

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

I. ACIDIC SOLUTIONS

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Investigation of the temperature dependence of the rate of an electrochemical reaction can provide important information on the mechanism of the electrode process. The presently available experimental data on the temperature dependence of the hydrogen overpotential in acidic solutions at electrodes for which the hydroxonium ion discharge stage is retarded are relatively few [1-10]. The most reliable data are for a mercury cathode [1, 2, 10]. For other metals most of the results were obtained in dilute solutions of acids, where it is necessary to make a correction for the ψ' effect, and this makes their theoretical interpretation difficult.

In the present work measurements of the temperature coefficient of the hydrogen overpotential at dropping electrodes of gallium, mercury, and indium-gallium (16.4 at.% In) and mercury-gallium (2.1 at.% Hg) alloys were made in such a way as to avoid distortions introduced by the existence of the ψ' potential and its temperature dependence. For this purpose the polarization curves were recorded in acidic solutions containing an excess of the salt, i.e., in 0.1 N HCl + 0.9 N KCl for mercury and in 0.1 N HClO₄ + 0.9 N NaClO₄ for gallium and the alloys.* The following starting materials were used for the electrodes: mercury distilled three times under vacuum; grade GL-000 gallium of 99.9998% purity; indium of 99.999% purity. The acids were twice distilled under vacuum, the potassium chloride and sodium perchlorate were recrystallized three times, and the potassium chloride was in addition calcined. The investigated solutions were subjected to electrochemical purification for 12 h at a periodically renewed mercury cathode with agitation of the solution by gaseous hydrogen. The temperature in the cell was maintained with an accuracy up to 0.1°C by means of a water thermostat.

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

The values obtained in the present work for the hydrogen overpotential η agree well with the published data for mercury [2], gallium, and indium-gallium [4]† with correction for the different compositions of the solutions. (The measurements were made in 0.1 N hydrochloric acid in [2] and 0.1 N perchloric acid in [4].) Lower values for η are given in [3]. (In [3] the measurements were made at 35, 50, and 65°C.)

To determine the real [11] activation energies and preexponential factors k curves were plotted against Arrhenius coordinates ($\log i_{\eta} = \text{const} \cdot 1/T$), and the E° and $\log k$ values for a fixed value of η^*

* The composition of the solutions were chosen so that the nature of the anion did not affect the kinetics of hydrogen evolution in the investigated region of potentials.

† In [4] the concentration of indium in the indium-gallium alloy corresponded to 19.2 at.%. The measurements were made at two temperatures, 32 and 58°C.

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TABLE 1

t, °C	Ga			In - Ga			Hg - Ga			Hg		
	a, V	b, V	α	a, V	b, V	α	a, V	b, V	α	a, V	b, V	α
15										1,459	0,114	0,50
25										1,444	0,118	0,50
30				1,294	0,122	0,49						
32	1,097	0,116	0,52				1,405	0,118	0,51			
35										1,426	0,121	0,50
40	1,081	0,118	0,52	1,270	0,124	0,50	1,370	0,119	0,52	1,420	0,128	0,49
45												
50	1,067	0,120	0,53	1,250	0,126	0,51	1,342	0,124	0,52	1,404	0,132	0,49
55												
60	1,049	0,122	0,54	1,229	0,128	0,52	1,310	0,126	0,52	1,394	0,137	0,49
65												
70	1,038	0,125	0,54	1,208	0,128	0,53	1,276	0,128	0,53	1,388	0,146	0,48
75												
80				1,183	0,128	0,53	1,248	0,131	0,54			

TABLE 2. Activation Energy E^\ddagger , kcal/mole

η , V	Ga	In - Ga	Hg - Ga	Hg
0,7	9,2 \pm 0,3			
0,8	8,2 \pm 0,2	10,0 \pm 0,4		
0,9	7,8 \pm 0,3	9,9 \pm 0,2	16,3 \pm 0,7	11,9 \pm 0,1
1,0		9,4 \pm 0,1	15,4 \pm 0,4	10,5 \pm 0,3
1,1			14,6 \pm 0,2	9,2 \pm 0,5
1,2				7,7 \pm 0,3

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

η , V	Ga	In - Ga	Hg - Ga	Hg
0,7	3,1 \pm 0,2			
0,8	3,3 \pm 0,1	3,2 \pm 0,2		
0,9	3,9 \pm 0,3	3,9 \pm 0,2	7,4 \pm 0,4	4,2 \pm 0,1
1,0		4,3 \pm 0,1	7,6 \pm 0,3	4,0 \pm 0,2
1,1			7,8 \pm 0,2	3,8 \pm 0,2
1,2				3,6 \pm 0,2

TABLE 4

	Ga	In - Ga	Hg	Hg - Ga
E_0^\ddagger , kcal/mole	17,6	20,1	21,9	27,0
E_{M-H} , kcal/mole	37,2	32,2	29,0	18,5
lg k_{av}	3,4	3,8	3,9	7,6

were determined from the slope of these curves and from the intercept on the ordinate axis. Typical log i , $1/T$ curves are given in Fig. 2. It is seen that the experimental points fit well onto straight lines.

The mean values of E^\ddagger and log k and the maximum deviations from the mean, calculated from the results of three series of measurements with each electrode, are given in Tables 2 and 3.

By means of the Brönsted-Polanyi equation

$$\alpha(E_{M-H} - E_{Hg-H}) = (E_{\alpha(Hg)}^\ddagger - E_{\alpha(M)}^\ddagger),$$

which relates the difference in the energies of adsorption of hydrogen on metals (E_{M-H} , E_{Hg-H}) to the difference in activation energies with constant α , in particular with $\alpha = 0$ ($E_0^\ddagger(Hg)$, $E_0^\ddagger(M)$), an attempt was made to evaluate the energy of adsorption of hydrogen on gallium and indium-gallium and mercury-gallium alloys (Table 4). The E_0^\ddagger value was obtained by extrapolation of the E^\ddagger values determined for various

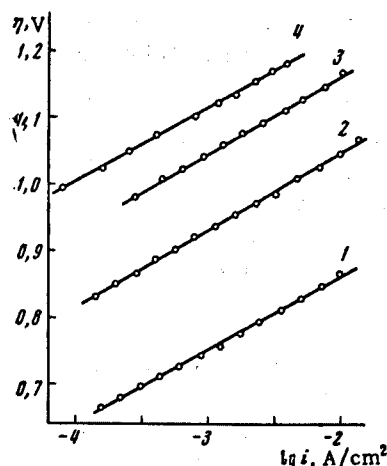


Fig. 1

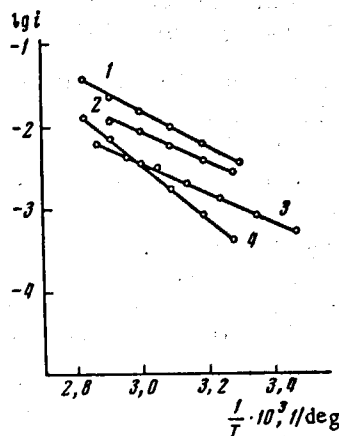


Fig. 2

Fig. 1. Polarization curves: 1) At gallium at 32°C; 2) at indium-gallium at 30°C; 3) at mercury-gallium at 32°C; 4) at mercury at 15°C.

Fig. 2. Dependence of $\lg i$ on $1/T$ for: 1) Indium-gallium with $\eta = 1.0$; 2) gallium with $\eta = 0.8$; 3) mercury with $\eta = 1.1$; 4) mercury-gallium with $\eta = 1.0$.

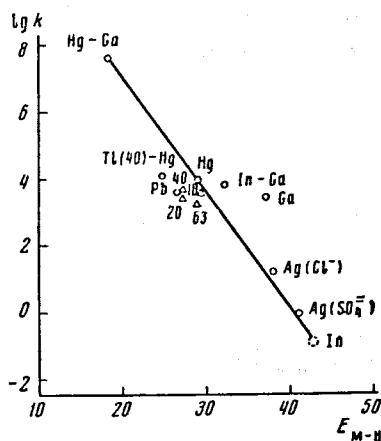


Fig. 3. Dependence of $\lg k$ on the bond energy E_{M-H} . The $\lg k$ values were calculated in [9] from data for indium [7], silver [8], thallium amalgam (40.6 at.% Tl) [5], indium amalgams [In(x)-Hg] [6], and lead [9]. The figures indicate the mole fractions of indium in the amalgam. The $\lg k$ values for gallium, mercury, indium-gallium, and mercury-gallium were calculated from the results of the present work.

η values to $\eta = 0$. The value of α was taken as $1/2$. The mean values of E_0^\ddagger and E_{M-H} are given in Table 4. The E_{Hg-H} value was taken as 29 kcal/mole [10].

At the mercury electrode the value which we calculated for E_0^\ddagger (21.9 kcal/mole) proved close to the value (21.7 kcal/mole) calculated in [11] from data in [1] for 0.25 N H_2SO_4 + 1 N Na_2SO_4 and from data in [2] for 0.1 N HCl. According to the data from the present work, the average value of $\lg k$ at mercury is 3.9 and occupies an intermediate position between the values of 3.3 and 4.0, calculated in [11] from data in [1] and [2] respectively. A similar value for $\lg k$ (3.0) was obtained in [10] for barrier-free discharge of hydrogen ions.

The E_0^\ddagger values which we obtained at gallium and indium-gallium are close to the values $E_0^\ddagger(Ga) = 17.8$ kcal/mole and $E_0^\ddagger(In-Ga) = 21.0$ kcal/mole obtained in [4] in 0.1 N perchloric acid with allowance for the diffuseness of the double layer, but the $E_0^\ddagger(Ga)$ value differs significantly from the value of 22.5 kcal/mole obtained in [3] in 0.1 N hydrochloric acid. The $\lg k$ values for gallium and indium-gallium presented in Table 4 are close to the values $\lg k(Ga) = 3.3$ and $\lg k(In-Ga) = 4.1$, which we calculated for 0.1 N perchloric acid from data in [4].

The $\lg k$ values and bond energies E_{M-H} are compared in Fig. 3. It is seen that all the points fit satisfactorily into a single relationship and to a first approximation give a straight line.

From comparison of Tables 1 and 4 it is seen that at gallium, indium-gallium, and mercury both the activation energy and the hydrogen overpotential η increase with decrease in the energy of the M-H bond. However, the mercury-gallium alloy falls outside this series, and the η value for this alloy is only a little lower than the value for mercury (18 mV lower at 32°C, $i = 10^{-3.5}$ A/cm²), while E^\ddagger is considerably higher, but this is compensated for by the large k . This value of $\lg k$ itself is unexpectedly large, exceeding the theoretical estimates of the upper limit of $\lg k$ values (for the ideal preexponential $\lg k \sim 7$ [12], for the real expo-

nential ~ 5 [13]). It is possible that in the case of mercury-gallium the temperature dependence bears the impression of a change in the structure of the surface of the alloy at various temperatures.

The effect of a simultaneous decrease in the activation energy and preexponential factor with increase in the energy of the M-H bond (the so-called compensation effect) is frequently observed in various reactions. For the electrochemical evolution of hydrogen this was observed in [14] and was examined in more detail in [9]. An explanation was given on the basis of the quantum-mechanical theory of the elementary hydrogen discharge event [15], which presupposes activation by reorganization of the solvent. According to this theory, the magnitude of the preexponential factor is determined by the probability of tunnelling by the proton, which depends on the overlap of its wave functions in the initial and final states. On a metal with a lower bond energy E_{M-H} the proton is less localized in the adsorbed state, and consequently the overlap of the wave functions of the adsorbed proton and the proton in the hydroxonium ion is greater in this case. In accordance with this the probability of tunnelling α increases and $\log k$ increases. The theory of Horiuti and Polanyi, which presupposes extension of the O-H bond in the process of activation, leads to directly opposite conclusions, which contradict experiment [9, 16, 17]. In the present work the correlation of the $\log k$ and E_{M-H} values was confirmed with more extensive and accurate material.

From Table 3 it is seen that at gallium and indium-gallium there is a tendency for $\log k$ to increase, by an amount somewhat exceeding the probable experimental error, with increase in potential.* This agrees with the analogous conclusion reached in [16, 17] during investigation of the isotope effect. In [13] direct indications were obtained of a substantial increase in the preexponential factor with considerable (on the order of 1 V) increase in the electrode potential. Within the scope of the quantum-mechanical model the increase of $\log k$ with η is due to decrease in the distance of the transfer of the proton on account of attraction of the hydroxonium ion towards the electrode with increase in its negative potential ϕ .

It should be noted that gallium (and, possibly, indium-gallium alloy) falls somewhat outside the general relationship in Fig. 3. This discrepancy may be due to the different orientation of the water at the surface of these electrodes [18], which leads to somewhat different orientation of the hydroxonium ions and, consequently, to some change in the conditions for the tunnelling of the proton.

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* The variations in $\log k$ with overpotential for electrodes of mercury-gallium and mercury are values on the order of the experimental error and are not therefore discussed here.