Using Contact Resistance to Measure Adsorption of Gases on Metals

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The contact resistance between electrodes of molybdenum and tungsten is used to investigate the adsorption of nitrogen and oxygen. It is found that, on clean metals, the initial period of fast adsorption gives rise to a surface resistivity of about 4×10^{-10} *ohm-cm*^{2}*, corresponding to a layer of the order of 1.6 Angstroms thick on each surface. To remove, within a minute or so, the layers resulting from adsorption beyond this initial period, temperatures near 1700°K are required for all four metal-gas combinations.*

Some of the oxygen adsorbed at a pressure of a few torr at room temperature can be removed by lowering the pressure, but such an effect was not observed for nitrogen. Nitrogen or oxygen adsorbed during the initial period of fast adsorption on clean molybdenum or tungsten at a temperature of 100°K is not removed in times of the order of one hour by lowering the pressure, in disagreement with some results in the literature. The rate of migration of adsorbed oxygen into and out of the region between closed contacts is found to be much lower than that reported in an earlier experiment of the same type.*

I. INTRODUCTION

Measurement of the contact resistance between metal electrodes can be used to study surface films of nonconducting substances such as adsorbed gases. In comparison with other techniques it has the following advantages:

1. It can be used in the presence of the gas.
2. It can be used over a wide temperature range.
3. It does not depend primarily on the change in work function, which might be small for some adsorbates.

* Throughout this paper the unit of pressure will be the "torr", a unit widely used in Europe to designate one millimeter of mercury of pressure, i.e., 1.332×10^3 dynes/cm^2. (See, for example, W. H. Westphal, *Physikalisches Wörterbuch*, Springer Verlag, Berlin, 1952). This avoids the awkward "millimeters of mercury of gas *X*."

4. Under many conditions it does not destroy the surface film.

5. Adsorption can be studied on the bulk metal, which can be degassed by vigorous heating; i.e., dispersed conditions such as powders or porous films are not required.

In general, the contact resistance arises from two effects, the constriction of the lines of current flow into a relatively small region of contact and the resistance offered by a surface film. The pioneering paper in this field is due to Holm and Meissner,[1,2] who resorted to low temperatures to minimize the constriction resistance and showed that, for reasonably clean metals, there remained a resistance due to the surface film of the order of 5×10^{-9} ohm-cm^2. Although the method has been applied by a number of authors under a wide range of conditions,[3 to 10] only J. J. Went[11] attempted to obtain clean surfaces under high vacuum and then to investigate the adsorption of gases under controlled conditions. The present investigation is an attempt to extend these measurements using the improved vacua now available, and to interpret the results in terms of the advances in the knowledge of adsorption gained since that paper was published.

II. PRINCIPLES OF THE METHOD

For a single circular contact area of diameter, d, much smaller than the dimensions of the electrodes, the "constriction" or "spreading" resistance is given by (Ref. 2, p. 16):

$$R_s = \rho/d, \tag{1}$$

where ρ is the bulk resistivity of the metal.

A surface film gives rise to an additional resistance inversely proportional to the contact area (Ref. 2, p. 79), A:

$$R_t = \sigma_t/A, \tag{2}$$

where σ_t is called the "surface resistivity."

Although R_s is not completely independent of R_t because of the rearrangement of the lines of current flow, the change is negligible for our purposes (Ref. 2, p. 18), and we may write:

$$R = R_s + R_t \tag{3}$$

Since R_s is proportional to $1/d$ and R_t is proportional to $1/d^2$, smaller diameters of the contact area lead to an increase in the ratio R_t/R_s. Thus, for sufficiently small contact forces and hard metals it is not necessary to go to extremely low temperatures to measure R_t. In this

manner Went[11] was able to perform some of his experiments on molybdenum at room temperature.

The theory accounting for the resistance R_l for films less than about 20 Angstroms thick, valid for small potential drops (less than a few tenths of a volt), is based on a model in which the adsorbed gas is regarded as simply a spacer holding the metal contacts apart. The electrons flow by means of quantum mechanical penetration of the potential barrier. The result of calculations based on the potential barrier illustrated in Fig. 1, is:[2,12,13,14]

$$\sigma_l = \frac{h^2 l}{e^2\sqrt{2m\varphi}} \exp\left(\frac{4\pi l}{h}\sqrt{2m\varphi}\right) \text{statohm-cm}^2$$
$$= 3 \times 10^{-11}(l/\sqrt{\varphi}) \exp(l\sqrt{\varphi}) \text{ ohm-cm}^2, \tag{4}$$

where h, e, and m have their usual significance, l is the thickness of the film and φ the work function of the metal. The second form of the expression is valid for φ in volts and l in Angstrom units.

This resistance is ohmic (i.e., current proportional to voltage) according to both theory and experiment.[1, 2] A further refinement involves the inclusion of the electron image forces,[2, 14] and the result of this calculation is plotted in Fig. 2. It may be seen from (4) that the exponential factor is dominant so long as $l\sqrt{\varphi}$ is greater than one and that, under this condition, the resistance is extremely sensitive to l and slightly less sensitive to φ. This is the case for all practically attainable values of l and φ.

To interpret the data one must have some knowledge of the dimensions of the contact area. For perfectly smooth electrodes under most of the experimental conditions, the contact force could, in principle, be supported elastically. Because of the roughness of practical surfaces,

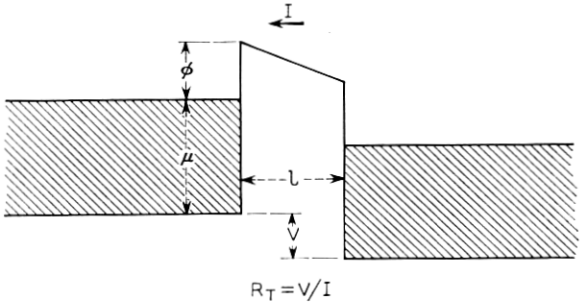

Fig. 1 — Potential diagram illustrating the model used in the derivation of equation (4).

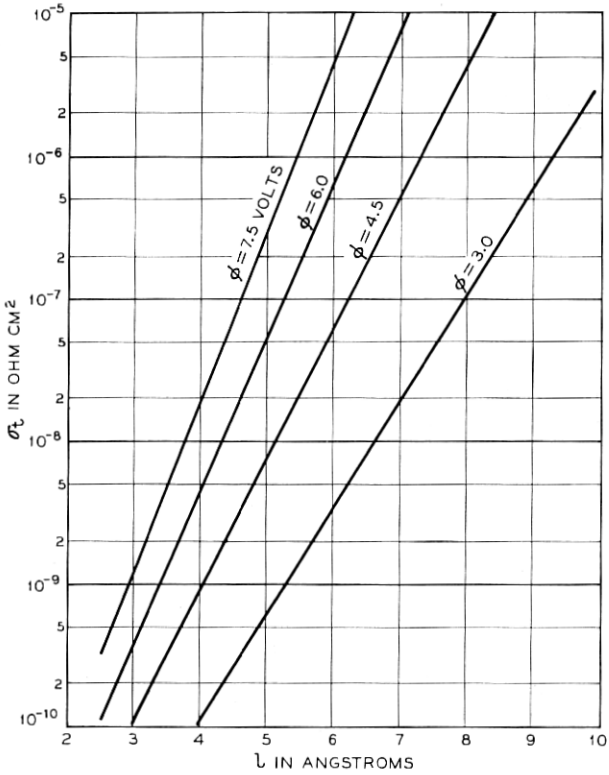

Fig. 2 — Contact resistivity, σ_t, versus film thickness for various values of the work function. The electron image force has been taken into account, modifying the potential barrier illustrated in Fig. 1.

however, the load is in fact supported by squashing a small contact region inelastically. Under this condition the contact area can be calculated approximately if the hardness of the metal is known:

$$d = \sqrt{\left(\frac{4}{10^5\pi}\right)\frac{P}{H}}, \tag{5}$$

where P is the contact load in grams and H is the hardness on the Vickers scale.

III. EXPERIMENTAL APPARATUS

The apparatus used in these experiments (Fig. 3) consisted essentially of two mechanically polished crossed wires (diameter 15×10^{-3} in.)

mounted on flat molybdenum springs. The lower of these was connected to a quartz yoke which could be pulled up by a micrometer screw operating through a sylphon bellows. The force constant of the spring on which the upper wire was mounted was measured both before mounting and after dismantling, and the constancy of the force constant as the spring was cycled between room and liquid nitrogen temperature was verified in a separate experiment. The motion of the upper spring as a function of the micrometer setting was calibrated with a cathetometer.

The tube was mounted in a vacuum system (mercury diffusion pump and liquid nitrogen trap) capable of reducing pressure to the order of 10^{-10} torr as measured on an ionization gauge. A gas-handling manifold was provided and isolated from the system by a Westinghouse-type

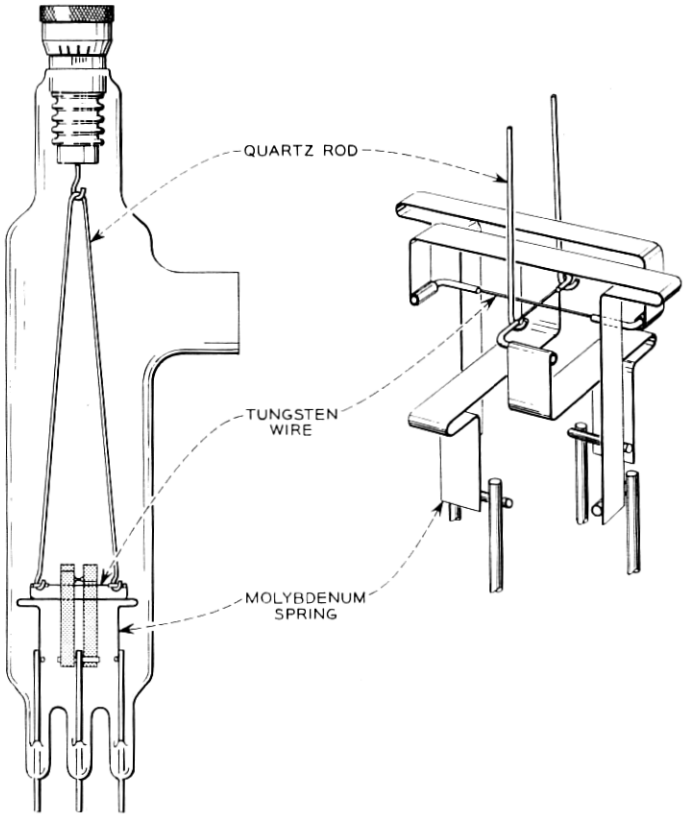

Fig. 3 — The tube in which these experiments were performed.

vacuum valve.[15] The gases were of spectroscopic grade supplied by the Air Reduction Company. The test wires could be flashed by conduction.

The contact resistance was measured in the region near 50 milliamperes and one millivolt by a four-terminal method using a milliammeter and microvoltmeter, exactly as described by Went.[11]

IV. EXPERIMENTAL RESULTS

Experiments were performed on tungsten and molybdenum electrodes using nitrogen and oxygen as adsorbates. The behavior of the two metals is very similar, and that of the two gases differs only at relatively high pressures. The experiments are subdivided as follows:

1. The behavior of clean metals.
2. The resistance due to gas adsorbed at room temperature.
3. The temperature of flash necessary to remove the adsorbed film in a reasonable time.
4. Adsorption at lower temperature.
5. The creeping in and out of adsorbed gas between closed contacts.

One is limited in these experiments by the scatter in the data. In a run of ten closures at the same force the largest value of the resistance was usually about twice the smallest, and the average deviation from the mean about 20 per cent. After the electrodes had been exposed to the same conditions of gas pressure for equal intervals at widely different times during the course of the experiment even the average of ten resistance measurements sometimes varied by as much as a factor of two. This scatter is partly due to differences in local hardness because of the polycrystalline nature of the wires, but also could be caused by differences in annealing, as the wire was flashed and then work-hardened in the contact region. It may also be due to local differences in adsorptive properties. In any case, as a consequence little weight can be attached to small differences and only fairly gross effects can be interpreted reliably.

Some of the relevant physical properties of tungsten and molybdenum are given in Table I.

4.1 *Clean Surfaces*

The metal surfaces were presumed to be clean after having been flashed repeatedly at a temperature of 2000°K for molybdenum, and at a somewhat higher temperature for tungsten, in a measured residual gas pressure of about 2×10^{-10} torr. By measuring the increase in the maximum pressure during a flash as a function of the cold interval, it

TABLE I — PROPERTIES OF MOLYBDENUM AND TUNGSTEN

		Present Work*	Other References
Resistivity, ρ, 300°K.	Mo	—	5.9×10^{-6} ohm-cm†
	W	—	5.85×10^{-6} ohm-cm†
Ratio of Resistivity, $\frac{\rho_{300°K}}{\rho_{78°K}}$	Mo	10.2	9.3‡
	W	9.3	8.4‡
Hardness, H, 300°K	Mo	230	160–225§
	W	480	290–488§
Ratio of Hardness, $\frac{H_{300°K}}{H_{78°K}}$	Mo	0.53	—
	W	0.62	—

* Measured resistivity ratios are for wires after outgassing in high vacuum. The hardnesses were measured on larger pieces from different samples. In the case of tungsten, the hardness samples had also been vacuum annealed, but the molybdenum hardness sample was not so treated.

† Ref. 16, pp. 2357–2363

‡ Refs. 17 and 18

§ Ref. 19, pp. 1140, 1144

was verified that about five hours were required to reach a constant value. The experiments to be reported in this section were performed within a period less than one-half hour after the flash.

For a force of 1 gm (±5 per cent) the contact resistance averaged between 10 and 16 milliohms for molybdenum and between 14.5 and 28 milliohms for tungsten. This range of values is for different samples and for measurements taken at different times during the course of these experiments. If the values of the hardness and resistivity listed in Table I are used in equations (1) and (5), one computes 22 and 36 milliohms for the two metals. Considering that the load is supported elastically to some extent and that the contact region may not be exactly circular, this agreement is satisfactory. It is assumed in latter portions of this paper that contact areas obtained from the measured resistivities under these conditions are more reliable than those computed from the hardness.

The contact resistance between clean metal electrodes, according to (1) and (5), should vary as the inverse square root of the force, and it does so within the limits of experimental error, as can be seen in one of the curves of Fig. 4.* However, to obtain this result it is necessary to

* For the opposite extreme, when $R_l \gg R_s$ rather than $R_s \gg R_l$, one would expect R to vary as the inverse first power of the force if the load is supported by plastic deformation. The other curve of Fig. 4, obtained for the thickest film observed during the course of these experiments, shows that this is also verified experimentally.

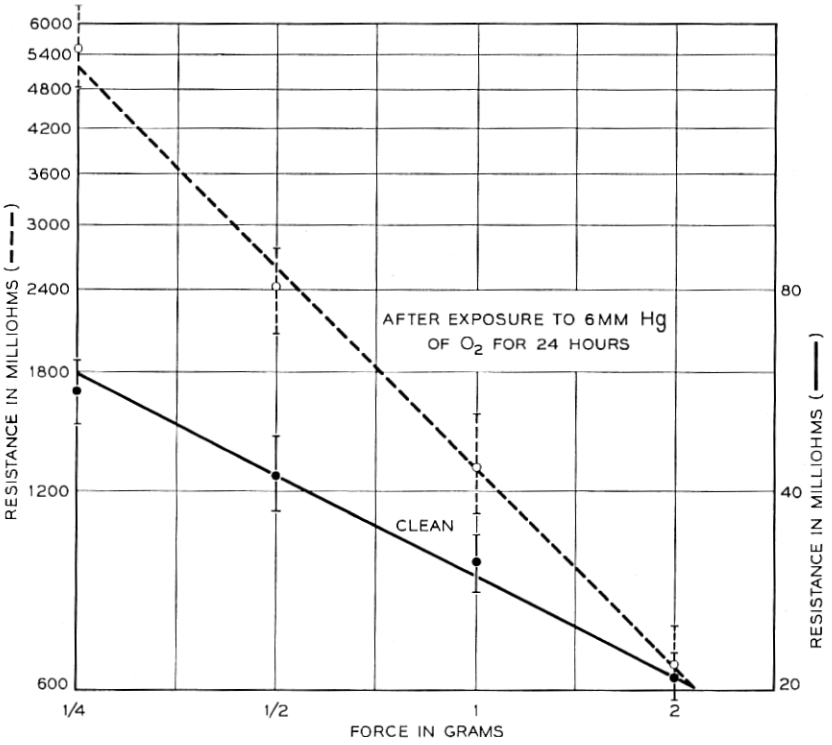

Fig. 4 — Contact resistance versus contact force for clean tungsten electrodes and for electrodes which have been exposed to 6.5 torr of oxygen for 24 hours. Each point is the average for five closures.

increase the force to its final value and not to overshoot and come back. The effect of cycling is shown in Fig. 5. There is also a relatively slow increase in contact area with time and a typical curve of the resulting decrease in resistance is shown in Fig. 6.

The assumption that the load is supported on regions formed, for the most part, by plastic flow is thus confirmed by the following observations:

1. The approximate agreement of the measured value of R_s with that computed on this assumption. The contact resistances computed for an elastically supported load are considerably smaller than those found experimentally.

2. The slopes in Fig. 4, which are 0.5 clean and 1.0 with a thick film, as expected for plastic deformation, rather than 0.3 and 0.7, as would be expected for purely elastic deformation.

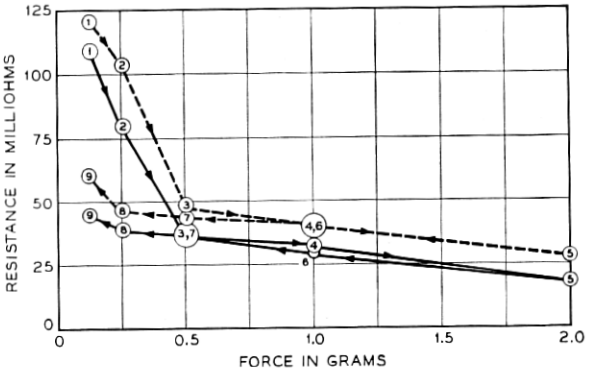

Fig. 5 — The contact resistance of clean tungsten with increasing and decreasing contact force. The numbers on the experimental points give the sequence of the measurements.

3. The irreversibility exhibited in Fig. 5.

4. The slow changes shown in Fig. 6.

The second point also shows that any surface film still present on the nominally clean surface contributes very little to the measured resistance.

The results of attempts to check the effect of lowering the temperature on the contact resistance of clean metals were inconclusive because:

1. The long time (about one-half hour) required for the contacts to cool down to liquid nitrogen temperature after flashing made the vacuum requirements much more severe.

2. Inadequate radiation shielding made the actual temperature of the contacts uncertain.

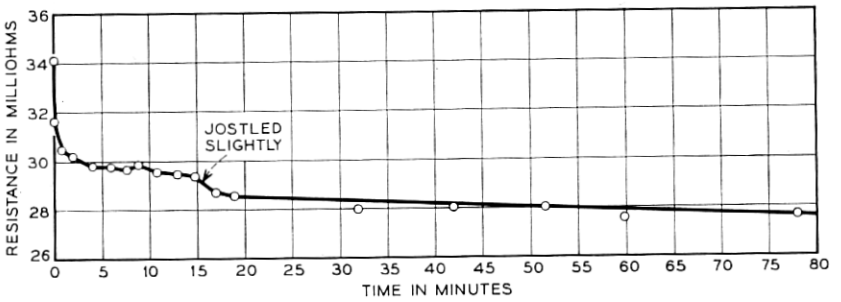

Fig. 6 — The contact resistance between closed clean tungsten contacts (force = 1 gm) as a function of time. The tube was jostled slightly by passing footsteps at the time indicated.

For both metals, the contact resistances measured when the contacts were closed with the tube immersed in a liquid nitrogen bath were lower by a factor of about four than the contact resistances measured at room temperature with the same contact force. The resistivity and hardness ratios of Table I, however, would lead one to expect a factor of about seven.*

In summary, the results of these experiments are consistent with the behavior expected for clean metals plastically deformed by the contact load. The contact areas for a force of 1 gm at room temperature are about 2×10^{-7} cm^2 for molybdenum and 5×10^{-8} cm^2 for tungsten.

4.2 *The Contact Resistance Due to Gases Adsorbed at Room Temperature*

A series of experiments in which the contact resistance was measured after tungsten contacts were exposed to nitrogen and oxygen at various pressures and for various intervals is reported in Appendices A and B and summarized in Figs. 11 and 12. The gas was usually admitted by opening a metal valve very slightly and allowing the gas to leak in while the system was continuously being pumped. Because of the pumping action of the ion gauge and the glass walls, which decreased as they became saturated, the pressure showed a steady increase with time. However, for nitrogen, except at the lowest pressures, the effect was small, so that the rate of change in pressure could be ignored in computing the pressure-time product, here called the "exposure". For oxygen, on the other hand, the effect was quite large and had to be taken into account. The corresponding desorption during the interval of pumping out the gas resulted in higher pressures after a given time with oxygen than with nitrogen.

To interpret these results, it is helpful to review some of the results of measurements obtained by other methods. When nitrogen (and perhaps oxygen) molecules strike a clean molybdenum or tungsten surface at room temperature, the sticking probability, s, is relatively constant and of the order of tenths until a coverage of roughly 1.7×10^{14} molecules per cm^2 is attained, at which point it falls off rather sharply to a much lower value.[20, 21, 22] Thus, after a few seconds at 10^{-6} torr or a few minutes at 10^{-8} torr, this coverage is attained, after which the coverage changes relatively slowly. The sticking probability continues to fall off with increasing coverage until, after a considerably longer time (of the order of 15 minutes for nitrogen at 10^{-6} torr, when the coverage is above 3.5×10^{14} molecules per cm^2), the sticking probability remains relatively constant at a value of roughly 10^{-4}. When the coverage reaches approxi-

* Went[11] reports a factor of only 2.3.

mately 5.5×10^{14} molecules per cm^2, the sticking probability for nitrogen falls off to an immeasurably small value.[21] The "exposure" for the first step of rapid adsorption is, for nitrogen, approximately 3×10^{-8} torr-min, and exposure needed for a relatively constant low value of s is approximately 10^{-5} torr-min. To attain the immeasurably low sticking probability the exposure is roughly 10^{-3} torr-min.*

The results given in Appendix A and Fig. 11 for nitrogen on tungsten may be summarized as follows: Exposures corresponding to the completion of the critical period of rapid chemisorption give rise to a surface resistivity of 3.5×10^{-10} ohm-cm^2, while exposures corresponding to the attainment of immeasurably low sticking probability give rise to a surface resistivity of 12×10^{-10} ohm-cm^2. Higher values of the surface resistivity observed for much greater exposures may be due to impurities in the gas. No appreciable part of the adsorbed layer giving rise to the observed values of σ_t could be removed at room temperature by pumping out the nitrogen.

The results given in Appendix B and Fig. 12 for oxygen on tungsten yield $\sigma_t = 5 \times 10^{-10}$ ohm-cm^2 at the completion of the initial period of rapid absorption, and $\sigma_t \approx 10 \times 10^{-10}$ ohm-cm^2 for exposures roughly ten times as great. However, at pressures above 10^{-5} torr the resistance continues to increase at a measurable rate up to the longest times observed (24 hours) and eventually exceeds any of the values observed for nitrogen on tungsten. This is attributed to the formation of one of the stable oxides of tungsten (perhaps WO_3). For the growth of such films a logarithmic law, the "Elovich" equation, has been widely observed,[23] but no attempt to follow this growth quantitatively will be made in the present paper. For the thickest film observed, resulting from the exposure to 6 torr of oxygen for 24 hours (Fig. 4), σ_t was equal to 6×10^{-8} ohm-cm^2.

When the pressure has been as high as several torr of oxygen, loosely held molecules on the oxide film contribute to the contact resistance. These can, however, be pumped off at room temperature.

While the data on molybdenum are less extensive, the values of σ_t for the first and second steps of adsorption on the two metals are similar, as is the behavior of oxygen at a pressure of a few torr.

4.3 *Temperature of Flash Necessary to Remove the Adsorbed Film*

In these experiments, the contacts were exposed to a few torr of the gas in question for a few minutes, and the system was then pumped

* The sticking probability may be a function of pressure at high pressure; i.e., processes other than the arrival rate may control the rate of reaction.

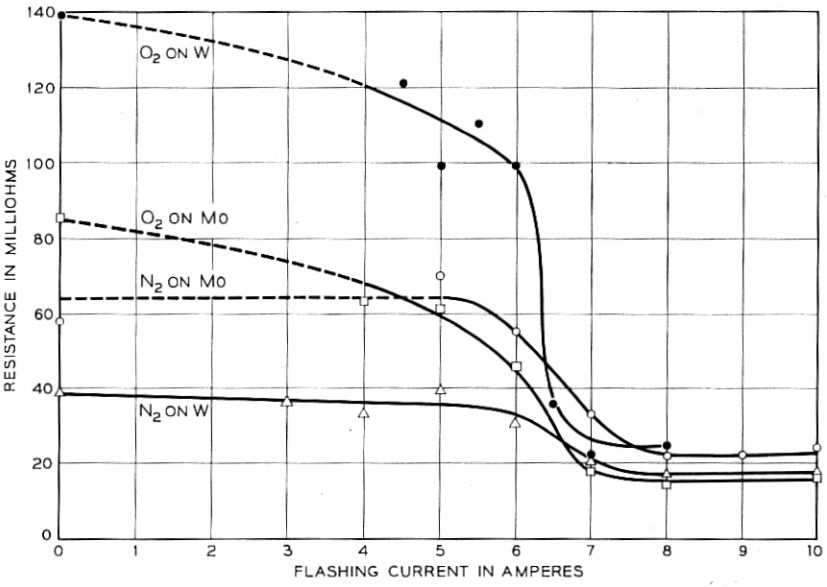

Fig. 7 — The contact resistance at room temperature (force = 1 gm) after heating for 30 sec with various currents for molybdenum and tungsten contacts which have been exposed to a few torr of oxygen or nitrogen.

down to a pressure of about 10^{-8} torr before the flashing procedure* was started.

The heating current was maintained for 30 seconds, after which 5 minutes were allowed for cooling. The results are given in Fig. 7, where each point is the average for five closings.

Flashing at about 1000°K causes some lowering of the contact resistance for oxygen on either metal, whereas for nitrogen there is no observable effect below 1450°K on molybdenum, and below a somewhat higher temperature on tungsten. For all four combinations of gas and metal there is a sharp drop in resistance after flashing at 6.5 amperes (1600 ± 50°K for molybdenum, 1750 ± 100°K for tungsten) and the curve is essentially flat above about 1725°K for molybdenum, and above 1800°K for tungsten.

The molybdenum temperatures were measured with an optical pyrometer and suitably corrected for the emissivity and reflection in the glass.

* Even at this lower pressure, a layer corresponding to the fast adsorption (first step) can be adsorbed in the few minutes necessary for the electrodes to cool, so that it was not possible to determine whether the metal had been completely cleaned, but only whether the thicker layers had been flashed off.

Unfortunately, the wall of the tube in the tungsten experiment had been coated with evaporated metal before such a temperature measurement was taken, so that these temperatures are taken from the tables of Jones and Langmuir,[24] with an estimated correction for cooling at the ends.

The data for oxygen on molybdenum are consistent with those of Went,[11] who finds some reduction in resistance after heating to 1000°K for 5 minutes and a more marked drop after heating to 1750°K. A rise in resistance observed by Went at 1400°K was not observed in the present experiment.

For oxygen on tungsten the results of field emission microscope experiments are roughly consistent with the present experiments. These results have been interpreted to be due to these successive actions: partial desorption from some crystal planes in one minute at 800°K; a temperature region (800 to 1400°K) where there is no further desorption; a resumption of desorption (perhaps of WO_3) from all planes in the region from 1400 to 1700°K.[20,25]

The observation of some relatively loosely bound oxygen is also in agreement with Morrison and Roberts,[26,27] who suggest that these molecules are adsorbed on isolated empty sites for the chemisorption of an atom, where the molecule is prevented from dissociating by the lack of an adjacent empty site.

For nitrogen on tungsten the present result differs from that of Becker and Hartman,[28] in that we do not observe a decrease in contact resistance after 30 seconds at temperatures in the neighborhood of 1100°K even when, in their notation, $\theta \approx 2$ (second step of adsorption complete), under which condition they observe a measurable rate of desorption. However, there is rough agreement as to the temperature necessary to clean the metal surface.

4.4 *Adsorption at Lower Temperature*

Went[11] and de Boer and Kraak[29] present evidence that oxygen is only physisorbed and may be pumped off when it is admitted to a nominally clean molybdenum surface at a temperature near 100°K. On the other hand, Gomer[25,30] has shown that, even at 40°K, oxygen is rapidly chemisorbed on a clean tungsten surface. One is tempted to conclude that the vacuum techniques at the time of the experiments of Went and de Boer and Kraak were not adequate to maintain a clean surface during preparations necessary before oxygen was admitted (cooling down after flashing, in the case of Went, and pre-sintering the evaporated film, in

the case of de Boer and Kraak). The reversible adsorption they observe may thus apply to surfaces already covered with chemisorbed atoms. The arguments presented by Went to show that his surface was essentially clean can be shown to be inconclusive. One possible exception may be the high temperature required to recover his "clean" state, but the evidence that the surfaces remained clean while cooling down to liquid oxygen temperature is unconvincing.

The present experiments were performed in a liquid nitrogen bath for oxygen on tungsten, nitrogen on tungsten and nitrogen on molybdenum. The results of these experiments are tabulated in Appendix C. In no case was the initial state of cleanliness recovered by pumping at the low temperature. In the case of nitrogen on tungsten, there was an increase in resistance during the pumping interval, possibly due to the accumulation of impurity gases on the surface.

The temperature of the contacts in these experiments was somewhat above that of the liquid nitrogen bath, because of inadequate radiation shielding. With all exposed parts of the tube packed with dry ice to reduce thermal radiation, the resistance of one of the tungsten wires was used as a thermometer. Using this procedure, the temperature in the above experiments was estimated to be $95 \pm 10°K$.

In summary, the bulk of the nitrogen and oxygen taken up during the initial period of fast adsorption at 95°K cannot be removed in a few hours by merely reducing the gas pressure to a much lower value. This is in disagreement with some early results,[11,29] but is in agreement with more recent experiments.[25,30]

4.5 *The Creeping in and out of Adsorbed Gas Between Closed Contacts*

Went (Ref. 11, Fig. 10) reports that physisorbed layers of oxygen at room temperature can migrate in and out of the region between contacts of molybdenum. He presents arguments to show that this is possible. In the present experiments the observed effects were smaller by at least one order of magnitude.

After the sequence of measurements of Fig. 6, where the fall in contact resistance with time on clean metal is attributed to a slow increase in area, 5 torr of oxygen were admitted to the closed tungsten contacts. The contact resistance as a function of time is shown in Fig. 8(a). The increase in resistance in 100 minutes is small and occurs in a single jump, and so may be due to a jarring of the apparatus.

If the contacts are closed in the presence of the gas, the resistance between the contacts decreases with time [Fig. 8(b)]. This is not necessarily due to the squeezing out of gas, as it is of the order to be expected

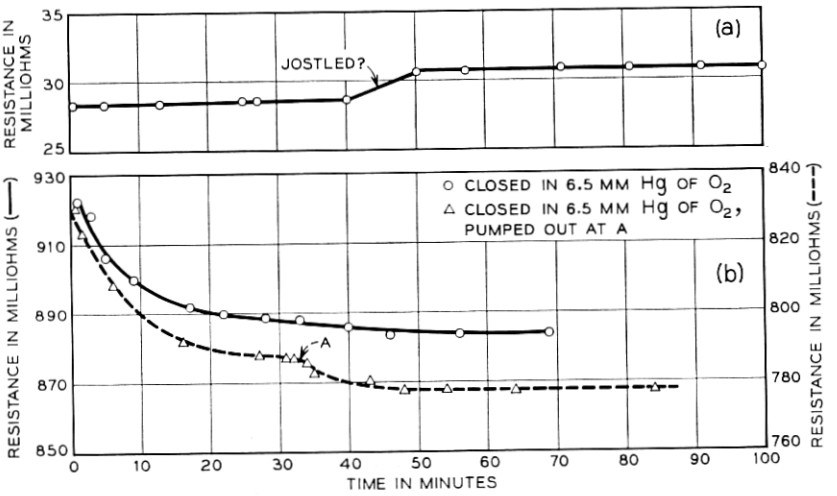

Fig. 8 — (a) The resistance between closed tungsten contacts (force = 1 gm) as a function of time when 5 torr of oxygen are admitted at $t = 0$. This sequence actually follows that of Fig. 6. While no actual disturbance was noted at the time marked "jostled?" the flatness of the curve for earlier and later times indicates that this is very likely the reason for the sudden small increase in resistance during this interval. (b) The resistance between closed tungsten contacts as a function of time after exposure to 6.5 torr of oxygen. At the point marked "A" on one of the curves the gas was pumped out without disturbing the closed contacts.

because of slowly increasing area, judging from the rate of change of the resistance between clean contacts (Fig. 6). If the gas is pumped out during such a sequence, a small discontinuity sometimes results [Fig. 8(b)] which may be due to gas molecules migrating out of a small region near the edge of the contact area.

A similar sequence for oxygen on molybdenum is shown in Fig. 9. However, this is for a somewhat lower pressure and smaller time of exposure before closing than that used by Went[11] (2.7 torr rather than 10 torr and two hours rather than ten hours).

V. INTERPRETATION AND DISCUSSION

The experiments on clean metal (Section 4.1) show that the assumptions leading to equations (1), (2), (3) and (5) are approximately valid, and give a means for measuring the contact area.

To interpret the data on films adsorbed at room temperature (Section 4.2) by means of (4) it is necessary to assign a value to the work function, φ. The changes in contact potential during the adsorption of nitrogen or oxygen show that the work function is increased,[21, 31] but in

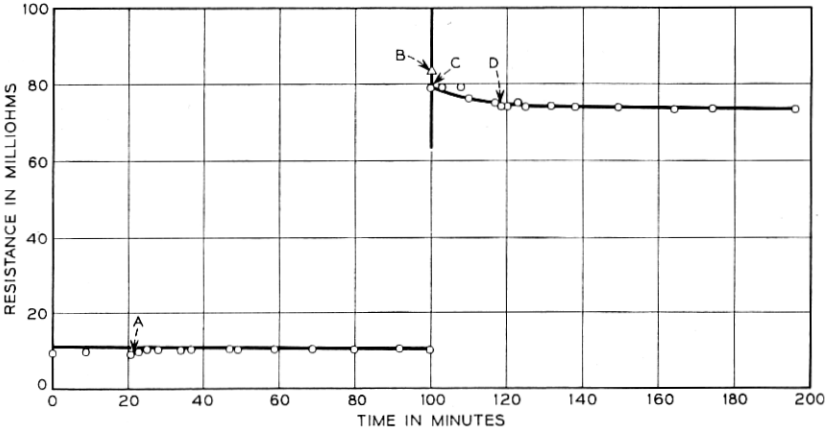

Fig. 9 — The resistance between closed, initially clean, molybdenum contacts (force = 1 gm) as a function of time at room temperature. At point A, 2.7 torr of oxygen were admitted to the system. Point B is the average resistance for ten closings in the presence of the gas. Beginning at point C the contacts were again left closed. At point D the gas was pumped out.

the presence of such an adsorbed film the potential diagram of Fig. 1 is an oversimplification and the values of l obtained by the use of (4) can have only an approximate meaning. Furthermore, the film may not be uniform over the contact area, in which case the measured values are averages heavily weighted toward a value appropriate to the thinnest film within the contact area. The values of l according to (4), using the data of Section 4.2, are given in Table II. Here, $\varphi = 5.0$ volts for nitrogen on tungsten; $\varphi = 6.0$ volts for oxygen on tungsten.

For the thickness of the layer on a single surface these values of l should be approximately halved. Thus, the entire range of thickness of the layers on each surface in these experiments is from 1.5 to 2.6 Angstroms, i.e., one or two atom diameters in thickness. The interpretation of this distance on an atomic model, however, offers considerable diffi-

TABLE II — THICKNESS OF ABSORBED FILM ON TUNGSTEN

Coverage, Molecules/cm²	Surface Resistivity Due to Film, σ_l, ohm-cm²		Thickness of Film, l, Angstrom Units	
	Nitrogen	Oxygen	Nitrogen	Oxygen
1.7×10^{14}	3.5×10^{-10}	5×10^{-10}	3.3	3.1
3.4×10^{14}	1.2×10^{-9}	1×10^{-9}	4.0	3.4
More than 4×10^{14}	$\sim 5 \times 10^{-9}$	up to 6×10^{-8}	4.5	up to 5.1

culty, as is illustrated diagrammatically in Fig. 10. This difficulty is connected with the problem of where to place the potential barrier (as illustrated in Fig. 1) with respect to the positions of the atoms in the surface plane[32].

In Section 4.3 the range of temperatures necessary to remove these films from the surface is found to be in general agreement with that determined by other techniques. It is perhaps surprising how similar the behaviors of nitrogen on tungsten, oxygen on tungsten, nitrogen on molybdenum and oxygen on molybdenum are to one another: All require a temperature in the vicinity of 1700°K to remove a large fraction of the adsorbed gas within about 30 seconds. The heat of adsorption of the desorbing molecules is thus of the order of five electron volts.[33]

In Section 4.2 it was shown that some of the oxygen giving rise to the measured resistance after relatively great exposures could be pumped off at room temperature. This was not the case for nitrogen. The result reported in Section 4.3 — that temperatures sufficient to remove a considerable amount of oxygen had no observable effect on the nitrogen layers — confirms the conclusion that additional oxygen is bound, though with relatively weak bonds, on top of the more firmly held layers.[26,27,34] Nitrogen, on the other hand, shows little tendency to stick to the completed nitrogen layers at room temperature, although some

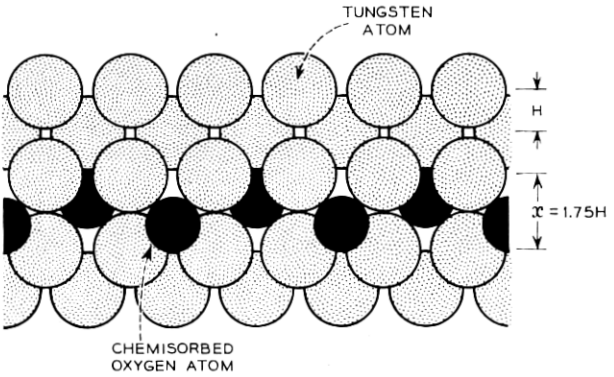

Fig. 10 — A conceivable arrangement of atoms when two (100) faces of a body centered cubic lattice are opposed, with chemisorbed gas atoms on each surface in one quarter of the lattice sites. If the coverage were twice as great, the opposing lattice planes would not necessarily be farther apart — the alternate empty positions could simply be filled in. The relative radii are approximately those appropriate to oxygen on tungsten. The distance, x, between the nearest opposed (100) planes is 1.75 times that in the normal lattice, H, i.e., about 2.8 A. The distance l to be used in (4) should perhaps lie between this value and $X - H$, the increase over the normal distance, which is about 1.2 A.

of the gas adsorbed at liquid nitrogen temperature is released as the contacts are allowed to warm up (Appendix C, Table VII).

The differences between the results of Section 4.4 on adsorption at 95°K and those reported by Went[11] are unexplained.

In Section 4.5 the effects of migration of adsorbed molecules between closed contacts are found to be much smaller than those observed by Went (Ref. 11, Fig. 10). This might be due to low-frequency mechanical vibration in his experiments resulting from footsteps etc., which may have rocked the contacts, allowing different regions to be exposed.[7] Extensive precautions against vibrations were necessary to obtain the results presented in Figs. 6, 8 and 9.

VI. ACKNOWLEDGMENT

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APPENDIX A

We interpret the values of σ_t for the entries in Table III numbered 2 through 6 and 12 and 13, for exposures between 7×10^{-8} and 6×10^{-5} torr-min as due to a layer corresponding approximately to the completion of the first step of rapid chemisorption. The average value of σ_t is 3.5×10^{-10} ohm-cm^2 (± 30 per cent). Entries numbered 7, 8, 15 through 21 and 23 through 27, for exposures between 1.7×10^{-4} and 8×10^{-1} torr-min, we attribute to a layer somewhere in the second or third steps of slower chemisorption. The value of σ_t averages 1.2×10^{-9} ohm-cm^2 (± 25 per cent).

The higher values of σ_t in entries 28 through 34 corresponding to exposures from 1.0 to 85 torr-min might possibly be attributed to an impurity in the gas. Oxygen, if present in a few parts in 10^5, could account for such an effect, while spectroscopically unobservable impurities might be present in concentrations of the order of a few parts in 10^4. The highest value of σ_t observed in the presence of nominally pure nitrogen is $\sim 5 \times 10^{-9}$ ohm-cm^2.

Entries 9, 10, 20, 21, 33 and 34 show that none of the adsorbed gas

TABLE III — THE ADSORPTION OF NITROGEN ON TUNGSTEN AT ROOM TEMPERATURE (Fig. 11)

Treatment	Contact Resistance (Milliohms) Average of Five Closures Force = 1 gm	σ_t (ohm-cm^2)	Total Exposure of Electrodes to Gas Since Previous Flash (torr-min)
1. Flash repeatedly; allow to cool for 10 min in residual pressure 1.1×10^{-10} torr	17	0, assumed	0
2. Admit 7×10^{-9} torr of N_2 ; wait 10 min	22	5×10^{-10}	7×10^{-8}
3. Wait 35 min	21	4×10^{-10}	3×10^{-7}
4. Wait 35 min	20	3×10^{-10}	5.5×10^{-7}
5. Admit 2×10^{-7} torr of N_2 ; wait 5 min	20	3×10^{-10}	1.5×10^{-6}
6. Wait 50 min	21	4×10^{-10}	1×10^{-5}
7. Admit 8×10^{-5} torr of N_2 ; wait 5 min	30	1.3×10^{-9}	4×10^{-4}
8. Wait 30 min	37	1.9×10^{-9}	3×10^{-3}
9. Close leak from N_2 source; pump for 5 min, pressure down to 5×10^{-7} torr	36	1.8×10^{-9}	—
10. Pump for 16 hours, pressure down to 8×10^{-9} torr	40	2.2×10^{-9}	—
11. Flash repeatedly, pressure falls to 1×10^{-9}; wait 10 min	17.5	0, assumed	0
12. Admit 4.5×10^{-6} torr of N_2 ; wait 3 min	20	2×10^{-10}	1.3×10^{-5}
13. Wait 10 min	22.5	4.5×10^{-10}	6×10^{-5}
14. Wait 10 min	25	7×10^{-10}	1.0×10^{-4}
15. Wait 15 min	33	1.4×10^{-9}	1.7×10^{-4}
16. Wait 10 min	31	1.2×10^{-9}	2.2×10^{-4}
17. Wait 15 min	33	1.4×10^{-9}	2.8×10^{-4}
18. Wait 40 min	35	1.6×10^{-9}	4.6×10^{-4}
19. Wait 50 min	31	1.2×10^{-9}	6.9×10^{-4}
20. Close leak from source; pump for 5 min, pressure down to 1×10^{-7} torr	30	1.1×10^{-9}	—
21. Pump for 16 hours, pressure down to 3×10^{-9} torr	31	1.2×10^{-9}	—
22. Flash repeatedly, residual pressure down to 1×10^{-9} torr; wait 10 min	14.5	0, assumed	0
23. Admit 4×10^{-3} torr of N_2 ; wait 5 min	19	6×10^{-10}	2×10^{-2}
24. Wait one hour	21	8.5×10^{-10}	2.6×10^{-1}
25. Wait one hour	22	1.0×10^{-9}	5×10^{-1}
26. Admit 1.4×10^{-2} torr of N_2 ; wait 5 min	21	8.5×10^{-10}	6×10^{-1}
27. Admit 3×10^{-2} torr of N_2 ; wait 5 min	23	1.1×10^{-9}	8×10^{-1}
28. Admit 1.5×10^{-1} torr of N_2 ; wait 2 min	33	2.4×10^{-9}	1.0
29. Wait 30 min	28	1.8×10^{-9}	5.5
30. Admit 9×10^{-1} torr of N_2 ; wait 5 min	26	1.5×10^{-9}	10
31. Admit 3.3 torr of N_2 ; wait 3 min	58	5.7×10^{-9}	20
32. Wait 20 min	42	3.7×10^{-9}	85
33. Open valve to pumps; in 5 min, pressure down to 3×10^{-7} torr	51	4.8×10^{-9}	—
34. Wait 30 min, pressure down to 2.5×10^{-8} torr	53	5.0×10^{-9}	—

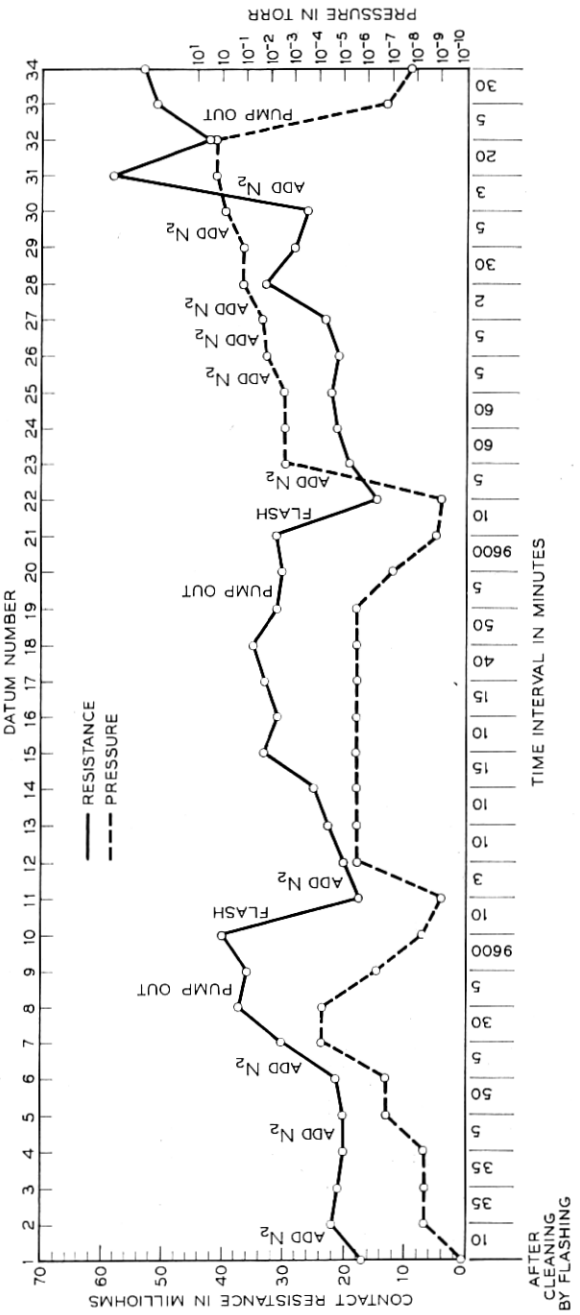

Fig. 11 — Nitrogen on tungsten, at room temperature.

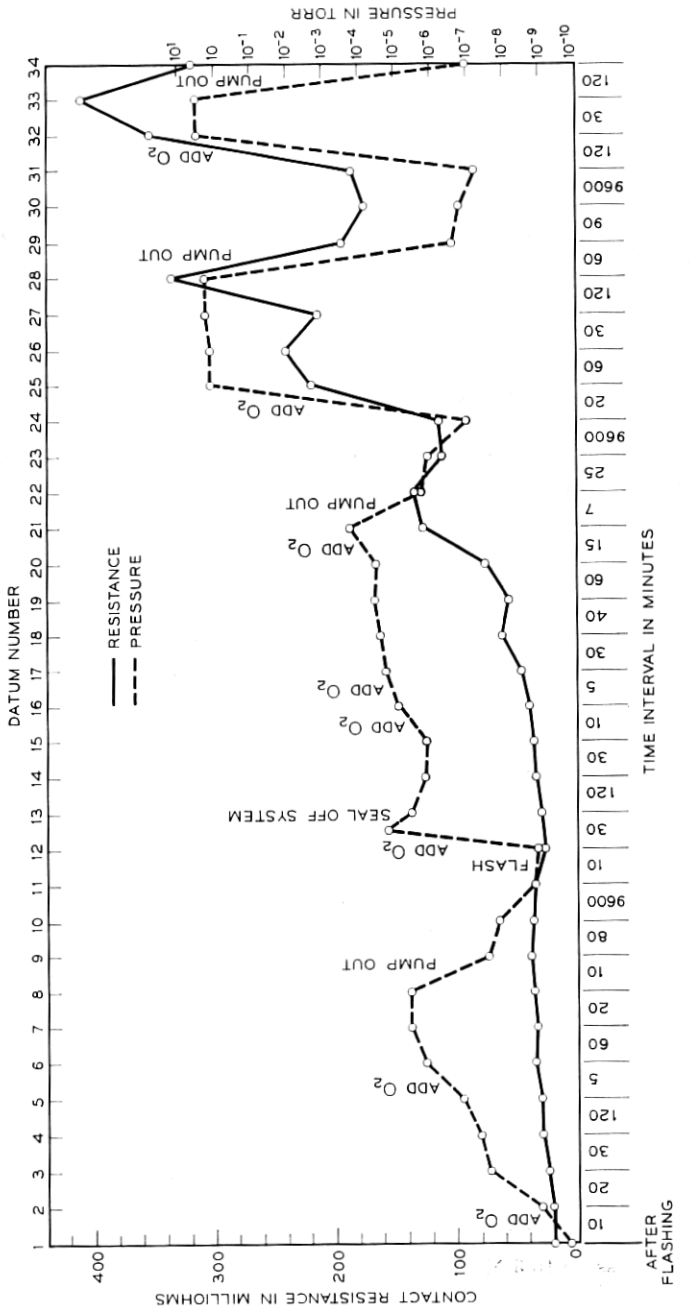

Fig. 12 — Oxygen on tungsten, at room temperature.

TABLE IV — THE ADSORPTION OF OXYGEN ON TUNGSTEN AT ROOM TEMPERATURE (Fig. 12)

Treatment	Contact Resistance (Milliohms) Average of Five Closures Force = 1 gm	σ_t (ohm-cm^2)	Total Exposure of Electrodes to Gas Since Previous Flash (torr-min)
1. Flash repeatedly in residual pressure 2×10^{-10} torr; wait 10 min	20	0, assumed	0
2. Flash in presence of 1×10^{-9} torr of O_2; wait 10 min, during which pressure rises to 2.5×10^{-9} torr	20	0	2×10^{-8}
3. Wait 20 min, during which pressure rises to 3.5×10^{-8} torr of O_2	23	2×10^{-10}	4×10^{-7}
4. Wait 30 min, pressure up to 6.5×10^{-8} torr	29	6×10^{-10}	2×10^{-6}
5. Wait 2 hours, pressure up to 2.7×10^{-7} torr	30	7×10^{-10}	2×10^{-5}
6. Reduce pumping speed, pressure rises to 2×10^{-6} torr; wait 5 min	33.5	9.5×10^{-10}	3×10^{-5}
7. Wait 1 hour, pressure up to 5×10^{-6} torr	33	9.9×10^{-10}	2×10^{-4}
8. Wait 20 min, pressure up to 6×10^{-6} torr	34.5	1.0×10^{-9}	3.2×10^{-4}
9. Close valve to O_2 source; increase pump speed; wait 10 min, pressure down to 5×10^{-8} torr	37	1.2×10^{-9}	—
10. Pump for 80 min, pressure down to 1.5×10^{-8} torr	35	1.1×10^{-9}	—
11. Pump for 16 hours, pressure down to 2×10^{-9} torr	35	1.1×10^{-9}	—
12. Flash repeatedly, pressure falls to 1.3×10^{-9} torr; wait 10 min	25	3×10^{-10}	1.3×10^{-8}
13. Admit O_2 to closed system at $\sim 2 \times 10^{-5}$ torr; wait 30 min, pressure falls to 5×10^{-6} torr	28	6×10^{-10}	$\sim 3 \times 10^{-4}$
14. Wait two hours, pressure down to 1.8×10^{-6} torr	33	9×10^{-10}	$\sim 10^{-3}$
15. Wait 30 min, pressure down to 1.6×10^{-6} torr	35	1.1×10^{-9}	$\sim 10^{-3}$
16. Admit O_2 to pressure 9×10^{-6} torr; wait 10 min	39	1.3×10^{-9}	$\sim 10^{-3}$
17. Admit O_2 to pressure 3×10^{-5} torr; wait 5 min	46	1.8×10^{-9}	$\sim 10^{-3}$
18. Wait 30 min, pressure 4×10^{-5} torr	61	2.8×10^{-9}	$\sim 2 \times 10^{-3}$
19. Wait 40 min, pressure 5×10^{-5} torr	55.5	2.5×10^{-9}	$\sim 3 \times 10^{-3}$
20. Wait one hour, pressure 5×10^{-5} torr	74.5	3.8×10^{-9}	$\sim 10^{-2}$
21. Increase pressure to 3×10^{-4} torr, wait 15 min	127	7.5×10^{-9}	$\sim 10^{-2}$

TABLE IV — *Continued*

Treatment	Contact Resistance (Milliohms) Average of Five Closures Force = 1 gm	σ_t (ohm-cm^2)	Total Exposure of Electrodes to Gas Since Previous Flash (torr-min)
22. Close O_2 leak; increase pumping speed; wait 7 min, pressure down to 2.5×10^{-6} torr	132	7.7×10^{-9}	—
23. Wait 25 min, pressure 1.2×10^{-6}	110	6.3×10^{-9}	—
24. Pump for 16 hours, pressure 1.1×10^{-7} torr	111	6.4×10^{-9}	—
25. Admit O_2 to pressure 1.4 torr; wait 20 min	219	1.4×10^{-8}	~30
26. Wait one hour	240	1.5×10^{-8}	100
27. Increase pressure to 2.1 torr; wait 30 min	215	1.4×10^{-8}	175
28. Wait 2 hours	335	2.2×10^{-8}	400
29. Open valve to pumps; wait one hour, pressure 5×10^{-7} torr	193	1.2×10^{-8}	—
30. Pump for 1½ hours, pressure 2.5×10^{-7} torr	175	1.1×10^{-8}	—
31. Pump for 16 hours, pressure 7×10^{-8} torr	184	1.1×10^{-8}	—
32. Admit 5.5 torr of O_2; wait 2 hours	354	2.3×10^{-8}	~1,000
33. Wait 30 min	410 (2 unusually large readings not included in average ~1400)	2.7×10^{-8} ($\sim 1.0 \times 10^{-7}$)	~1,000 —
34. Open valve to pump; wait 2 hours, pressure down to 1×10^{-7} torr	319	2.0×10^{-8}	—

giving rise to the measured resistance pumps off at room temperature even after the nitrogen pressure has been as high as 3 torr.

APPENDIX B

We attribute entries in Table IV numbered 3 through 6 for exposures from 4×10^{-7} to 3×10^{-5} torr-min to the first step of fast adsorption, with $\sigma_t \approx 5 \times 10^{-10}$ ohm-cm^2. Entries 7 through 11, 14 and 15, for exposures from 2×10^{-4} to about 10^{-3} torr-min, are attributed to the completion of the second step, with $\sigma_t \approx 1.0 \times 10^{-9}$ ohm-cm^2. For pressures of oxygen above $\sim 10^{-5}$ mm of mercury, the resistance continues to increase at an observable rate (entries 16 through 33).

Entries 28 through 31, 33 and 34 show that, after exposure to a few torr, a considerable decrease in resistance occurs on pumping out the gas.

APPENDIX C

Adsorption and Desorption at Low Temperatures

TABLE V — OXYGEN ON TUNGSTEN

Treatment	Contact Resistance (Milliohms)
1. Expose to 10^{-6} torr of O_2 at room temperature for a few minutes; measure resistance with force = 1 gm	50
2. Close contacts with force = 2 gm	37
3. Apply liquid N_2 and wait 30 min with contacts remaining closed	17
4. Increase O_2 pressure to 10^{-5} torr; allow contacts to stand open 15 min; measure resistance with force = 1 gm	140
5. Wait 2 hours	160
6. Open valve to pumps, wait 1 hour until pressure is 10^{-7} torr; measure resistance with force = 1 gm	160
7. Remove liquid N_2; allow system to warm 10 minutes, pressure = 2×10^{-7} torr (force = 1 gm)	120
8. Pump 16 hours at room temperature, pressure = 10^{-8} torr (force = 1 gm)	90

TABLE VI — NITROGEN ON MOLYBDENUM

Treatment	Contact Resistance (Milliohms) Force = 1 gm
1. Flash contacts in liquid N_2 bath; allow 30 min to cool, pressure = 7×10^{-11} torr	6
2. Admit N_2, pressure = 5×10^{-6} torr; wait 10 min	22
3. Open valve to pumps; wait 1 hour, pressure = 1×10^{-9} torr	23
4. Admit nitrogen, pressure 6.0 torr; wait 10 min	41
5. Open valve to pumps; wait 10 min, pressure = 10^{-6} torr	41

TABLE VII — NITROGEN ON TUNGSTEN

Treatment	Contact Resistance (Milliohms) Force = 1 gm
1. Flash in liquid N_2 bath; wait 30 min, pressure 2×10^{-10} torr	8
2. Admit 1.0 torr of N_2; wait 40 min	85
3. Open valve to pumps; wait 5 min, pressure down to 3×10^{-6} torr	124
4. Wait 1 hour, pressure 3×10^{-7} torr	150
5. Remove liquid N_2; wait 15 min to allow system to come to room temperature, pressure = 10^{-8} torr	60

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