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# K. Sabo, I. A. Bagotskaya

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**Abstract**

**Full Text**

**PHYSICAL CHEMISTRY**

**K. Sabo, I. A. Bagotskaya**

## **STUDY OF THE HYDROGEN OVERVOLTAGE ON SOLID AND LIQUID GALLIUM IN A SULFURIC ACID SOLUTION**

*(Presented by Academician A. N. Frumkin, 6 XII 1962)*

In order to clarify the influence of various factors on the kinetics of the electrochemical evolution of hydrogen on an electrode as a function of its state of aggregation, in the present work we studied the hydrogen overvoltage on solid and liquid gallium in a 1 *N* solution of H<sub>2</sub>SO<sub>4</sub>. The melting point of gallium, 29.78°, lies close to room temperature, which facilitates the experimental conditions and permits measurements to be carried out in aqueous solutions of different concentration. The data available in the literature on the relation between the overvoltage values on solid  $\eta_t$  and liquid  $\eta_l$  gallium are contradictory. According to the works of Bowden <sup>(1)</sup> and Stelling,  $\eta_t < \eta_l$ , whereas Khristov and co-workers <sup>(3)</sup> observed the opposite relation,  $\eta_t > \eta_l$ .

The measurements were carried out in the apparatus shown in Fig. 1: pieces of solid gallium were placed in cell *A*, and the entire volume of the apparatus was filled with hydrogen. Then a solution of 1 *N* H<sub>2</sub>SO<sub>4</sub>, saturated with hydrogen and previously purified on a gallium electrode by prolonged cathodic polarization, was pumped into vessel *B*. The gallium was melted and, by hydrogen pressure, forced through tube *a* into cup *b* with a platinum contact in such a way that no gallium remained in tube *a*. The upper end of tube *a* projected into cell *A*, which made it possible to take the gallium from the bulk of the metal. Complete expulsion of the gallium from tube *a* was necessary in order to avoid cracking of the tube upon freezing of the gallium, accompanied by an increase in its volume. In addition, we kept the walls of tube *a* and vessel *A* moist, wetting them with 1 *N* H<sub>2</sub>SO<sub>4</sub> solution to prevent the gallium from adhering to the glass. The drop of gallium forced into cup *B* served as the electrode under investigation. The size of the electrode was determined with a microscope and was  $\sim 1$  cm<sup>2</sup>. A platinum electrode (*I*) served as the anode; the potential was measured relative to a hydrogen electrode in the same solution (*II*). On liquid gallium the measurements were carried out at 32°, and on solid gallium at 28°. To freeze the liquid gallium, cooled alcohol was passed through the jacket of cell *B*. Gallium of 99.99% purity was used in the work; the H<sub>2</sub>SO<sub>4</sub> was twice distilled.

**Fig. 1**

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

Figure 2 gives the data on the overvoltage values on solid (curve 1) and liquid (curve 2) gallium. As is seen from the figure,  $\eta_t$  is 25-30 mV lower than  $\eta_l$ ; the slope of the polarization curves on solid and liquid gallium is practically the same and is equal to 0.095 V. If the electrolyte solution is not sufficiently carefully saturated with hydrogen or if it is passed through

If several bubbles of air are then passed through it,  $\eta$  on solid gallium proves, depending on the section of the polarization curve, to be 0.096-0.166 V higher than the value that occurred in the solution containing no oxygen (Fig. 2, curve 3); the slope of the polarization curve increases to 0.130. The hydrogen overvoltage on liquid gallium remains unchanged. Upon subsequent purification of the solution from oxygen and cathodic polarization of the electrode with a current of  $1 \cdot 10^{-1}$  A/cm<sup>2</sup>, the oxide film on solid gallium is reduced and  $\eta$  on solid gallium decreases, approaching the value that occurred in the solution containing no oxygen. With cathodic polarization of the solid oxidized gallium electrode by a current of  $1 \cdot 10^{-3}$  A/cm<sup>2</sup>, reduction of the electrode is not observed.

**Fig. 2.** Dependence of the overvoltage ( $\eta$ ) in 1 N H<sub>2</sub>SO<sub>4</sub> on solid gallium (1), liquid gallium (2), and oxidized solid gallium (3).

Figure 3 gives data from a series of measurements demonstrating the change in  $\eta$  during successive oxidation and reduction of a gallium electrode. The experiment was carried out as follows. In a solution carefully saturated with hydrogen, the  $\eta, \lg i$  curve was recorded on liquid gallium (curve 2). Then several bubbles of air were passed through the solution, the gallium was frozen, and the polarization curve was again recorded (curve 3). Upon subsequent purification of the solution from traces of oxygen and cathodic polarization of the electrode with a current of  $1 \cdot 10^{-1}$  A/cm<sup>2</sup>, the oxide film on the electrode surface was reduced and the overvoltage decreased (curve 1). After melting the electrode under these conditions, the initial value of  $\eta$  on liquid gallium was observed (curve 2). During the introduction of traces of oxygen into the solution, subsequent saturation of the solution with hydrogen, and also during transfer of gallium from one aggregate state to another, the electrode was polarized with a current of  $1 \cdot 10^{-3}$  A/cm<sup>2</sup>.

From the data presented it follows that traces of oxygen, which increase  $\eta$  on solid gallium, do not change  $\eta$  on liquid gallium. In order to clarify the reason for the absence of an effect of oxygen on  $\eta$  on liquid gallium, we performed the following experiment. A solid oxidized gallium electrode, under cathodic polarization with a current of  $\sim 10^{-3}$  A/cm<sup>2</sup>, was melted and then frozen again.

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

After careful removal of oxygen from the solution,  $\eta$  on the refrozen gallium electrode proved to be lower than the value that had occurred on the liquid electrode and corresponded to  $\eta$  on the solid reduced gallium electrode. From this experiment it follows that the oxide film on liquid gallium, unlike that on solid gallium, is readily reduced, and that a solid oxidized gallium electrode, after passing through the liquid state, proves to be reduced. A more ready passivation of solid gallium in comparison with liquid gallium was observed by Schwabe<sup>4</sup>, who studied the anodic dissolution of gallium.

**Fig. 3.** Change in  $\eta$  during successive oxidation and reduction of gallium in 1  $N$   $H_2SO_4$ .

**I** –freezing of gallium in the presence of traces of  $O_2$ ;

**II** –reduction of a solid oxidized gallium electrode with a current of  $1 \cdot 10^{-1}$  A/cm<sup>2</sup> and removal of  $O_2$  from the solution;

**III** –melting of reduced gallium.

Using an alternating-current bridge, we recorded capacitance curves  $C$  on liquid, solid reduced, and oxidized gallium electrodes in 1  $N$   $H_2SO_4$ . In all three cases the same gallium droplet served as the electrode under study; by the method described above it was converted from one state to another. To monitor the state of the gallium surface ...

...electrode, capacitance measurements were always accompanied by measurements of  $\eta$ . In alternating-current measurements the auxiliary electrode was a large platinized platinum electrode introduced into the solution. The measurements were carried out at 5 kc. In Fig. 4, capacitance values, referred to the entire surface of the electrode, are compared at different  $\eta$ . In accordance with the data of work (<sup>5</sup>), on liquid and solid reduced gallium electrodes the values of  $C$  practically coincided. However, on the solid oxidized electrode  $C$  was 1.5–1.7 times lower than on the reduced one. We compared the changes with time of  $C$  and  $\eta$  on a solid oxidized gallium electrode during its reduction. As the electrode was reduced,  $\eta$  decreased, whereas  $C$  increased.

**Fig. 4.** Dependence of capacitance on potential in 1  $N$   $H_2SO_4$  on a solid reduced gallium electrode (1), a liquid electrode (2), and a solid oxidized gallium electrode (3).

On the basis of the experimental material obtained in the present work, it seems to us unambiguously proved that on gallium  $\eta_s < \eta_l$ . The opposite relation between the values  $\eta_s$  and  $\eta_l$  observed in work (<sup>3</sup>) is apparently connected with

the fact that the solid gallium in the experiments of the cited authors was oxidized by traces of  $O_2$  introduced into the  $H_2$  solution because of its insufficient purification. As the authors indicate, in order to obtain stable values of  $\eta$  on solid gallium they had to saturate the solution with  $H_2$  for not less than 1/2 day. It follows from this that oxidation of gallium in their experiments proceeded slowly with time because of the small amount of  $O_2$  in the solution. In a special experiment we showed that the correct relation between  $\eta$  on solid and liquid gallium can be observed even when the initial droplet of liquid gallium was placed in the cup ( ) in air and then immersed in the acid solution. After thorough removal of  $O_2$  from the solution and cathodic polarization of the liquid electrode for some time by a current not exceeding  $4 \cdot 10^{-4}$  A/cm<sup>2</sup>,  $\eta_l$  proves to be higher than  $\eta_s$ , although the scatter of points on the polarization curves themselves, recorded under these conditions, increases. The latter is apparently connected with the presence of impurities in the solution, which we usually removed from the solution by preliminary prolonged cathodic polarization of the gallium electrode. It should be noted that the values of  $\eta$  on liquid gallium observed in work (3) are close to ours.

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

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