OXIDATION: DISCUSSION

Mechanism of Electrochemical Oxidation by V. I. Veselovskii

A. L. Shlygin. The report of V. I. Veselovskii on the reactivity of adsorbed oxygen or oxides is very interesting. We also have a considerable amount of accumulated material on the reactivity of adsorbed oxygen. Thus, if the potential is not raised above 1.3 v, then the adsorbed oxygen is found to have a low activity. We studied its activity with respect to many substances and convinced ourselves that the oxidation proceeds at a very low rate. However, it seems to me that oxidation proceeds at a satisfactory rate in this potential region not due to adsorbed oxygen, but due to hydroxyl radicals. I cannot object to the second thesis of V. I. Veselovskii on the high activity of oxides formed at high anode potentials. It is possible that this is actually so.

There has been some discrepancy in the points of view in the present discussion on the mechanism of electrooxidation.. I consider that some discrepancy in opinions is quite natural in connection with the unsatisfactory state of the theory of electro-oxidation and only closer and more continuous contact between investigators is required.

A. N. Frumkin. I am not quite clear what physical meaning V. I. Veselovskii attributes to the additional term in the expression for overvoltage. At constant solution concentration and without allowance for the dipole nature of the surface oxides, this expression may be written in the following form:

$$\eta = \frac{RT}{\alpha F} \ln i + A.$$

The additional term may appear as a result of allowance for the structure of the electrical double layer. It is easily shown that in the case of oxidation reactions, $A = (\beta + n/\beta)_{\psi_1}$, where n is the charge of the reacting particle and ψ_1 is the potential at a distance from the electrode surface equal to its radius. In a one-electron transfer, $0 < \beta < 1$. Let us examine from this point of view the solution of platinum in HCl, to which electrostatic ideas were first applied in a somewhat different form by B. V. Ershler. According to the latter author, the rate of anode solution of platinum in HCl is determined by the discharge of Cl^- ion; thus, in this case $n = -1$. If we consider that $\beta = 1/2$, then A equals $-\psi_1$. The appearance of an oxide film makes the ψ_1 potential more negative and consequently it must increase η, i.e., retard the reaction. The objection that such an effect should disappear at a sufficiently high total concentration is probably eliminated by the fact that in a more strict treatment, the expression for η should contain the ψ_1 potential at a point at the center of the charges of the transition complex*; the latter lies closer to the electrode surface than the center of the reacting particle in its initial position, which leads to an increase in the effective value of ψ_1.

Another possible interpretation of the physical meaning of the term A refers to a reaction on a partly filled surface when this term allows for the decrease in adsorption energy of the reaction product as the surface is filled. This treatment of the problem was first given in the work of A. N. Frumkin and N. A. Aladzhalova. A similar interpretation was recently used by Delahay to explain the sharp increases in overvoltage during the liberation of oxygen on platinum. As follows from the theory of M. I. Temkin, if the discharge occurs on a heterogeneous surface to which the logarithmic adsorption isotherm applies, then the term A expresses the displacement of the equilibrium potential of the adsorbed layer of reaction product as the filling of the surface increases. It seems to me that the falls in current on anode polarization curves on a Pt electrode are produced mainly by changes in

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*In rejecting the simplifying assumptions which are normally made in the derivation of the relation of the slow discharge theory, it may be stated that the value of i is expressed by the product of some function $f(\varphi - \psi_1)$ and the concentration of the transition complex, which is proportional to $(-n\psi_1 F)/(RT)$.

adsorption energy; in any case, the electrostatic interpretation is not applicable to the liberation of oxygen from water molecules since when n = 0, $A = \psi_1$ and consequently, a displacement in ψ_1 in a negative direction should produce a fall rather than an increase in η. In other cases, for example, in the oxidation of molecular hydrogen on a Pt electrode, the fall in current is also produced by a change in the adsorption energy of the product, which is formed, however, as a result of not an electrochemical, but a purely chemical stage of the process $H_2 \rightarrow 2H_{ads}$.

I would like to issue a warning against an inaccurate understanding of the meaning of relation (1) in its second interpretation. This relation may also be written in the form:

$$\eta = \eta_1 + \eta_2 \qquad (2)$$

where η_1 is the overvoltage of discharge on an unfilled surface and η_2 is the reduction in adsorption energy due to filling of the surface. As was pointed out above, the term η_2 may be roughly interpreted as the equilibrium potential of the surface reaction products, i.e., as the overvoltage produced by their slow removal. The value of η_2 may be much greater than that of η_1 as is probably observed in the liberation of oxygen on platinum at high current densities. However, this does not give grounds for considering that the measured potential of an electrode may be regarded as the equilibrium potential of the adsorbed layer or surface compounds. The latter would be correct if the rate of the reaction opposite to the discharge reaction were close to the rate of the forward reaction, which is possible only when $\eta_1 \ll RT/F$. If, as is normally the case, $\eta_1 > RT/F$, i.e., the discharge stage is irreversible despite the slowness of removal, then the measured overvoltage should be regarded as the overvoltage of discharge on a partly filled surface, which is only expressed in the form of the sum $\eta_1 + \eta_2$ as a result of some mathematical transposition. The irreversibility of the discharge stage in the case of oxygen liberation on platinum from acid solutions is confirmed by the absence of exchange between the surface layer and the water of the solution, which was observed by M. A. Gerovich and R. I. Kaganovich in the liberation of O_2 from a solution of perchloric acid labeled with O^{18} under conditions when ClO_4^- anion participates in the anode process.

Mechanism of Electrooxidation of Some Compounds on Platinum by A. I. Shlygin and G. A. Bogdanovskii

A. P. Tomilov. As a rule, the anode oxidation of organic substances is accompanied by the formation of not one product, but a series of substances so that it is extremely difficult to describe the processes occurring by one simple stoichiometric equation. This characteristic was first pointed out by Bunge in the last century in a study of the electrolysis of carboxylic acids. For example, acetic acid yields ethane, methane, methyl acetate, ethylene, and other products. Available literature data on the quantitative and qualitative composition of substances formed by anode oxidation of organic materials are not systematic and are frequently contradictory. From what has been said it is clear that for an accurate understanding of anode oxidation of organic substances it is necessary to use modern methods of physicochemical investigation and complete qualitative and quantitative analysis of all the products formed is essential.

In this connection, some comment should be made on the work of A. I. Shlygin and G. A. Bogdanovskii. The authors consider that alcohol is oxidized on the anode to aldehyde, which is then oxidized to acetic acid. This is reasonable from the point of view of organic chemistry, but according to the literature, in addition to acetaldehyde and acetic acid, the anode oxidation of ethanol forms methane, ethane, ethylsulfuric acid, and other products. It is clear that the mechanism proposed by A. I. Shlygin for the oxidation of ethanol is only an approximate scheme and cannot represent completely the actual, more complex process occurring on the anode.

A. I. Shlygin. The following should be said on the treatment of the fall in polarizing current at a definite potential observed in the electrooxidation of alcohol and sulfur dioxide.

In our opinion, this fall is connected with the fact that the oxidation of alcohol yields acetaldehyde, which partly displaces alcohol molecules from the surface and thus retards the electrooxidation of the latter. The accuracy of this hypothesis is demonstrated conclusively by the fact that the addition of acetaldehyde to the alcohol actually produces a sharp fall in the current strength. We attempted to show that adsorbed oxygen is absent in this potential region. As is known, oxygen gives to platinum a potential of 1 v. Hence, if the observed current fall is connected with the formation of an oxygen film, then switching off the current should lead to a displacement of the potential by not more than 1 v. This is not confirmed by experiment. If the current is switched off, the potential is instantaneously displaced in a negative direction by 0.4 v, which unequivocally demonstrates the complete absence of oxygen. It should also be noted that maintaining the electrode at a constant potential for some time leads to a continuous fall in current strength, which is readily explained by the accumulation of acetaldehyde but is difficult to explain by the presence of oxygen. In the case of SO_2, we adhere to the hypothesis that the fall in current is produced by the appearance of adsorbed oxygen because its presence may be demonstrated by the given method. However, I would like to present yet another clear demonstration. If platinum is poisoned with mercury, the electrooxidation of SO_2 proceeds well. At a certain potential there is also a fall in polarization current and the electrode becomes black, indicating its oxidation. This is quite a conclusive demonstration of the fact that we are dealing with oxygen here. The electrooxidation of alcohol cannot be represented as dehydrogenation as this is improbable at normal temperature and, in addition, the beginning of electrooxidation in this case should be observed at a potential indicating the presence of hydrogen.

A. N. Frumkin. In connection with the interpretation of the current fall on the polarization curves of alcohol oxidation given by A. I. Shlygin, I would like to point out that similar current falls are also observed when these curves are plotted on a rotating electrode under strictly stationary conditions, as follows from the article submitted to the Journal of Physical Chemistry, Akad. Nauk SSSR by U. V. Pleskov and E. A. Aikazyan. Elementary calculation shows, however, that the appearance of a maximum and a current fall on the polarization curve under stationary conditions cannot be explained by retardation of the process as a result of the accumulation of reaction products. I consider that the anomalous form of the polarization curves in the anode oxidation of alcohol is connected with the appearance of chemisorbed oxygen or oxide films on the platinum surface.

Mechanism of Anodic Discharge in the Electrolysis of a Cryolite - Alumina Melt by V. P. Mashovets and A. A. Revazyan

S. I. Rempel'. V. P. Mashovets expressed the opinion that ion exchange between the carbon anode and the electrolyte melt is produced by carbon ions, which have semiconductor properties. However, I would like to note that there is no need to resort to additional hypotheses. The ion exchange may be explained more simply. In the electrolyte there are oxygen-containing ions and in the carbon anode, chemisorbed oxygen in the form of carbon-oxygen complexes. Thus, ion exchange is achieved by transfer of oxygen.

Study of the Mechanisms of the Electrochemical Formation of Oxygen Compounds of Chlorine by Polarography by T. S. Filippov and E. I. Yakovleva

G. A. Tedoradze. In connection with the work of T. S. Filippov and E. I. Yakovleva, I should point out that we investigated the oxidation of Cl^- in HCl solutions with concentrations of 0.003 to 0.12 M. H_2SO_4 and $HClO_4$ solutions were used as indifferent electrolytes. Anode polarography on a rotating disk electrode (rotation rate from 26 to 1200 rev/min) gave the following results.

The form of the polarogram depended both on the concentration of chlorine ions and the rotation rate of the electrode. If the Cl^- ion concentration was low (about 0.01 M), then the polarogram at low acidity was a curve with an inflection at a potential of 1.65 v, while a plateau appeared at these potentials at high acidities. The form of the curve was independent of stirring at low Cl^- ion concentrations, but changed with an increase in the Cl^- ion concentration. At high electrode rotation rates, the curve showed a characteristic "hump"; the "hump" disappeared with a decrease in the rotation rate, and a plateau appeared with the whole of the curve displaced in an anodic direction. Hysteresis was observed with the voltage applied in the opposite direction, and this was more sharply expressed, the higher the potential at the beginning of the reverse plot. A linear relation was found between the maximum current and the Cl^- ion concentration over the range of 0.03 - 0.12 M with an accuracy of 5%. A change in pH had a strong effect on the maximum current. It increased in proportion to the square root of the H^+ ion concentration. Electrolysis products of HCl, ClO_3^- and ClO_2^- ions, were determined by the method proposed by Bilyk. The data we obtained apparently do not conform the hypothesis of T. S. Filippov on the mechanism of Cl^- ion oxidation. In actual fact, if the reaction proceeds by the mechanism proposed by T. S. Filippov through oxygen compounds of platinum, then it is incomprehensible why the accumulation of adsorbed oxygen hampers the oxidation of Cl^- ions, as follows from our data. Even if this is explained by an increase in the strength of the bond of oxygen with platinum, then it remains incomprehensible why the rate of Cl^- ion oxidation increases with an increase in the acidity of the solution; an increase in acidity does not promote the formation of adsorbed oxygen atoms. This is also incomprehensible after the explanation given by V. I. Veselovskii.

As regards the formation of ClO_3^- ion, the mechanism proposed by T. S. Filippov is not sufficiently accurate. Let us actually examine two mechanisms for the oxidation of Cl^- ions:

DISCUSSION

According to T. S. Filippov, the first reaction proceeds in dilute solutions and the second, in more concentrated solutions. Our data also confirm this. However, if this is so then it is evident that in the formation $HClO_3$, each chlorine atom requires six times as much oxygen as in the oxidation of Cl^- ion to chlorine atoms. Consequently, the relation of the current strength to the concentration of chlorine ions should be approximately that which is illustrated in Fig. 1.

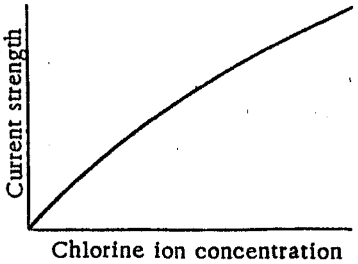

Fig. 1. Relation of current strength to Cl ion concentration.

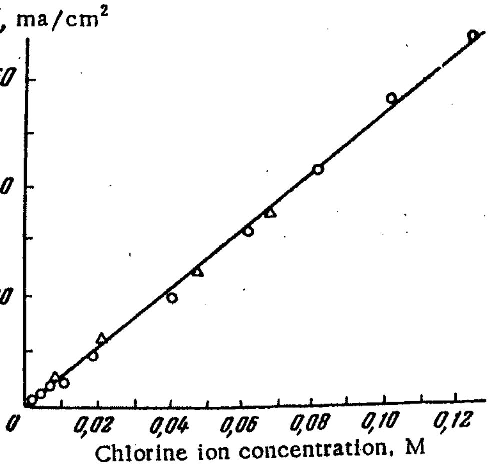

Fig. 2. Relation of maximum current to Cl ion concentration. Base electrolyte: O – 0.645 N H_2SO_4, pH 0.91; Δ – 0.154 N $HClO_4$, pH 0.92.

At low HCl concentrations, the current should be somewhat greater than corresponds to a linear relation as six times as much oxygen is consumed per chlorine atom as in electrolysis in more concentrated solutions. However, we obtained an almost linear relation by means of polarography (Fig. 2). If the polarization curves are measured at constant potential, then the opposite picture to that in Fig. 1 is obtained. The curve is concave in the opposite direction. This is undoubtedly connected with stronger passivation of platinum in solutions with a low concentration of Cl ions. (Fig. 3).

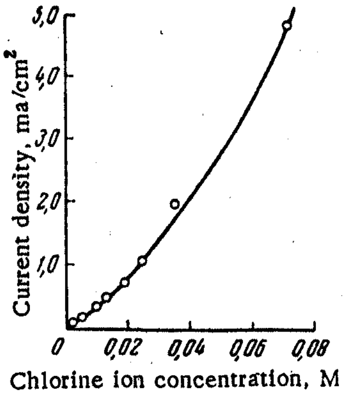

Fig. 3. Relation of current density to chlorine ion concentration.
m = 150 rev/min, φ = 1.010 v.

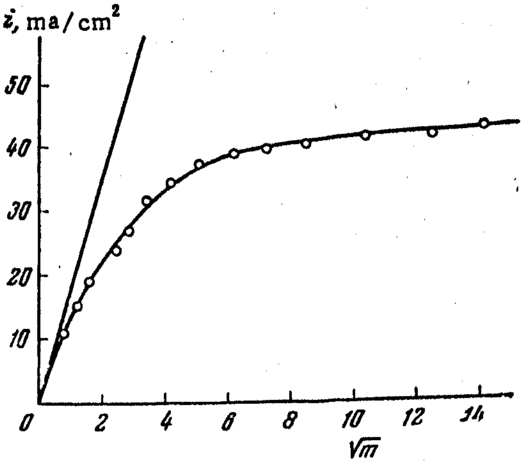

Fig. 4. Relation of maximum current to the square root of the number of electrode rotations (m) per sec.

DISCUSSION

In the light of the facts presented, it seems probable that the maximum on a polarogram of Cl^- ion oxidation has a complex character and is the result of the superposition of the hindering process of adsorbed oxygen formation on the oxidation of Cl^- ions.

With weak stirring, the oxidation of Cl^- ions is also hindered by the accumulation of elementary chlorine on the electrode. If it is considered that the formation of $HClO_3$ is due to the decomposition of water, i.e., is the result of the reaction

$$6Cl + 3H_2O \rightarrow ClO_3^- + 6H^+ + 5Cl^-,$$

then this eliminates the difficulties mentioned above, which were associated with the fact that the current is linearly dependent on the Cl^- ion concentration right down to very low concentrations. Finally, it should be noted that T. S. Filippov's comments on the Heyrovsky equation are incorrect as this equation is accurate only for reactions occurring in the diffusion region, while the oxidation of chlorine ions proceeds in the kinetic region under the conditions of stirring used by T. S. Filippov (Fig. 4).