Influence of Sorption on the Electric Conductivity of Pulverized Metals. I.

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Introduction. As the recent development of catalyst chemistry, it has become very important to make clear the state of sorbed hydrogen on metals, especially on transition elements, which are frequently used as catalyst. Generally speaking, from various experiments it is verified that above certain temperatures the sorbed hydrogen by metal is present in the atomic or in the ionic form. By the method of electron diffraction, Germer[1] has found that in some range of temperature and pressure, hydrogen exists in the atomic form on Ni surface and that the individual hydrogen atoms are so arranged around the lattice centers as to have twice the interatomic distances of the Ni atoms. On the other hand, the experiment of Coehn[2] is sufficient to make us believe that the hydrogen is present in metal in the form of protons. Coehn has found that when electromotive force is applied to palladium wire, protons are concentrated toward cathodic side. Similar result has also been found by Hirota and Horiuti[3]. Moreover, according to the experimental data on the diffusion of hydrogen through metals, we can suggest that the hydrogen exists in the atomic form. These experiments elucidate the state of hydrogen on the surface or in the bulk of metal to some extent; there remains, however, some ambiguities. The present author has found that hydrogen has characteristic influence on the electric conductivity of various metal powders and attempted to make clear the state of sorbed hydrogen from these experimental data.

Experimental. The experiments were carried out on such metals as Ni, Co, Cu, Ag, Pt, and Au, of which Ni, Co. Cu, and Ag were prepared by ignition of nitrates and by reduction in hydrogen, while Pt and Au were prepared by reduction of chlorides in hydrogen. The conductivity was measured by current-voltage method. The hydrogen used was perfectly free from oxygen and water vapour, and its pressure can be controlled at will, while the conductivity is measured. Before measurements, the metals were thoroughly reduced again by hydrogen. Then the measurement of conductivity at constant temperature under various pressures of hydrogen shows that the influence of hydrogen pressure on the conductivity is characteristic for each metal. We can classify them in the three types as follow:

(1) The conductivity increases as the hydrogen pressure rises:—Pt.

(1) L. Germer, *Z. Physik*, **54** (1929), 408.
(2) A. Coehn, *Z. Elektrochem.* **35** (1929), 676.
(3) K. Hirota and Horiuti, *Oyo Buturi*, **8** (1939), 266.

(2) The conductivity decreases as the hydrogen pressure rises:—Ni, Co, Ag, and Cu.
(3) No effect:—Au.

Detailed observations will be described for each of these metals.

Nickel. It is well-known that the conductivity of nickel oxide increases with oxygen pressure, but no report is found on the effect of hydrogen on the conductivity of Ni powder.

When hydrogen is introduced on Ni oxide at temperatures higher than 200°C., the conductivity decreases as the reduction proceeds, the velocity of which is slower than that of reduction. The result of kinetic observation, which is carried out at 250°C., is shown in Fig. 1. In the reduction process, a stationary state is attained in 30 minutes, while in the oxidation process, it takes more than 5 hours to attain the stationary state.

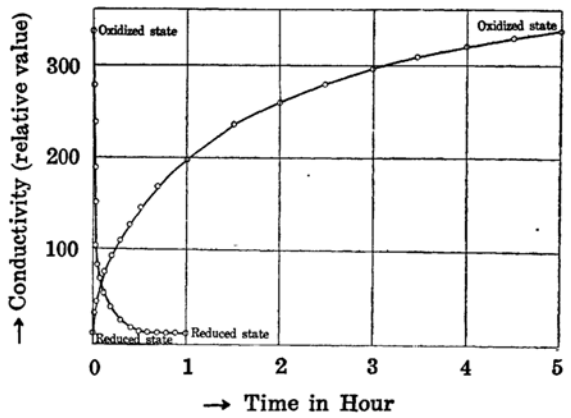


Fig. 1. Oxidation and reduction process for Ni at 250°C.

As the temperature coefficient of the conductivity is large, the conductivity-temperature relation is determined on oxidised and reduced states at constant oxygen and hydrogen pressures, respectively. The measurements show that conductivity increases with temperature and that the relation between the conductivity and the temperature is expressed exactly by the following exponential formula:

$$\sigma \propto e^{-E/RT},$$

in the oxidised as well as in the reduced state. The relation is shown in Fig. 2 and 3 by plotting the logarithm of σ against the reciprocal of the absolute temperature. The inclinations of these straight lines give the activation energies, and which are calculated to be 3.50 kcal and 6.98 kcal for oxidised and reduced states, respectively. The activation energy for reduced state is about twic that of the oxidised state.

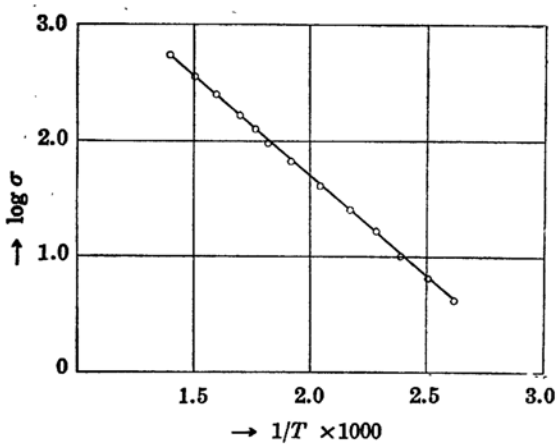


Fig. 2. Conductivity-temperature relation for oxidized Ni.

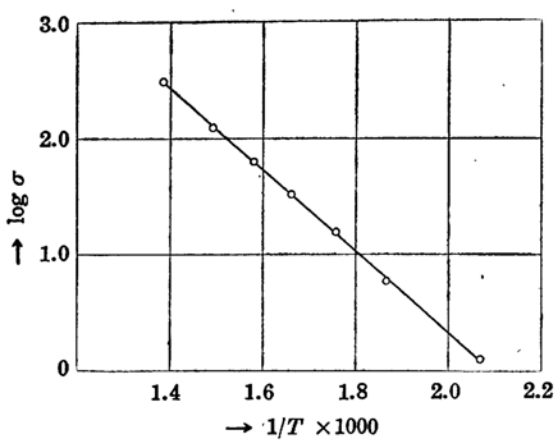
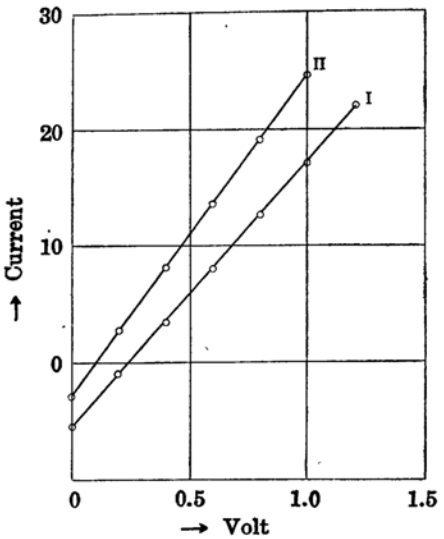


Fig. 3. Conductivity-temperature relation for reduced Ni.

In the determination of the conductivity, we must assume the Ohm's law. Here is checked the applicability of Ohm's law, both in the oxidized and the reduced Ni. The results of measurement are graphically shown in Fig. 4. In the figure, we see that the current-voltage relation is strictly linear, but the lines do not pass the origin. In both cases, the measurements were carried out after the specimen were electrolysed several hours. In the case of the oxide, $i=0$ at $V=0.24$ volt, and it shows negative current at $V=0$, while in the case of reduced Ni, $i=0$ at $V=0.1$ volt, and it also shows negative current at $V=0$. These results suggest that the electric current is at least partially conducted by the ions.



I. Oxidized state
II. Reduced state

Fig. 4. Current-voltage relation.

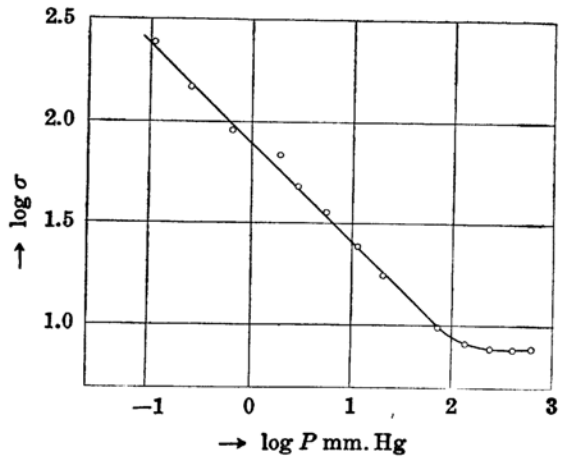


Fig. 5. Conductivity-pressure relation for Ni at 300°C.

Now, the relation between the conductivity and the hydrogen pressure will be described. As is mentioned above, the conductivity decreases as the hydrogen pressure increases. The relation between the conductivity and hydrogen pressure from 0.1 mm. Hg to 100 mm. Hg by the following formula:

$$\sigma \propto P^{-1/n},$$

where P is the pressure of hydrogen and n is a constant. The logarithm of σ and P is shown graphycally in Fig. 5, which shows that the above relation holds from 0.1 mm. Hg to 100 mm. Hg, and above 100 mm. Hg the conductivity does not change any more. In the region where the above relation holds, n is found to be 2.0. This relation gives some hints as to the mechanism of conduction and the state of the sorbed hydrogen on nickel.

Summary.

(1) The electric conductivity of such pulverized metals as Pt, Au, Ni, Co, Cu, and Ag has been measured in the atmosphere of hydrogen.

(2) The effect of hydrogen on the conductivity is characteristic for each metal, and can be classified in three types:

a) The conductivity increases as the hydrogen pressure rises:—Pt.
b) The conductivity decreases as the hydrogen pressure rises:—Ni, Co, Cu, and Ag.
c) No effect:—Au.

(3) In the case of nickel, more detailed observations were carried out as regards the oxidation and the reduction velocities, the relation between the conductivity and the temperature, the relation between the current and the voltage both in the cases of oxidized and reduced nickel, and finally the relation between the conductivity and the hydrogen pressure.

(4) A relation between the conductivity and the hydrogen pressure is expressed from 0.1 mm. Hg up to 100 mm. Hg by the following expression:

$$\sigma \propto P^{-1/n},$$

and above 100 mm. Hg a saturation in conductivity is attained.

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