Physical Chemistry

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1965

SovietRxiv

Abstract

Full Text

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Kinetics of Hydrogen Oxidation on Clean Platinum Surfaces

In a previous communication (^{1}) we described certain kinetic regularities observed in the oxidation of hydrogen on clean Pt and Pd surfaces, and proposed an equation for the reaction rate in the form

$$w = \frac{k a_{O_2}^m P_{O_2}^m a_{H_2}^n P_{H_2}^n}{\left(1 + a_{O_2} P_{O_2} + a_{H_2} P_{H_2}\right)^{m+n}}, \tag{1}$$

which describes the passage of the reaction rate through a maximum when the composition of the mixture is changed, a phenomenon first observed in the work of Boreskov and coworkers (^{2}).

Further study of the kinetics confirmed the applicability of this equation to the reaction on Pt and Pd and made it possible to give it a more definite form suitable for experimental verification.

The specific form of equation (1) does not allow one to determine the values of the exponents m and n at comparable pressures of the components; therefore it was necessary to study the reaction kinetics, respectively, at a large excess of H_2 and a large excess of O_2. In this case the denominator of equation (1) and the partial pressure of the component present in excess, which stands in the numerator, remain practically constant during the experiment. The only variable quantity under these conditions is the partial pressure of the other component, which makes it possible to determine the value of the corresponding exponent.

Fig. 1. Reaction kinetics at different mixture compositions:
I $-P_{H_2} = 2P_{O_2}$; II $-P_{O_2}$ (excess) $= 0.5 \cdot 10^{-2}$ mm Hg; III $-P_{O_2}$ (excess) $= 8 \cdot 10^{-2}$ mm Hg; IV $-P_{H_2}$ (excess) $= 4.5 \cdot 10^{-2}$ mm Hg.

We followed the course of the reaction from the decrease in the pressure of the gas mixture, which was measured with a Pirani manometer and automatically recorded by an EPP-092M one-second potentiometer. The inertia of the system was determined with a Pirani manometer and was equal to 2–3 sec. Figure 1

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Fig. 2. Scheme of the transition complex

Figure 2: Fig. 2. Scheme of the transition complex

shows typical kinetic curves obtained in excess H_2 (IV) and O_2 (III). In these experiments, the excess gas was first introduced into the reaction vessel, and then at the moment $\tau = 0$ a definite portion was admitted.

of the stoichiometric mixture $H_2 + O_2$, to which the initial rise in pressure corresponds. The slowing of the rise in the region of the maximum and the fall of the curve after it occur as a result of the catalytic reaction. By graphical differentiation of the curves obtained, the values of m and n were calculated; they proved to be very close, respectively, to 1 and 2.

From our adsorption and catalytic data it follows that $a_{\mathrm{O2}}P_{\mathrm{O2}} + a_{\mathrm{H2}}P_{\mathrm{H2}} \gg 1$; therefore we finally arrive at the equation:

$$w = \frac{ka_{\mathrm{O2}}P_{\mathrm{O2}}a_{\mathrm{H2}}^2P_{\mathrm{H2}}^2}{\left(a_{\mathrm{O2}}P_{\mathrm{O2}} + a_{\mathrm{H2}}P_{\mathrm{H2}}\right)^3}. \tag{2}$$

Fig. 2. Scheme of the transition complex

Since P_{O2} and P_{H2} enter this equation with integer powers, its simplest interpretation reduces to the assumption that undissociated molecules participate in the stepwise mechanism.* In this case two variants are possible: (a) interaction of two H_2 molecules and one O_2 molecule adsorbed on the same or on neighboring centers, and (b) preliminary formation of a reversible surface complex $H_2 \cdot O_2$, which then reacts with $H_{2\,\mathrm{ads}}$.

In both cases the activated complex of the rate-controlling step includes two H_2 molecules and one O_2. It may be represented, for example, by the scheme shown in Fig. 2. In the second variant it is easier to explain the formation, observed by some authors ([3]), of appreciable amounts of H_2O_2. This mechanism is described by the following stages:

Fig. 3. Straightening of curves III and IV of Fig. 1

Figure 3: Fig. 3. Straightening of curves III and IV of Fig. 1

Fig. 4. Dependence of the initial reaction rate on an Ag film on the mixture composition at 400°C

Figure 4: Fig. 4. Dependence of the initial reaction rate on an Ag film on the mixture composition at 400°C

Fig. 3. Straightening of curves III and IV of Fig. 1

Fig. 4. Dependence of the initial reaction rate on an Ag film on the mixture composition at 400°C

$$H_2 \xrightarrow{k_1} H_{2\,\mathrm{ads}};$$

$$O_2 \xrightarrow{k_2} O_{2\,\mathrm{ads}};$$

$$H_{2\,\mathrm{ads}} + O_{2\,\mathrm{ads}} \underset{k_3'}{\overset{k_3}{\rightleftharpoons}} H_2 \cdot O_{2\,\mathrm{ads}};$$

$$H_2 \cdot O_{2\,\mathrm{ads}} + H_{2\,\mathrm{ads}} \xrightarrow{k_4} 2H_2O_{\mathrm{ads}} \rightarrow 2H_2O;$$

$$H_2 \cdot O_{2\,\mathrm{ads}} \rightarrow H_2O_{2\,\mathrm{ads}} \rightarrow H_2O_2.$$

* If the reaction components participate in the form of atoms, then for second order with respect to H_2 and first order with respect to O_2 the corresponding transition complex would have to be formed from 4 H atoms and 2 O atoms, which is unlikely.

Applying to these stages the method of steady-state concentrations and taking into account that $k_4 \ll k_3''$ (4), we obtain the following expression for the rate:

$$w = \frac{k_3' \cdot k_4}{k_3''}\,[\mathrm{H_{2ads}}]^2 \cdot [\mathrm{O_{2ads}}]. \qquad (3)$$

Substituting into it the values of the surface concentrations of H_2 and O_2 from the Langmuir equation, we arrive at equation (2). At high coverages, a similar result is also obtained for broadly heterogeneous surfaces (5).

This equation describes well the following regularities observed by us:

1. The dependence of the rate only on the ratio of the partial pressures of the components, and not on their absolute values. This is easily verified if the numerator and denominator are divided by P_{H2}^3 and the ratio $P_{\mathrm{O2}}/P_{\mathrm{H2}}$ is replaced by Z:

$$w = \frac{k a_{O2} a_{H2}^2 Z}{(a_{O2} Z + a_{H2})^3}. \tag{4}$$

The resulting equation does not contain the pressures of the individual components.

2. Passage of the reaction rate through a maximum at a certain ratio P_{O2}/P_{H2} constant for a given temperature. Several experimental examples of this were given in the preceding communication (1). Indeed, setting the derivative of the right-hand side of equation (4) equal to zero, we obtain the condition for the maximum rate in the form:

$$(P_{O2}/P_{H2})_{\max} = a_{H2}/2a_{O2} = \text{const.}$$

At $T = 293$°K, the experimental value $(P_{O2}/P_{H2})_{\max} \simeq 3$.

3. Zero order of the reaction for a stoichiometric mixture (see curve I in Fig. 1). It follows directly from equation (4), since in this case $Z = \text{const}$.
4. Acceleration of the reaction and its subsequent slowing with a small excess of oxygen (curve II in Fig. 1). This effect is explained by the fact that, in the course of the reaction, the ratio P_{O2}/P_{H2} in a mixture with an excess of oxygen increases, which should cause an increase in the rate up to the maximum and its subsequent decrease.
5. Slowing of the reaction in an excess of either component (curves III and IV in Fig. 1), which also follows directly from equation (4). These curves, as is evident from Fig. 3, are well straightened by means of expressions obtained by transformation of equation (2):

$$\sqrt[3]{1/k_1^2 Z^2 w} = (1 + 1/k_2 Z) \quad \text{(with excess H}_2\text{, straight line 1)},$$

$$\sqrt[3]{k_1 Z/w} = (1 + k_2 Z) \quad \text{(with excess O}_2\text{, straight line 2)},$$

where $k_2 = a_{O2}/a_{H2}$, $k_1 = kk_2$.

In contrast to Pt, silver in the form of clean degassed films and wires catalyzed the reaction $H_2 + O_2$ only at elevated temperatures; moreover, the same dependence of the initial rate on the ratio P_{O2}/P_{H2} as for Pt and Pd was observed (Fig. 3).

The maximum of the reaction rate on Ag upon changing the composition of the mixture, but with the condition $P_{O2} + P_{H2} = \text{const}$ maintained, was observed earlier by Pshezhetskii and Vlodavets (6). With independent variation of P_{O2} and P_{H2} (as in our experiments), the reaction mechanism proposed by these authors would not give a maximum of the rate.

Analysis of the literature data shows that kinetics analogous to ours has also been observed for some other reactions on massive pure metals: the interaction of CO with O_2 (7), H_2 with CO_2 (8), and NH_3 with NO (9) on Pt; isotope exchange of NH_3 with D_2 on Fe (10); and ortho-para conversion of H_2 on elements of the first transition series (11). However, in most studies on the oxidation of H_2 on Pt carried out under less pure conditions (with possible influence of mercury vapors, grease, etc.), different kinetic dependences were obtained. The presence of major contradictions in the results of these studies gives grounds to regard factors of this kind as an important reason for the discrepancy with our data. With partial poisoning of the surface, other centers may operate, and a change in the rate-controlling step is possible. This is supported by the difference in the magnitudes and character of the isotope effects for hydrogen. Thus, in separately conducted oxidation of D_2 and H_2 without sufficient protection from grease and mercury vapors, $w_{D2}/w_{H2} = 1$ (12), whereas in our experiments $w_{D2}/w_{H2} = 2$, i.e., an inverse isotope effect is observed.

It should be noted that the appearance of regularities similar to those observed in this work is, in principle, also possible owing to mutual compensation of surface charges caused by adsorbed particles of different polarity. The resulting change in the catalyst work function may acquire independent significance.

A more detailed analysis of this question, as well as of the temperature dependence of the rate and other kinetic characteristics of the reaction, is impossible within the scope of this publication.

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Received
29 I 1965

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Note: Figure translations are in progress. See original paper for figures.