THE CROSSED POLARIZED METALLIC THREAD METHOD FOR DETERMINING ZERO CHARGE POINTS

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The problem of determining the zero charge points of metals is known to be of very great importance in present day electrochemistry [1]. Some of the existing methods are indirect [2]. In a number of cases, such as platinum for example, different methods give substantially differing values for the zero points [3]. The work presented here is an attempt to find a new and direct method of measuring the zero charge points of metals*. The method is based on measuring the force barrier preventing contact between polarized metallic threads immersed in a solution of an electrolyte. In a solution of an electrolyte, the barrier is primarily due to the repulsive forces produced when the ionic atmospheres overlap. With small electrolyte concentrations and not too small charges in the double layer, the repulsive forces can outweigh the molecular attraction forces at moderate distances of the order of thickness of the ionic atmosphere [5]. At substantially smaller distances, the molecular attraction forces are known to predominate. Accordingly when an external force overcomes the force barrier, the threads come into contact, as may be seen from the

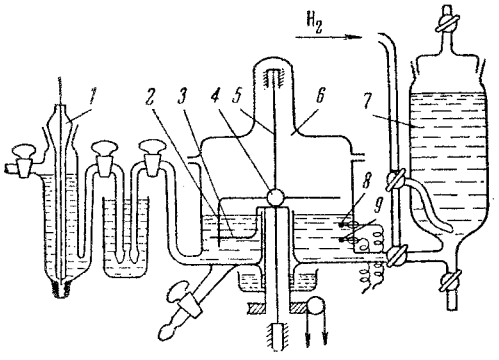

Fig. 1. Diagram of apparatus for measuring force barriers between smooth metallic conductors.

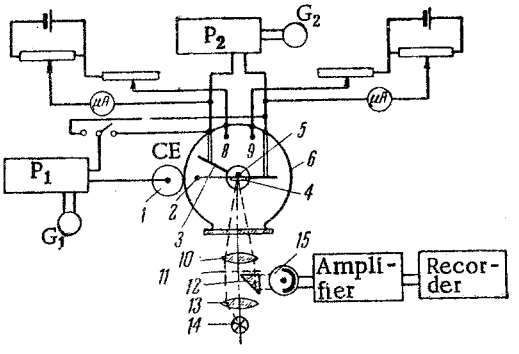

Fig. 2. Diagram of equipment. The numbers 1-9 have the same meaning as in Fig. 1.

discontinuous disappearance of the electrical resistance between them. According to the simple theory of [5, 6], at the zero charge point the force barrier will disappear or take on a minimum value if repulsive forces of some other kind are present.

EXPERIMENTAL PART

The threads used were two smooth wires 200-300 μ in diameter. The wires are made of the metal whose zero charge point we wished to measure. The wire 2 was soldered to an elastic suspension 5, and formed the arm of a torsion balance (Fig. 1). The suspension 5 of phosphor bronze had a rectangular cross-section and was calibrated in advance. The angular deflection of the suspension was measured with the mirror 4 attached to it. The thread 3 was soldered to the stopper passing through the entrance to the vessel 6. The stopper was connected by a worm drive through a transmission system to a D.C. motor. It was thus possible to move thread 3 slowly and evenly up to or away from thread 2. To keep the threads from rubbing together while they were moving, they were mounted so as to have the same axis of rotation. This was done by constructing the apparatus in such a way as to have the elastic suspension 5 with the thread 2 exactly in the center of the rotating stopper with the thread 3 fastened to it. The two threads meeting at an angle of 90° were placed in the ring-shaped hermetically sealed vessel 6. The electrolyte solution was

*For the first report on this work see [4].

introduced into vessel 6 from vessel 7, where it went through a preliminary purification, and after use was let out through the drain. The system of connected glass tubing made it possible to saturate the solution in vessels 6 and 7 with electrolytic hydrogen. The vessel 6 was connected with the comparison electrode 1 through an electrolyte switch. The threads were polarized by the auxiliary electrodes 8 and 9 made of platinum wire and sealed into vessel 6. All the glass parts of the apparatus were made of "pyrex" glass.

TABLE

Polarization	Current density m A/cm^3	Time, min.
Cathode	40-50	180-240
Anode	2-3	15
Cathode	40-50	15
Anode	2-3	15
Cathode	40-50	15

The construction of the apparatus was such as to permit charging each of the wires to any desired value of potential. The threads were polarized by means of the scheme shown in Fig. 2, where each thread had its own voltage source and could be polarized to any value of potential independently of the other thread. The potentials of the threads were measured with the potentiometer P_1 against a calomel electrode when measuring in KCl solutions and against a mercury-sulfuric acid mercurous oxide electrode in $MgSO_4$ and H_2SO_4 solutions. Since it is necessary to find the instant at which the threads come in contact in order to determine the force barrier, a small potential difference (0.01 V) was set up between the threads, and measured by the potentiometer P_2. As soon as they came together, the potentials on the threads became equal, the balance of the system was destroyed, the automatic equipment was actuated and thread 3 was moved away from thread 2.

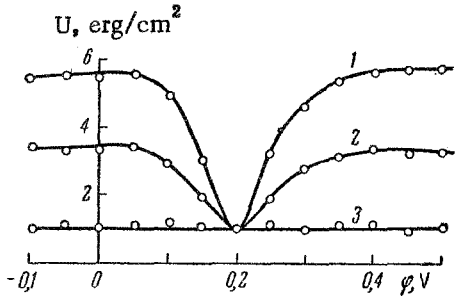

Fig. 3. Force barrier as a function of potential of platinum wires in KCl solutions: 1) 0.001 N; 2) 0.01 N; 3) 0.1 N.

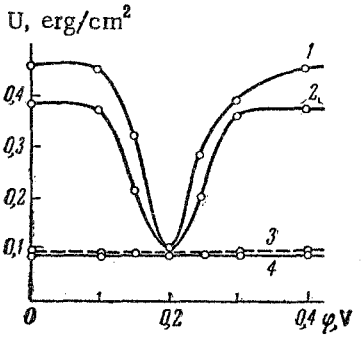

Fig. 4. Force barrier as a function of potential of platinum wires in $MgSO_4$ solutions: 1) $3 \cdot 10^{-4}$ N; 2) 10^{-5} N; 3) 10^{-1} N; 4) 10^{-2} N.

The angular deflection of the elastic suspension was measured by means of a grating photorelay, which worked as follows. The light rays from the lamp 14 passed through the condensing lens 13, and the grating 11, consisting of alternate light and dark bands of equal width, then through the objective lens 10 and were focused on the mirror 4, fastened to the elastic suspension, were reflected from the mirror and passed through the same objective lens 10 and prism 12 and were deflected to the photo cell 15. Thus half of the grating 11 was projected on the other half. Accordingly, when the mirror rotated, the lines on the one half of grating 11, reflected by the mirror 4, were displaced with respect to the lines on the other half, thus reducing or increasing the illumination uniformly over the whole area of the photo cell. At the instant the bright lines of both halves of the grating are completely in coincidence, the illumination of the photo cell is a maximum. With further rotation of the mirror, the dark lines of one half of the grating begin to cover up the bright spaces in the other half of the grating. This causes the illumination of the photo cell to decrease, and it reaches a minimum when the bright spaces are completely covered up by the dark lines, then again increasing to a maximum etc. The width of the bands in the grating is such that when making measurements, the maximum angle of rotation of the arm, and accordingly the maximum change in illumination of the photo cell occurs in a range where the illumination varies approximately linearly with the angle of rotation of the mirror. Linearity is maintained over a considerable part of any of the half periods except in the immediate vicinity of the maximum or minimum illumination. The photo cell signal, after passing through a vacuum tube amplifier, was recorded on the ÉPP-09, where the scale had already been calibrated in units of force. On account of the sensitivity of the equipment to various types of shock, the most sensitive part was put on a damping plate mounted on a post set in the ground and insulated from the field. Further, in order not to introduce additional mechanical or other disturbances, the equipment was remote controlled.

At the start of the experiment, the threads were separated some distance from one another. The zero position of thread 2 (see Fig. 1), fastened to the elastic suspension, was marked on the scale of the ÉPP-09 electronic potentiometer. Next, known potentials were applied to the threads. Then thread 3 was carefully brought up close to thread 2. If thread 3 was close enough to thread 2, and a force barrier was present, thread 2 began to move in the same direction as thread 3, rotating the suspension through the angle recorded on the ÉPP-09 potentiometer and proportional

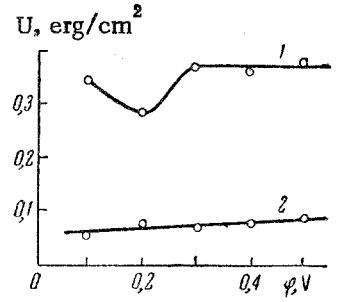

Fig. 5. Force barrier as a function of potential of platinum wires in H_2SO_4 solutions: 1) 10^{-3} N; 2) 10^{-2} N.

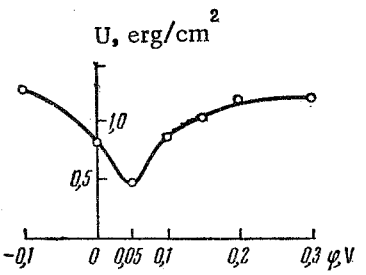

Fig. 6. Force barrier as a function of potential of gold wires in 0.001 N KCl solution.

to the interaction force between the threads. At the instant the force barrier was overcome and the electrolyte film was penetrated, thus putting the threads in contact with one another, the reading on the electronic potentiometer chart gave the magnitude of the force barrier between the threads. Before the measurements, all the glass parts of the apparatus were carefully washed with dichromate and acid or hot sulfuric acid, and then with double distilled water. The salts used to make up the solutions were recrystallized and baked. The platinum and gold threads* were cleaned in the following way: they were put into concentrated sulfuric acid for 3 minutes, then placed in vessel 6 and further cleaned electrochemically in 1 N sulfuric acid without taking the threads out of the vessel. The sequence of the electrochemical operations is given in the table. After the above treatment, the sulfuric acid solution was replaced by hydrogen and the vessel containing the threads was washed several times with the electrolyte solution in which the measurements were to be made, and was then finally filled with the solution. Before the measurements, the iron wires were immersed for 3-4 min in hot 10% NaOH solution, and then washed with double distilled water. In order to free

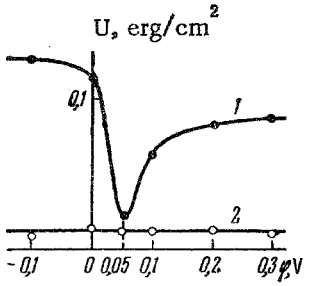

Fig. 7. Force barrier as a function of potential of gold wires in $La(NO_3)_3$ solutions: 1) $5 \cdot 10^{-4}$ N; 2) 10^{-3} N.

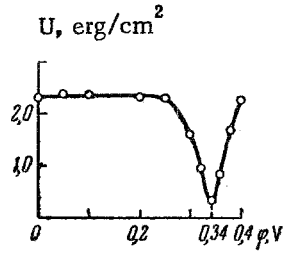

Fig. 8. Force barrier as a function of potential of iron wires in 0.01 N NaOH solution.

the solution of surface active organic contaminants and oxygen, a platinized platinum screen was placed in the vessel, and hydrogen was passed through for a considerable time. The repulsive forces can only be measured on the above apparatus in the ranges of potential where no gas is liberated on the electrode wires.

The values of the force barriers were measured as a function of the potentials of the wires and the concentration of electrolyte. Both wires were charged to practically equal potentials (the difference between them being 0.01 V).

*The threads were used without any preliminary mechanical treatment, since mechanical treatment (for example cleaning the surface with moist powdered glass, which does not settle after 7 minutes in water) causes rapid breakdown of the electrolyte film, so that it is impossible to measure the force barrier.

All the potentials are given with reference to a normal hydrogen electrode. It was assumed in making the calculation that the potential of a saturated calomel electrode against a normal hydrogen electrode is equal to 0.247 V, and 0.617 V for a mercury sulfate electrode. Figure 3 shows how the force barrier changes with the potentials on the platinum wires. The measurements were made in KCl solutions (0.1, 0.01, and 0.001 N). A clearly defined minimum is observed at a potential of 0.20 ± 0.01 V, the minimum gradually flattening out with increase in electrolyte concentration, and, in 0.1 N solution, where the surface charge is not appreciably diffuse [6], it disappears completely. The same picture is also observed in $MgSO_4$ and H_2SO_4 solutions (Figs. 4, 5).

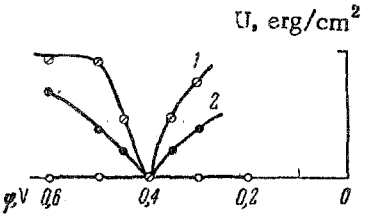

Fig. 9. Force barrier as a function of potential of iron wires in HCl solutions: 1) $3 \cdot 10^{-3}$ N; 2) 10^{-2} N; 3) 10^{-1} N.

Measurements of the force barriers on gold were made in 10^{-3} N KCl solution (Fig. 6), and in $3 \cdot 10^{-4}$ N $La(NO_3)_3$ (Fig. 7). In both cases the minimum in the curve corresponds with the potential 0.05 V. This value is in agreement with the only published data on the zero point of gold [7]. Further, values were measured for the force barriers of iron using 200 μ diameter wires. In 10^{-2} N NaOH solution (Fig. 8) in which iron is passive, the force barrier minimum occurs at 0.34 V; in HCl solutions, where the iron is active, the force barrier minimum is observed at − 0.4 V (Fig. 9), i.e., at a potential of 0.74 V more negative than the zero potential of passive iron. This value is in agreement with the data taken by Ayazyan [8].

Our data, taken on iron in HCl solutions give the best agreement with classical electric double layer theory and the results of determining zero points from the capacity in dilute solutions [9] which is also based on making use of the increase in diffuseness of the double layer with dilution. This case is, however, apparently complicated, since our experiments showed that in HCl solutions using platinum and gold wires, we were not able to observe repulsive forces at any potentials. In all the other solutions, considerable repulsive forces are found to exist at the zero point, but the nature of the forces is not entirely clear. This result cannot be accounted for by saying that there are different crystal faces of the metal with different zero potentials at the point of contact, since repulsive forces of the same magnitude are observed in strong solutions where the forces are independent of the potential. The good reproducibility of the experiments, and the careful purification given the solutions are against any possible assumption of extraneous solid particles falling in by chance, which would make it difficult to get the wires closer together than the radius of the ion cloud.

For platinum and gold, the potential for minimum repulsive forces turned out to be independent of the nature of the anion. This may be accounted for by the fact that there is no appreciable difference in the specific adsorption of Cl^- and SO_4^{2-} on platinum or of Cl^- and NO_3^- on gold in millinormal solutions. The actual potential for minimum potential forces in the most completely studied case of platinum (+ 0.2 V) differs by 0.1 V from the result for the zero charge potential found in acidulated 1 N Na_2SO_4 solution by the adsorptive method (+ 0.11 V) and lies between this value and the one found by one of the authors using the edge angle method [3]. The capacity method [10] in this case gave uncertain results, in qualitative agreement however with our data. Good agreement with the theory of Guy and Stern is shown by the fact that in a 2-2 charge electrolyte, the maximum concentration at which a minimum is still to be observed in the repulsive forces on platinum is an order of magnitude less than in a 1-1 charge electrolyte.

SUMMARY

1. A technique has been developed which makes it possible to use a measurement of the force barrier between smooth solid metals as a function of potential to find the zero charge potential of the metals.

2. Curves have been obtained for the force barriers as a function of potential at various electrolyte concentrations. Measurements were made of the force barriers occurring when bringing together wires made of platinum, gold, and iron.

3. The zero charge points found are for platinum, 0.20 V, for gold, 0.05 V, for passive iron, 0.34 V, and for active iron − 0.4 V.

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