SURFACE LAYERS ON TUNGSTEN AND THE ACTIVATION OF NITROGEN BY ELECTRON IMPACT[1]

By Carl Kenty and Louis A. Turner

Abstract

A fine tungsten filament at 400°C in active nitrogen is quickly covered with a layer which produces a lowering of the resistance of the filament. This lowering of the resistance is apparently the result of a lowering of the temperature of the filament which occurs because heat is more readily conducted away from the coated filament by the gas than from the clean filament. At a given temperature, 15–20 percent more heat is conducted away by the gas with the layer present. The same effect is produced by activating the nitrogen by bombardment with electrons. In a tube with a large nickel anode the production of the active agent could be detected down to 10.8 ± 0.5 volts. In a tube with a hot tungsten spiral anode of small area the effect could be detected down to the ionizing potential (16.3 volts). Traces of oxygen cause the spontaneous formation of a layer which renders the filament insensitive to active nitrogen. Traces of hydrogen prevent the formation of the nitrogen layer and remove it if already present. Experiments with a tube of small volume containing tungsten disks of large area show that the amount of nitrogen adsorbed is of the order of magnitude of the quantity necessary to produce a layer of single atoms. Activation of a stream of nitrogen reduces the thermionic emission from a tungsten filament in the stream. Similarly, the striking of an arc in nitrogen under suitable conditions gives a momentary slight increase of current followed by a great decrease, the emission apparently being cut down by the active form of nitrogen produced in the arc. Upon subsequent breaking of the same arc by reducing the anode voltage the current drops and then quickly rises to its much higher former value at that voltage. With an interrupted arc in pure nitrogen, and in argon containing a small percentage of nitrogen, an emission of the D lines persists for several hundredths of a second after the extinction of the arc. The sodium is evaporated from an oxide-coated filament and excited by some active form of nitrogen produced in the arc, presumably atomic nitrogen.

DURING an attempt to measure ionizing potentials in a stream of active nitrogen it was noticed that the thermionic current from a tungsten filament underwent a considerable temporary reduction as the activated nitrogen passed over it. Subsequent experiments, to be described below, have shown that this decrease was probably caused primarily by an increase of the work function of the filament, but it was thought at the time that the decrease of current might be accounted for as the result of the cooling of the filament by the active nitrogen, assuming the latter to contain nitrogen atoms and thus to have a thermal conductivity higher than that of ordinary nitrogen. Accordingly, a tungsten filament placed in the steam of nitrogen was connected as one arm of a Wheatstone bridge. The nitrogen could be activated by a condensed discharge passed between two tungsten electrodes up-stream from the filament. It was found that when the filament was white hot the active nitrogen increased the resistance slightly. When it was at a

[1] A preliminary account of these experiments was given in Nature, **120**, 1927.

temperature of approximately 400°C, however, the active nitrogen caused a considerable lowering of its resistance which was permanent. This effect was permanent in the sense that the filament maintained its new lowered resistance after the activated nitrogen had passed on. This is, of course, contrary to what one would expect if the filament were to be cooled simply because of increased thermal conductivity of the active nitrogen, for this latter effect would last only as long as the active nitrogen were present. The permanent lowering of the resistance must have been the result of a change of the filament. It could be restored to its original condition by flashing it at a white heat.

For subsequent experiments the following simpler arrangement was used. The filament, which was of tungsten of a diameter of one mil and 2 cm long, was connected in series with a much larger resistance so that the current flowing through it was very little affected by small changes of its own resistance. The larger changes could be measured directly from the change in the voltage drop as measured by a voltmeter. Smaller changes were measured by a potentiometer, the voltage drop across the filament being balanced against a constant potential difference. A micro-ammeter was used as an indicating galvanometer. Any small change of the resistance of the filament would cause a proportional change in the voltage drop across it, thus putting the arrangement out of balance, the current through the micro-ammeter being to a first approximation proportional to the change of the resistance. The nitrogen used in these experiments was commercial nitrogen taken from a tank and passed over hot copper shavings. It still contained a small percentage of oxygen as was evidenced by the brilliance of the glow of active nitrogen. It was impossible to obtain a brilliant glow in the pure nitrogen used later.

The effect was investigated for various pressures ranging from 0.04 to 5 mm of Hg. It increased rapidly with pressure being negligible at 0.04 mm whereas at 5 mm the resistance of the filament changed by 20 percent. The relative changes of resistance were largest when the filament was at a temperature such that it was just perceptibly red in a dark room. If the filament were made much hotter the changes became temporary. The resistance would drop while the active nitrogen was present and then slowly recover its original value after the active nitrogen had passed.

The following experiment would seem to indicate that the effect of the active nitrogen is to form some kind of a layer upon the surface of the filament, rather than to change its volume conductivity. The resistance of the filament at room temperature was measured by ordinary methods. It was then warmed, treated with active nitrogen which caused the drop in its resistance and then allowed to cool to room temperature. Its resistance was then the same as it had been in the first place. That the effect of the active nitrogen had not been lost before this second measurement of the cold resistance was shown by warming the filament again, measuring the voltage drop across it, and then flashing it at white heat whereupon its resistance rose to the value it had had before the active nitrogen had passed over it.

The reduced resistance could not be, however, simply the result of the low specific resistance of a thin surface layer, for experiments described below indicate that this layer, if uniform, was of a thickness of the order of magnitude of atomic diameters and would thus have had to have an extremely low specific resistance at the higher temperatures in order to influence the measured resistance appreciably. At room temperature its specific resistance would have had to be much larger in order that the change in resistance caused by the presence of the layer should be inappreciable. Such hypothetical properties of the layer are fantastic. It seemed more reasonable to believe that in some way the layer caused a lowering of the temperature of the filament, the fall of resistance being only that which would be connected with such a change of temperature of any tungsten filament.

Such a cooling would result from an increase in the efficacy of any one of the processes by which heat is dissipated from a hot filament. Part of it is conducted away by the leads, part is radiated away, and part is conducted away by the gas. One would not expect the first process to be affected appreciably by the formation of a layer but the last two could be so affected.

The efficacy of the dissipation of the energy by radiation would have been increased if the layer had caused an increase of the emissive power of the surface. If this were the principal cause of the cooling however, one would have expected the effect to be most prominent for low pressures of gas for which the loss of heat by conduction by the gas would have been negligible in comparison with the loss by radiation. As mentioned above, the observed effect behaved in the opposite way, increasing rapidly with increasing pressure. The following experiment also gave a fairly direct indication that the presence of the layer did not increase the emissive power. A coarser tungsten wire was placed in the stream of nitrogen. Its surface could be cleaned by flashing it at a high temperature. A source of white light was arranged so that the light was reflected from this wire and could be observd with an eye-piece. The wire was flashed and then brought to a very dull red so that it was barely visible in the dark. After the activation of the nitrogen up-stream the wire became quite dark when the active nitrogen reached it showing that the layer was being formed and the wire cooled in the normal fashion. No change in intensity or color of the reflected white light could be detected, however, showing that the coefficient of absorption of the tungsten surface for visible light was not markedly affected by the presence of the layer. Since, according to Kirchhoff's law, the coefficient of absorption and the emissive power are in the same ratio to each other for all bodies at the same temperature it is evident that the formation of the layer did not produce any great increase of the emissive power of the filament for visible light. This was most probably also true for the infra-red radiation actually emitted by the warm filament, although not certainly so.

If it were possible to bring the filament to the same temperature for all pressures with and without the layer, one could study the conduction by the gas since the heat lost by conduction to the leads and by radiation would

be the same in all cases (assuming the emissive power to be the same with and without the layer). The changes in the energy supplied to the filament to maintain it at the given temperature would be the changes in the amounts of heat conducted away by the gas. This ideal experiment was realized to a first approximation by adjusting the current through the filament so that the resistance was always the same. Equal resistances would mean equal temperatures provided that the conductivity of the layer itself was negligibly small and that the variation of temperature along the filament was the same in all cases. The experiment described above indicates that the first condition was probably satisfied but undoubtedly with higher pressures and more energy being lost by the filament the variation of temperature along it was altered so that equal resistances gave equal temperature conditions of the filament to a first approximation only. Fig. 1 shows the results of the experiments. The abscissas are the pressures and the ordinates are the amounts of power supplied to the filament to bring it to a resistance of 14.2 ohms,

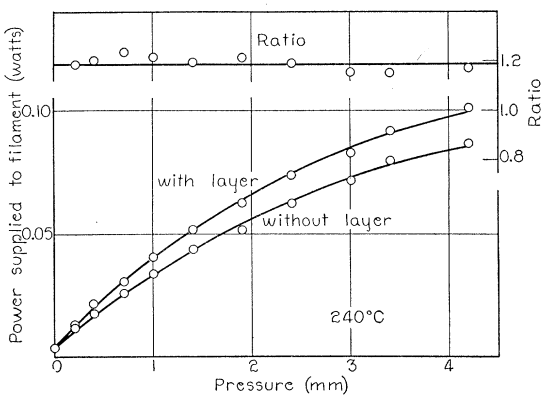

Fig. 1. Variation with pressure of the power input necessary to heat the filament to a resistance of 14.2 ohms (240°C).

corresponding to a temperature 240°C. The resistance of the leads was negligible. (The data for Fig. 1 were actually obtained by producing the layer by means of an arc in very pure nitrogen in the tube with the spiral anode described below. Results of the same sort but less complete were obtained with the ordinary active nitrogen. There was no reason to believe that there was any difference between the results obtained by forming the layer in the two different ways.)

The curve obtained with the layer present being higher, shows that heat was more readily conducted away by the gas when the layer was present. The fact that the intercepts of the two curves are the same indicates that the amount of energy radiated was not appreciably affected by the presence of the layer. Its small magnitude shows that the heat lost by conduction to the leads and by radiation was very small compared to that conducted away by the gas at the higher pressures. If it be assumed that this amount of power

was dissipated by metallic conduction and radiation at all pressures, the amounts dissipated by gas conduction are obtained by subtracting this intercept from the observed power values. These have been computed and the ratio of the two values obtained with and without the layer at each pressure also plotted in Fig. 1. Within the experimental error these values are all the same, the average being 1.19. The difference between the two curves must depend upon a difference in the effectiveness of the transfer of heat from the filament to the gas molecules since the thermal conductivity is a constant of the gas at a given pressure and is not dependent upon the properties of particular surfaces. The transfer of heat from solids to gases has been studied by many workers. Knudsen[2] introduced and defined the accommodation coefficient, the ratio of the amount of heat conducted away from the surface of a solid by a gas molecule to the amount which would have been conducted away had the gas molecule reached thermal equilibrium with the surface. Langmuir[3] showed that the value of the accommo-

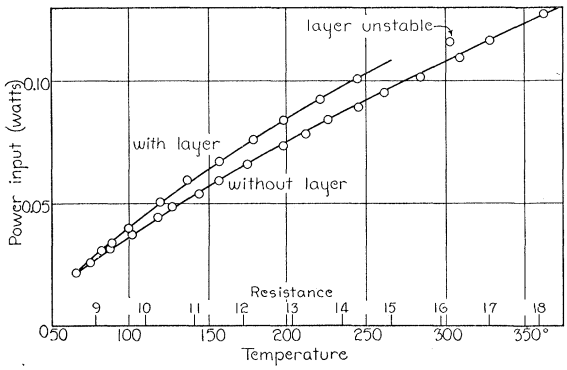

Fig. 2. Variation with temperature of the power input, with and without the layer, at 4.2 mm pressure.

dation coefficient for different surfaces and gases depended upon the presence of surface layers. The present experiments indicate that this coefficient is increased by the presence of the layer by about 19 percent at 240°. Our apparatus was not one such that it could be used to determine the actual value of the accommodation coefficient.

In order to see how this effect depended upon the temperature, readings of current and voltage were made from which could be calculated the power inputs for different resistances both with and without the layer at a pressure of 4.2 mm. The results are shown in Fig. 2. The temperatures were calculated roughly by the use of an average value of 0.005 for the linear coefficient of resistance of tungsten. The resistance at 22° was 7.15 ohms. The percentage increase caused by the layer seems to be very nearly constant for all temperatures down to 150° below which it seems to decrease.

[2] M. Knudsen, Ann. d. Physik **34,** 593 (1911).
[3] I. Langmuir, Phys. Rev. **8,** 149 (1916).

The experiments were not very accurate and show merely that there was no great change with changing temperature.

This cooling effect presents a sensitive indicator for the presence of extremely small concentrations of active nitrogen. It seemed that it would be of interest to endeavor to produce active nitrogen by electron bombardment and if possible to determine the critical voltage for its formation. A tube which had been designed originally for determing ionizing potentials by the Hertz-Kingdon method was used for these experiments. A diagram of the tube is shown in Fig. 3. F_1 is the source filament, a source of electrons which were accelerated by the voltage applied between it and the grid in the side of the cylindrical anode A. This was 4 cm in diameter and 8 cm long. F_2 was the filament which served as the detector of active nitrogen or as the source of a thermionic current limited by space charge when the tube was being used to measure the ionizing potential. The nickel anode was thoroughly de-gassed by the repeated use of an induction furnace. Experiments with this tube showed that there was a production of some layer-forming agent upon raising the voltage above approximately ten volts. Fig. 4 shows typical curves. The abscissas are the times and the ordinates are the readings of the micro-ammeter of the potentiometer circuit. Changes in the latter are proportional to changes in the resistance of the filament. Curve A shows how the resistance changed with time when no accelerating voltage was applied. The break in Curve B comes at the instant that the accelerating voltage from F_1 was applied.

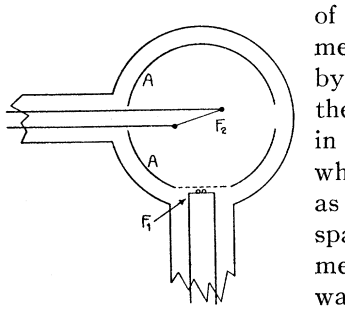

Fig. 3. Diagram of tube.

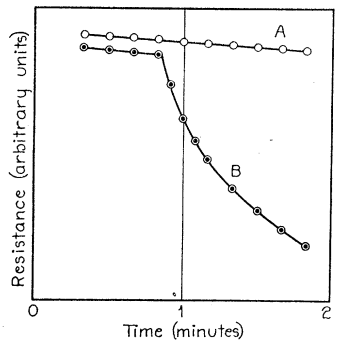

Fig. 4. Typical curves showing change of resistance of filament with time.

This fall in the resistance with no applied voltage was observed in many of these experiments and previous to the activation in all the experiments with ordinary active nitrogen. It indicates the formation of a layer by the unactivated gas. This can be attributed to the oxygen present as an impurity in the gas. It was found that if the gas was circulated through a tube containing a white-hot tungsten filament a deposit of blue tungsten oxide was formed and that the rate of formation of the layer on the test filament by the unexcited gas was steadily reduced. In all the later experiments pure nitrogen made by Waran's method was employed but even this contained enough oxygen to cause the spontaneous formation of a layer until it had been circulated for some time over the hot purifying filament. By the introduction of a very slight amount of oxygen (0.1 percent) the original condition could be restored and the whole series of effects repeated. When sufficient

oxygen was present the layer would form spontaneously so quickly that the resistance reached a steady value before the effect of activating the nitrogen could be tried. Under these conditions no further cooling was caused by the active nitrogen but occasionally a slight warming of the filament was detected. This may have been produced by the combination of nitrogen atoms at the surface or by some other chemical reaction. Experiments of this general sort were performed by Willey and Rideal[4] with filaments of various metals, including tungsten. They found that the active nitrogen heated all the metals but the effect was small for tungsten. Since they made no mention of flashing the filament immediately before each experiment in order to clean it, it may be that this was not done and that the effect which they observed was the same as ours with the already coated filament. Our experience indicates that this layer would probably have formed slowly in spite of the high purity of the nitrogen which they used. We also found that the addition of a slight amount of hydrogen would quickly clean off a nitro-

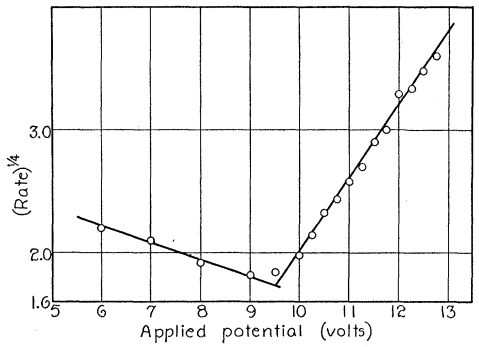

Fig. 5. Curve indicating critical potential for the formation of the active substance.

gen layer already formed and would prevent the formation of any further nitrogen layer. It did not seem to affect the oxygen layer. These experiments explained many puzzling, apparently contradictory results obtained before the effects of traces of oxygen and hydrogen were recognized as such. The experiments with oxygen suggest the use of such a test filament for the detection and measurement of small quantities of oxygen in other gases which do not affect the filament.

The nitrogen was activated by electron impact first with an oxide-coated platinum strip as a source of electrons and then with a tungsten filament for a source thus showing that the effect could not be attributed to anything being driven out of the oxide-coated filament by the bombardment of it by positive ions. The cooling effect obtained in this way showed the same increase with pressure as that obtained with ordinary active nitrogen. It persisted as the gas was made as pure as possible by circulating it through the tube containing the hot tungsten filament and through liquid air traps which kept mercury from the circulating pump from entering the tube. It

[4] E. J. B. Willey and E. K. Rideal, Jour. Chem. Soc. London, p. 2188 (1927).

was independent of the potential of the test filament, showing that the layer was formed by neutral atoms or molecules.

With the oxide-coated filament an attempt was made to determine the critical potential for the formation of the active substance. The time necessary for the micro-ammeter to change between two arbitrarily chosen values as the filament cooled was measured for each accelerating voltage, the filament having been flashed before each observation in order to remove any layer already accumulated. The reciprocals of these times gave measures of the rates of formation of the active substance. In Fig. 5 the fourth roots of these rates are plotted against the corresponding voltages. The fourth roots were chosen simply because two straight lines can be drawn through the points plotted in this way. The break indicates a critical potential of 9.5 volts but the determination of the ionizing potential in the same tube with the same gas at nearly the same time indicates that this value should be corrected to 10.8 ± 0.05 volts, assuming the value of the ionizing potential to be 16.3 volts.[5] The drop in the rate at the lower voltages is independent of the applied voltage, such a progressive change being shown by rates obtained with no applied voltage. It indicates a gradual purification of the gas during the course of the experiment.

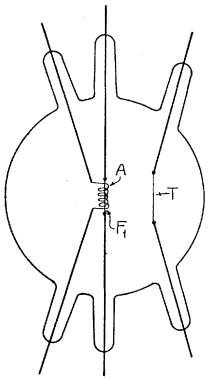

Fig. 6. Design of tube to reduce area of metal surface.

Because of the apparent extreme sensitivity of the test filament it seemed desirable to construct a tube in which there would be less metal surface in order to be free from any such effects which might arise from substances driven from the surface of the metal parts by bombardment by the accelerated electrons. The tube shown in Fig. 6 was constructed with this end in view. The straight filament F_1 was the source of the bombarding electrons. The anode A was coiled tungsten wire which could be kept hot so as to keep its surface clean. The test filament T was placed at the side as indicated. The tube was thoroughly baked out before any experiments were made. The results obtained with this tube were much the same as those obtained with the first one except that the ionizing potential was the minimum voltage at which any formation of the layer could be detected. The cooling effect was obtained when the anode was heated to a bright yellow temperature so as to drive off any layer which might have been formed upon it previously thus showing that the active substance was not produced by bombardment of the anode. It was also obtained when a strong magnetic field was produced along the axis of the filament F_1, preventing any electrons from striking the outer walls of the tube, thus eliminating the loosening of substances from the walls of the tube by electron bombardment as a possible explanation for the effect. It appears that the active layer-forming substance can be produced by bombardment of pure nitrogen by electrons having more than 16.3 volts of energy. The lower value obtained with the

[5] C. A. Mackay, Phil. Mag. **46**, 828 (1923).

tube containing the large nickel anode is presumably a critical value for the releasing of either oxygen or nitrogen from the surface of the nickel and it is nearly the same value as that found by Kistiakowsky[6] for the production of ions by the bombardment of various metals, including nickel, which had been exposed to nitrogen. He found that the adsorbed film formed upon the surface of a clean iron target very rapidly when a small amount of nitrogen was admitted to the tube, without activation. In the present experiment, however, the layer which forms spontaneously is apparently one of oxygen, upon the tungsten at least.

The use of a small test filament in a large volume is liable to give spurious results because with even a very small percentage of an impurity there is enough of it to coat a fine filament. It seemed desirable to construct an apparatus of small volume containing tungsten surfaces of large area so that the formation of a layer one atom deep on the tungsten surface would give a reduction of the pressure far in excess of the possible partial pressure of any impurity. An apparatus as indicated in Fig. 7 was made. The main bulb contained 42 circular tungsten disks supported on a heavy tungsten wire and kept apart by small rings made of tungsten wire. Each disk was 8 mm in diameter so that the total area of the tungsten surface was 42 sq cm. The nitrogen could be activated by passing a condensed spark between the two electrodes E or in a later experiment by running an arc between a hot filament and an anode put in above the disks. The filament F was put in in order to test for oxygen by cleaning it up with this filament. The pressure was measured by means of the previously calibrated hot-wire pressure gauge G of small volume. The total volume of the tube and gauge and connecting tubing to the trap which could be made to cut off the tube from connection with the pump was 18 cc. Assuming that a single nitrogen atom occupies an area of one square Angstrom unit (probably a little too small) it follows that there would be 4.2×10^{17} atoms in a uniform layer of single atoms covering the 42 sp cm of tungsten surface. If driven off these would give a pressure of

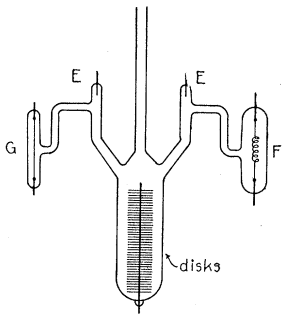

Fig. 7. Design of tube of small volume and large area of tungsten.

$$\frac{4\cdot2\cdot10^{17}\cdot760\cdot22.4\cdot10^{3}}{2\cdot6\cdot10^{23}\cdot18}=0.33\text{ mm of }N_2$$

in this tube having a volume of 18 cc, such a pressure being easily measured with the gauge.

One complete experiment was made as follows. The tube was baked out at 440° for 3/4 of an hour. Nitrogen to a pressure of 1.9 mm was admitted to the tube and a spark passed between the electrodes, to drive gas out of

[6] G. B. Kistiakowsky, J. Phys. Chem. **30**, 1356 (1926).

them, until they were red hot. The bulb was kept at 330° during this process. The gas was pumped out and the process repeated. The filament F was freed of gas by heating it to a high temperature for some time and then the tungsten disks were out-gassed by heating them to a high temperature with the induction furnace. The system of small volume was then cut off from the pump and it was found that when the disks were glowed for a half minute at a high temperature that only a few hundredths of a mm of gas were given off. Pure nitrogen was then admitted to give a pressure of 1.9 mm and the system of small volume again shut off. While the disks were kept at a dull red by intermittent use of the induction furnace hot sparks were passed between the electrodes, also intermittently so as to avoid undue heating of the electrodes. After the tube had cooled it was found that the pressure had dropped to 1.4 mm. The tube was then evacuated and again shut off. The furnace was put around it and the tube heated to about 400° for 15 minutes and the filament flashed. Approximately 0.05 mm of gas were thus recovered. The tube was exhausted for 10 minutes being kept at a temperature of 400°. It was then immersed in liquid air, shut off again, and the disks heated yellow for about thirty seconds. This had to be done intermittently because of the necessity of replenishing the liquid air which boiled away rapidly. It was used in order to avoid the possible evolution of gas by the heating of the walls during the flashing of the disks. Approximately 0.2 mm of gas was thus recovered. The tube was immersed in water and the filament run at a bright yellow for 3/4 of an hour. There was no clean-up of the gas and no blackening of the walls of the tube as there would have been had the gas contained an appreciable quantity of oxygen or of water vapor. The spectrum of the gas was examined with a small hand spectroscope when it was excited by passing a spark between the electrodes. It gave the spectrum of nitrogen but the $H\alpha$ line was not present as it would have been had the gas contained a small amount of hydrogen or water vapor. It is thus seen that the amount of gas recovered was much greater than could be accounted for as an impurity in the supposedly pure nitrogen, it gave the spectrum of nitrogen, and did not behave as either oxygen or hydrogen would. The tungsten had adsorbed a quantity of nitrogen of the order of magnitude of the amount necessary to cover it with a single layer of atoms.

Further experiments of this sort showed that the layer was not put on the tungsten unless the nitrogen was activated by a hot spark or an arc and that the layer did not form as readily upon cold tungsten. Experiments with a similar bulb containing no tungsten showed that no gas could be recovered by heating the bulb after sparking although a small clean-up had been observed. Other similar experiments were made with a different tube containing a coiled heavy tungsten wire instead of the disks which could be heated by passing a current through it. The area of tungsten in this tube was only 18 sq cm so that the amounts of gas recovered were smaller but the ratios of the amounts recovered to the area of tungsten were nearly the same as before. The two tubes were of nearly the same size which shows that it was the area of the tungsten and not that of the glass which was important.

There is, of course, no proof that the cooling effects discussed above result from the formation of a layer like the one here studied but they were most readily understood as resulting from the formation of a layer such as the one whose existence is here demonstrated.

The original observation that the thermionic emission from a tungsten filament suffered a considerable temporary reduction as ordinary active nitrogen passed over it was repeated and the effect found when the nitrogen was more nearly free from oxygen than that originally used. A similar effect has been obtained with pure nitrogen activated by an arc discharge in the tube with the hot spiral anode described above (Fig. 6). As the voltage applied to the anode was raised the current increased in the normal way until a value in the neighborhood of the ionizing potential was reached. For voltages above that the current showed a tendency to fall off with time slowly, it being necessary to wait several minutes after raising the voltage before the current became steady. At about 26 volts an arc struck, the current showed an instantaneous increase and then quickly fell off to a

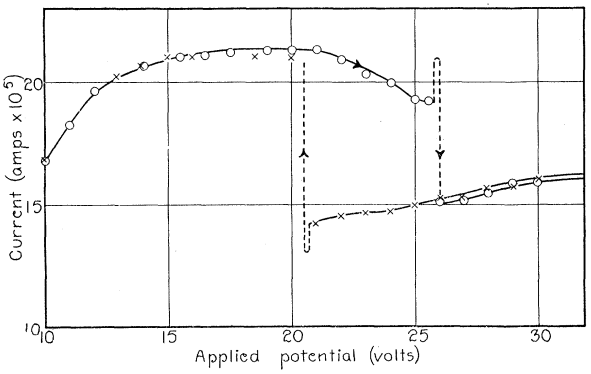

Fig. 8. Typical curve showing variation of thermionic current from a tungsten filament in pure nitrogen.

value lower than that which it had had before the arc struck. Further increases in the voltage produced increases in the current in a normal way. Upon decreasing the voltage the current fell off until the arc broke at a voltage lower than that at which it had struck. When the arc broke the current dropped instantaneously but then quickly rose to the value which it had had before at that voltage as the voltage was being raised. This current might be several times as large as it had been before the arc broke. For still lower voltages the same values of the current as at the beginning were obtained. Fig. 8 shows the actual currents in one particular typical experiment. If the pressure or the temperature of the filament was too high this effect was not observed. Several times it was possible to adjust conditions so that slow oscillations of a period of a second or so were obtained. The arc would strike, the current drop off until it would break again, the current then rise until it struck again, and so on.

The slow falling off of the current was accompanied by a slow cooling of the test filament present in the bulb, and the striking of the arc caused a very rapid cooling of the test filament, suggesting that both effects are evidences of the presence of the same active substance. The fall in the current would occur if a layer formed upon the surface of the hot filament increasing the work function for the surface. No cooling of the hot filament was observed so that the effect must be attributed to a change of the work function rather than to a diminution of the temperature. Langmuir[7] found such a diminution of the thermionic current but with much lower pressures of nitrogen and at higher voltages.

It has been suggested that this effect might be the result of the formation of charged layers on the surface of the bulb. We believe that this is not the case because such charged places would be effectively shielded by the formation of space-charge sheaths. Further, it has been found that there is no such effect with pure argon at the same pressure in the apparatus and with similar currents. If the argon contained a slight amount of nitrogen, however, indications of the beginning of such an effect were observed.

The filament which was the source of the electrons in these experiments was heated to a high temperature such as was reached in flashing the test filament of the earlier experiments in order to drive off the layer. The layer which was responsible for the drop of the thermionic emission must have been, therefore, a temporary one present only in an atmosphere of the active substance. This was shown by the rapidity with which the current rose to its former value after the breaking of the arc. (Fig. 8.) It has been shown that in certain other cases[8] the work function of a filament was greatly changed when but a small fraction of the surface was covered with atoms of a different sort. The same condition may hold here, the effect being produced by a layer covering but little of the surface.

Ordinary active nitrogen is probably a rather complicated mixture of various atoms and molecules,[9] so that from experiments with that alone it would be impossible even to guess what it was that produced the layer. The experiments with the gas activated by electron bombardment and those with the tube containing the disks show that the layer is one of nitrogen. The effective activated variety might be either atomic nitrogen or metastable excited nitrogen molecules. The experiments do not give any definite evidence conclusively in favor of either one of these possibilities but the fact that the large production of the layer-forming agent occurred in the neighborhood of 20 volts is suggestive since the experiments with positive rays[10] have indicated that atomic ions are produced at about 24 volts. These ions are produced by the breaking up of unstable molecular ions. It is not impossible that similar unstable excited molecules might be produced at lower

[7] I. Langmuir, Phys. Rev. **2,** 450 (1913).

[8] K. H. Kingdon, Phys. Rev. **24,** 510 (1924).

[9] J. Kaplan and G. Cario, Nature, **121,** 906 (1928).

[10] H. D. Smyth, Proc. Roy. Soc. **104A,** 121 (1923); T. R. Hogness and E. G. Lunn, Phys. Rev. **26,** 786 (1925).

voltages although there is no evidence for this. The cooling effect undoubtedly does begin close to the ionizing potential of nitrogen but may result from a further ionization of the relatively stable ordinary molecular ions.

Although the layer is produced by ordinary active nitrogen and by the electronically activated nitrogen it does not necessarily follow that the two varieties are the same. Experiments were made with heavy arcs in streaming nitrogen in an attempt to produce ordinary glowing active nitrogen in this way. They were unsuccessful but it is not surprising since ordinary active nitrogen could not be made to pass through a tube containing such hot metal electrodes. A tube was next arranged with a commutator so that it could be run intermittently, the space between the electrodes being examined spectroscopically, after the current was cut off, by use of a sectored disk on the shaft of the commutator. It was hoped that it might be possible to detect the after-glow bands characteristic of active nitrogen before it had disappeared. No indications of them were found when the space was viewed 0.0005 sec. after the arc had been cut off. The *D* lines were found to persist, however, several hundredths of a second if the voltage across the arc had been 21 volts or more but not for lower values. It was also noticed that the *D* lines could not be detected in the arc itself for voltages below 21. Some rearrangement of the arc took place and the current increased at that voltage. The sodium was apparently present in the oxide used in preparing the filament. These persistent *D* lines were found with mixtures of argon and nitrogen even when the amount of nitrogen was less than one percent but disappeared when the nitrogen was removed by circulating the gas through a tube containing a misch metal purifying arc. It was in the course of these experiments that the argon after-glow,[11] discussed elsewhere was noticed. Here again there is no direct proof of the presence of any particular variety of active nitrogen but the persistence of the *D* lines is greater than one would expect if they had been excited by collision with metastable molecules. It seems probable that the activated nitrogen formed by the impact of electrons is atomic nitrogen although this has not been conclusively established. It will be difficult to do so because so few of the properities of that elusive substance are definitely known.

In conclusion we wish to express our thanks to Professor K. T. Compton, Dr. K. K. Darrow, and Dr. Saul Dushman for helpful suggestions made by them in discussing this work with us.

PALMER PHYSICAL LABORATORY,
PRINCETON, NEW JERSEY,
June 15, 1928.

[11] Carl Kenty, Phys. Rev. **32,** 624, (1928).