

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

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The present work has involved a study of the hydrogen overvoltage on solid and liquid gallium in 1 N H_2SO_4 , the aim being to elucidate the effect of certain factors, including the state of aggregation, on the kinetics of hydrogen evolution at an electrode. The fact that the melting point of gallium (29.78°) is close to room temperature makes for ease in carrying out such experiments and opens the possibility of performing measurements in aqueous solutions of various concentrations. The literature contains contradictory statements concerning the relation of the overvoltages on solid (η_s) and liquid (η_l) gallium. The work of Bowden [1] and Stelling [2] would indicate that $\eta_s < \eta_l$, while Christov and his coworkers [3] report the reverse relation, namely, $\eta_s > \eta_l$.

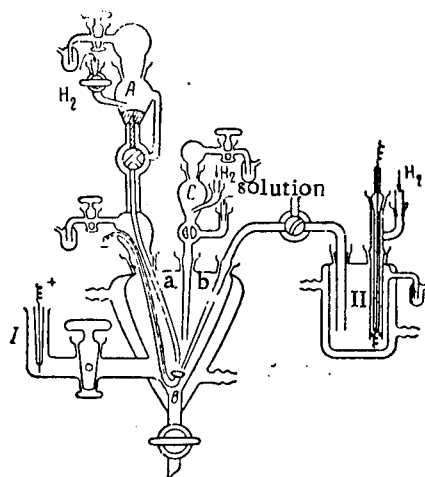


Fig. 1.

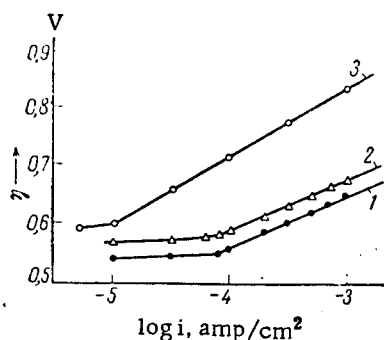


Fig. 2. Variation of the overvoltage (η) on: Solid gallium (1), liquid gallium (2), and oxidized solid gallium (3), in 1 N H_2SO_4 .

Measurements were carried out in the apparatus shown in Fig. 1. Lumps of solid gallium were placed in the cell A and the entire apparatus then filled with hydrogen. A hydrogen-saturated 1 N H_2SO_4 solution which had been previously purified by extended cathodic polarization on a gallium electrode was then transferred into the vessel B. The gallium was melted and forced by the hydrogen pressure through the tube a into the cup b with the platinum contacts, working so that none of the metal was left in a. The upper end of the tube a projected up into the cell A so that gallium could be obtained from the bulk of the metal. It was necessary to completely remove the gallium from tube a in order to avoid cracking the tube when the gallium froze and expanded. In addition, adherence of the metal to the glass was prevented by keeping the walls of tube a and cell A moist with the 1 N H_2SO_4 solution. The drop of gallium which protruded into the cup served as the working electrode. The dimensions of the electrode were determined microscopically and proved to be $\sim 1 \text{ cm}^2$. The anode was the platinum electrode I; potentials were measured with respect to the hydrogen electrode II which was placed in the same solution. Measurements were carried out at 32° with the liquid gallium and at 28° with the solid. The liquid gallium was frozen by passing cooling alcohol through the jacket of cell B. The gallium used in this work had a purity of 99.99% and the H_2SO_4 had been redistilled twice.

Data on the overvoltages on solid gallium (curve 1) and liquid gallium (curve 2) are shown in Fig. 2. It is seen that η_s is 25-30 mV

lower than η_l and that the slopes of the two polarization curves are practically identical at 0.095 V. By failing to entirely saturate the electrolytic solution with hydrogen or by introducing air bubbles, η values can be obtained for solid gallium which are 0.096-0.166 V higher than the value obtained with a solution free of oxygen, the difference depending on the segment of the polarization curves (Fig. 2, curve 3), the curve slope increasing at the same time to

0.130. These same factors have no effect on the hydrogen overvoltage on liquid gallium. Subsequent removal of oxygen and cathodic polarization at $1 \cdot 10^{-1}$ amp/cm² reduces the oxide film on the solid gallium and causes η to fall to approximately the same value that it had in the oxygen-free solution. Reduction is not observed when the oxidized solid gallium electrode is cathodically polarized with a current of $1 \cdot 10^{-3}$ amp/cm².

Data from a series of measurements demonstrating the effect of successive oxidation and reduction of the gallium electrode on η are shown in Fig. 3. These experiments were carried out in the following manner. The η , log i

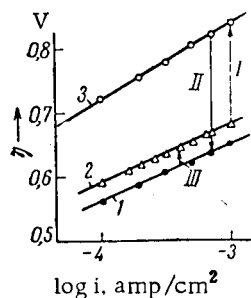


Fig. 3. Alteration in η during successive oxidation and reduction of gallium in 1 NH_2SO_4 . I) Gallium frozen in the presence of traces of O_2 ; II) oxidized solid gallium electrode reduced by a current of $1 \cdot 10^{-1}$ amp/cm², with removal of O_2 from solution; III) reduced solid gallium melted.

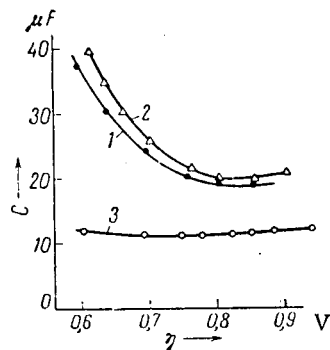


Fig. 4. Relation between capacity and potential in 1 $\text{N H}_2\text{SO}_4$ on: Reduced solid gallium electrode (1); liquid gallium electrode (2), oxidized solid gallium electrode (3).

curve for liquid gallium was first developed in a solution which had been thoroughly saturated with hydrogen (curve 2). Several air bubbles were then passed through the solution, the gallium was frozen, and a new polarization curve developed (curve 3). The oxide film on the electrode surface was reduced by removing the traces of oxygen from the solution and carrying out cathodic polarization with a current of $1 \cdot 10^{-1}$ amp/cm², thus causing the overvoltage to fall (curve 1). The electrode was melted and it was observed that η returned to the original value for liquid gallium (curve 2). The electrode was under polarization by a current of $1 \cdot 10^{-3}$ amp/cm² during the introduction of oxygen into the solution, and during subsequent saturation of the solution with hydrogen, and during passage of the gallium from one state of aggregation to another.

It follows from these figures that traces of oxygen will increase the value of η for solid gallium but leave the value for liquid gallium unaltered. The following experiment was carried out to explain the fact that oxygen had no effect on the η value for liquid gallium. The oxidized solid gallium electrode was melted while undergoing cathodic polarization with a current of $\sim 10^{-3}$ amp/cm², and then refrozen. On carefully freeing the solution of oxygen, the value of η on the newly frozen gallium electrode proved to be lower than the value for the liquid electrode and corresponded to the η value for the reduced solid gallium electrode. It follows that the oxide film on liquid gallium differs from the corresponding film on solid gallium in that it is readily reduced, with the result that an oxidized solid electrode can be carried through the liquid state into the reduced condition. Schwabe, studying the anodic dissolution of gallium [4], observed that solid gallium is more readily passivated than liquid.

An alternating current bridge was used to develop capacity curves for liquid, reduced solid, and oxidized solid gallium electrodes in 1 $\text{N H}_2\text{SO}_4$. The same drop of gallium served as the electrode in all of these measurements, this being carried from one aggregation to another in the manner described above. In order to check the surface state of gallium electrode, the measurements of capacity, C , were always accompanied by companion measurements of η . A large platinized platinum plate was introduced into the solution to serve as the reducing electrode for the alternating current measurements. These measurements were carried out at 5 kc/sec. A comparison of capacities referred to the entire surface area of the electrode at various values of η is given in Fig. 4. The data of [5] have shown that the C values for liquid and reduced solid gallium electrodes are practically identical. On

the other hand, the value of C for the reduced solid electrode is 1.5-1.7 times greater than C for the oxidized solid electrode. We have compared the time variation of C and η during reduction of the oxidized solid gallium electrode, finding that η fell and C increased as electrode reduction proceeded.

The experimental material collected in the present work appears to us to give definite proof that $\eta_s < \eta_l$ for gallium. The fact that the inverse relation was observed in [3] is indication of oxidation of the solid gallium by traces of O_2 carried into solution through imperfectly purified H_2 . The authors themselves pointed out that it was necessary to saturate the solution with H_2 for at least a half day in order to obtain reproducible η values. It follows that the oxidation of gallium in these experiments must have proceeded slowly because of the small amount of O_2 in solution. Special experiments showed that the correct relation for η on solid and liquid gallium can be obtained even if the

liquid metal drop was introduced into the cup B in air and then immersed in the acid solution. After thoroughly removing O_2 from the solution and carrying out cathodic polarization of the liquid electrode with a current no greater than $4 \cdot 10^{-4}$ amp/cm², η_l proved to be higher than η_s , although the point scatter on the polarization curves developed under these conditions was higher than before. This scatter is obviously due to the presence of those solution contaminants which were usually removed prior to extended cathodic polarization of the gallium electrode. It is to be noted that the η values reported in [3] are close to our own.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.
