The electrical resistance of metal contacts can be divided into two parts, a "convergence resistance", which is determined by internal properties of the contact material, and a "transition resistance", which depends upon the properties of the surface of contact. In this article the transition resistance is studied of clean metal contacts, particularly of molybdenum. By heating the contact surfaces in a vacuum to temperatures of 1500—1600° C the transition resistance can be made to disappear completely. A study is made of the way in which the transition resistance of a contact cleaned in this way changes when the surfaces of contact are exposed to oxygen at room temperature and at —160° C. Conclusions may be drawn from the observations about the adsorption phenomena at metal surfaces.

In almost every piece of electrical apparatus there are numerous places where the electrical current must pass from one electrical conductor to another which is pressed against it with a certain pressure. In this transition the electric current in general experiences a resistance of from several thousandths of an ohm to twenty or thirty ohms, depending upon the nature of the contact. In practice it is desirable to make this resistance as small as possible.

In an earlier article in this periodical 1) a discussion was given of the phenomena which determine the resistance of a contact. The resistance was divided into two components: the convergence resistance $R_u$ which occurs in the interior of the contact materials due to the fact that the current lines of force must be constricted in the very small contact surface, and the transition resistance $R_0$ proper, which occurs at the surface of contact itself. In that case it was chiefly the convergence resistance $R_u$ which was dealt with, and its dependence upon the pressure of contact and the hardness of the material of the contact. In this article we shall consider somewhat more closely the transition resistance $R_0$. The investigation of this transition resistance is not only of technical interest, but is, moreover, found to furnish surprising insight into the adsorption phenomena at the surface of the contact material. It is mainly from this point of view that the subject will be treated in what follows.

The method of measurement

In order to be able to measure the transition resistance satisfactorily it is of importance to choose the experimental conditions such that the transition resistance $R_0$ between the surface of contact is considerably larger than the convergence resistance $R_u$. This necessity leads to measuring conditions which are exactly opposite to the conditions which are striven for in the practical technical use of contacts. If $a$ is the radius of the surface of contact, assumed to be circular, then the convergence resistance $R_u$ is proportional to $1/a$, as was explained in the article already referred to. The transition resistance on the other hand is inversely proportional to the area of the surface of contact and thus proportional to $1/a^2$. The ratio $R_u/R_0$, which must be made as small as possible for the investigation in question, is therefore proportional to $a$. The radius $a$ must therefore be as small as possible, which, for our investigations, also involves the advantage that the absolute value of the resistance is also relatively large, and therefore easy to measure. In the case of technical contacts, on the other hand, every attempt is made to keep the absolute value of the resistance as low as possible, and thus to make the radius $a$ as large as possible.

In order to keep the radius of the surface of contact small, low contact pressures must be used and, moreover, a contact material must be chosen with a relatively great hardness. In this case two molybdenum rods were used as contact pieces, and they were laid crosswise over each other with a contact pressure of a few grams. In order to reduce the ratio $R_u/R_0$ still more, part of the measurements were done at a low temperature (−160° C). At this temperature the specific resistance of molybdenum, and with it the proportional convergence resistance, is considerably lower than at room temperature, while the transition resistance changes only slightly with the temperature 2).

Several observations

It was at first ascertained whether it is possible to make the transition resistance disappear completely by cleaning the contact surface thoroughly.


For this purpose the molybdenum rods were placed in a vacuum tube and heated for a long time at a temperature of about 1500° C. The contact resistance measured at room temperature was indeed found to become smaller and smaller and finally to approach a final value which differs only slightly from the theoretically calculated pure convergence resistance. This would mean that the transition resistance has practically disappeared.

A confirmation of this result could be obtained by ascertaining how the contact resistance depends upon the temperature. The contact resistance is composed of the convergence resistance which changes very much with temperature, and the transition resistance which is practically independent of the temperature. As the contribution of the transition resistance becomes smaller, the temperature coefficient of the total contact resistance will therefore have to increase in order finally to reach a value which is equal to that of the specific resistance of the contact material.

This is found experimentally to hold. According as the total contact resistance decreases, its temperature coefficient increases. The ratio $R_{160}:R_{190}$, which was taken as a measure of the temperature coefficient, finally reaches a value of 2.1, while the ratio of the specific resistances of molybdenum at these temperatures amounts to 2.3. If it is assumed that $R_0$ is entirely independent of the temperature, it follows from these values that the residual transition temperature at room temperature amounts at the most to 10 per cent of the convergence resistance.

After a perfectly clean contact had been obtained in this way, oxygen at a temperature of —160° C was admitted to the tube in order to find out what effect it has upon the transition temperature. The result is reproduced in fig. 1. The transition resistance already exhibits considerable increase at oxygen pressures of the order of $10^{-4}$ mm, and at a pressure of about 0.01 mm it reaches a saturation value which amounts to about 0.013 ohm with the contact in question. The relation between the resistance and the pressure is easily reversible: when the oxygen is pumped off, the resistance changes according to the same curve as during admittance of the oxygen, and finally disappears entirely. No time lag was observed in reaching the resistance corresponding to each pressure. It may be concluded from this that the contact resistance adapts itself to the oxygen pressure in less than 10 sec. (i.e. the time necessary for the measurement).

If the same experiments are repeated at room temperature, the results are less simple. In the first place the contact resistance is not a function of the pressure alone, but depends very much upon the time during which the contact metals have been exposed to the oxygen (see fig. 2 curve I). Moreover, the relation between oxygen pressure and contact resistance is not reversible; if at a given moment the oxygen is pumped off, a certain resistance persists, which is given by curve II of fig. 2. It may be seen that the two curves as functions of the time rise steadily without it being possible to speak of saturation.
Explanation and completion of the observations

The change in the contact resistance upon the admission of oxygen indicates that the metal surfaces are attacked in one way or another by the oxygen. Upon this assumption, in order to understand the difference between the behaviour at low temperature and at room temperature, at least two processes must be assumed to take place: a reversible process which proceeds rapidly, and an irreversible process which only occurs at a higher temperature, and proceeds much more slowly. Both processes are of such a nature that the molybdenum becomes covered with a layer which has a resistance of the order of $10^{-8}$ to $10^{-6}$ ohm/cm².

For further identification of these processes one must begin with the existing information about the adsorption of gases on metals.

a) Van der Waals adsorption

If a metal surface is exposed to oxygen, it becomes covered with a monomolecular layer of oxygen. The molecules of this oxygen layer are bound to the metal surface by relatively weak forces of attraction, which are always present between molecules, even though the molecules exhibit no chemical activity with respect to each other. These forces are called van der Waals forces, because they are found to be of the same type as those which van der Waals considered responsible for the condensation of gases.

Although the strength of the van der Waals bond generally amounts to only a few per cent of that of the chemical bond, it is large enough to give rise to a dense covering of the metal with oxygen molecules at an oxygen pressure of less than 0.01 mmHg. The result is that the two pieces of metal cannot approach each other more closely than to a distance equal to twice the thickness of an oxygen molecule. It is obvious that the electrons passing from one part of the contact to the other will experience a certain resistance in passing through this space.

In order to calculate the magnitude of this resistance, we consider the contact as consisting simply of two pieces of metal situated at a definite distance from each other, and take no account of the fact that the space between these pieces of metal is filled with oxygen. The electrons which must pass from one part of the contact to the other must then leave the metal and enter the empty space, for which a certain $\varphi$ (work function) is necessary, and they may then enter the second part of the contact, whereby the work function is regained.

Since the kinetic energy of practically all the electrons in the metal is smaller than the work function, it might be expected that the electrons would not be able to leave the metal, so that the contact resistance would be infinitely large. With a distance between the electrodes which is not too small (for instance larger than $10^{-5}$ cm) this is indeed true. If, however, the distance becomes smaller than $10^{-6}$ cm, electrons with a kinetic energy smaller than the work function also have a certain chance of passing from one part of the contact to the other. This is a result of the wave nature of matter which makes itself felt when the motion of electrons is considered over distances which are not very large compared with their wavelengths 3). If on the basis of wave mechanics one calculates the transition resistance of a contact with a surface of contact $O$, a distance $d$ between the parts of the contact and a work function $\varphi$, then as a first approximation one obtains:

$$R_o = \frac{h^3 d}{\sqrt{2m\varphi} O} \exp \left( \frac{\pi d}{h} \sqrt{2m\varphi} \right), \quad (1)$$

where $h$ is Planck's constant and $m$ the mass of the electron. In fig. 3 the relation is shown between $R_o$, $O$ and $d$ for different values of the work function $\varphi$. When it is kept in mind that the surface of contact of contacts is in general only of the order of $10^{-8}$ cm², it may be seen that an appreciable conductivity between two metal surfaces can only occur for distances $d$ between these contacts up to about $10^{-5}$ cm.

In the case of molybdenum contacts the work function has a value of about 3.8 volts. If one

3) A qualitative explanation of this phenomenon was given in this periodical in an article on blocking-layer rectifiers: Philips techn. Rev. 4, 100, 1939.
calculates the distance between the metal surfaces for this value from the transition resistance observed, one finds a variation as a function of the oxygen pressure such as is indicated with a broken line in fig. 1. It is striking that the distance between the metal surfaces seems already to approach its final value at a considerably lower oxygen pressure: between 0.0005 and 0.06 mm oxygen pressure the distance changes by only 19 per cent, the transition resistance $R_0$, however, is more than doubled by this change.

The final value of the distance $d$ amounts to 5.4 Å. Since the thickness of an oxygen molecule, according to research with the help of electron diffraction, is 2.72 Å, this agrees exactly with what would be expected if each of the parts of the contact were covered with a monomolecular layer of oxygen (see fig. 4). A contact resistance about 100 times greater is sometimes observed at high oxygen pressures. This corresponds to a distance $d = 8$ Å. Apparently in these cases one of the parts of the contact is also covered with a second layer of oxygen molecules.

b) Activated adsorption

If the contact surfaces are exposed to oxygen at room temperature, as already stated a gradual increase of the contact resistance with time is observed, which upon pumping the oxygen away only gradually disappears again. Apparently the oxygen bound by van der Waals forces passes gradually over into another state in which it adheres much more strongly to the surface, so that the molecules cannot immediately be removed by evacuation.

A phenomenon by comparison with which this behaviour may be explained is known to chemistry under the name of activated adsorption. Molecules which are adsorbed by van der Waals forces are converted by a certain activation process into a state in which the bond is much stronger. In the case of oxygen, for example, it is known that in some cases the adsorbed molecules are split into atoms which are then bound chemically by the underlayer; this chemical combination is indeed much stronger than the bond due to van der Waals forces.

A representation of this process may be given by plotting the binding energy of an oxygen molecule and of the atoms formed from it as a function of the distance between the molecule (or atom) and the surface of the metal. A diagram is obtained such as that shown in fig. 5. The potential energy of the adsorbed molecule or atom is plotted vertically. For a definite distance the potential energy has a minimum, and this is at a distance from the wall at which the adsorbed particle is in equilibrium. For the atom this distance is always smaller than for the molecule, since the atom has a smaller diameter. Furthermore the depth of the minimum for the atom is considerably greater, since the chemical bond is much stronger than the bond due to van der Waals forces.

![Fig. 5. Potential energy as a function of the distance from the molybdenum surface: 1 for an oxygen molecule, 2 for two oxygen atoms. The atoms are bound more firmly and at a smaller equilibrium distance from the surface than the molecules.](image)

We now see that a molecule will first be found by van der Waals forces and thereby reach the potential minimum $I$. At a sufficiently low temperature it will remain in this minimum. At room temperature, however, the molecules are sufficiently strongly agitated to carry out vibrations, and it may occur that the point $P$ is suddenly exceeded: This means that the molecule can dissociate into atoms without any further addition of energy. The atoms now behave as may be deduced from potential curve 2, i.e. they are chemically bound at a distance given by the position of the potential minimum $II$.

1) This view or activated adsorption was first given by J. E. Lennard Jones, Trans. Farady Soc. 28, 333, 1932.
This distance can again be determined by calculating the distance between the parts of the contact from the contact resistance measured. The difficulty is here encountered, however, that the work function $\varphi$ is not known in the case of activated adsorption. If the molybdenum surface is covered with a layer of molecules, as in the case of adsorption by van der Waals forces, then — as has been done above — it may be assumed that the work function of an electron will not differ appreciably from that of an electron from the clean molybdenum surface, which is 3.8 volts. If, however, the surface is covered with chemically bound oxygen atoms, the latter are negatively charged. The electrons which leave the metal are pushed back by this negative charge and the work function is hereby increased to for instance 6 volts or more.

Since the correct value of the work function is not known, we have calculated $d$ for two values of $\varphi$: a value of 3.8 volts, which is certainly too small, and a value of 7 volts, which is very probably too large. The broken-line curves of fig. 2 give the results; these have been derived from curve II.

It is found that the thickness of the layer of oxygen no longer changes to any extent after 5 hours. With $\varphi = 3.8$ volts a distance of 5.8 Å between the parts of the contact is calculated, while with $\varphi = 7$ volts a distance of 3.8 Å is found. The actual distance is probably less than 5 Å, and in any case less than the distance which prevails with adsorption by van der Waals forces, as was also assumed in drawing the potential curves.

Migration of oxygen molecules over the surface

In the experiments described until now, when oxygen was admitted or pumped off, the parts of the contact were taken apart so that the contact surfaces could easily be reached by the surrounding oxygen molecules. If, however, the perfectly clean contacts are pressed together, and then only oxygen is admitted, it is found that at a low temperature ($-160^\circ$ C) no increase of the resistance occurs at all. At room temperature the resistance begins to increase gradually, much more slowly, however, than when there is direct contact between the oxygen and the molybdenum (see fig. 6).

It may be concluded from this that the molecules adsorbed by van der Waals forces remain in position at low temperatures, but at room temperature they migrate over the surface and in doing this penetrate between the surfaces of contact. At the same time the above-described process of activated adsorption takes place, i.e., the molecules at a certain moment pass into the dissociated state; the thus formed oxygen atoms are bound chemically and thus their migration interrupted.

In this way the molybdenum becomes gradually covered with an atomic layer of oxygen, and this also takes place between the surfaces of contact. When this covering is complete, it might be imagined that on the top of the layer of oxygen atoms a layer of oxygen molecules might be formed which also penetrates between the surfaces of contact. This can be studied by finding out how the resistance changes when the oxygen is pumped off. If a layer of oxygen molecules were present, upon decrease in pressure this layer should creep away gradually from between the surface of contact, so that the transition resistance would decrease. If, however, the oxygen layer between the surfaces consists entirely of oxygen atoms, then even at room temperature they will remain in their places, so that the contact resistance upon pumping off the oxygen will not change at all.

This last was actually observed when the parts of the contact were exposed to oxygen for about

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Footnote: This has been found from investigations of the electron emission of tungsten which is chemically closely related to molybdenum.
three hours while being pressed together. It follows from this that the molecules which creep between the contact surfaces are all split up into atoms. If on the other hand the open contact is exposed to oxygen, it is found that the contact resistance, after closing the contact and pumping off the oxygen, again partially disappears, as curve III of fig. 6 shows. With an opened contact, therefore, a layer of molecules is apparently formed on top of the layer of oxygen atoms.

If it is desired to make the transition resistance disappear entirely, the molybdenum must be heated so highly during evacuation that the chemically bound oxygen atoms also evaporate. As was mentioned in the beginning, the melting point of molybdenum is high enough for this to be done; heating to 1500° C gives the desired result.

What exactly happens when this is done cannot be stated with certainty. It seems as if the atomic oxygen layer does not evaporate directly, but is first transferred into a different state. If the molybdenum is heated to a lower temperature, for instance 1100° C, no decrease in the resistance is observed, but, on the contrary, a fairly considerable increase. It is possible that this may be ascribed to the formation of molecules of molybdenum oxide (MoO₃). This oxide has a considerably higher vapour tension than molybdenum itself, so that upon heating to 1500° C the molecules can evaporate and the surface becomes perfectly clean.

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STANDARDIZATION OF ACOUSTIC QUANTITIES

In February 1937¹ tables were given in this periodical for the sound pressure and the velocities of the air particles at different sound levels, as well as for the frequency of the different musical tones. The remark was there made that it was extremely unfortunate that different standards were used in different countries by different investigators. Since this situation has recently been changed by international regulation, it will perhaps be useful to give the tables once more, brought into agreement with this regulation.

The sound level is indicated in “phon”, i.e. the number of decibels above a definite threshold value. As threshold value, i.e. as the sound intensity to which the level of zero phons is ascribed, the intensity 10⁻¹⁵ watts/cm² was decided upon at a conference in June 1937 in Paris, called together on the initiative of the C.C.I.F. (Comité Consultatif International Téléphonique). This intensity corresponds to an effective sound pressure of 2 × 10⁻⁴ dynes/cm². In table I the effective values of the sound pressure and of the velocity of the air particles are given for the sound levels from 0 to 120 phons. With the help of the values given for the levels from 60 to 80 phons, increasing by intervals of 1 phon, interpolation can be carried out in the main table, as explained in the accompanying text.

The regulation as to the frequencies of the musical tones was arrived at in May 1939 in London; at a meeting of one of the committees of the I.S.A. (International Federation of Standardizing Asso-

¹ R. Vermeulen, Octaves and Decibels, Philips techn. Rev. 2, 47, 1937.