analysis is one that is suited to a wide variety of studies of surface conditions, and we shall therefore call attention to the scheme of procedure. The filament is subjected to processes which take place in three separate steps. First, the surface is "conditioned"; by this we mean that a given state of the surface is chosen to be the initial condition for a series of experiments, and the filament is brought to this condition. For example, in the preceding paragraph the filament was conditioned by being flashed in vacuum and then held at 80°K while it was brought into contact with hydrogen. In general, the treatment chosen for conditioning a surface is one that is accurately reproducible, so that different sets of experiments may be started from identical initial conditions.

The second step is to "treat" the filament, by which we mean that it is subjected to processes of a nature which tend to alter the condition of the surface, causing it to depart from the initial condition. Very often the treating is done in many consecutive repetitions of the same operation, these repetitions taking place at measured intervals of time or of temperature. In order to measure the effect of "treating" the filament we must have the third step, which is "testing" the filament. This is done by measuring some one property of the surface which changes whenever the surface changes; in our experiments this property was the heat loss to the gas at a given temperature. Since most properties of surfaces are functions not only of the state of the surface but also of its temperature, it is important that data taken for the purpose of testing the state of the surface should all correspond to a single temperature. For this reason it is generally far more satisfactory to adopt the practice of testing the surface at a given "testing temperature" which is the same for all tests, than to risk the uncertainties involved in converting data by calculation to the values that correspond to one temperature.

Our practice consisted, therefore, in treating a suitably conditioned filament in a given manner for a given length of time, and then lowering the temperature to that corresponding to a "testing resistance"; it is clear that the testing temperature should be chosen well outside of the range of the "treating temperatures" wherever this is possible, so that the condition of the surface will undergo no change during the time required to make the test. The data plotted in the curves in Fig. 3 were obtained at a testing resistance of 6 ohms which corresponded to $T_m = 568°K$, $T_r = 357°K$. They represent the wattage required to bring filament *b* to this resistance after the filament had been treated for 1 minute in hydrogen at the treating temperature which is plotted as abscissa.

Curve (1) represents a surface conditioned in the same way as for the "initial" curve in Fig. 2, that is, the filament was flashed in vacuum before each heat treatment in hydrogen. Similarly Curve (3) corresponds to the "final" curve in Fig. 2, for the points were measured consecutively as the treating temperature was lowered in short steps. In Curve (2) the surface received the same "treating" as in Curve (1), but started from a different initial condition, for it was conditioned by being cooled suddenly from 1100°K or higher temperatures in hydrogen, instead of being flashed in vacuum. The heating at 1100°K and rapid cooling were repeated after each point on Curve (2) was obtained, so that the filament was always brought to its initial condition in which it consumed 0.881 watt at the testing resistance before the next measurement on this curve was made.

At $T_r = 1000°K$ Curve (3) starts to fall rapidly with decreasing temperature reaching its lowest value in the neighborhood of $T_r = 640°K$, and we have made the hypothesis that this falling off in the heat loss is due to a hydrogen film which forms on the filament. Curve (2), on the other hand, follows the course of Curve (3) rather closely between $T_r = 900°$ and $T_r = 1000°K$, but departs from it widely at lower temperatures. The difference between the two curves is due to the slow rate of formation of the hydrogen film at low temperatures. For in Curve (2) the filament has only 1 minute at each temperature for the film to form, whereas in Curve (3) with slowly falling temperature the film reaches the equilibrium value characteristic of each temperature.

In other words, Curve (3) is the limit which Curve (2) would reach after a great length of time. The equilibrium value must represent a balance between the rate at which hydrogen attaches itself to tungsten and the rate at which it evaporates. For this reason the film is not complete at temperatures above about 770°K, for the rise in Curve (3) at $T_r = 640°K$ is due to the temperature of the hottest part of the filament which is then at $T_m = 770°K$. It is clear from the low-temperature end of Curve (2) that the rate at which hydrogen attaches itself to tungsten increases rapidly with increasing temperature; it is also clear from Curve (3) that the rate at which hydrogen evaporates from tungsten increases rapidly with temperature; and from the shape of Curve (2) which passes through a minimum and then ascends to higher values, we see that the rate of evaporation of the film must increase more rapidly with temperature than the rate of formation.

The appearance of the high-temperature ends of these curves is deceiving. The horizontal line drawn at 0.881 watt above 1000°K does not properly represent the state of the hydrogen film in this region, for it must be borne in mind that these measurements were all made at a low testing temperature after the filament had been cooled through the critical temperature range in which the film partly formed during the rapid cooling. Curve (1) indicates that the wattage of a filament entirely free from this type of film would be at least 1.0 watt. For this reason it appears probable that the film does not completely leave the tungsten at $T_r = 1000°K$, but at a temperature 100 or 200 degrees higher.

The data in Fig. 3 were found to be consistently reproducible, having been checked on many different occasions, and the same effects were observed in three different tubes. Some of the effects which we observed with hydrogen tubes, which will be described presently, were dependent upon the amount of oxide present upon the walls of the tube, the effects diminishing with a decreasing supply of oxygen. But the observations that have been described in this section were entirely independent of this factor, and are to be attributed solely to the interaction of pure hydrogen with a surface of pure tungsten.

Technique for producing state X. The family of X-curves in Fig. 4 represents the heat loss from filament *b* when the surface of the filament was more or less contaminated by a foreign substance. We have already said that with the tube in liquid air the way to produce contamination on the surface of the filament was to burn a neighboring filament in hydrogen. The rate at which the contamination was produced by this treatment varied with the temperature of the neighboring filament, increasing rapidly with temperature. But it was also found that for any given temperature of the neighboring filament the rate varied over a wide range, depending on the previous history of the experiment, and this variation was found to be due to the amount of oxide present on the walls of the tube. The rate was always highest immediately after baking the tube, for there was a fine deposit of tungsten on the walls and every time the tube was baked sufficient water vapor was driven out of the glass to oxidize some of this tungsten. But after either of the filaments had been run for some time at a temperature at which atomic hydrogen was produced, the rate at which one filament could then contaminate the other was cut down to a marked degree.

Fig. 5 illustrates what is meant by the rate at which the burning of one filament contamintes the other. Filament *b*, when clean, consumed 6.25 watts when it had a resistance of 21 ohms in hydrogen; when contaminated till it showed its minimum heat loss (state *X*), it consumed 2.29 watts at the same resistance. Curve *YX* in Fig. 7 is a typical curve of a filament in a state intermediate between *Y* and *X*, the heat loss having been reduced by this type of treatment from 6.25 to 5.2 watts at 21 ohms. The curves in Fig. 5 represent the rate at which the transition from one state to the other takes place in filament *b*, when filament *a* is burned at the temperatures marked on the graph. In every case filament *b* was cold while filament *a* was running, then filament *a* was shut off while filament *b* was tested at the testing resistance 21 ohms. In order that data of this type should be reproducible, it was imperative that some standard initial condition of the tube be adopted with regard to the amount of oxide on the walls, and for this purpose the tube was torched at about 450°C, while connected to the vacuum pump, preceding each run.

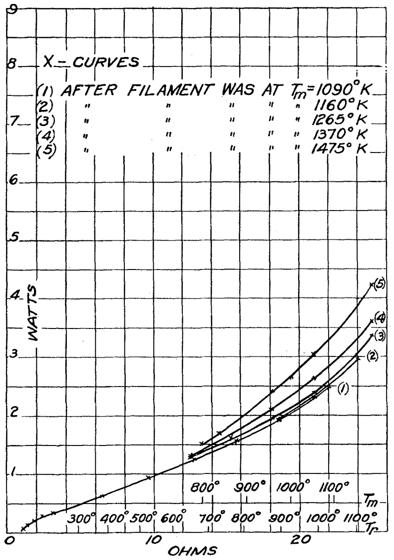

Fig. 4. Heat loss curves for filament *b* after oxygen has adhered to it in the presence of atomic H. The series shows the temperatures in degrees K at which oxygen leaves the filament.

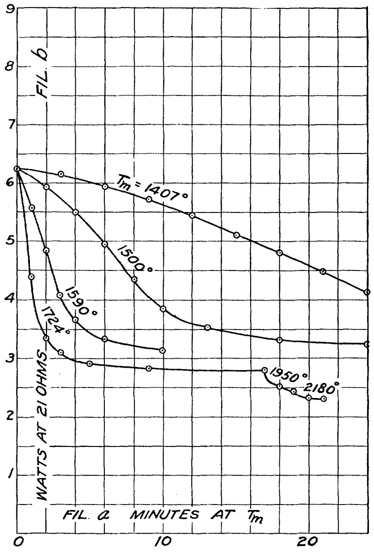

Fig. 5. Curves which give the rate at which the burning of filament *a* causes oxygen to be deposited on filament *b*, shown as a function of the temperature in degrees K of filament *a*.

The atomic hydrogen produced by burning filament *a* is the agent which gives rise to the contamination that arrives at filament *b*. This was shown by plotting the logarithm of the reciprocal of the time required in each of the four runs to bring the wattage to 5.5, 5.0, 4.5 and 4.0 watts, against $1/T$. The plot gave four parallel straight lines, and when the logarithm of the degree of dissociation of hydrogen[13] at these temperatures was plotted on the same graph, all five lines were found to have the same slope. In other words, the surface of filament *b* was altered by a mechanism which was the same in every run and varied in its rate of activity only in proportion to the degree of dissociation of the hydrogen. A second run, however, taken immediately after any one of these at the same temperature but without an intervening torching of the tube, would show a greatly lessened rate of progress, a rate about one half as great having been measured in most instances. Moreover, when filament *a* was run at 2000°K for a long time till the greater part of the oxides in the tube were reduced, it could then be burned at 1500°K and have almost no effect at all upon filament *b*. From these observations we conclude that atomic H dislodges oxygen or an oxide from walls cooled in liquid air, and that it is this product and not the atomic H itself which causes the reduced heat loss exhibited by a filament when it is in the condition that we have called state *X*.

Examination of the curves in Fig. 5 shows that the rate at which filament *b* becomes coated is rapid at first, and then slows down very greatly after the coating is about two thirds complete. After the rate has become very slow at one temperature, it can be speeded up by raising the temperature of filament *a*; this is shown at the end of the curve measured at 1724°, where the temperature was raised twice consecutively. A limit is finally reached at which raising the temperature will not avail to reduce the heat loss any further. This limit must represent the maximum coating of oxide which can be in equilibrium with atomic H and its products. Evidently a higher concentration of atomic H and its accompanying products is favorable to a more complete oxidation of the tungsten.

When filament *a* is employed to oxidize filament *b*, filament *a* itself also becomes oxidized, and for this reason the current through filament *a* must be lowered as often as proves necessary in order to hold the resistance constant. At the beginning of a run it may need to be lowered every ten seconds, at the end every minute. The oxidation proceeds to a less degree, however, than on filament *b*, because of the higher temperature of filament *a*. Part of the oxidizing substance leaves the surface when the temperature is high; this is shown by the family of *X*-curves in Fig. 4. Curve (1) represents the minimum heat loss from filament *b* that could be obtained by burning filament *a* at any temperature and for any length of time in hydrogen. Filament *b* was not heated above $T_m = 1090°$K until after the points on Curve (1) had been measured. The temperature was then raised to $T_m = 1160°$K for 30 sec., and the resulting measurements gave Curve (2). Similarly Curves (3) (4) and (5) were obtained after heating the filament to 1265°, 1370° and 1475°K respectively, the heating lasting for 30 sec. in each case, after which the points were measured consecutively as the temperature was lowered. From these curves we conclude that the oxidizing substance leaves the filament by evaporation and reduction until the surface concentration is reduced to an amount that is more nearly stable at these temperatures. Most of the removal takes place in the first 30 sec., and further heating at any given temperature produces only a very slow change.

It is now apparent that the oxygen films produced by the processes just described can be readily distinguished from the hydrogen films that were discussed in connection with Fig. 3, because of the difference in temperature range at which the two films are stable on tungsten. The hydrogen film is practically gone at 1055°K (21 ohms), whereas the oxygen film is so stable at this temperature that it was chosen as the suitable testing temperature for the experiments of Fig. 5, in which it was important that the film should not change in composition while being tested.

Experiments were made in order to learn whether a *hydrogen* film could be caused to adhere to one filament as a result of producing atomic H by the other. Such a film should be stable on filament *b* at a testing resistance of 6 ohms but disappear at 21 ohms. These experiments were made when the oxides in the tube were so well reduced that oxygen films were deposited on filament *b* only very slowly even when filament *a* was run at 1724°K. No evidence was found for the formation of a hydrogen film; for any change which took place at 6 ohms also persisted at 21 ohms and was therefore attributed to oxygen.

When the data for the X-curves in Fig. 4 are drawn on a volt-ampere plot instead of a watt-ohm plot, they show that a temperature discontinuity occurred in the neighborhood of 200°–300°K. This appears in Fig. 4 as a point of inflection as the curve passes through this range, but on this plot the change in curvature is small. The actual changes in current, however, as the filament temperature passed through the discontinuity from a low temperature at which it was stable to the next higher temperature at which it was again stable, were of considerable proportions. For example, the point plotted at 2.35 ohms corresponded to a current of 0.340 amp. at 0.80 volt, whereas at 6.42 ohms the values were 0.313 amp. at 2.01 volts. In other words, the filament passed through a region of "negative resistance", so that it consumed less current at the higher temperature than it did at the lower. This effect is not uncommon in volt-ampere characteristics of filaments in which nearly all of the heat generated by the filament is lost to a gas or to the leads.[14] The explanation is to be found in the fact that under these conditions there is apt to be a certain temperature range in which the heat loss to the gas or to the leads is even greater than the heat input, and as the filament cannot maintain these temperatures, the temperature falls until the heat balance is restored to equilibrium. In the experiments of Fig. 4 the heat loss to the gas and to the leads was evidently such that it required 0.27 watt at 2.35 ohms and 0.63 watt at 6.42 ohms, which could be secured only by having the higher current at the lower temperature.

FILAMENTS OXIDIZED BY TORCHING TUBE

A clean filament can be oxidized by torching the tube containing the filament with a Bunsen burner until water vapor is driven out of the walls, even though the tube has been baked many times before. This provides a simple method of preparing a filament with a thin oxygen film evenly distributed along its length. When the tube containing such a filament was cooled and immersed in liquid air, and hydrogen then admitted, the heat loss from the filament was found to have the values shown in Fig. 6 which lay along curves which will be called Z-curves.

Series Z (1), Fig. 6, were measured after the tube containing the filament had been torched for 1 minute, Series Z (2) after the filament had been more completely oxidized by a 6 minute torching. In Series Z (1) the dotted curve, which represents a filament being heated for the first time after it had been cooled to 80°K immediately after the torching, shows a hump at temperatures below $T_r = 200$°K (2.9 ohms) which disappears between 200°K and 250°K (3.9 ohms) and does not return when the filament is cooled. This is to be attributed to water vapor or possibly carbon dioxide which adhered to the tungsten as the tube cooled after it had been torched. A similar hump appeared in Series Z (2) but is not shown on the graph.

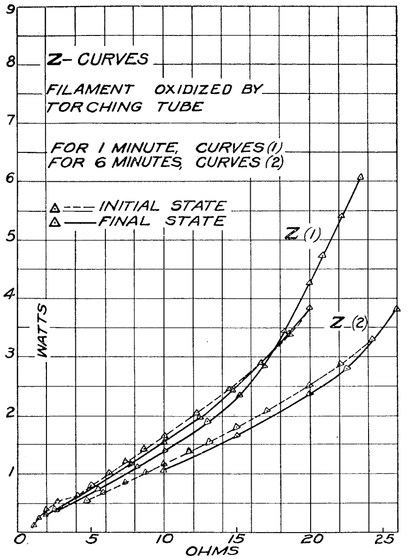

Fig. 6. Heat loss curves from a filament oxidized by torching the tube containing the filament.

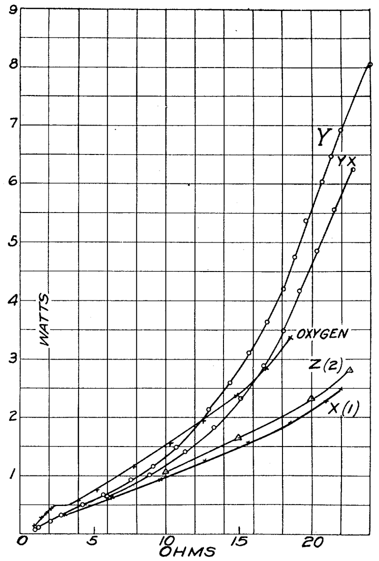

Fig. 7. Comparison of curves from Figs. 2, 4, and 6. The YX curve represents an intermediate stage as the state of the surface changes from Y to X.

When the oxidized filament in the experiment Z (1) was first heated in hydrogen to 20 ohms ($T_r = 947$°K) and then cooled, the curve of descending temperature, marked by the solid line, departed from the ascending curve to a small extent, in the manner shown in Fig. 6. This is the type of departure which in the case of a clean filament indicates that hydrogen is attaching itself to the surface, and it may have the same interpretation in the case of an oxidized filament. When, however, the filament was heated to 23.5 ohms ($T_r = 1082$°K), the departure was much more marked and acted in opposite directions at the two ends of the curve. Whatever change took place in the surface composition of the filament, due to its being heated at this temperature, had the effect of raising the heat loss from the surface at high temperatures and lowering it at low temperatures, so that the curve approached much more nearly the shape of the curve for a clean filament shown in Fig. 2. This suggests that a considerable fraction of the oxygen had been removed from the surface by heating it at 1082°K in hydrogen. The curves in experiment Z (2) show, on the other hand, that when the surface layer of oxygen is more nearly complete, the filament can be heated to 26 ohms ($T_r = 1180°$K) without raising the heat loss on the descending curve appreciably above that of the ascending curve at corresponding temperatures. This is in accord with the X-curves of Fig. 4 which show only a very small change in the surface composition after heating at these temperatures; a curve corresponding to a heating at $T_r = 1180°$ would lie between (2) and (3) in Fig. 4. Curve Z (2) closely resembles one of the lower X-curves, as can be seen from Fig. 7. We conclude that curve Z (1) corresponds to a composite surface layer of oxygen and hydrogen, in which some of the oxygen was replaced by hydrogen more readily than in curve Z (2) because of the fact that the original oxygen layer was incomplete.

A curve of each type, taken from Figs. 2, 4 and 6, together with a YX curve, is plotted in Fig. 7, which also shows the curve obtained at low temperatures when a very small quantity of free oxygen is added to the hydrogen mixture. The charcoal U-tube was removed, the experimental tube evacuated and the filament flashed, and a small amount of oxygen admitted which was then pumped down to 0.001 mm. The data for the curve were taken after a pressure of 0.20 mm of hydrogen had been added to the oxygen and the tube had been allowed to stand in liquid air for one hour. When oxygen is present in the gas phase, the heat loss at low temperatures often creeps toward higher values as time elapses, so that the experimental values have not as yet been reproduced with nearly the precision of the experiments made in the absence of oxygen. This is particularly true of the measurements made above 800°K, for at this temperature oxygen reacts with tungsten in such a way as to form successive layers of oxide on the surface, so that the filament is continually changing. For this reason the data in the section of the oxygen-curve which lie below 3 ohms were taken before the filament had been heated to higher temperatures in the presence of oxygen, and the higher end of the curve must be regarded as only an approximate continuation of the lower end but was sufficiently reproducible to make it plain that the oxygen-curve always crosses the Y-curve. Farkas has observed the same phenomenon.

The oxygen curve has a hump at its lower end which closely resembles the hump in the Z-curves of Fig. (6), but unlike the Z-curves the hump in the oxygen curve is retraced when the filament is heated to higher temperatures and then cooled. Hence we know that the increased heat loss at low temperatures, represented by the hump, is the result of a film of oxygen which settles on the tungsten surface when there is free oxygen present in the gas phase.

These results are to be compared with those of Roberts[15] who measured accommodation coefficients in helium and found the coefficient of a "dirty surface", i.e., a tungsten filament which had stood over night in the apparatus, was increased 3-fold over that of a clean filament. His paper does not tell at what temperatures these coefficients were measured, but presumably they were not far from room temperature.

Calculation of Accommodation Coefficient

Fig. 8 shows the data from which the accommodation coefficient α, was calculated. The values of α, calculated from Eq. (8) are tabulated in column 6 of Table II and plotted against T_r in Fig. 9. W_Y and W_X in column 2 represent the heat loss from the entire filament to the gas. T_a in column 3 was calculated from Eqs. (2) and (3) using the value for the diameter of the tube $b = 5.0$ cm, derived from the average distance of filament b from the walls. λ in column 4 represents the mean free path length of a hydrogen molecule at temperature T_a and 0.20 mm pressure, calculated for an ideal gas from the value $\lambda = 14.6$ cm at 25°C and 0.001 mm. Column 5 gives the average values of β for the temperature range T_a to T_r. Column 7 shows what the heat loss from the filament would be if α were equal to unity; column 8 the corresponding values of T_a. Similar calculations of α for the case of filament b in hydrogen containing 0.5 percent of oxygen are given in Table III.

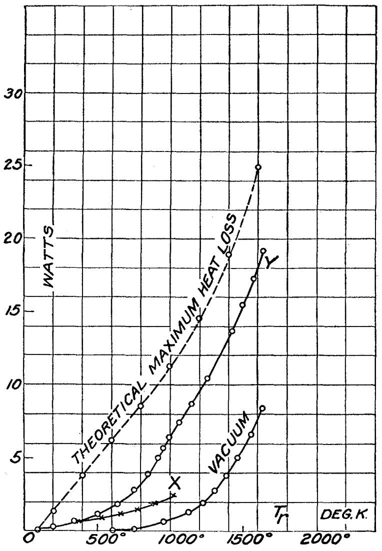

Fig. 8. Data from which α is calculated.

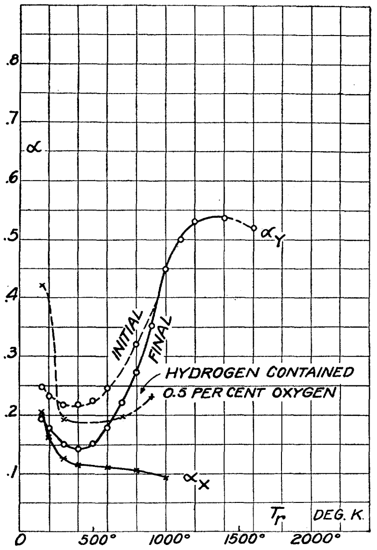

Fig. 9. Accommodation coefficient of hydrogen at 0.20 mm pressure in contact with tungsten. α_Y represents tungsten free from oxygen. α_X represents tungsten to which oxygen has adhered in the presence of atomic H.

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[15] J. K. Roberts, Proc. Roy. Soc. **129A,** 146 (1930).

TABLE II.

		Observed W				Theoretical W calc. for $\alpha=1$	
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
T_r deg. K	W_Y "Final" Watts	T_a deg. K	λ cm	β Average T_a to T_r	α_Y	W_Y Watts	T_a deg. K
150	0.215	86	0.021	1.84	0.195		
200	0.346	91	0.022	1.97	0.180	1.38	115
300	0.570	96	0.024	2.17	0.151		
400	0.80	102	0.025	2.27	0.143	3.82	155
500	1.11	109	0.027	2.34	0.153		
600	1.56	118	0.029	2.38	0.179	6.15	184
700	2.21	130	0.032	2.42	0.222		
800	3.03	143	0.035	2.46	0.274	8.34	209
900	4.21	160	0.039	2.49	0.354		
1000	5.69	178	0.044	2.52	0.449	10.54	229
1100	6.79	192	0.047	2.55	0.500		
1200	7.77	203	0.050	2.57	0.531	12.70	247
1400	9.17	216	0.053	2.61	0.537	14.86	264
1600	10.17	226	0.055	2.65	0.519	16.97	280
	W_Y "Initial"						
150	0.262	88	0.022	1.84	0.248		
200	0.435	93	0.023	1.97	0.233		
300	0.78	102	0.025	2.17	0.219		
400	1.15	110	0.027	2.27	0.220		
500	1.58	118	0.029	2.34	0.226		
600	2.04	127	0.031	2.38	0.248		
	W_X				α_X		
150	0.228	86	0.021	1.84	0.207		
200	0.317	90	0.022	1.97	0.163		
300	0.487	94	0.023	2.17	0.126		
400	0.66	99	0.024	2.27	0.116		
600	1.03	107	0.026	2.37	0.111		
800	1.36	115	0.028	2.44	0.106		
1000	1.56	118	0.029	2.49	0.094		

Values of α calculated for filament b of tungsten wire, length 40.7 cm, diameter 0.00779 cm, in 0.20 mm pressure of pure hydrogen.

α_Y refers to a filament free from oxygen.

α_X refers to a filament to which oxygen has adhered in the presence of atomic H.

TABLE III. *Values of α calculated for filament b in a mixture consisting of 0.20 mm pressure of hydrogen and 0.001 mm pressure of oxygen.*

(1) T_r deg. K	(2) W_Y Watts	(3) T_a deg. K	(4) α
150	0.410	92	0.422
300	0.70	100	0.193
500	1.32	114	0.189
700	2.00	127	0.198
900	2.99	143	0.232

The outstanding feature of the α_Y curves in Fig. 9 is the sharp drop with decreasing temperature from $\alpha_Y=0.531$ at 1200°K to $\alpha_Y=0.143$ at 400°K for the "final" condition of the filament surface. The drop in α_Y in Fig. 9 occurs in the same temperature range as the change in filament surface represented by Curve (3), Fig. 3. In Fig. 3 the change in the condition of the surface caused the heat loss from the filament at $T_r = 357°K$ to be decreased, so that α_Y at this temperature had the values shown in Fig. 9 which are 0.219 for the "initial" curve and 0.145 for the "final" curve. In discussing Fig. 3 this change was attributed to a hydrogen film which attaches itself to tungsten at these lower temperatures, and we now attribute the entire drop from the maximum $\alpha_Y = 0.54$ to the presence of adsorbed hydrogen. The data of Fig. 9 enable us to amplify our theory of this adsorption.

We assume that at $T = 1300°K$ the tungsten is bare, all hydrogen films having evaporated from the surface, and that $\alpha_Y = 0.54$ therefore represents the accommodation coefficient of hydrogen striking a bare tungsten surface. Above 1400°K the determinations of α_Y are subject to inaccuracies resulting from the dislodging of oxygen from the walls by atomic H. The conclusion that the surface is bare was reached in an earlier paper[16] which dealt with measurements made over a wide range of pressures. In the early work the measurements were made with the walls of the tube at room temperature, which accounts for the low value $\alpha_Y = 0.19$ obtained at $T = 1500°K$; for under these conditions the filament would be attacked by water vapor as soon as atomic H was formed in the tube, with the result that the surface would not be free of oxygen until it reached $T > 2000°K$, at which temperature oxygen evaporates rapidly from tungsten.[17]

The value $\alpha_Y = 0.54$ is to be compared with calculations of α_D, the fraction of hydrogen molecules striking a tungsten surface which are dissociated and leave the surface as atoms. At very high temperatures α_D is the same as α_2, calculated in 1915, and is derived from the following considerations. The heat consumed by the dissociation of gas molecules constitutes, at high temperatures, the greater part of the heat loss from a tungsten surface in hydrogen. It was found experimentally in 1915 that the heat loss due to dissociation increased with rising temperature, but that at low pressures it reached a limiting value at 2700°K and kept this value at higher temperatures. This maximum was considerably less than the heat loss that would have resulted if all the molecules striking the surface had been dissociated and had left the surface as atoms. Hence it is evident that only a limited fraction of the molecules could be thus dissociated. Recent recalculation* of the 1915 data gives $\alpha_D = 0.49$ as the value for this fraction.

The rather close agreement between $\alpha_Y = 0.54$ and $\alpha_D = 0.49$ does not necessarily mean that the mechanisms which fix these limits are the same in the two cases. In the case of α_Y the value 0.54 may represent either an average in which all of the gas striking the filament takes up 54 percent of the amount of energy which would bring the gas to thermal equilibrium with the

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[16] I. Langmuir, J.A.C.S. **38,** 1155 (1916).

[17] I. Langmuir and D. S. Villars, J.A.C.S. **53,** 486 (1931).

* The heat loss due to dissociation, in watts per cm length of the filament is $W_D = (4.19 \pi d)\alpha_D n Q/N$, where Q is the heat of reaction at constant volume in the reaction $H_2 = 2H$, and

surface; or an average in which 54 percent of the gas reaches thermal equilibrium while the rest rebounds from the surface with zero change in energy. We have no way of distinguishing between these two general alternatives. In the case of α_D, on the other hand, we know that 49 percent are dissociated while the remaining 51 percent leave the surface without carrying away with them a quantity of heat which would correspond to partial dissociation; for any such quantity of heat should increase with rising temperature and no increase was observed at temperatures above 2700°K.

We shall now consider the region in Fig. 9 where α_Y has low values. At every temperature from 150° to 1200°K α_Y is less than 0.54, and in the greater part of this range α_Y is less than 0.25. When α_Y is less than 1.0, that is, when a molecule striking a surface fails to reach thermal equilibrium with the surface, it means that the time τ during which the molecule remains on the surface is too brief. In general, a molecule striking a surface is adsorbed, and after an interval of time τ it evaporates, the length of life on the surface depending on the temperature and nature of the surface and of the gas. When τ is so brief that it equals the time of collision between two molecules, that is, a time of the order of 10^{-13} sec. for hydrogen, we commonly say that the molecule is not adsorbed on the surface but is reflected from it. We assume that the life τ_T which a molecule requires in order to reach thermal equilibrium on a surface, depends on the nature of the surface, since different surface layers because of their chemical composition or geometrical configuration do not lend themselves equally readily to a rapid interchange of energy with molecules of the gas in question. When $\tau < \tau_T$ we have $\alpha_Y < 1$.

Since τ is inversely proportional to the rate of evaporation, we know that τ for any given surface increases as the temperature of the surface decreases. If, then, the tungsten suffered no change in composition of its surface layer as its temperature was lowered from 1200°K, we should expect α_Y to increase

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N is the number of molecules in a gram mol. (6.06×10^{23}). Q has the value 101,200 cals. per gram mol. at 2800°K. W_D is derived from the observed heat loss W_H after calculating W_C by Eq. (7), since $W_D = W_H - W_C$. With a filament of diam. 0.00706 cm, at 2800°K, the quantities involved were as follows, calculated for $\alpha_Y = 0.54$ and $\alpha_Y = 0.80$ in Eq. (7):

Press. mm	W_H Watts/cm	α_Y	T_a deg. K	W_C Watts/cm	W_D Watts/cm	α_D
0.015	0.191	0.54	303	0.028	0.163	0.490
0.039	0.50	0.54	315	0.070	0.430	0.506
0.015	0.191	0.80	305	0.042	0.150	0.452
0.039	0.50	0.80	322	0.102	0.398	0.474
				Weighted mean		0.49

We know that $\alpha_Y = 0.54$ at 1300°K and have no evidence that it rises above this value at higher temperatures. The table shows, however, that even if α_Y were 0.80 the calculated values of α_D would not be greatly altered. The difference between $\alpha_2 = 0.68$, calculated in 1915, and $\alpha_D = 0.49$, given above, is due mainly to a difference between the old values of Q and new values published in 1926.

as the temperature falls. Since α_Y on the contrary decreases, we conclude that the surface is no longer bare tungsten at these lower temperatures, but that hydrogen adheres to it in a film. This conclusion must be applied to both the "initial" and the "final" states of the filament, since in both states α_Y falls far below 0.54. The films in the two states are not identical, however, and we need to consider the relationship that exists between them.

Langmuir, Taylor[18] and others have come to the conclusion that films adsorbed on surfaces must be classified according to the mechanism of adsorption which holds them, and that adsorption processes must consequently be divided into at least two general types. In general, molecules attach themselves to a surface by a process of the first type, called "normal" adsorption, and the adsorbed layer then changes over into the second type, called "modified" adsorption, slowly at low temperatures and more rapidly at higher temperatures. In the case of hydrogen on tungsten the experiments show that the "initial" film forms from molecular hydrogen at any low temperature that we have employed, whereas the "final" film forms only slowly at temperatures under 1000°K. The final film has an accommodation coefficient which at 400°K is two thirds of that for the initial film, which suggests that the field of force of the tungsten is more completely saturated by the final than by the initial film. We consider that these data afford a typical instance of an adsorbed film which becomes modified in such a way that the bonds uniting the atoms within the molecules acquire a new alignment, some of these bonds being taken over by the tungsten atoms.

It seems safe to assume that the final film is a modified form of the initial film, but we are left uncertain with regard to the nature of the initial film itself. Since this film covers the tungsten completely at temperatures as high as $T_m = 600°\mathrm{K}$, the film must have a heat of evaporation many times greater than the heat of evaporation of hydrogen from a liquid hydrogen surface. This means that the molecules in this initial film are held to the underlying tungsten by such close bonds, that their reaction with the surface must be of the nature of a chemical reaction. The question arises, therefore, of whether this close binding is formed instantaneously as the molecules strike the surface, or whether the reaction requires a period of time, the time required being less than 5 minutes at 100°K. In other words, the initial film may itself represent a modification of the form in which the molecules originally attach themselves to the surface, the original form being by definition "normal" adsorption. If this is the case there exists a normal film which has a heat of evaporation only a few times greater than that of hydrogen evaporating from a hydrogen surface. This would represent the type of adsorption in which a molecule suffers little if any internal change by becoming attached to the surface. If such a film exists we should expect to be able to detect its presence if these experiments were repeated with the tube cooled in liquid hydrogen; we have found no indication of it in the present experiments.

The present experiments also afford no means of deciding whether the

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[18] I. Langmuir, J.A.C.S. **38,** 2221 (1916); **39,** 1848 (1917); **40,** 1361 (1928). H. S. Taylor, J.A.C.S. **53,** 578 (1931).

hydrogen in the initial film is held as separate atoms or as pairs of atoms.* It has been generally assumed by those[12,19] who have studied the catalytic activity of metals in converting parahydrogen to orthohydrogen, that some of the hydrogen adsorbed on the tungsten is held in the form of separate atoms at temperatures as low as liquid air temperature. Farkas made experiments with approximately one half litre of a mixture consisting of 47 percent parahydrogen and 53 percent orthohydrogen, at 50 mm pressure. He found that when this mixture was brought into the presence of a tungsten filament of diameter 0.01 cm and length 20 cm at 273°K, the mixture was converted to 36 percent parahydrogen and 64 percent orthohydrogen in about 12 seconds. According to the theory advanced by Bonhoeffer and Farkas, both forms of hydrogen are dissociated when they are adsorbed on tungsten so that the distinction between para and ortho structures disappears while the gas remains on the surface. Then when the separate atoms combine to form molecules which evaporate from the surface, the molecules are formed in the proportions characteristic of ordinary hydrogen at the temperature of the filament. These proportions at 273°K and higher temperatures are known to be 25 percent parahydrogen and 75 percent orthohydrogen. Since the amount of conversion which takes place in 12 seconds at 273°K in the absence of a catalyst is practically zero, they conclude that the conversion takes place on the surface of the tungsten.

Calculation shows that this means that 11 percent of the molecules present in the gas, or approximately 10^{20} molecules, are converted in 12 seconds by contact with a surface of area 0.63 cm^2, which area could hold 6×10^{14} to 9×10^{14} molecules in contact with the tungsten at any one time. Thus the average time it would take for the atoms of one molecule to be separated from each other on the surface and for each to combine with another atom and evaporate from the surface, could be not more than 10^{-4} sec. If the hypothesis of Bonhoeffer and Farkas is correct, the initial film in our experiments represents a surface covered with hydrogen which is experiencing this type of rapid dissociation and rebuilding of molecules. The gas used in our experiments was an ordinary hydrogen mixture, that is, it was not enriched with parahydrogen as was the gas that Farkas used, but the mechanism of dissociation at the surface should operate in either case.

It now remains to offer a theory that will explain how our initial film may become modified to form a second type, or final film, which we know to be very stable at temperatures below 600°K. If the experiments of Bonhoeffer and Farkas can be explained on the basis of any mechanism other than the dissociation of hydrogen, we should expect that the final state represented a film of separate atoms, as distinguished from an initial state of atoms held in pairs. On the other hand, if the hydrogen is dissociated in the initial state, the

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* A mathematical treatment of the properties of hydrogen adsorbed on tungsten was given in an earlier paper.[16] Two sets of equations were derived for the following alternative hypotheses: (a) Hydrogen exists on the surface in the form of atoms only; (b) Atoms and molecules of hydrogen can exist on the surface at the same time. In this case the equations took into account the rate at which each form of hydrogen changed over into the other.

[19] K. F. Bonhoeffer and A. Farkas, Zeits. f. physik Chem. (B) **12**, 231 (1931).

hydrogen atoms may possess the property of gradually modifying the tungsten atoms on the surface by a process which is very slow in comparison with the process of dissociation of the hydrogen. The distinction between the two processes may possibly be explained on the basis that the atoms, when first dissociated, share with the tungsten only electrons which are comparatively free to move about over the surface, these being electrons which give to the metal its property of electrical conductivity. Some of the adsorbed atoms may then gradually achieve a closer binding in which each hydrogen atom shares with a tungsten atom a pair of electrons situated in the kernel of the tungsten atom.

We have some evidence that the hydrogen which evaporates from the modified film leaves as atoms rather than as molecules. This evidence is shown by the following calculation. From Fig. 3 in which Curve 3 departs from Curve 2 in the neighborhood of $T_m = 1000°\mathrm{K}$, we conclude that the life of the modified hydrogen on the surface is about 1 min. at 1000°. This follows from the fact that Curve 3 represents equilibrium conditions for a given temperature, whereas Curve 2 represents the result of treating the filament for one minute at the same temperature. At $T = 1000°\mathrm{K}$ the surface is approximately one half covered with modified hydrogen, so that if we assume that the surface density of hydrogen in a complete film is the same as that of the underlying tungsten atoms, or 10^{15} molecules per cm^2, the surface density at 1000°K is 5×10^{14} molecules or 10^{15} atoms per cm^2. Hence if the modified hydrogen has a life on the surface $\tau = 60$ sec., it leaves the surface as atoms or molecules at a rate which is the equivalent of 8.3×10^{12} molecules cm^{-2} sec.$^{-1}$. From entirely separate considerations we can fix an upper limit to the number of atoms which can evaporate from the surface at this temperature. The degree of dissociation of hydrogen in the gas phase[13] is $x = 2.29 \times 10^{-7}$ where x is expressed as the fraction of the hydrogen molecules which have been dissociated into atoms. The number of molecules which come from a region where $T_a = 160°\mathrm{K}$ (see Table II, $T_r = 900°\mathrm{K}$) and strike the filament can be calculated from Eq. (4) and is $n = 3.95 \times 10^{20}$ cm^{-2} sec.$^{-1}$. The number of molecules which is dissociated and leaves the surface as atoms cannot be greater than $nx = 9.05 \times 10^{13}$ cm^{-2} sec.$^{-1}$, but may be less than this number, so that we may very well have 8.3×10^{12} molecules leaving the surface as atoms.

We have no satisfactory explanation of the rise in both the α_Y and α_X curves in Fig. 9 when the temperature is lowered below $T_r = 300°\mathrm{K}$. It is not accounted for on the basis of the altered value which the specific heat would have if the hydrogen were changing from a mixture which is in equilibrium at room temperature and therefore contains parahydrogen and orthohydrogen in the proportions 1:3 to a mixture representing equilibrium at liquid air temperature which has the proportions 1:1. It is improbable that this change took place in our experiments for it is known to proceed extremely slowly at liquid air temperature except when the hydrogen is passed through a tube containing a very large volume of charcoal, and we used only 1.7 cc of charcoal. However, it can be shown from data taken from Table V of a paper by Beutler[20] that the term $(\beta+1/2)$ which we use to calculate α by Eq. (8) has the value 2.1166 for a 1:3 mixture and 2.2227 for a 1:1 mixture. This is a range of only 5 percent in $(\beta+1/2)$ for the two extreme cases, which is much too small to account for the observed rise in α.*

OXYGEN FILMS

We have already pointed out that the rising values of α obtained when the filament temperature is lowered below 300°K when 0.5 percent of oxygen is present in the hydrogen, gives evidence that an oxygen film forms on the filament at this low temperature. The film departs from the filament at 300°K but forms again whenever the temperature is lowered to 200°K or lower temperatures. These data add to the knowledge which we already have of the formation of oxygen films on tungsten.[17,21] It is commonly found that if oxygen is admitted to a vacuum tube containing a clean tungsten filament while the filament is at room temperature or at liquid air temperature, and the oxygen is then pumped out of the tube, and the last traces removed by "getters", a film remains on the cold filament which continues to adhere when the temperature is raised to 1300°K. This can be shown by testing the filament for electron emission since the presence of oxygen on a tungsten surface reduces the electron emission to a small fraction of its value for pure tungsten. In order to test the surface for electron emission it must be heated to about 1500°K (at which temperature oxygen gradually evaporates from tungsten) for at lower temperatures the emission is too small to be measured. But since the test which reveals the presence of oxygen on the surface is made with the filament in vacuum, we know that the adsorption took place at the low temperature at which all free oxygen was pumped out of the tube. The heat of evaporation of oxygen from tungsten has been found to be 162,000 cals. per *gram atom* of oxygen[17] when only a small fraction of the tungsten surface is covered with oxygen; when more than one third of the surface is covered, the heat of evaporation is less.

In the present experiments the film which forms at 200°K and leaves at 300°K forms on a surface which already has a layer of oxygen adsorbed on the tungsten. It has been customary to refer to the latter surface as an OW surface, so we shall call the former an OOW surface. If we assume that the OOW film covers one half of the surface at 150°K, calculation shows that the fraction of the surface covered at 300°K would be about 0.5×10^{-5}, which is an amount too small to affect α to a measurable degree, so that at 300°K the surface would have the properties of an OW surface so far as measurements of α are concerned.

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[20] H. Beutler, Zeits. f. Physik **50,** 581 (1928).

* In calculating α we have assumed that parahydrogen and orthohydrogen have the same accommodation coefficient since we have found no evidence to the contrary. If it so happens that the accommodation coefficient of parahydrogen is considerably greater than that of orthohydrogen, this would account for differences greater than 5 percent between α_Y at 80° and at 300°K.

[21] K. H. Kingdon, Phys. Rev. **24,** 510 (1924).
I. Langmuir and K. H. Kingdon, Proc. Roy. Soc. **A107,** 61 (1925).
I. Langmuir and K. H. Kingdon, Phys. Rev. **34,** 129 (1929).

In Fig. 9, α_X gives the lowest values which we have found for the accommodation coefficient at temperatures above 300°K, and we have abundant evidence that α_X represents a surface layer containing oxygen. If we make the hypothesis that α_X represents an OW surface in which the tungsten is completely covered with oxygen, then the OW layer in the experiments in which 0.5 percent of oxygen was present in the hydrogen was not a complete layer over the surface. On the other hand, if we make the hypothesis that the experiments in which oxygen was present in the gas gave a complete OW layer at say 300°–700°K (at which temperatures we should not expect hydrogen to remove the oxygen from the tungsten) then α_X represents another type of oxygen layer, possibly oxygen plus hydrogen or hydroxyl. In either case it is clear that the effect of an OW surface is to keep α at a low value at temperatures above 600°K, in the range in which α_Y is increasing rapidly. We attribute this effect to the saturation of the field of force of the tungsten atoms on the surface by the adsorbed oxygen atoms, so that impinging hydrogen molecules encounter such a weak field of force that they are held to the surface for too brief a time to reach thermal equilibrium.

Below 200°K the oxygen which is held comparatively loosely to the OW surface in an OOW layer may serve to prolong the duration of stay of hydrogen molecules on the surface, for the oxygen atoms may constitute a loose network in which the impinging hydrogen molecules are caught. We take exception to the explanation offered by Farkas to account for the effect of oxygen in increasing α at low temperatures. Farkas says that this effect illustrates the working of a mechanism discussed by Baule[22] whereby the exchange of energy which takes place when gas molecules are reflected from a wall is limited by the relative masses of the molecules of the gas and of the wall; the more nearly equal the masses, the greater the exchange of energy. This theorem would account for a higher α for hydrogen in contact with an OW surface than with a bare W surface; but we believe that we never have a bare W surface in contact with hydrogen at low temperatures, but instead of this an HW surface, and this should give the maximum α from the point of view of Baule's theorem.

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[22] B. Baule, Ann. d. Physik **44,** 145 (1914).