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ON THE APPEARANCE OF FREE ATOMIC HYDROGEN ON THE MERCURY CATHODE AND THE MECHANISM OF THE CATHODIC REDUCTION OF WO_3

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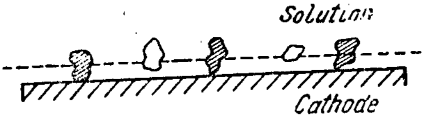
The conception of free atomic hydrogen participating as an intermediate product in reactions of cathodic reduction of dissolved substances is one frequently encountered in electrochemical literature. According to this view, it was considered that the evolution of hydrogen in the atomic or some other active state (*in statu nascendi*) constitutes the first stage which precedes its chemical interaction with the reducible substance. Molecular-kinetic considerations, howerer, lead to the conclusion that at least for those reactions that occur at potentials which are not very negative, the rôle of the free atomic hydrogen as an intermediate substance must be extremely insignificant. For instance, it is possible to calculate its equilibrium pressure according to the Nernst formula. Assuming the free energy of dissociation of the hydrogen molecules into atoms to be equal to 96700 cal./mole (1), we obtain for an electrode in equilibrium with the atomic hydrogen at pressure of one atmosphere the value of the potential equal to —2.096 V with respect to the potential of the standard hydrogen electrode in the same solution. For potentials of —0.6 and —0.8 V the equilibrium pressure of the atomic hydrogen is, consequently, equal to only $5 \cdot 10^{-26}$ and 10^{-22} atmospheres (at 25° C). Only in the event of considerable adsorption of the hydrogen atoms on the surface, is their participation in the reduction process conceivable. There is also, however, the possibility of a direct electrochemical mechanism of reduction by means of immediate interaction of the reducible substance with the electrons supplied by the surface, and—when this is necessitated by the stoichiometry of the reaction—with the hydrogen ions from the solution. Direct contact between the reducible molecules or ions and the surface of the electrode is a condition essential for the reaction to take place, whether electrochemically or through the agency of the adsorbed hydrogen atoms. The possibility of tunnel effects during electrochemical reactions will not be entered into here.

In 1930 Kobosew and Nekrassow (2) published a paper on the appearance of free atomic hydrogen during the cathodic polarization of metals in a solution of H_2SO_4. The reduction of the yellow anhydride of tungstic acid WO_3 into the blue compound of lower valency was evidence of the existence of atomic hydrogen near the cathode. The change in coloration affords a convenient means of following the process of the cathodic reduction of WO_3. The reaction imparts an uniform blue colour to the separate grains of the powdered substance, not merely to their points of contact with the electrode. Hence it follows that the WO_3 molecules which are not directly affected by the electrode surface and the hydrogen atoms adsorbed on it, also undergo reduction. To explain this phenomenon Kobosew and Nekrassow assumed the partial evaporation of the hydrogen atoms from the surface into the solution, where they retain their activity for some time. This supposition was subsequently adopted by Hickling and Salt (³) as the basis for a modified recombination theory of hydrogen overvoltage.

However, an attempt to give such an assumption a molecular-kinetic interpretation encounters serious difficulties. Thus, for example, in calculating the rate of evaporation of the hydrogen atoms from the electrode surface into vacuum, according to the formula for the number of collisions of the molecules of an ideal gas with the walls $Z=p(2\pi mkT)^{-1/2}$ and assuming the pressure p to be equal to the equilibrium pressure of the atomic hydrogen for potentials of —0.5 and —0.8 V, which is in accord with the fundamental assumptions of the recombination theory that the above-mentioned authors adopted as a basis, we obtain the values of 0.08 and 200 atoms/cm²·second for the rate of evaporation. Even smaller values are obtained when we calculate the rates of the hydrogen atoms' diffusion into the solution to a distance of the order of the thickness of the Nernst diffusion layer, beyond which transfer by convection begins. Assuming the thickness of this layer to be equal to 10^{-4} cm, the diffusion coefficient of the hydrogen atoms in the solution to be equal to 10^{-5} cm²·sec. and the solubility coefficient of the atomic hydrogen to be unity, we obtain for two above-mentioned potentials rates of diffusion of the order of 10^{-7} and 10^{-4} atoms/cm² · sec. Naturally, such insignificant rates, calculated moreover under the most favourable assumptions (absence of influence of recombination of atoms, *etc.*), exclude the possibility of the atomic hydrogen actually taking part in the process of the cathodic reduction of WO_3, which, according to the data of Kobosew and Nekrassow, proceeds quite rapidly in the specified region of potentials.



The difficulties which are encountered in explaining the cathodic reduction of tungsten trioxide can be overcome, if we take into consideration the fact that this substance possesses an appreciable electron conductivity. The electron conductivity of WO_3 has been studied by a number of workers both in this country and abroad (⁴). According to the data of Meyer and Friederich, the electronic conductivity sharply increases with the gradual reduction of this substance.

The simple experiments described below were undertaken with the purpose of elucidating the mechanism of the cathodic reduction of WO_3.

1. An individual grain of WO_3 is reduced only when in contact with the surface of the electrode at least in one point. Several grains, of the order of 1 mm in size, were fixed in the neighbourhood of the surface of the mercury electrode with the help of gauze so that part of them were in contact with the mercury, while the rest were approximately at a distance of 0.1—0.2 mm from the surface (see figure). The electrolyte was a solution of 0.2 N H_2SO_4. During the cathodic polarization of the mercury to an overvoltage value of the order of —0.8 V the entire visible surface of the particles in contact with mercury became blue after 10—20 sec., whereas the other particles which were not in contact with the electrode did not change their colour at all, even after 15 min. It can be seen from this experiment that the reduction of WO_3 is caused by a process taking place along the surface or in the bulk of the grains, but not by diffusion into the

solution of the intermediate producs of reduction formed at the surface of the cathode (*e. g.* hydrogen atoms, reduced soluble admixtures, *etc.*).

2. The reduction of an individual grain begins around the point of its contact with the surface of the electrode, but rapidly spreads over the entire surface of the grain. After a short cathodic polarization of the mercury (lasting from 2 to 4 sec.) it is possible to observe how the lower part of the grain acquires a pronounced bluish tint, while the yellow coloration of the upper part does not alter.

After the cathodic polarization was switched off, it could be seen how the blue tint spread to those parts of the moist grain's surface which were not yet reduced. During the space of 20—30 min. the grain acquired a uniform blue-green colour.

3. The spreading of the reaction of reduction in yellow tungsten trioxide without the participation of the polarized metallic electrode can also be observed if a glass tube is filled with the yellow and blue tungsten oxides in layers with a sharply defined boundary, the oxides then being slightly wetted with the electrolyte solution. After a certain time we observe the formation and spreading of a green zone in the yellow layer, the colour of the blue layer simultaneously growing lighter.

These experiments indicate that between the unchanged and the reduced parts of the surface there occur reactions as a result of which the former are partly reduced, whereas the latter are partly oxidized. At low temperatures these processes do not take place with perfectly dry specimens.

4. The oxidation-reduction reactions, mentioned in § 3, are accompanied by a transition of electrons from the reduced to the oxidized sections. This can be demonstrated, if the yellow and blue tungsten oxides, pressed into tablets, are partly submerged in an electrolyte solution (an acidified solution of KCl or a solution of H_2SO_4). Immediately after the dry parts of the tablets are connected by means of a metal wire, the yellow tablet begins to acquire a bluish tint. A galvanometer inserted in the circuit shows the existence of a rather strong current (under the conditions of our experiment, of the order of 10^{-5}A).

This current in the external circuit serves as an indication of electrode reactions which take place on the boundaries of the oxide tablets and the solution and which are responsible for the observed changes in colour and composition. These reactions can proceed according to the following scheme, for instance:

$$2WO_3 + 2H^{\cdot} + 2e \rightleftarrows W_2O_5 + H_2O$$

The mechanism of the propagation of the reaction along the surface is thus determined by the movement of the electrons inside the WO_3 particles and by the movement of the hydrogen ions in the solution*.

Many authors believe in a more complicated composition of the blue tungsten oxide, for example W_4O_{11}(⁵). However, this cannot have any effect on the conclusions arrived at here.

When a tablet of pressed yellow WO_3, partly submerged in the solution, is subjected to cathodic polarization by means of an external source of electric current, we observe an instantaneous change of colour of the wetted part of the tablet which becomes blue.

The conclusion to be drawn from these experiments is that the reduction of the tungsten trioxide powder is a specific electrode reaction, made possible owing to the electron conductivity of the WO_3 and does not require the participation of free atomic hydrogen. The reaction of reduction is transmitted from each grain to those in contact with it by means of the action of local elements.

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* A rough determination of the potentials of the yellow and blue oxide tablets showed that the value of the first potential was 0.1—0.2 V more positive, and of the second, 0.1—0.2 V more negative than the potential of the normal calomel electrode.

In all probability the reaction of the reduction of WO_3 occurs with considerable kinetic hindrance which can partly be ascribed to purely physical causes (high resistance to electron transitions between the separate microcrystals forming aggregate-grains, poor contact between the grains and the surface of the electrode, *etc.*) and can partly be associated with the elementary mechanism of the electrode process itself which has not been studied up to the present. This accounts for the fact that, despite the comparatively positive value of the equilibrium potential, a marked cathodic polarization is required for the noticeable reduction of the powder. The relation between the intensity of reduction and the cathode potential was discussed already by Kobosew and Nekrassow, but these authors explained it by an increase of the emission of atomic hydrogen with the growth of the negative potential.

The experiments described and considerations put forward in the present paper do not as yet solve the problem of the mechanism of the propagation of the reduction reaction into the lattice of the separate microcrystals.

By simple grinding of the reduced grains into a powder it can be shown that the reaction of reduction is not confined to the surface of the individual particles. The necessity of explaining this phenomenon is not removed by any interpretation of the mechanism of the propagation of the zone of reduction over the surface.

A number of properties of WO_3 point to the comparatively easy mobility of the atoms (or ions) of oxygen inside the lattice:

a) reduction by molecular hydrogen in the gaseous phase begins at a comparatively low temperature (about 120° C); the oxidation of the powder slightly reduced on the cathode and dried in hydrogen begins at a sti lower temperature (85° C);

b) when pure WO_3 is heated *in vacuo* to 200—250°, a blue colour is imparted to the powder, this colour growing in intensity with the decrease of the oxygen content.

This mobility of the oxygen leads to the assumption that in the microcrystal being reduced from the surface there is a diffusion of the oxygen from the middle to the surface. Owing to the small dimensions of the microcrystals (of the order of 10^{-4} mm), this diffusion can proceed at a considerable rate and lead to a noticeable change in the composition of the lattice. It must also be taken into account that as reduction proceeds, there is a possibility of the loosening of the surface structure of the separate crystallites facilitating the penetration of the solution through micropores and even into the crystal lattice. This in turn increases the surface of contact between the powder and the solution and facilitates further reduction.

All observations on the reduction of tungstic trioxide WO_3 near the polarized electrode with high overvoltage can thus be explained without difficulty, if due consideration is given to the electron conductivity of WO_3 and especially of its reduction products. The explanation of these observations does not involve the assumption about the appearance of free atomic hydrogen in the solution near the cathode.

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