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The Platinum Electrode.

VII. VIII. The effect of poisoning on the capacity of the platinum electrode[1]

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In a number of papers[2] it has been pointed out that the investigation of the capacity of the platinized and smooth platinum electrodes is of considerable interest since it permits a number of problems to be solved which are connected with the state of the electrode/solution interface.

In the present investigation we studied the effect of poisoning on the character of the curves representing the charging of a smooth and of a platinized electrode with the hope of obtaining from this some additional information regarding the effect of poisoning on the adsorption phenomena on a platinum electrode, and on the kinetics of the ionization of adsorbed hydrogen.

Procedure

The procedure which we employed for obtaining the platinized and smooth electrode is described in previous papers. In order to poison the platinized electrode, a definite amount of the poison

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[1] In the present paper the authors examine the data obtained by A. Šlygin, M. Razumovskaya and K. Rosental on the poisoning of the platinized platinum electrode, and by B. Ershler on the poisoning of the smooth platinum electrode.

[2] Šlygin a. Frumkin, Acta Physicochimica URSS, 3, 791 (1935). Šlygin, Frumkin a. Medwedowsky, Acta Physicochimica URSS, 4, 911 (1936). Frumkin a. Šlygin, Acta Physicochimica URSS, 5, 819 (1936). Ershler a. Proskurnin, Acta Physicochimica URSS, 6, 195 (1937). Ershler, Acta Physicochimica URSS, 7, 327 (1937). Ershler, Deborin a. Frumkin, Acta Physicochimica URSS, 8, 565 (1938).

was introduced into the cell containing the electrode, after which hydrogen was passed through the liquid during one hour. Then the solution was poured off and subjected to analysis; the cell was filled with the initial solution in a current of hydrogen, and measurements of the cathodic and anodic polarization were carried out in the usual manner.

In order to poison the smooth electrode, a solution containing a definite amount of the poison was introduced into the cell. Then the electrode was introduced into it and, by means of cathodic polarization, was brought to a potential which was 0.08 V. more positive than the reversible hydrogen potential in the same solution. The electrode was maintained at this potential for a period of 2—3 hours during which the vessel was shaken from time to time. Since the quantity of liquid in the vessel amounted to only 0.007 cm.^{3}, we assumed that within this time interval all of the poison was adsorbed on the electrode. After this polarization data were obtained in the manner described in previous papers.

Experimental results

A. Poisoning by As_2O_3

Charging curves were obtained using an electrode poisoned by gradually increasing amounts of As_2O_3. For the platinized electrode, normal sulphuric acid served as the electrolyte; and for the smooth electrode, half normal solution of sodium sulphate acidified with 0.02 *N* sulphuric acid. The data for the platinized electrode are presented in the form of curves in Figs. 1, 2 and 3, and for the smooth electrode in Fig. 4. Along the ordinates are plotted the values of the potential (in volts) with reference to a reversible hydrogen electrode, in the same solution, and along the abscissae, the total quantities of electricity *Q* which passed through the electrode (in coulombs for the platinized electrode and in micro-coulombs for the smooth electrode[3]; these designations remain without change in all the figures presented).

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[3] The apparent surface of the platinized electrode was 44 cm.^{2}, and that of the smooth electrode, 0.74 cm.^{2}

Curve *I* of Fig. 1 was obtained with a platinized electrode under standard conditions, *i. e.*, in the absence of As_2O_3[4].

Curves *II*[5], *III* and *IV* of Fig. 1 and curves *I* and *II* of Fig. 2 were obtained with a platinized electrode which had been poisoned by 7×10^{-7}, 4.7×10^{-6}, 1.5×10^{-5}, 5.5×10^{-5} and $20.5 \times \times 10^{-5}$ gr. atoms of As respectively.

The polarizing current amounted to 2×10^{-3} A.

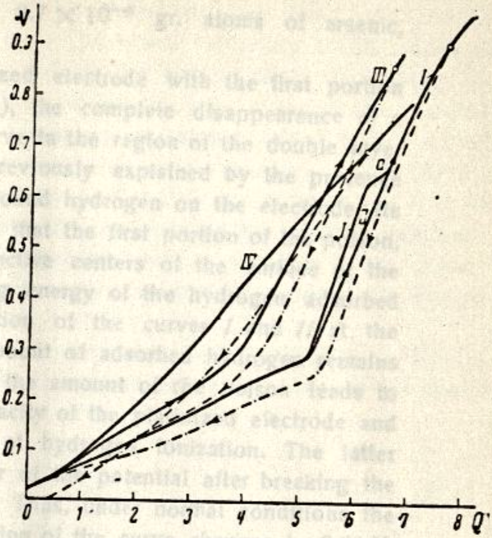

Fig. 1. Poisoning of a platinized electrode by As.

For the smooth electrode, curve *a* (Fig. 4) represents the data obtained with a non-poisoned electrode (polarizing current ca. 10^{-7} A); and curves *b*, *c*, *d* and *e*, the data obtained with electrodes poisoned by 5.4×10^{-11},

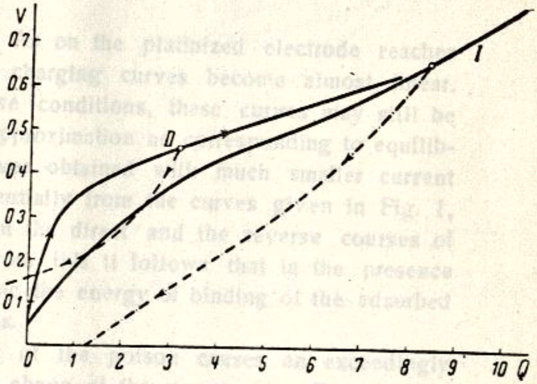

Fig. 2. Poisoning of a platinized electrode by large amounts of As.

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[4] The curves representing anodic polarization (forward course) for the platinized electrode are drawn as solid lines in all the figures, while the curves representing cathodic polarization (reverse course) are drawn in dotted lines.

[5] Curve *II* almost completely coincides with curve *I*, a difference being noticeable only in the middle portion of the curve showing the direct course.

2.7×10^{-10}, 5.4×10^{-10} and 2.7×10^{-8} gr. atoms of arsenic, respectively.

After poisoning the platinized electrode with the first portion of As_2O_3 (see curve *II*, Fig. 1), the complete disappearance of a short arrest on the charging curve in the region of the double layer is observed. This arrest was previously explained by the presence of a certain amount of firmly bound hydrogen on the electrode. Its disappearance attests to the fact that the first portion of the poison, being adsorbed on the most active centers of the surface of the electrode, decreases the binding energy of the hydrogen adsorbed on these centers. The intersection of the curves *I* and *II* at the point *a* shows that the total amount of adsorbed hydrogen remains constant. A further increase in the amount of the poison leads to a noticeable decrease in the capacity of the platinized electrode and to a decrease in the velocity of hydrogen ionization. The latter causes a change in the behaviour of the potential after breaking the circuit of the polarizing current. Thus, under normal conditions the potential in the double layer region of the curve changes by 0.01 V. in 2 hours after breaking the circuit, while after poisoning (1.5×10^{-5} gr. atom As), the decrease of the potential is already of the order of 0.03 V. after 30 min.

When the amount of As on the platinized electrode reaches 1.5×10^{-5} gr. atoms the charging curves become almost linear. However, even under these conditions, these curves may still be considered with a certain approximation as corresponding to equilibrium states, since the curves obtained with much smaller current densities do not differ essentially from the curves given in Fig. 1, and the divergence between the direct and the reverse courses of the curves is not great. From this it follows that in the presence of larger quantities of arsenic the energy of binding of the adsorbed hydrogen markedly increases.

A still larger quantity of the poison causes an exceedingly marked deformation in the shape of the curves (see Fig. 2). For example from curve *II* (Fig. 2) it is seen that the removal of hydrogen in noticeable amounts begins only after a potential of 0.38 V. has been attained. However, from this fact it is difficult to draw any conclusions regarding the magnitude of the binding energy, since these curves correspond already to clearly non-equilibrium states.

This is shown by the large loop between the direct and reverse courses of the curves, by the increased instability of the potential after breaking the circuit, and by the marked effect of a change in the density of the polarizing current upon the shape of the charging curve. Curve *I* (Fig. 3)[6] represents the data obtained with a current density 10 times smaller than the one usually adopted by the authors (electrode poisoned by 1.47×10^{-5} gr. atoms of As). A comparison of this curve with curve *II* taken under standard conditions leads to the following conclusion: With a decrease in the density of the polarizing current, the curve noticeably approaches a straight line in shape.

When large amounts of the poison are present the "double layer" region on the curve disappears completely. This is the result both of the slowing down of the desorption of hydrogen and of the earlier start of the oxygen adsorption, which is probably considerably facilitated if hydrogen is also present on the electrode.

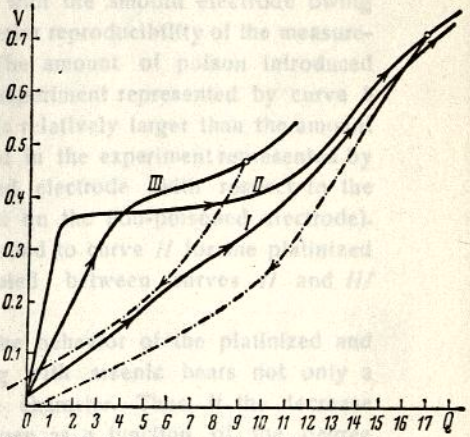

Fig. 3. Effect of the density of the polarizing current upon the charging curves of a platinized electrode poisoned by large amounts of As.

The experimental data given above can be represented in the form of a curve characterizing the activity of the poison by plotting the amount of the poison in gram atoms as abscissae against the corresponding decrease in the adsorption of hydrogen (gr. atoms) on the entire electrode as ordinates[7]. From an examination of curve *I* (Fig. 11) it follows that the activity of the first portions of the

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[6] Data taken from a 2nd series of experiments.

[7] The amount of hydrogen adsorbed on the electrode was determined from the polarization curve in the following manner: the linear portion of the curve, corresponding to the region of the double layer, was extrapolated to its intersection with the abscissa axis. The linear portion of the curve corres-

poison is much larger than the activity of the last portions. If small amounts of the poison are present, one atom of arsenic acts upon approximately 4 atoms of hydrogen; while if large amounts are present, the reverse is true, *i. e.*, 4 atoms of arsenic act upon only 1 atom of hydrogen.

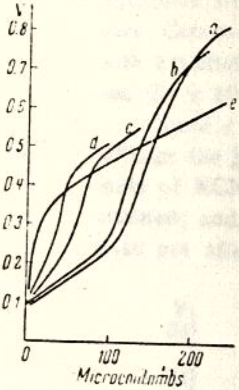

Fig. 4. Poisoning of a smooth electrode by As.

The behavior of the smooth electrode is in good agreement with the behavior of the platinized electrode. The first small amounts of arsenic (Fig. 4, curve *b*) already noticeably change the shape of the curve. (An arrest on the anodic curve for a non-poisoned electrode which is observed with a platinized electrode cannot always be obtained with the smooth electrode owing to the inferior reproducibility of the measurements). The amount of poison introduced in the experiment represented by curve *b* (Fig. 4) is relatively larger than the amount introduced in the experiment represented by curve *II* (Fig. 1) for the platinized electrode (with respect to the total amount of hydrogen adsorbed on the non-poisoned electrode). Therefore curve *b* does not correspond to curve *II* for the platinized electrode, but to a curve located between curves *II* and *III* (Fig. 1).

The observed similarity in the behavior of the platinized and smooth electrodes upon poisoning with arsenic bears not only a qualitative but also a quantitative character. Thus, if the decrease in the amount of adsorbed hydrogen as a function of the degree of poisoning of the surface is calculated from curves *b*, *c* and *d*, it turns out that, during the additions of the first portions of arsenic, each arsenic atom affects the adsorption of approximately 4 hydrogen atoms (3.7 for curve *b* and 3.8 for curve *c*), and then the ratio H/As decreases (2.1 for curve *d*).

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ponding to the region of hydrogen adsorption was also extrapolated to its intersection with the same axis. The intercept between the two points thus obtained gives the quantity of electricity equivalent to the amount of hydrogen adsorbed on the electrode at the equilibrium hydrogen potential.

B. Poisoning by KCN

Experiments with a platinized electrode were carried out under the same conditions as those in which As_2O_3 was used, the only difference being that normal KOH served as the electrolyte in this case. Curves *II*, *III* and *IV* in Fig. 5 represent the results obtained with a platinized electrode in solutions containing 7×10^{-7}, 7×10^{-5}, and 23×10^{-5} gr. mol of KCN, respectively.

Curve *I* is a normal charging curve in the KOH solution without the poison. Upon poisoning the electrode with 23×10^{-5} gr. mols of KCN, a certain limit for the decrease in the capacity is attained; and a further increase in the amount of the poison already does not affect the capacity of the electrode.

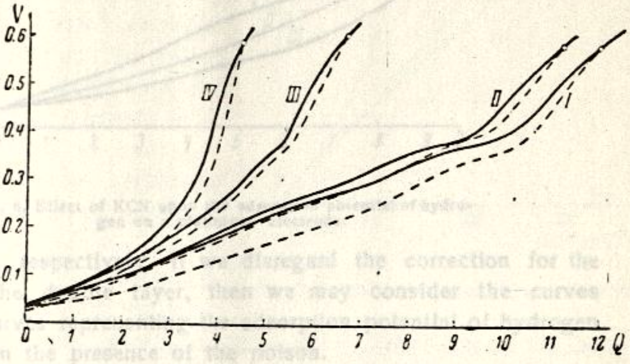

Fig. 5. Poisoning of a platinized electrode by KCN.

It is characteristic that, even if the electrode is poisoned with considerable amounts of KCN, the reversibility of the polarization curves does not decrease, and after the circuit has been broken, the potential also remains quite stable. Hence the conclusion may be drawn that, in all the experiments with an electrode poisoned with KCN, we have conditions which are close to equilibrium ones; and consequently we may attempt to calculate the change in the binding energy of adsorbed hydrogen as a function of the degree of poisoning of the surface.

If we confine ourselves to that part of the curves which refers to hydrogen adsorption (*i. e.*, up to the potential 0.4 V.), we must take into account the fact that the amount of adsorbed hydrogen at standard conditions (without the poison) and at different degrees of poisoning of the electrode changes markedly; and therefore, in order to compare the binding energy, it is necessary to refer the charging curves to a fixed amount of adsorbed hydrogen. This was effected by increasing the abscissa scale of the curves representing the data obtained with the poisoned electrode.

The results are presented in Fig. 6. Curve *I* corresponds to a non-poisoned electrode, while curves *II* and *III* refer to an electrode placed in a solution containing 7×10^{-5} and 23×10^{-5} gr.

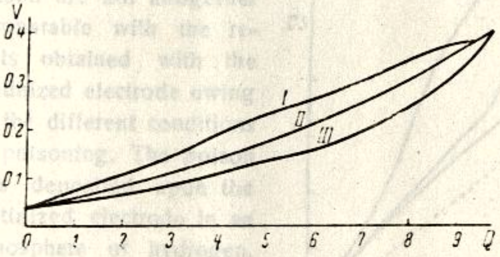

Fig. 6. Effect of KCN upon the adsorption potential of hydrogen on a platinized electrode.

mols of KCN, respectively. If we disregard the correction for the charging of the double layer, then we may consider the curves obtained as curves representing the adsorption potential of hydrogen on platinum in the presence of the poison.

From Fig. 6 it follows that, as the surface becomes covered with the poison, the adsorption potential of hydrogen noticeably decreases. The capacity in the region of the double layer also decreases as the electrode becomes poisoned.

The curve representing the activity of the poison in the case of KCN (curve *II*, Fig. 11) shows that KCN is more effective as a poison than arsenic. This is revealed especially when very small amounts of the poison are used. In this case 1 molecule of KCN influences the adsorption of 10 atoms of hydrogen. The decrease in the adsorption of hydrogen was calculated from the anodic polarization curves making use of the quantity of electricity necessary to attain the potential 0.35 V.

The calculation of the maximum amount of adsorbed KCN which we observed with the platinized electrode (33×10^{-5} gr. mols of KCN) shows that 3.7 molecules of KCN correspond in this case to every surface atom of platinum. This provides grounds for supposing that a surface compound — $Pt(CN)_4$ — forms on the electrode.

The results obtained with a smooth electrode in the presence of this poison are not altogether comparable with the results obtained with the platinized electrode owing to the different conditions of poisoning. The poison was deposited upon the platinized electrode in an atmosphere of hydrogen, the electrode possessing a hydrogen potential. In the case of the smooth electrode the poison was deposited upon the latter at an oxygen potential of 0.8—0.9 V. Therefore, in the latter case it could interact with the oxide film on the platinum and form products which affected the adsorption of hydrogen in a different way.

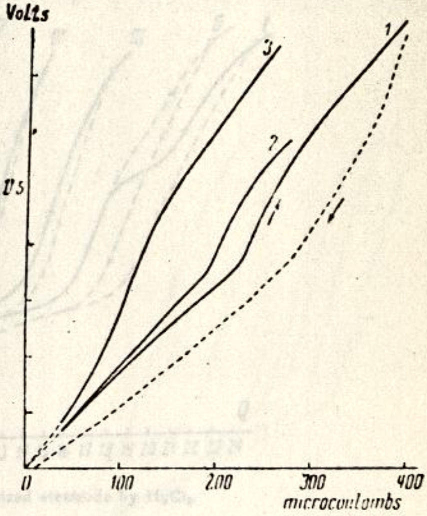

Fig. 7. Poisoning of a smooth electrode by KCN.

The results for the smooth electrode are presented in Fig. 7 in which curve *1* refers to a non-poisoned electrode and curves *2* and *3* refer to electrodes poisoned by 3.4×10^{-10} and 1×10^{-9} gr. mols of KCN, respectively. A half normal solution of sodium sulphate alkalified with $0.02\,N$ sodium hydroxide served as the electrolyte. In comparison with the curves for the platinized electrode, the polarization curves for the smooth electrode are less reversible and do not so clearly express the decrease in the binding energy of hydrogen as a function of the degree of poisoning.

C. Poisoning by $HgCl_2$

The experimental conditions were the same. A normal solution of H_2SO_4 served as the electrolyte for the platinized electrode. The data obtained with the platinized electrode are presented in Fig. 8

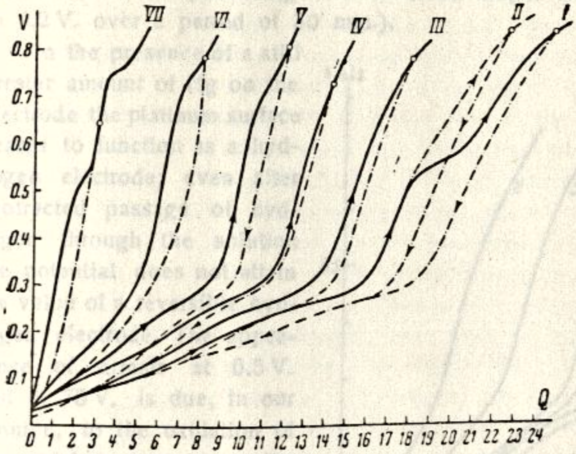

Fig. 8. Poisoning of a platinized electrode by $HgCl_2$.

in which curve *I* refers to a non-poisoned electrode and the remaining curves refer to electrodes poisoned by 3.5×10^{-7}, 2.7×10^{-6}, 2.6×10^{-5}, 5.2×10^{-5}, 9.4×10^{-5} and 12.9×10^{-5} gr. atoms of Hg. As can be seen from curve *II* Fig. 8, the presence of the first portions of the poison on the platinized electrode leads to a marked dwindling of the arrest observed at 0.6 V. just as in the case of poisoning with As_2O_3, the only difference being that the adsorption centers occupied by the poison (evidently in the form of Hg) already do not adsorb hydrogen at all.

An increase in the amount of the poison to 2.6×10^{-5} gr. atoms already begins to show an effect on the outer appearance of the platinized electrode: the color of the latter changes from dark to lighter grey. The capacity falls to 60% of the normal, while the reversibility does not decrease and the potentials remain constant after the interruption of the polarizing current. An arrest appears at the potential 0.75 V. (curve *V*) upon poisoning the electrode with 5.2×10^{-5} of a gr. atom of mercury. And finally, maximum poisoning (as follows from curve *VII*) leads both to an increase of the arrest at the potential 0.75 V. and to the appearance of a new arrest at the potential 0.5 V. The potential of the electrode after switching off the polarizing current is no longer constant (falling to 0.2 V. over a period of 30 min.).

In the presence of a still greater amount of Hg on the electrode the platinum surface ceases to function as a hydrogen electrode; even after protracted passage of hydrogen through the solution the potential does not attain the value of a reversible hydrogen electrode. The appearance of arrests at 0.5 V. and 0. 75 V. is due, in our opinion, to the oxidation of Hg which is present on the surface in an adsorbed state.

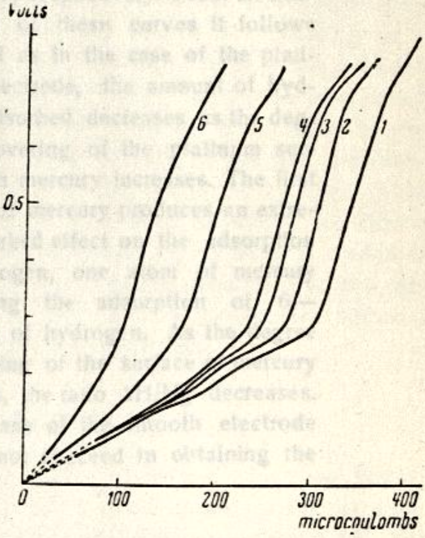

Fig. 9. Poisoning of a smooth electrode by $HgCl_2$.

A curve representing the activity of poison, plotted using the data obtained with a platinized electrode for the poison $HgCl_2$ in H_2SO_4, is shown in Fig. 11 (curve *III*). The decrease in the adsorption of hydrogen was calculated from the curve of the cathodic polarization using the quantity of electricity necessary to pass from the potential 0.35 V. to the reversible hydrogen potential as a measure of the quantity of hydrogen adsorbed. It is characteristic that this curve is very much steeper than the other or, in other words, the activity of $HgCl_2$ as a poison is very much greater than that of KCN and As_2O_3. This is exceptionally strongly pronounced when the amount of poison present is very small. In this case 1 atom of Hg influences the adsorption of as many as 40 atoms of hydrogen.

A series of cathodic curves are given (Fig. 9) for the smooth electrode, since these particular curves were used to calculate the amount of hydrogen adsorbed on the electrode. Curve *1* (Fig. 9) refers to a non-poisoned electrode, while curves *2*, *3*, *4*, *5*, and *6* refer to an electrode poisoned by 4.2×10^{-11}, 1.7×10^{-10}, 3.3×10^{-10}, 6.6×10^{-10} and 13.3×10^{-10} gr. atoms, of mercury respectively. From an examination of these curves it follows that, just as in the case of the platinized electrode, the amount of hydrogen adsorbed decreases as the degree of covering of the platinum surface with mercury increases. The first portion of mercury produces an extremely marked effect on the adsorption of hydrogen, one atom of mercury preventing the adsorption of 6—7 atoms of hydrogen. As the degree of covering of the surface of mercury increases, the ratio ΔH/Hg decreases. In the case of the smooth electrode we did not succeed in obtaining the

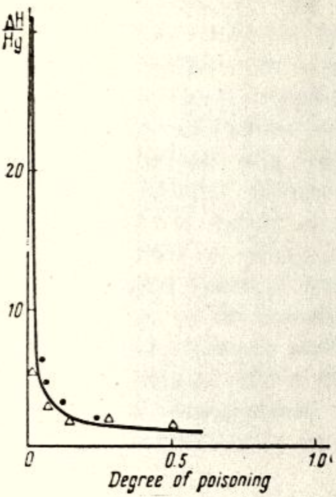

Fig. 10. A comparison of the poisoning of the smooth and the platinized electrodes by $HgCl_2$.

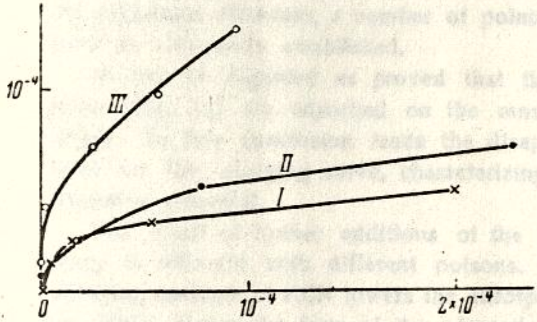

Fig. 11. Decrease of the amount of hydrogen adsorbed on the platinized electrode as a function of the amount of the poison: *I* — As_2O_3; *II* — KCN; *III* — $HgCl_2$.

value 40 for this ratio observed in the case of the platinized electrode. However, it is necessary to take into account that the magnitude of this ratio markedly changes with the degree of poisoning of the electrode, and such a large value for the platinized electrode is observed only when the amounts of the poison are very small. Such conditions are difficult to reproduce reliably with the smooth electrode. For a quantitative comparison of the action of mercury on smooth and platinized electrodes, a curve was constructed giving the dependence of $\Delta H/Hg$ upon the degree of poisoning of the electrode (Fig. 10). The values of the ratio $\Delta H/Hg$ are plotted as ordinates; whereas the abscissae represent the degree of poisoning of the surface as determined by the ratio of the number of gram atoms of mercury introduced into the surface to the total number of gram atoms of hydrogen present at the reversible hydrogen potential on the non-poisoned surface. The curve represents the data for the platinized electrode, while the points represented by circles and triangles refer to data obtained with smooth electrodes in two series of measurements. It is easy to see that a quantitative agreement is observed in the behavior of both electrodes.

Summary

The whole picture of the action of poison which we obtained is quite complex and requires further study before it can be definitely explained. However, a number of points can already be considered as sufficiently established.

It may be regarded as proved that the first portions of the poison (Hg, As) are adsorbed on the most active centers of the surface. To this conclusion leads the disappearance of the central arrest on the charging curve, characterizing spots with the largest adsorption potential.

The effect of further additions of the poison on the binding energy is different with different poisons. While the addition of increasing amounts of KCN lowers the adsorption potential of hydrogen, $HgCl_2$ leaves the form of the adsorption isotherm of hydrogen unchanged over a rather wide interval, and As (except for the first portions) even increases the binding energy of hydrogen. The influence of the poisoning by KCN on the hydrogen part of the curve reminds one somewhat of the effect which is observed in the presence of active but reversibly adsorbed anions like Br.

The activity of the poisons increases in the following order: $As_2O_3 < KCN < HgCl_2$. This becomes especially noticeable with small degrees of poisoning when 1 atom of As, 1 molecule of KCN and 1 atom of Hg show an effect upon 4, 10 and 40 atoms of hydrogen respectively. These effects of the "action at a distance" of the poisons on the surface of the electrode are difficult to explain as yet and require further study. There is no doubt, however, that these facts may be of importance for the theory of catalysis.

Upon increasing the degree of covering of the surface, the effectiveness of the poison always decreases very markedly. It follows from the data referring to the adsorption of hydrogen that the action of poisons cannot be reduced to a simple blocking of a part of the surface of the catalyst and that it is necessary to consider the specific forces of interaction between the adsorbed poison and the atoms of hydrogen.

This investigation makes it possible to compare the properties of smooth and platinized platinum electrodes. The nearly quantitative agreement in the behaviour of both electrodes, which is observed in the case of the poisoning by As and $HgCl_2$ leads to the conclusion that the surface of a smooth electrode is actually as inhomogeneous as the surface of a platinized electrode, and that their structures are similar.

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