ACTIVATION ENERGY AND PREEXPONENTIAL FACTOR FOR THE EVOLUTION OF HYDROGEN AT GALLIUM AND ITS ALLOYS

II. ALKALINE SOLUTIONS

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By comparison of the activation energies and preexponential factors for the evolution of hydrogen from acidic and alkaline solutions it is possible to compare the characteristics of the elementary discharge event of two particles with different nature, i.e., the hydroxonium ion in acidic solutions ($H_3O^+ + e \rightarrow H_2O + H_{ads}$) and the neutral water molecule in alkaline solutions ($H_2O + e \rightarrow H_{ads} + OH^-$).

However, there have so far been no published data on the temperature dependence of the hydrogen overpotential for the water molecule discharge reaction. This is evidently due to the difficulty of creating conditions which eliminate the effect of the entry of alkali-metal cations into the electrode on the kinetics and mechanism of the evolution of hydrogen from alkaline solutions.

In [1] it was shown that alkali metal cations are not discharged with an appreciable rate and do not have an effect on the kinetics of the evolution of hydrogen at liquid gallium up to −2.05 V (s.c.e.). For electrodes of indium–gallium alloys (16.4 at.% In) in solutions containing Li^+, Na^+, K^+, and Cs^+ cations and mercury–gallium alloys (2.1 at.% Hg) in solutions containing Li^+ [2, 3] it is also possible to single out a region of potentials in which the discharge rate of the alkali metal cations is in any case significantly less than the discharge rate of the water molecules, and possible discharge of the alkali metal cations does not affect the energy of adsorption of atomic hydrogen. With gallium, indium–gallium, and mercury–gallium electrodes it is thus possible to compare the activation energies and preexponential factors in acidic and alkaline solutions.

As for the discharge of the hydroxonium ion [4], the temperature dependences of the hydrogen overpotential for the discharge of water molecules at gallium, indium–gallium, and mercury–gallium were measured at dropping electrodes in 0.1 N NaOH (LiOH) + 0.9 N NaCl (LiCl) solutions. The sodium chloride and lithium chloride of special purity were calcined, the sodium hydroxide solution was obtained by decomposition of sodium amalgam, and chemically pure lithium hydroxide was used. The investigated solutions were purified and the temperature was controlled as described in [4].

Typical polarization curves for gallium, indium–gallium, and mercury–gallium are presented in Fig. 1. The parameters of the Tafel equation for these electrodes in the investigated range of temperatures are given in Table 1.

The dependences of log $i_{\eta = \mathrm{const}}$ on 1/T for gallium, indium–gallium, and mercury–gallium are given in Fig. 2. The activation energies $E^{\neq}$ and preexponential factors k, calculated from these curves, are presented in Tables 2 and 3. From Tables 2 and 3 it is seen that the $E^{\neq}$ and log k values increase with increase in the hydrogen overpotential in the order gallium, indium–gallium, and mercury–gallium. For mercury–gallium, as already mentioned in [4], the $E^{\neq}$ and log k values are anomalously high. As discussed earlier [4-6], the increase in the absolute value of log k on passing from gallium to indium–gallium and mercury–gallium may be due to decrease in the energy of adsorption of hydrogen. As a result of this, as follows from the quantum-mechanical theory of the elementary discharge event [7], the degree of over-

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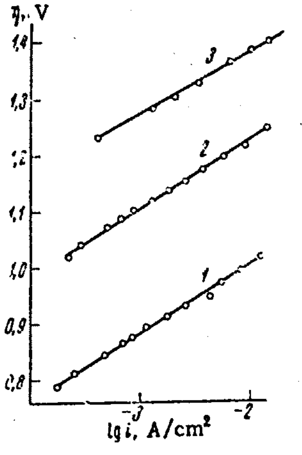

Fig. 1

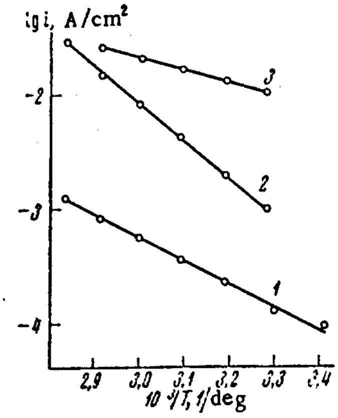

Fig. 2

Fig. 1. Polarization curves: 1) At gallium at 32°C; 2) at indium–gallium at 30°C; 3) at mercury–gallium at 40°C.

Fig. 2. Dependence of log i on 1/T for: 1) Indium–gallium with $\eta = 1.0$; 2) mercury–gallium with $n = 1.3$; 3) gallium with $\eta = 1.0$ V.

lap of the wave functions of the proton in the initial and final states increases, and the probability of tunnelling increases, i.e., the k value increases.

From Table 3 it is seen that at gallium and indium–gallium in alkaline solutions, unlike acidic solution [4], the log k value remains practically unchanged with increase in the overpotential and, accordingly, the negative charge of the surface. This is clearly due to the fact that the hydrogen is released from a neutral water molecule, the attraction of which to the negatively charged surface of the electrode is less clearly expressed than for the hydroxonium ion, and the degree of overlap of the wave functions depends little on the charge of the electrode. The different nature of the variation of log k with the electrode potential in acidic and alkaline solutions is consistent with data on the dependence of the separation factors for the hydrogen isotopes on the electrode potential [6].

During comparison of the experimental values for the preexponential factors for one and the same electrode in acidic and alkaline solutions it is necessary to take account of, firstly, the different concentration of the discharging particles (H_3O^+ ion and H_2O molecules) and, secondly, the fact that the real (according to Temkin [8]) and not the ideal preexponential factor is determined by the experiment. The real preexponential factor differs from the ideal by the exponential of the equilibrium standard change in entropy ΔS for the given electrode process. The ΔS value is inaccessible to direct experimental determination, and only approximate estimates are possible [9]. However, as will be shown below, the change in this correction on passing from acidic to alkaline solutions can be determined with a fairly high degree of accuracy.

The ideal preexponential factor for the discharge of the hydroxonium ion is equal to $k_{H_3O^+} \cdot n_{H_3O^+}$, where $k_{H_3O^+}$ is a constant determined by the range of vibrational frequencies of the polar medium and the

TABLE 1

t, °C	Ga			In — Ga			Hg — Ga		
	a, V	b, V	α	a, V	b, V	α	a, V	b, V	α
20				1,454	0.112	0.52			
30				1,440	0,113	0,52			
32	1,236	0,118	0,51						
40	1,231	0,122	0.51	1.420	0.114	0.54	1,630	0,110	0,55
50	1,230	0.128	0,50	1,406	0.117	0,55	1,570	0,112	0,57
60	1,228	0,134	0,49	1,402	0.123	0.54	1,546	0.116	0,57
70	1,222	0,138	0,49	1,392	0,126	0.54	1,512	0.118	0,58
80				1,385	0,130	0,54	1,490	0.124	0,56

TABLE 2. Activation Energy, kcal/mole

η, V	Ga	In — Ga	Hg — Ga
0,8	7,7±0,1		
0,9	6,3±0.3		
1,0	4,6±0,4	9,4±0,1	
1,1		8,0±0,3	
1,2		6,9±0,5	17,0±0.2
1,3			15,5±0,5

TABLE 3. The log k Values (preexponential factor k, A/cm²)

η, V	Ga	In — Ga	Hg — Ga
0.8	1,8±0.1		
0,9	1,7±0,1		
1,0	1,3±0,3	2,8±0,1	
1,1		2.8±0,2	
1,2		2,8±0,4	8,3±0,1
1,3			8,1±0,3

TABLE 4

	Ga	In–Ga	Hg–Ga
$\log k^r_{acid}$ [4]	3,4	3,8	7,6
$\log k^r_{alk}$	1,6	2.8	8,2
$\Delta\log k^{id}$	5,6	4.8	3.2

probability of a subbarrier transfer of the proton at the intersection of the electron–proton terms [7, 10], and $n_{H_3O^+}$ is the number of H_3O^+ ions per unit surface of electrode. In the absence of ψ_1 effects and specific adsorption of H_3O^+, $n_{H_3O^+} = n_{H_2O} \cdot x_{H_3O^+}$. Here n_{H_2O} is the corresponding number of water molecules, and $x_{H_3O^+}$ is the mole fraction of hydroxonium ions in the volume of the solution, which in a dilute solution is practically equal to $m_{H_3O^+}/55.5$, where $m_{H_3O^+}$ is the molarity of the H_3O^+ ions.*

As mentioned, the real preexponential factor differs from the ideal by $\exp(\alpha\Delta S_{ac}/R)$, where ΔS_{ac} relates to the equilibrium $^1/_2H_2 + H_2O = H_3O^+_m + e_{met}$. The subscript m indicates the concentration of hydrogen ions. Indicating the standard entropies by the superscript ^{0}, we obtain $\Delta S_{ac} = S^0_{H_3O^+} - R\ln m_{H_3O^+} + S_e - S^0_{H_2O} - {}^1/_2 S^0_{H_2}$. Similarly, for discharge from an alkaline solution the ideal preexponential factor is equal to $k_{H_2O} \cdot n_{H_2O}$, and the real preexponential factor differs from it by an $\exp(\alpha\Delta S_{al}/R)$, where $\Delta S_{al} = S^0_{H_2O} + S_e - S^0_{OH^-} + R\ln m_{OH^-} - {}^1/_2 S_{H_2}$ relates to the equilibrium $^1/_2H_2 + OH^-_m = H_2O + e_{met}$. Hence we obtain the ratio of the real preexponential terms:

$$\frac{k^r_{H_3O^+}}{k^r_{H_2O}} = \frac{k_{H_3O^+}}{k_{H_2O}} \cdot \frac{m^\beta_{H_3O^+}}{m^\alpha_{OH^-}} \cdot \frac{1}{55{,}5} e^{\frac{\alpha(S^0_{H_3O^+} + S^0_{OH^-} - 2S^0_{H_2O})}{R}}.$$

This expression contains the sum of the entropies of the two ions, i.e., a quantity which is amenable to determination. The tabular values for the ionic entropies are given on an arbitrary scale, in which it is assumed that $_{arb}S^0_{H^+} = S^0_{H_3O^+} - S^0_{H_2O} = 0$. On this scale $_{arb}S^0_{OH^-} = -2.57$ eu [12]. The sum included in the power index is $S^0_{H_3O^+} + S^0_{OH^-} - 2S^0_{H_2O} = {}_{arb}S^0_{H^+} + {}_{arb}S^0_{OH^-} - S^0_{H_2O} = 0 - 2.57 - 16.71 = -19.28$ eu, i.e., the exponential term is equal to $10^{-2.1}$ (with $\alpha = 0.5$). Thus, from the ratio of the real preexponential factor it is possible to obtain the ratio of the ideal constants and, since the solvent is the same in both cases, the ratio of the probabilities of the tunnelling of the proton:

$$\frac{k_{H_3O^+}}{k_{H_2O}} = \frac{k^r_{H_3O^+}}{k^r_{H_2O}} \left(\frac{m_{OH^-}}{m_{H_3O^+}}\right)^{1/2} \cdot 55.5 \cdot 10^{2.1} = \frac{k^r_{H_3O^+}}{k^r_{H_2O}} \left(\frac{m_{OH^-}}{m_{H_3O^+}}\right)^{1/2} \cdot 10^{3.85}.$$

Since under the conditions of our experiments $m_{OH^-} = m_{H_3O^+} = 0.1$, the ratio of the probabilities of tunnelling is $10^{3.85}$ times greater than the ratio of the experimental values for the real preexponential factors.

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*Strictly speaking, the specific adsorption of H_3O^+ ions in the first monolayer should be taken into account; without this it is difficult to explain a number of the relationships in the kinetics of hydrogen evolution [11]. The appropriate correction is, however, largely related to the difference in the energies of the ion in the volume of the solution and at the surface of the electrode and should therefore be reflected primarily in the activation energy and not in the preexponential factor. Of course, there is still a correction due to the change in the entropies of the H_3O^+ ion and H_2O molecules on adsorption, but these quantities can scarcely be large (probably not more than the entropy of the freezing of water in magnitude, i.e., ~6 eu) and what is most important, an analogous and similar (in magnitude) correction will apply to alkaline solutions (the entropies of the adsorption of water and OH^-) so that the difference in these effects can be neglected.

The mean real log k^r values for acidic and alkaline solutions and also the Δ log k^{id} values calculated on the basis of the preceding arguments are given in Table 4. It is seen that the ideal values of the pre-exponential factor are several orders of magnitude greater in acidic solutions than in alkaline solutions, and Δ log k^{id} decreases in the order gallium, indium–gallium, mercury–gallium, i.e., with increase in the absolute value of k. Within the scope of the model used previously in [6] the observed difference in the k values can be explained qualitatively by the stronger attraction of the H_3O^+ ions towards the electrode by the electric field compared with the water molecules. As a result of this the transfer of the proton takes place over a shorter distance in the discharge of H_3O^+ than in the discharge of H_2O, and the probability of this process increases. In addition, it is seen that in gallium and indium–gallium, where the absolute values of k are small and, consequently, the degree of overlap of the wave functions is small, the nature of the discharging particle has an appreciable effect on the magnitude of k. For the mercury–gallium electrode, where the k value is significantly larger, i.e., the overlap of the wave functions of the proton is large, change in the distance of the transfer does not significantly affect the probability of tunnelling. The observed ratio of the log k values in acidic and alkaline solutions is in qualitative agreement with data on the dependence of log k on the electrode potential.

LITERATURE CITED

1. K. Sabo, I. A. Bagotskaya, and N. B. Grigor'ev, Zh. Fiz. Khim., 38, 2059 (1964); I. A. Bagotskaya, N. M. Genkina, and V. G. Boitsov, Élektrokhimiya, 5, 132 (1969).
2. E. N. Potapova and I. A. Bagotskaya, Élektrokhimiya, 9, 702 (1973).
3. L. M. Dubova, N. B. Grigor'ev, and I. A. Bagotskaya, Élektrokhimiya, 8, 1395 (1972).
4. E. N. Potapova, L. I. Krishtalik, and I. A. Bogatskaya, Élektrokhimiya, 10, 49 (1974).
5. V. M. Tsionskii, Élektrokhimiya, 5, 1500 (1969).
6. V. M. Tsionskii and L. I. Krishtalik, Élektrokhimiya, 5, 1184, 1501 (1969); J. Electroanalyt. Chem., 31, 363 (1970).
7. R. R. Dogonadze, A. M. Kuznetsov, and V. G. Levich, Élektrokhimiya, 3, 739 (1967).
8. M. I. Temkin, Zh. Fiz. Khim., 22, 1081 (1948).
9. L. I. Krishtalik, Élektrokhimiya, 5, 3 (1969).
10. R. R. Dogonadze and A. M. Kuznetsov, Progress in Science, Electrochemistry, 1967 [in Russian], Izd. VINITI, Moscow (1969), p. 5.
11. L. I. Krishtalik, Élektrokhimiya, 6, 1165 (1970).
12. M. Kh. Karapet'yants and M. L. Karapet'yants, Fundamental Thermodynamic Constants of Inorganic and Organic Substances [in Russian], Khimiya, Moscow (1968).