PHYSICAL CHEMISTRY

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1960

SovietRxiv

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PHYSICAL CHEMISTRY

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STUDY OF THE ADSORPTION OF IODINE ON SMOOTH PLATINUM AND ITS DESORPTION BY THE TRACER-ATOM METHOD

(Presented by Academician A. N. Frumkin on 6 V 1960)

In a number of works it has been shown that a very strong adsorption of iodine takes place on platinized and smooth platinum ($^{1-3}$). The question of the nature of this adsorption and of the influence of various factors on it, however, has still remained not entirely clear.

The task of the present work was to study the adsorption of iodine on smooth platinum from acidic and, in part, alkaline sodium iodide solutions as a function of its concentration and of time, and also to study the desorption of iodine under various conditions. The work was carried out by the tracer-atom method using the isotopes J^{131} and Pt^{193}. Electrodes of smooth platinum were subjected to preliminary activation by alternating cathodic and anodic polarization in $1\,N\,\mathrm{H_2SO_4}$. To prepare the solutions, recrystallized chemically pure salts, twice-distilled sulfuric acid, and twice-distilled water were used. The experiments were conducted as follows: after activation the electrode was immersed for a specified time in the labeled solution* under the prescribed conditions, then removed into the air, rinsed with bidistillate (2 min), and placed in an end-window counter for measurement of its radioactivity, from the magnitude of which the adsorption was calculated. The adsorption measured in this way was previously conventionally called by us “irreversible”(^{1,5}). After this, experiments on desorption or exchange under various conditions were carried out.

It was found that in solutions of the commercial radioactive preparation of sodium iodide “without carrier,” containing the radiochemically pure isotope J^{131}, there are, in addition to simple anions J^-, impurities that include J^{131} in another chemical form and that possess considerably greater sorbability than the anion J^-. These may be, for example, complex ions of heavy metals. In this case, calculation of the amount of adsorption per unit surface, carried out on the assumption of complete identity of the stable and radioactive ions, gives results that are the more overestimated the greater the concentration of stable ions (^{5}). It turned out that this danger is completely eliminated by preliminary purification of the commercial labeled sodium iodide by sublimation of iodine after oxidation of J^- with potassium dichromate, followed by electrochemical

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

reduction to the J^- ion. Such purification was used in the present work, after which the reproducibility of the results also improved to ±15%.

The maximum value of irreversible adsorption of iodine on smooth platinum, obtained in this way with purified iodine isotope in a nitrogen atmosphere from a solution of $1\,N\,H_2SO_4 + 0.01\,N\,KJ$, is about $1.5 \cdot 10^{-9}$ g-ion/cm^2 of visible surface, which is close to the value required for the formation of one monolayer. The considerably larger values obtained for smooth platinum under the same conditions in work (^{1}) should apparently be attributed to the use of unpurified isotope J^{131}.

The magnitude of iodine adsorption on smooth platinum in an atmosphere of air or hydrogen from acidic solutions with a concentration above 10^{-3} N, under conditions in which it is measured immediately after washing the platinum with bidistillate, is practically independent of the adsorption time in the interval from 10 sec to several hours. In less concentrated solutions this dependence is observed, which may be associated with diffusion difficulties.

The isotherm of irreversible adsorption of iodine on smooth platinum, obtained from an acidic solution in an atmosphere of nitrogen, air, or hydrogen, is logarithmic in the concentration range from 10^{-6} to 10^{-4} N. With a further increase in concentration, saturation is observed* (Fig. 1).

Fig. 1. Dependence of the magnitude of irreversible iodine adsorption on the concentration of NaJ against a background of 1 N H_2SO_4 in an atmosphere of nitrogen. Γ at a concentration of $1 \cdot 10^{-6}$ N is equal to $8 \cdot 10^{-11}$ g-eq/cm^2.

Fig. 2. Desorption of iodine in 1 N H_2SO_4 at different potentials: 1—0.78 V; 2—1 V; 3—1.25 V; 4—1.35 V; 5—1.45 V; 6—1.55 V; 7—1.75 V; versus N.H.E.

The magnitude and rate of desorption of iodine from smooth platinum, adsorbed at the air potential from an acidic solution, depend on its potential in the desorbing solution. In 1 N H_2SO_4 at potentials less positive than 1.25 V versus N.H.E., desorption proceeds slowly, and in one hour about 20% of the total sorbed amount is desorbed. With increasing potential the rate of desorption increases sharply (Fig. 2). Complete desorption (residue 0.1%) is achieved at a potential of 1.7 V in several minutes.

In 1 N NaOH, at potentials more positive than 0.35 V, desorption likewise in-

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* In different experiments the solutions contained at most 0.4 mC of isotope per 1 g of dry NaJ.

Figure 3

Figure 3: Figure 3

creases with increasing potential. This effect of potential during anodic desorption can be explained by oxidation of the sorbed iodine to JO_3^-, which apparently is not sorbed by the surface of oxidized smooth platinum.

Desorption of iodine in sulfuric acid at the reversible hydrogen potential increases linearly with decreasing logarithm of the acid concentration, which can be explained by an increase in the magnitude of the negative surface charge, repelling iodine anions, when the potential shifts in the negative direction (Fig. 3). For the same reason, probably, in water and in 1 N NaOH in a hydrogen atmosphere, desorption of iodine proceeds still faster and more completely than in sulfuric acid. Complete desorption under these conditions is attained in 30-40 sec.

The same effect as when the concentration of sulfuric acid is decreased is achieved in 1 N H_2SO_4 by increasing the cathodic current density in the interval from 1.5 to 50 mA/cm^2. At the highest current density, in 5 min, desor- about 90% of the total sorbed amount is desorbed, i.e., practically the same amount as in $10^{-4}\,N$ sulfuric acid without polarization over the same time. The dependence of the amount of iodine during desorption by cathodic or anodic polarization in H_2SO_4 and NaOH, or by changing the acid concentration, on time is not logarithmic, but obeys a more complex law.

In the absence of polarization, in an atmosphere of air or nitrogen, in water, ethyl alcohol, and in a $1\,N$ NaF solution, desorption of iodine proceeds very slowly, reaching 30% over several days. In solutions of H_2SO_4, NaOH, and NaI under these conditions, a linear dependence of desorption on the logarithm of time is observed (Fig. 4, 1, 2, 6).

Fig. 3. Dependence of iodine desorption on the potential in H_2SO_4 of various concentrations. (Desorption time 30 min.)

The same dependence is observed in exchange processes in neutral sodium iodide solutions of various concentrations, with the exchange increasing as the concentration rises. If at a concentration of $1 \cdot 10^{-3}\,N$, in 10 min., about 20% of the total sorbed amount is exchanged, then at a concentration of $1 \cdot 10^{-1}\,N$ over the same time 40% is exchanged, and at a concentration of $1\,N$, 60%. The slope of the $\Gamma - \lg t$ curves decreases with increasing sodium iodide concentration (Fig. 4, 3–6).

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* The absence of dependence of the measured quantities on the gas atmosphere is probably associated with taking the platinum out into air for washing from the active solution and with the resulting change in its sorption properties, as well as with oxidation of J^-.

Figure 4

Figure 4: Figure 4

During adsorption of iodine on smooth platinum from acid solutions, we observed a shift in potential, as in the experiments of A. D. Obrucheva[6]. At an initial potential in 1 N H_2SO_4 equal to 0.8 V on the normal hydrogen scale, the shift of the potential in the negative direction on smooth platinum in an atmosphere of pure nitrogen is 80–100 mV when the concentration of added J^- is increased by an order of magnitude in the range from 10^{-3} N to 1 N, i.e., there is a dependence analogous to that observed in (?) on platinized platinum. During adsorption of iodine in an atmosphere of air, analogous shifts of the potential of smooth platinum in the negative direction are observed.

Fig. 4. Dependence of iodine desorption on the duration of desorption. 1–1 N H_2SO_4; 2–1 N NaOH; 3–10^{-3} N NaJ; 4–10^{-2} N NaJ; 5–10^{-1} N NaJ; 6–1 N NaJ. At $t = 0$, I for curves 1–6 is equal to 6200 ± 200 imp/min.

The potential of platinum in sulfuric acid in air, after washing out the KJ solution with bidistillate, has a value 150–200 mV more negative than the value of the potential before iodine adsorption, the amount of which, according to radioactivity measurements, changes little (by several percent) upon washing. Such a change in the air potential of platinum in sulfuric acid can be explained by a decrease, under the influence of sorbed iodine, in the oxygen exchange current responsible for the establishment of the potential.

The results obtained in acid solutions show that the principal part of the iodine is chemisorbed and is bound quite strongly to the platinum.

During adsorption of iodine from alkaline solutions on smooth platinum in air, no adsorption shift of the potential is observed, and the magnitude of adsorption according to radioactivity amounts to one tenth of a monolayer. Hydroxyl ions impede iodine adsorption at all negative platinum potentials.

less than 1.0 V on the normal hydrogen scale. At high anodic potentials (the oxygen-evolution potential) in an alkaline solution, however, considerable adsorption of iodine is observed, exceeding several monolayers when calculated per anion J^-. This can be explained by the formation of a stable surface chemical compound of iodine with platinum oxides formed under these conditions.

The resulting surface compound dissolves readily in acid, but is stable in an alkaline solution even under cathodic polarization. Thus, at a cathodic current density of 20 mA/cm^2, in 10 min about 20% of the measured amount passes into solution. This indicates slow reduction of the compound formed. Independent experiments with radioactive platinum showed that platinum also passes into a 1 N sulfuric acid solution together with the sorbed iodine. Under conditions where sorbed iodine is absent from the platinum surface, its passage into solution at the same potentials is several times smaller.

We express our gratitude to Academician A. N. Frumkin for his interest in the work and for valuable advice during its discussion.

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Received
6 May 1960

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