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Abstract

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ON THE KINETICS OF THE DECOMPOSITION OF ALKALI-METAL AMALGAMS IN ALKALINE ELECTROLYTE SOLUTIONS

(Presented by Academician A. N. Frumkin, 27 VI 1961)

Brensted and Kane in 1931 (^1) showed that the kinetics of decomposition of dilute sodium amalgams in phosphate buffers (pH $\sim$ 7—9) is described by the equation

$$i = kC_{\mathrm{am}}^{0.5}, \tag{1}$$

where i is the rate of decomposition of the amalgam, C_{am} its concentration, and k a constant. The validity of equation (1) for various amalgams and buffer solutions was confirmed in a number of works (^2-5), and its theoretical interpretation was given by A. N. Frumkin (^6) and by Gammat and Lorch (^7), who proposed considering the decomposition reaction of amalgams as an electrochemical process in which the discharge of hydrogen ions is the slow stage determining the rate of the entire process.

The data on the decomposition of alkali-metal amalgams by solutions with a high pH value (> 10), obtained by various authors (^1-4, ^8-10), differ greatly from one another; therefore the interpretation of the experimental results also differs. In work (^8) the above electrochemical concept was applied to the process of amalgam decomposition in a strongly alkaline medium. It was found that, when the dependence of the activity of amalgams on concentration is taken into account, the exponent of C_{am} in equation (1) must exceed the value 0.5. Bockris and Uotson (^9), in order to explain differences in the regularities of decomposition of amalgams of alkali and alkaline-earth metals, assumed a chemical interaction of the surface atoms of the metal of the amalgam with water molecules; however, in deriving the kinetic dependences they proceeded from equation (1), which follows from the electrochemical theory. Volkov (^10) showed that, in studying the kinetics of amalgam decomposition, removal of surface contaminants plays an important role, as a result of which it is possible sharply to reduce the rate of decomposition.

Thus, on the basis of the data obtained, there was no doubt that the kinetics of decomposition of alkali-metal amalgams in buffer solutions with pH $\sim$ 7—9

Fig. 1

Figure 1: Fig. 1

follows the electrochemical theory and obeys kinetic equation (1). In the case of strongly alkaline solutions (pH > 10), however, the discrepancy of the data does not permit an unambiguous judgment about the kinetics and mechanism of the process.

The present work is devoted to the study of the kinetics of decomposition of alkali-metal amalgams by aqueous electrolyte solutions under conditions of maximum purity of reagents and apparatus.

The rate of decomposition was determined by a gasometric method. The concentration of the amalgam, prepared by electrolysis, was determined by titration of the excess acid added to the amalgam. To avoid contamination from glass, the experiments were carried out in a polystyrene apparatus. Organic impurities that could pass from the polystyrene into the solution, at the high negative potentials characteristic of alkali-metal amalgams, should be desorbed from the electrode surface and cannot affect the decomposition kinetics. The solutions from which the amalgams were obtained and in which they decomposed were subjected to prolonged cathodic purification.

Platinum contacts were eliminated, and the potentials of the amalgams were found by calculation or by measurement in a separate cell. The system was not stirred, since under the conditions of our experiments it had no effect on the kinetics of decomposition.

Fig. 1

The apparatus in which the measurements were made, shown in Fig. 1, consisted of a polystyrene beaker with a screw-on lid. It was filled with the solution under study and purged with hydrogen. The amalgam from vessel A was transferred through a three-way stopcock into cup B. The hydrogen evolved entered the bell and then the gas burette C. The bell and burette were made of glass, since adhesion of hydrogen bubbles to polystyrene made it difficult to measure the gas volume. As is seen from Fig. 1, the amalgam did not come into contact with glass, which, as experiment showed, accelerates the decomposition process. Contact of the solution with glass, however, did not noticeably affect this process during the experiment.

The surface of the amalgam was cleaned by discarding, with the aid of lever P, the layer of amalgam containing centers of enhanced hydrogen evolution. The discarded layer was removed from the apparatus through stopcock K. Before measuring the volume of hydrogen evolved, the bubbles on the surface of the amalgam were transferred by lever P into the gas burette. The temperature of the experiments was $20 \pm 1°$. The volume of solution was 500 ml. The area of the amalgam surface was 20 cm^2. Since, as a result of the high negative potential of

Fig. 2

Figure 2: Fig. 2

Figure 3

Figure 3: Figure 3

the amalgam, the solution is drawn in between the walls of the apparatus and the amalgam, the true area of contact between it and the solution exceeds the visible area; therefore the values of the current densities for decomposition of the amalgams should be regarded as somewhat overestimated.

Fig. 2. Dependence of the decomposition rate of Li (1), Na (2), and K (3) amalgams on their concentration in aqueous electrolyte solutions: *a*—Li amalgam in 0.1 N LiOH solution; *b*—Na amalgam in 0.1 N NaOH solution; *v*—K amalgam in 0.1 N KOH solution; *g*—the same in 0.1 N KOH + KH_2PO_4 solution with pH 10.6; *d*—the same in 0.1 N KOH + KH_2PO_4 solution with pH 11.4; *e*—the same in 1 N KOH solution.

Figure 2 shows the dependence of the decomposition rate of Li, Na, and K amalgams on their concentrations in various solutions, obtained by the method described above. As can be seen, there is a direct proportionality between the concentration of the amalgam and the rate of its decomposition, which corresponds to the kinetic equation

$$i = kC_{\text{am}}. \tag{2}$$

(i is expressed in A/cm^2, C_{am} in g-equiv/l.) Below we give the values of the constants k:

	Li	Na	K
k, A/cm$^2\cdot$ l/g-equiv	$3\cdot10^{-3}$	$2.4\cdot10^{-5}$	$3\cdot10^{-5}$

In Fig. 3, the data on the decomposition of Li, Na, and K amalgams in 0.1 N electrolyte solutions are presented in coordinates: potential—logarithm of the decomposition current density. At low concentrations of Na and K amalgams there is a linear dependence φ–$\lg i$ with a slope coefficient of 0.06–0.07 V. On passing to concentrated amalgams, whose activity coefficient increases, an increase in the slope is observed. In the case of Li amalgam, for which the dependence between the logarithms of the activity coefficient and the amalgam concentration in the concentration range under consideration is linear ([11]), a straight line φ—$\lg i$ is obtained with a slope coefficient of 0.073-0.075 V.

Fig. 3. Curves φ—$\lg i$: 1 —Li amalgams in 0.1 N LiOH; 2 —Na amalgams in 0.1 N NaOH; 3 —K amalgams in 0.1 N KOH (a) and in 0.1 N solution of KOH + KH_2PO_4 (b)

Table 1 summarizes the results of experiments on the decomposition of Li amalgam of approximately constant concentration in various solutions.

Table 1

$C_{\text{am}}(N)$	Composition and conc. of electrolyte	i, A/cm^2	φ, V vs. n.h.e.
0.54	0.1 N LiCl	$1.8 \cdot 10^{-3}$	2.413
0.51	0.55 N LiCl	$1.6 \cdot 10^{-3}$	2.374
0.47	2.0 N LiCl	$1.5 \cdot 10^{-3}$	2.313
0.45	10.8 N LiCl	$2.0 \cdot 10^{-3}$	2.111
0.50	0.63 N LiOH	$1.6 \cdot 10^{-3}$	2.352
0.50	2.20 N LiOH	$1.6 \cdot 10^{-3}$	2.325
0.50	5.0 N LiOH	$1.5 \cdot 10^{-3}$	2.307

From the data of Fig. 2 and Table 1 it is evident that the decomposition rate of Li and K amalgams does not depend on the composition, concentration, or pH of the solution. The only factor determining the rate of decomposition of the amalgams under the given conditions is their concentration.

To compare the data obtained by us with the data of earlier works, Table 2 gives the decomposition current densities of 0.55 N Li and K amalgams in electrolyte solutions (pH $\sim$ 12—13) according to various authors*. Since the expression of experimental results in a number of works differs greatly from one another, we carried out the corresponding recalculation.

Contaminants on the surface of the amalgam, introduced for example from glass, change not only the magnitude of the decomposition rate but also the character of the kinetic dependence. Figure 4 gives experiments on the decomposition of Li amalgam in 0.1 N LiOH. With careful removal of contaminated areas from the surface of the amalgam (curve 1), the decomposition rate proves to be the smallest and proportional to the concentration of the amalgam. Curve 2 refers to the case when the contaminated areas remained unremoved. After their removal at the moment indicated by the arrow, the decomposition rate drops sharply and approaches the rate expressed by straight line 1. After glass fragments are introduced onto the clean surface of the amalgam (curve 3), the decomposition rate increases somewhat and is no longer proportional to the concentration of the amalgam.

Table 2

Decomposition current density of 0.55 N amalgams	Decomposition current density of 0.55 N amalgams	Source
Li	K	Source
$15 \cdot 10^{-3}$	$6 \cdot 10^{-3}$	(4)
$6 \cdot 10^{-3}$	$1 \cdot 10^{-4}$	(8)

Fig. 4. Dependence of the decomposition rate of Li amalgam on its concentration in 0.1 N LiOH under different purification conditions

Figure 4: Fig. 4. Dependence of the decomposition rate of Li amalgam on its concentration in 0.1 N LiOH under different purification conditions

Decomposition current density of 0.55 N amalgams	Decomposition current density of 0.55 N amalgams	Source
$5 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	(9)
$1.6 \cdot 10^{-3}$	$1.6 \cdot 10^{-5}$	Our data

* In (10), for the case of decomposition of ~ 0.2 N Na amalgam in a saturated NaCl solution, $i = 3.47 \cdot 10^{-7}$ A/cm^2 was obtained. The experiments were carried out under conditions where complete harmonicity was not ensured.

···gram. In this case, as in the case of curve 2, the decomposition process is better described by equation (1).

The experiments we carried out showed that cathodic polarization of Li amalgams in a solution of $N(CH_3)_4J$ up to a potential of 2.73 V on the n.h.e. does not affect the rate of their decomposition. It was also found that a mixed Li and K amalgam decomposes in a solution of LiOH + KOH at a rate that is the sum of the decomposition rates of Li and K amalgams separately.

Fig. 4. Dependence of the decomposition rate of Li amalgam on its concentration in 0.1 N LiOH under different purification conditions

On the basis of the data we obtained, one may conclude that the process of decomposition of alkali-metal amalgams by solutions with high pH, provided the experiment is carried out with sufficient purity, proceeds through the direct interaction of surface atoms of the amalgam metal with water molecules according to the simplified scheme (3), without separation into cathodic and anodic processes:

$$\mathrm{Me(Hg)} + \mathrm{H_2O} \rightarrow \mathrm{Me^+} + \tfrac{1}{2}\mathrm{H_2} + \mathrm{OH^-} + \mathrm{Hg}. \tag{3}$$

This conclusion is in agreement with the assumption expressed by Bockris and Watson, although under the conditions of their experiments reaction (3) could not have been observed, since (see Table 2) the rates of decomposition of amalgams obtained by these authors are considerably higher than those found by us, i.e., the surface of the amalgams in the experiments of Bockris and Watson was contaminated. However, in contrast to what was assumed by the authors of work (9), the kinetics of the reaction of amalgam decomposition in a strongly alkaline medium is expressed by the first-order equation (2). The entry of impurities, on which the hydrogen overvoltage is reduced, onto the amalgam surface leads to separation of the cathodic and anodic processes. The kinetics of amalgam decomposition under these conditions is close to the dependence expressed by equation (1) and arising from electrochemical considerations. As will be shown in the following paper, the kinetics of amalgam decomposition in phosphate buffer solutions at pH < 10 follows equation (1) and obeys an electrochemical mechanism even under conditions of maximum purity.

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