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THE NATURE OF ADSORPTION BONDS OF HYDROGEN AND OXYGEN ON PLATINUM

I. Change in the Electrical Resistance of Thin Pt Wires due to Adsorption of H₂ and O₂

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Abstract

Measurements of the resistance of thin platinum wires were made to study the adsorption effects of H₂ and O₂ gases. It has been found that adsorption of hydrogen increases the resistance in contrast to the previous results of an exceptional decrease in the resistance observed by SUHRMANN *et al.* and PONEC; on the other hand, the effect of adsorption of oxygen is similar to the results obtained by PONEC. The followings are concluded from experiments: the resistance of Pt as well as other transitional metals is increased by adsorbed hydrogen and oxygen, *i. e.*, the adatom-conduction electrons interaction is important for the adsorption bonds, while some peculiar properties of evaporated films of Pt seem to cause the decrease of the resistance owing to adsorption of hydrogen.

I. Introduction:

Many experimental works have verified the general tendency of the electrical resistance of thin metals to increase due to adsorption of various kinds of gas molecules. This fact implies rather strong interactions between adsorbates and the conductive s-electrons even on surfaces of transitional metals. This problem was theoretically discussed in a previous paper¹⁾, in which adsorbate cross sections which represent the strength of the s-electron interaction were calculated.

However, there are a few exceptional cases of a decrease in the resistance after adsorption. Though some of them²⁾ seem to be attributed to enhanced rearrangements of surface atoms due to adsorbates, the resistance decrease of evaporated platinum films by adsorption of hydrogen^{3),4)}, on which we are going to focus our interest, is not yet well understood. It

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is to be noted that there is a simultaneous increase of the work function³, which apparently conflicts with the conventional understanding of both changes. Though PONEC *et al.*⁴) tried to explain it by d-bond formation, their explanation is not fully plausible. Another possible explanation is that the decrease is not a general characteristic but is due to some peculiar properties of evaporated platinum films, *e.g.*, an island structure of the film or a special surface structure. The above idea seems to be supported by the facts that (1) it is rather difficult to obtain thin, smooth films of platinum because of its low vapor pressure and high melting temperature; and (2) the decrease in the resistance is sensitive to film conditions such as temperature, as pointed out by SACHTLER and DORGELO⁵). Based on the above facts, measurements of the resistance change of thin platinum wires owing to adsorption were intended. We encountered a few difficulties in the measurements of the resistance of thin wires, *i.e.*, first: the resistance change due to adsorption is smaller by two orders of magnitude than that for usually used thin films (of which order can be theoretically estimated by the Boltzmann-Fuchs equation⁶). Second: a very slight difference in temperature

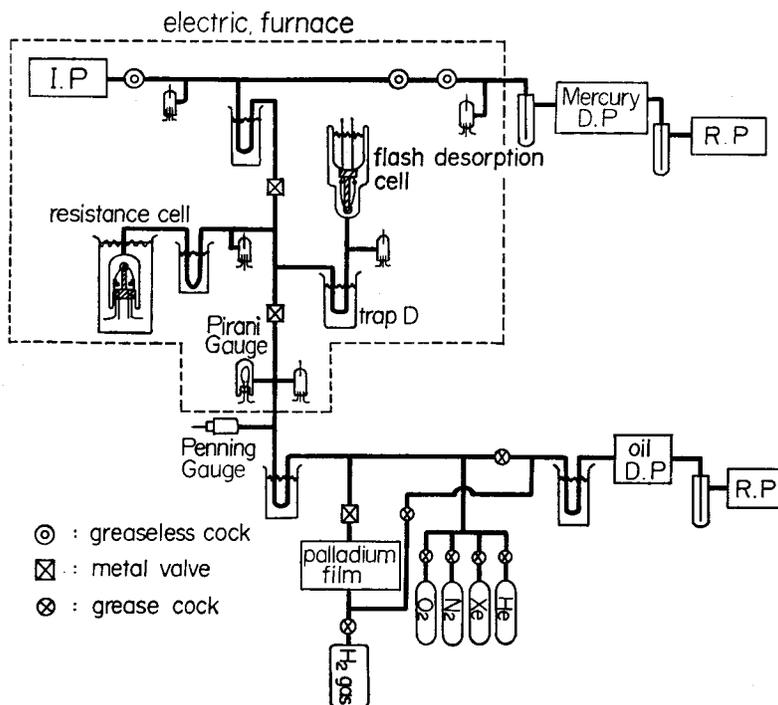


Fig. 1. Diagram of the ultrahigh vacuum and gas introduction systems.

between the platinum wire and dosed gases causes a relatively large change in the resistance. Carefully performing the resistance measurements, we obtained an increase in the resistance due to adsorption of hydrogen in contrast to the previous result of thin film measurements showing a decrease in the resistance. The details of analysis of the resistance change is presented in the following paper (Part II) and the electronic states of adsorbed hydrogen and oxygen will be also discussed in Part II.

II. Experiment:

The measurements were made in an ultrahigh vacuum system, which is diagrammatically shown in Fig. 1. The residual gas pressure was 5×10^{-10} Torr near the measuring cell, shown in detail in Fig. 2. Platinum foils were rolled round the glass wall of the cell (Fig. 2) to give a uniform temperature in the cell. When the cell was immersed in liquid nitrogen, it took about 30 minutes for the wire specimen to be at 78°K. The platinum wire was directly heated by a D.C. current. The temperature of the wire fell exponentially after heating the wire, so that it took a rather long time to achieve the equilibrium temperature. In addition a D.C. current of 0.5 to

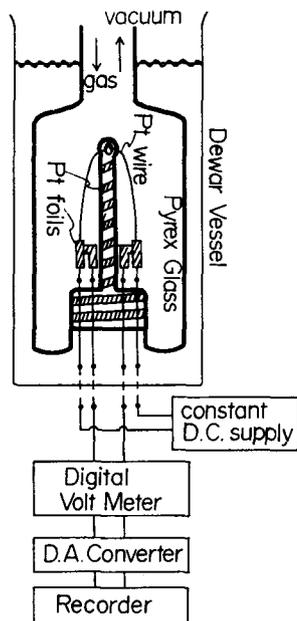


Fig. 2. The cell for resistance measurements and the block diagram of the voltage detection unit.

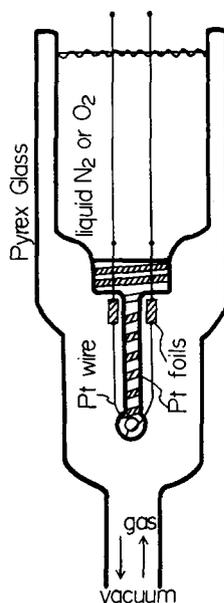


Fig. 3. The cell for flash desorption.

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0.9 mA run in the wire specimen to obtain a measurable potential drop caused a small increase in the temperature of the wire. These increased the temperature of the wire specimen in all by 0.2 to 0.5 degree above the temperature of the heat bath. The platinum wires, 99.99% pure and produced by Johnson-Matthey Company were 9.8μ in diameter as measured by an optical microscope. The wire specimens were thermally treated as follows: the platinum wires were heated up to about 950°C with oxygen and hydrogen gases (10^{-3} Torr at maximum) alternatively introduced to the wires to make the surfaces carbon-free and clean. This process was repeated many times until no change in the resistance was observed. The resistance measurements were made at 273°K , 195°K , 90°K and 78°K . Detectable changes in the resistance were observed at 78°K for adsorption of hydrogen and 90°K and 78°K for adsorption of oxygen. At the time of the resistance measurements, every endeavor was made to eliminate background noises generated by the thermoelectric power at the contacts of different lead wires. Hydrogen gas was purified as usual by a palladium film. The purity of oxygen gas, which was passed two times through traps of liquid nitrogen, was 99.9%.

The amount of adsorbed gas on a Pt wire was determined by measuring the flash desorption spectra. The cell for the flash desorption measurement is shown in Fig. 3. A typical desorption spectrum observed by use of a

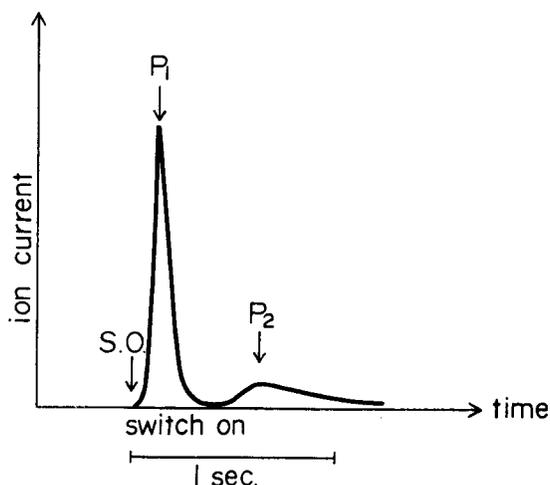


Fig. 4. A typically observed desorption spectrum of oxygen. P_2 peak depends on construction of the vacuum system and almost disappears when trap D in Fig. 1 is removed. Therefore, it is not an important peak.

sufficiently electron-bombarded B-A gauge is shown in Fig. 4. This was obtained by the following processes: first, a gas at certain pressure was introduced into the cell for few minutes; next, the cell was evacuated and then a sudden D.C. current (a step function current) heated the wire specimen to about 750°C within one second. A linear increase of temperature of the Pt-wire is not expected in our experiments, but it seems that the temperature rises monotonously with a very high rate of rising (order of 1000°/sec). Hence the amounts of irreversibly adsorbed gas, *i. e.*, the gas not immediately desorbed after the evacuation, can be relatively estimated by changing the gas pressures and measuring the peak area, so far as we are not concerned with the shape of the desorption spectra. The second small, broad peak in Fig. 4 appeared for all kinds of gases used and we noticed it becoming small when the trap D in Fig. 1 was removed. So, we concluded it was not due to desorption from the wire. The adsorbed amount was measured from the height and area of the first peak. The difference in the relative sensitivity for ionization of oxygen and hydrogen in the B-A gauge is corrected according to the result by ALPERT⁸⁾, *i. e.*, $S_{O_2}/S_{H_2} = 0.85/0.53 = 1.6$, and the approximation is made that all of the hydrogen and oxygen molecules are atomized when the ion currents are detected by the B-A gauge^{9),10)}.

III. Experimental Results:

The resistance due to adsorption of oxygen, which is experimentally known to be the largest among those of simple gases, was measured first. The observed resistance versus time curves are shown in Figs. 5 and 6 along with the pressure of dosed oxygen. The five-digit numbers of the potential drop were observable and the last three-digits were recorder-traced. The measurement was started about ten minutes after flashing the wire, so the gradual exponential decrease in the resistance before the gas introduction was due to the decreasing temperature of the wire. The large reversible and rapid resistance decreases caused by heat conduction from oxygen gas to the platinum wire when 1.2×10^{-5} Torr and 2.0×10^{-5} Torr oxygen doses are admitted at 78°K and 90°K, respectively, are remarkable. This effect was observed for all gases tried (O₂, H₂, Xe and He), though there was a difference in the critical pressures for the rapid decrease, *i. e.* lower for oxygen and higher for He. This effect is, as is well known, the principle of the Pirani-Gauge. The true resistance change for Xe was not clear and was within the background error.

Another fact observed was an irregular and small change in the resist-

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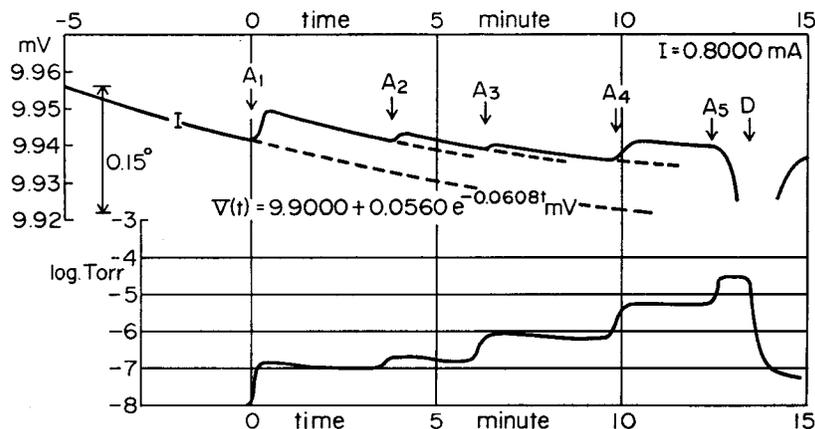


Fig. 5. The adsorption effect of oxygen on the resistance and the pressure of dosed oxygen at 78°K. The gradual decrease of the resistance due to decrease of temperature of the wire, is expressed by $V(t)$ equation, which is experimentally determined. The whole decrease of temperature during the measurement is shown at the left hand side. Mark I shows the range of the error of measurements.

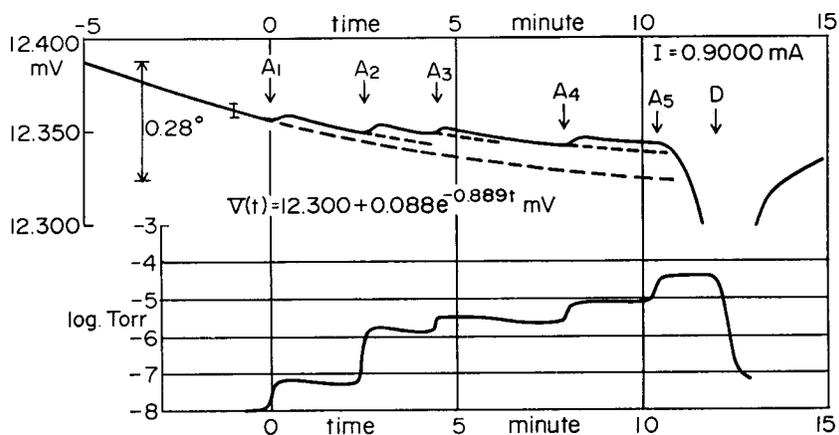


Fig. 6. The adsorption effect of oxygen on the resistance and the pressure of dosed oxygen at 90°K.

ance for the first dose of oxygen at 10^{-8} Torr. This is readily explainable as due to adsorption of CO molecules expelled from the glass wall by oxygen gas. The above interpretation is supported by results of the flash desorption as will be seen later (see Fig. 8). Therefore, the measurements of

the resistance change and the flash desorption were made after contacting the glass wall with oxygen gas.

The result of H₂ adsorption at 78°K is shown in Fig. 7. The resistance change due to adsorption above 90°K was not clear. To be noted in Fig. 7 is that no decrease in the resistance was observed for the wire specimen

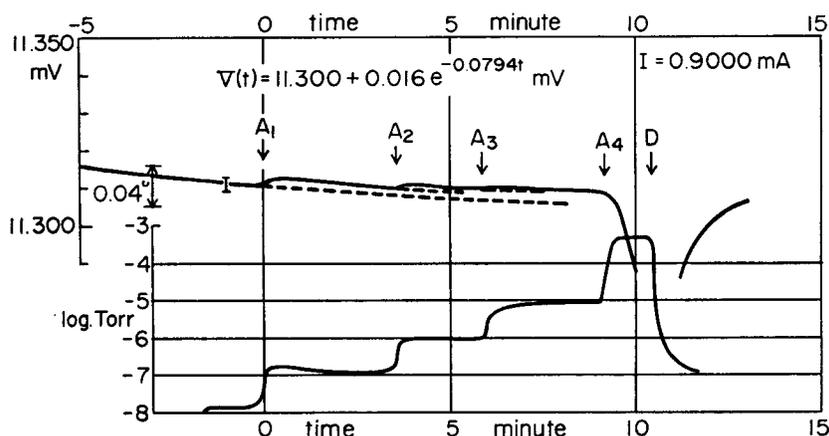


Fig. 7. The adsorption effect of hydrogen on the resistance at 78°K.

in contrast to evaporated film specimens^{3),4)} except that due to the heat transfer from hydrogen gas to the specimen as for oxygen gas.

The results of the flash desorption measurements, which were made to estimate the amounts of adsorbed oxygen and hydrogen, are shown in Fig. 8 for oxygen and in Fig. 9 for hydrogen. We intended simply to measure the area of desorption spectra but fortunately we could obviously observe different shapes of the desorption spectra for oxygen and hydrogen in spite of the very high rate of rising temperature as mentioned in Section II. The spectrum shape of the first dose of oxygen (Fig. 8, (a)) is very different from those of latter doses. This effect was observed only for oxygen. Therefore, it is explained, as already stated, by CO molecules expelled from the glass wall of the vacuum apparatus; the same effect has been reported by a few experimentatists^{19),20)}. The desorption spectra of oxygen at 90°K were so similar to those at 78°K (Fig. 8) that those are not shown. Fig. 9 shows the spectra for adsorbed hydrogen at 78°K. A characteristic of these spectra is two peaks overlapping in the main spectra, which seem to correspond to the two stable species denoted by γ and δ of TSUCHIYA, *et al*⁷⁾, who studied the temperature programmed desorption of

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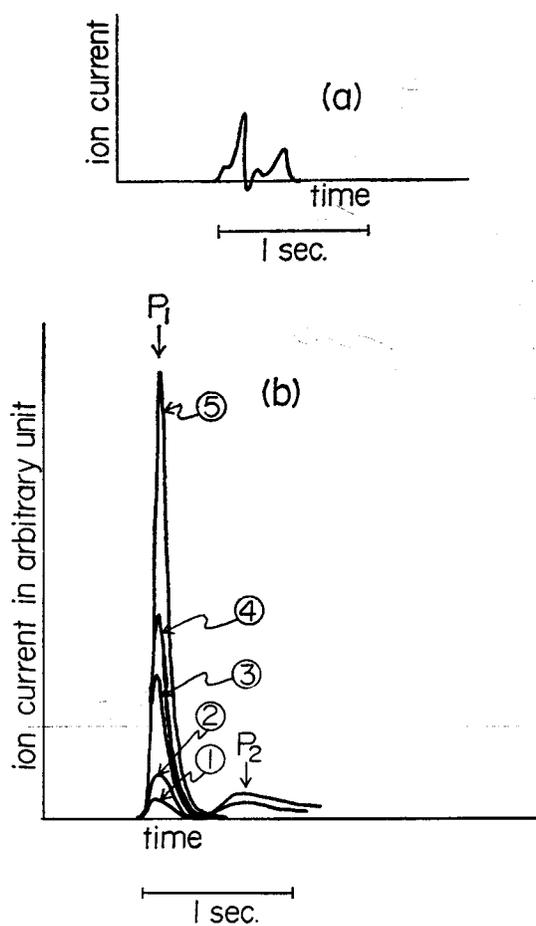


Fig. 8. Flash desorption spectra of oxygen adsorbed on the Pt wire at 78°K . (a): the spectrum of first dosed oxygen (6.5×10^{-8} Torr), which is different from spectra of the later doses in (b). The pressures of dosed oxygen are: (1): 5.8×10^{-8} Torr, (2): 2.0×10^{-7} Torr, (3): 5.0×10^{-7} Torr, (4): 1.0×10^{-6} Torr, (5): 9.5×10^{-6} Torr. P_2 is an insignificant peak as discussed in Section II.

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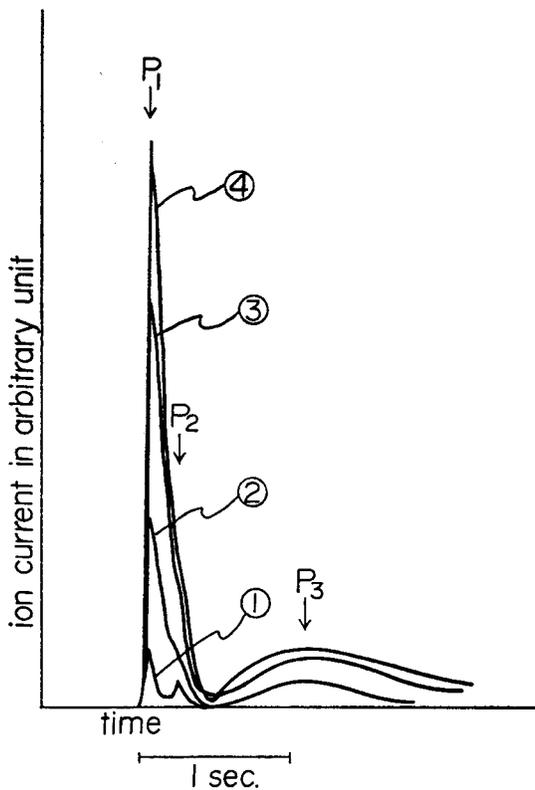


Fig. 9. Flash desorption spectra of hydrogen adsorbed on the Pt wire at 78°K. The pressures of hydrogen are: (1): 1.0×10^{-9} Torr, (2): 4.5×10^{-8} Torr, (3): 1.0×10^{-6} Torr, (4): 5.0×10^{-5} Torr. P_3 is an insignificant peak as for oxygen desorption in Fig. 8.

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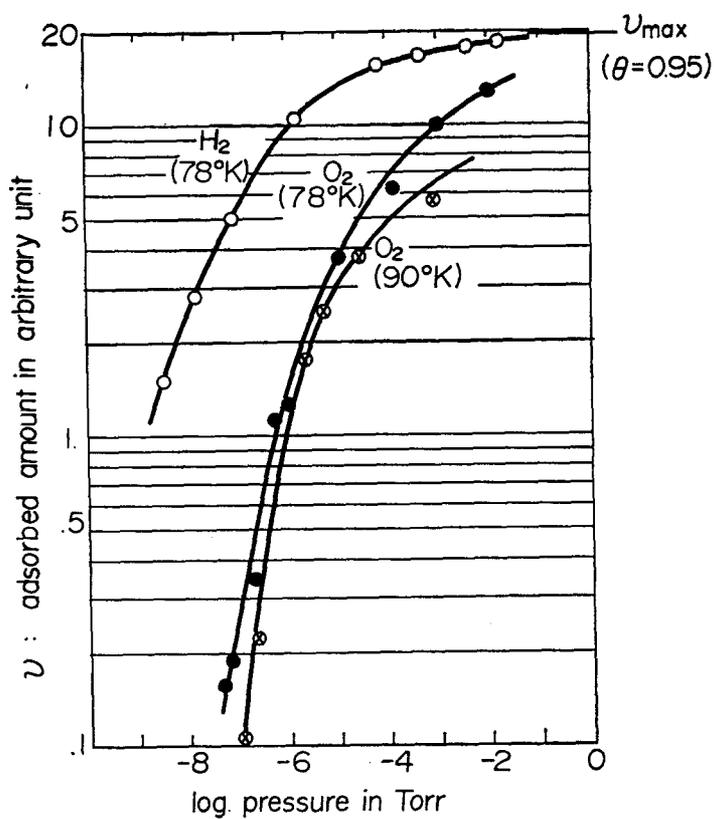


Fig. 10. Log-log isotherm of irreversibly adsorbed hydrogen and oxygen. $\theta = 0.95 = 1.19 \times 10^{15}$ atom/cm² is defined by the saturated value (v_m) of the isotherm of hydrogen according to VANNICE *et al.*¹¹⁾ and BRENNAN *et al.*¹²⁾

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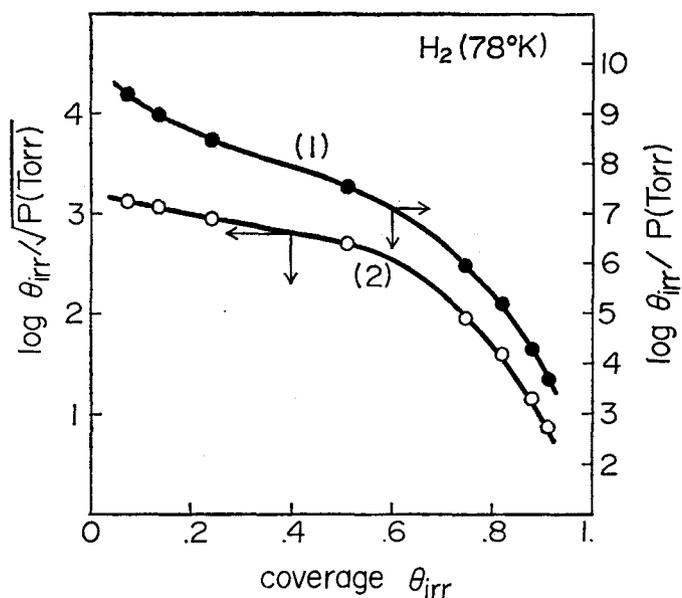


Fig. 11. Langmuir isotherm of irreversibly absorbed hydrogen. (1) isotherm of molecular adsorption: $\log \theta_{irr}/p = \log a \frac{\theta_{max} - \theta_{irr}}{\theta_{max}}$, (2) isotherm of dissociative adsorption: $\log \theta_{irr}/\sqrt{p} = \log a \cdot \theta_{max} - \theta_{irr}/\theta_{max}$.

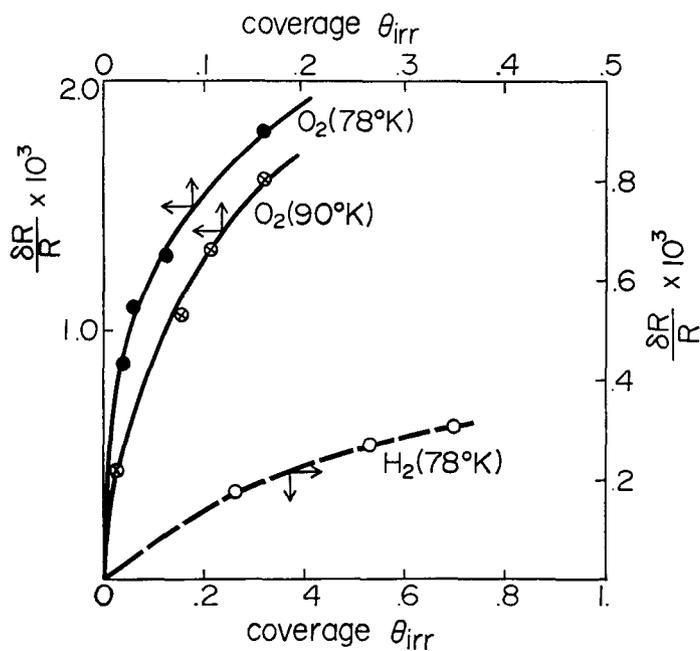


Fig. 12. The resistance change due to adsorption of H₂ and O₂ versus coverage.

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hydrogen adsorbed on platinum black.

Since the flash desorption was measured after contacting the Pt-wire with certain pressure of oxygen or hydrogen gas at 78°K or 90°K, we could obtain the adsorption isotherms from Figs. 8 and 9, which are shown in Fig. 10 plotted with log-log scales. From the results we can say that the three isotherm curves do not obey the Freundlich isotherm and that of hydrogen seems to obey the Langmuir isotherm for a dissociative form of adsorption, plotted as $\log \theta_{\text{irr}} \sqrt{p}$ vs. θ_{irr} as shown in Fig. 11, when the coverage is small. Here θ_{irr} denotes the coverage of irreversibly adsorbed hydrogen.

We finally obtain Fig. 12 showing $\delta R/R$ against θ_{irr} from the data in Figs. 5, 6, 7 and 10. It is assumed for the definition of the coverage that full coverage, $\theta=1$, signifies 1.25×10^{15} atoms/cm² and the saturated value of adsorbed hydrogen in Fig. 10 is equivalent to $\theta=0.95$ according to VANNICE *et al.*¹¹⁾ and BRENNAN *et al.*¹²⁾

IV. Discussion and Conclusions:

The results which should be emphasized are: though the effect of O₂ adsorption on the resistance is similar to the previous results,⁴⁾ the effect of H₂ adsorption is very different from those results.^{3),4)} From a theoretical viewpoint, the order of magnitude of the observed resistance increases is what we can expect from the Boltzmann-Fuchs-Dingle equation¹³⁾ and we can obtain very reasonable values of the scattering cross sections of H and O atoms using our experimental results¹⁴⁾ as will be discussed in Part II.

A few comments about the adsorbed amounts of hydrogen and oxygen are as follows. The flash desorption technique determines the relative amounts of irreversibly adsorbed species, while the resistance change due to adsorption is caused by both reversibly and irreversibly adsorbed species. However, according to the experimental results by SUHRMANN *et al.*^{15),16)} reversibly adsorbed hydrogen and oxygen contribute little to the resistance change when the coverage is small: a weakly adsorbed adatom interacts weakly with the conduction electrons as discussed in the previous paper¹⁾.

It should be pointed out that the bulk and surface structures of the wire specimens used are well-defined compared with those of evaporated films; the successive and alternative doses of oxygen and hydrogen gases ensure clean, carbon-free¹⁷⁾ and rather smooth surfaces of platinum. Therefore, it is concluded that the decrease in the resistance due to hydrogen observed by SUHRMANN *et al.* and PONEC should be attributed to peculiar properties of evaporated platinum films and is not a general characteristic

of Pt: adsorbed hydrogen scatters the conductive s-electrons resulting in increase of the resistance of Pt as it does for other transitional metals. The reason why a decrease in the resistance was observed for evaporated Pt films is not yet clear. However, generally speaking, it is rather difficult to produce smooth and defect-free thin films of platinum because of its low vapor pressure and the rather high melting temperature. The results by SUHRMANN *et al.*³⁾ and by PONEC *et al.*⁴⁾ are essentially the same and the latter produced thin films by directly heating Pt wires, which produces a very slow rate of the evaporation because the vapor pressure of Pt is 2×10^{-6} Torr even at the melting temperature. On the other hand, it might be experimentally said that adsorption of other simple gases increases the resistance without sensitive effects of structure of the films, *e.g.*, according to SUGITA *et al.*¹⁸⁾ CO increases continuously the resistance of an extremely thin platinum film with 12 atomic layers on the average, which is considered to be in an island structure. The decrease in the resistance of platinum films might, thus, be comprehended as the effects both of the small atomic size of hydrogen as stated by PONEC *et al.*²¹⁾ and of some special structures of the films.

It should be finally pointed out that our simple method of flash desorption found two irreversibly adsorbed states of hydrogen and one state of oxygen at 78°K, which seem to be consistent with the results by TSUCHIYA *et al.*⁷⁾; and initially adsorbed hydrogen obeys a Langmuir isotherm for dissociative adsorption.

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