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## Abstract

## Full Text

# PHYSICAL CHEMISTRY

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# ON THE KINETICS OF THE DECOMPOSITION OF ALKALI-METAL AMALGAMS IN BUFFER SOLUTIONS

It was shown earlier (1) that the rate of the reaction of decomposition of alkali-metal amalgams by electrolyte solutions with a high pH value ($> 10$), in the absence of catalytically active impurities, does not depend on the composition, concentration, or pH of the solution, and is determined only by the concentration of the amalgam, obeying the kinetic equation:

$$i = kC_{\text{am}}, \tag{1}$$

where $i$ is the rate of decomposition of the amalgam, A/cm$^2$; $C_{\text{am}}$ is its concentration, g-eq/l; $k$ is a constant. These facts led to the conclusion that, in a strongly alkaline medium, decomposition of amalgams proceeds by direct interaction of the metal atoms of the amalgam with water molecules without separation of the cathodic and anodic processes, which occurs only in the presence of impurities that lower the hydrogen overvoltage.

Fig. 1. Curves $\varphi$—lg $i$ for potassium and mercury amalgams, obtained in 0.33 *N* phosphate buffer solutions: 1 —pH 9.8; 2 —pH 9.0; 3 —pH 7.9; 4 —pH 7.0; 5 —pH 6.7; 6 —pH 6.1; 7 —pH 4.6

On the other hand, according to literature data (2), the decomposition of dilute amalgams in buffer solutions with pH $\sim$ 7-9 obeys the Brønsted-Kane equation

$$i = kC_{\text{am}}^{0.5}, \tag{2}$$

Fig. 2 and Fig. 3

Figure 2: Fig. 2 and Fig. 3

which is readily derived on the basis of electrochemical concepts ([3,4]). It therefore seemed essential to determine whether there is a real difference in the mechanism of decomposition of amalgams at higher and lower pH values, or whether the decomposition of amalgams by an electrochemical mechanism in the cited studies depended only on the presence of catalytically active impurities. To clarify this question, we carried out an investigation of the kinetics of decomposition of potassium amalgams in 0.33 *N* phosphate buffer solutions in the pH range 7-10, using a procedure for purifying the solutions and amalgams and for measuring the decomposition kinetics that practically did not differ from that described in ([1]). The buffer solutions were prepared by mixing the necessary quantities of 0.33 *N* solutions of KOH and $KH_2PO_4$. The polystyrene apparatus in which the measurements were made was analogous to that used in work ([1]), but had smaller dimensions: solution volume 100 ml, amalgam surface area 4.5 $cm^2$, temperature $20 \pm 1°C$.

The data we obtained on the rate of decomposition of K amalgams of various concentrations (from 0.02 to 1.4 *N*) in 0.33 *N* phosphate buffer solu-

solutions (pH 7-10) are presented in Fig. 1 in the coordinates: amalgam potential with respect to N.C.E.—logarithm of the decomposition current density (curves 1-4). In more acidic buffer solutions we also carried out direct polarization measurements of hydrogen evolution on mercury (curves 5-7).

As is seen from Fig. 1 (curves 2-4), between the potentials of the amalgams and the logarithms of the rates of their decomposition there is a Tafel dependence with a slope coefficient $b$ close to 0.115 V. An analogous dependence is also observed in acidic buffer solutions during cathodic polarization of mercury (curves 5-7), and at high current densities K amalgam begins to form. In this case the polarization curve was recorded by the procedure described in ([5]). The probable reason for the break in curve 1 will be discussed below.

Fig. 2. Dependence of the electrode potential on pH at $i = 10^{-4}$ A/$cm^2$: 1—our data; 2—data of Bagotskii and Yablokova

Fig. 3. Dependence of the logarithm of the hydrogen-evolution current density on the pH of the buffer solution at $\varphi = -2.100$ V: 1—points obtained on K amalgams; 2—on mercury

The data of Fig. 1 were used to construct Figs. 2 and 3. Fig. 2 presents the dependence of the electrode potential on the pH of the solution at $i = 10^{-4}$ A/$cm^2$. For comparison, the same figure gives analogous data obtained earlier by V. S. Bagotskii and I. E. Yablokova ([6]) in polarization measurements in acidic buffer solutions prepared by adding HCl to a 0.3 *N* solution of $K_3PO_4$. As can be seen, these data are very close to those obtained by us.

Examination of Fig. 2 shows that there is a continuous rectilinear dependence between the electrode potential at $i = \text{const}$ and the pH of the solution up to pH $\sim 10$, with a slope close to the theoretical value of 0.111 V. This means that both in an acidic medium on mercury and in a moderately alkaline medium on amalgams, the discharge of $H_3O^+$ ions proceeds by an electrochemical mechanism, while the rate of discharge is determined by the magnitude of the hydrogen overvoltage on mercury under the given conditions. The preservation of a constant slope of the straight line $\varphi$–pH ($i = \text{const}$), as well as of the straight lines $\varphi$–$\lg i$ (curves 5-7 in Fig. 1), up to high current densities also shows that the alkali metal dissolved in mercury does not substantially affect the magnitude of the hydrogen overvoltage. Analysis of the curve in Fig. 2 leads to the conclusion that up to pH $\sim 10$ neither buffer anions nor water molecules participate directly in the electrode process. The discharge of the latter, apparently, occurs only at more negative potentials, attained, for example, during cathodic polarization of mercury in solutions of tetraalkylammonium salts ($^7$).

Fig. 3 illustrates the dependence of the logarithm of the hydrogen-evolution current density during polarization of mercury and during decomposition of K amalgams in buffer solutions on the pH of the solution at $\varphi = \text{const}$. As is seen from the figure, there is a direct proportionality between the rate of hydrogen evolution

hydrogen (including during decomposition of the amalgam) and by the concentration of $H_3O^+$ ions. As follows from the theory of delayed discharge, an increase in the total electrolyte concentration at pH = const should increase the hydrogen overvoltage and decrease the rate of discharge of $H_3O^+$ ions, since the negative value of the $\psi_1$-potential decreases. The experiments whose results are given in Table 1 confirmed this conclusion*.

**Table 1**

| Composition of solution | pH | $C_{\text{am}}(N)$ | $-\varphi$ | $-\lg i$ |
|---|---|---|---|---|
| 0.1 $N$ (KOH+ $KH_2PO_4$) | 7.6 | 0.048 | 2.130 | 3.31 |
| 0.1 $N$ (KOH+ $KH_2PO_4$)+ 1.25 $N$ KCl | 7.6 | 0.044 | 2.062 | 4.10 |

Thus, the kinetics of decomposition of alkali-metal amalgams in buffer solutions with pH $< 10$, in agreement with the literature data, depends not only on the concentration of the amalgam, but also on the composition, concentration, and pH of the solution, and obeys regularities derived on the basis of the assumption of an electrochemical mechanism of the process. On the other hand, as was shown in ($^1$), in a strongly alkaline medium a chemical reaction takes place between the metal of the amalgam and water molecules. The difference in mechanisms leads to a difference in the kinetic equations (1) and (2). In order to give a general picture of the process of decomposition of alkali-metal amalgams in aqueous solutions, it may be assumed that at any pH value two independent and simultaneous reactions occur:

a) an electrochemical reaction consisting of coupled stages—the ionization of the metal of the amalgam:

$$\mathrm{MeHg} \rightleftarrows \mathrm{Me}^+ + \mathrm{e}^- + \mathrm{Hg} \tag{3a}$$

and the irreversible stage of discharge of $H_3O^+$ ions:

$$\mathrm{H_3O^+} + \mathrm{e}^- \rightarrow \tfrac{1}{2}\mathrm{H_2} + \mathrm{H_2O}; \tag{3b}$$

b) a chemical stage proceeding in a single act according to the scheme:

$$\mathrm{MeHg} + \mathrm{H_2O} \rightarrow \mathrm{Me}^+ + \tfrac{1}{2}\mathrm{H_2} + \mathrm{OH}^- + \mathrm{Hg}. \tag{4}$$

The kinetic equation for reaction (3b), obtained by combining the equation of electrochemical kinetics for the process of discharge of $H_3O^+$ ions

$$i = k[\mathrm{H_3O^+}]\, e^{-\alpha\varphi F/RT} \tag{5}$$

and the thermodynamic relation connecting the potential of the amalgam with its concentration,

$$\varphi = \varphi_0 - \frac{RT}{F}\ln\frac{a_{\mathrm{Me}}}{a_{\mathrm{Me^+}}} = \varphi_0' - B\lg C_{\mathrm{am}}, \tag{6}$$

has the form:

$$i_{\mathrm{e}} = k_1[\mathrm{H_3O^+}]C_{\mathrm{am}}^{B/0.116} = k_1[\mathrm{H_3O^+}]C_{\mathrm{am}}^{n} \qquad (n \gtrless 0.5) \tag{7}$$

(the coefficient $B$, which takes into account the deviation of amalgams from the properties of ideal solutions, is equal to 0.058 V at 20° for dilute amalgams, increasing strongly in the case of amalgams close to saturation). Equation (7) for dilute amalgams and at constant pH of the solution passes into the Brønsted—Kane equation (2). The kinetics of reaction (4) is determined by the equation:

$$i_{\mathrm{x}} = k_2' C_{\mathrm{am}}[\mathrm{H_2O}] = k_2 C_{\mathrm{am}}. \tag{1a}$$

According to the assumption stated above, the current density of amalgam decomposition in any case is the sum of the current densities of the elecof the electrochemical and chemical components of this process and is determined by the equation:

$$i_{\text{decomp}} = i_{\text{e}} + i_{\text{x}} = k_1[\text{H}_3\text{O}^+]C_{\text{am}}^n + k_2C_{\text{am}}. \tag{8}$$

In buffer solutions with not very high pH, the quantity $k_1[\text{H}_3\text{O}^+]$ in equation (7) is sufficiently large; therefore the current of the electrochemical component (7) is considerably higher than the current of the chemical reaction (1a), whose rate constant $k_2$ is small ($^1$). The kinetics of the process of amalgam decomposition under these conditions is determined by the rate of reaction (3b) and obeys equation (7), of which equation (2) is a special case.

In solutions with a high pH value ($> 10$), the quantity $k_1[\text{H}_3\text{O}^+]$ becomes so small that the current density of the chemical reaction (1a) becomes higher than the current of the electrochemical component (7). In this case the kinetics of the process of amalgam decomposition is determined by the rate of reaction (4) and obeys equation (1).

In the region of solution pH around 10, where the values of $i_{\text{e}}$ and $i_{\text{x}}$ are comparable with one another, kinetic regularities of a mixed type occur. The latter is confirmed by consideration of the shape of curve 1 (Fig. 1), which refers to a solution with pH 9.8. Calculation shows that at potentials of the lower part of curve 1, discharge of $\text{H}_3\text{O}^+$ ions by the electrochemical mechanism predominates; but upon reaching significant amalgam concentrations, the value of the current calculated from (1a) increases and, adding to the current of the electrochemical component, distorts the Tafel dependence. Using the value of the constant $k_2$ for K amalgam obtained by us in ($^1$), we introduced a correction for the decomposition current according to scheme (4). As a result of this correction, instead of the upper part of curve 1 there was obtained a dotted straight line, which is a continuation of the initial rectilinear portion of this curve.

The interpretation given here of the process of hydrogen evolution from phosphate buffers is, however, incomplete, since we have not considered the question of the sources replenishing the discharging $\text{H}_3\text{O}^+$ ions. In the case of the solutions investigated by us, diffusion of $\text{H}_3\text{O}^+$ ions from the bulk of the solution is practically of no significance because of the low concentration of the latter, and the donors of protons in the bulk of the solution must be water molecules or anions of phosphoric acid. Calculation shows that dissociation of water can provide current densities not exceeding $3 \cdot 10^{-6}$ A/cm$^2$ at pH 8 and $3 \cdot 10^{-7}$ at pH 10 ($^{8,9}$). Thus, the principal source of protons in the case under consideration must be buffer anions. The kinetic limitations imposed on the hydrogen-evolution process by the finite rate of dissociation of the anion were considered

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* In more concentrated buffer solutions, however, with increasing buffer concentration, a decrease in the hydr

in (10). Comparison of the conclusions of that work with our results will be the subject of further investigation.

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