THE POTENTIAL OF A CARBON ELECTRODE AS A FUNCTION OF SOLUTION pH UNDER ISOELECTRIC CONDITIONS*

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The potential of an electrode in equilibrium with hydrogen or oxygen at constant gas pressure as a function of solution pH is given by well known thermodynamic relations that have been repeatedly confirmed by experiment. Much less study has been devoted to the question of the variation with pH of the potential of an electrode on which oxygen or hydrogen is adsorbed, if the pH change is brought about under conditions such that there is no possibility of reacting with the volumn gas phase or the dissolved gas, and in addition there is no passage of current in the external circuit. This condition maintains constancy of the quantity $\varepsilon \pm AF$, where ε is the charge density on the electrode surface, and A is the amount of adsorbed gas in g-equiv/cm^2, with the + sign for oxygen and the - sign for hydrogen [1]. The correctness of this relation follows from the fact that under the above conditions, a change in the value of ε can only occur as the result of ionization of the adsorbed gases. The absorbed hydrogen or oxygen may thus be regarded as potential sources of electric charge, and keeping the value of $\varepsilon \pm AF$ constant may be regarded as the isoelectric condition in the experiment.

A potential change under isoelectric conditions may be determined by different factors. The potential changes occurring as the result of specific adsorption of halogen anions or various cations have recently been investigated by Obrucheva [2]. In the present paper, we are considering the changes associated with transition from acid to alkaline solutions. The electrode behavior in this case depends on the relation between the quantities $|AF|$ and $|\varepsilon|$. If $|AF| >> |\varepsilon|$ in both the initial and the final state of the electrode, possible changes in ε cannot produce any substantial change in the relative value of AF. In other words, the amount of adsorbed gas, and hence its activity,† change comparatively little with change in solution pH, and the change in the potential difference between the electrode and the solution will not be too greatly different from the one which occurs in the case of an electrode in equilibrium with the gaseous phase.

This case realized by Frumkin and Shlygin [1], who investigated the dependence on solution pH of the potential of a platinum electrode with considerable amounts of hydrogen adsorbed on the surface. The other case, corresponding to the condition $|AF| << |\varepsilon|$or, in the limit, A = 0 which, if satisfied, reduces the constancy condition on $\varepsilon \pm AF$ to the condition ε = const, is realized on an ideally polarized mercury electrode. The potential of such an electrode under isoelectric conditions remains constant with change in pH, as follows, for example, from the fact that the potential maximum on the electrocapillary curve is independent of solution pH. It will be seen from the material given below that a carbon electrode occupies an intermediate position between these two limiting cases.

EXPERIMENTAL

The study of the potential shift of carbon with change in solution pH as a function of the initial carbon potential in 0.01 N H_2SO_4 was conducted in the following way. The electrode, made of sol-free sugar charcoal, was placed in 0.01 N H_2SO_4 solution, through which was passed nitrogen carefully freed of oxygen, and was subjected to cathode

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†This conclusion is however of an approximate nature, since the bond energy of the adsorbed hydrogen and oxygen is, generally speaking, dependent on solution pH.

polarization with a current of 10 mA up to some potential. After the current was turned off and a steady state potential was set up on the carbon electrode, an alkaline solution saturated with nitrogen was added to the apparatus, and the pH of solution was brought to a value in the vicinity of 12. The results of these experiments are shown in Fig. 1. It may be seen from the curves given that after the alkali has been added to the solution, a discontinuous shift in potential occurs in the negative direction, after which the potential shift occurs more slowly. The total amount of the shift depends on the steady state potential to which the carbon has been polarized. Experiments at initial values of $\varphi > 0.2$ were made with carbon on the surface of which a certain amount of oxygen had been chemisorbed from the gaseous phase, as described in [3]. The experiment with the initial value of $\varphi = 0.65$ gives the behavior of carbon in contact with air. Figure 2 gives the negative potential shift $\Delta\varphi$ of the carbon electrode as a function of the initial carbon potential in 0.01 N H_2SO_4 The minimum in the curve comes at a potential of -0.03 V.

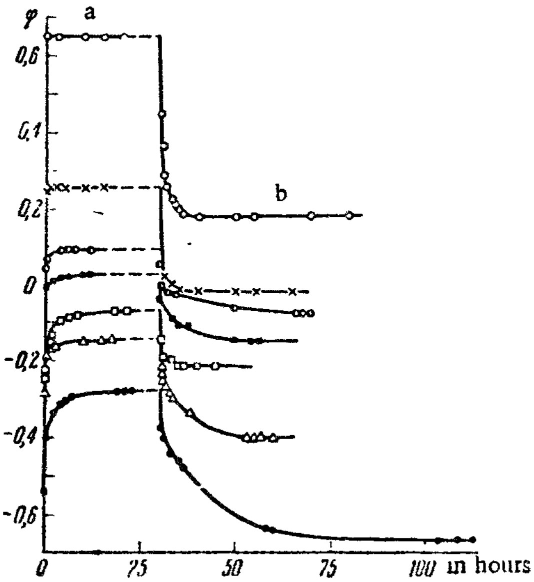

Fig. 1. Change in potential of a carbon electrode when 0.01 N H_2SO_4 is replaced by 0.01 N KOH under isoelectric conditions: a) potential in acid; b) in alkali.

The results obtained in this way were checked by taking charging curves, a method first applied to the carbon electrode along with adsorption measurements in [4]. The charging curves were taken in the following way. A carbon electrode weighing 0.075 g was immersed in 0.01 N H_2SO_4 solution through which nitrogen carefully freed of oxygen was being passed. The carbon electrode was given a long cathode polarization with the current gradually reduced until a potential of + 0.130 V (n.c.e.) was reached, which is nearly the same as that taken on by degased carbon in 0.01 N H_2SO_4 solution. The potential stayed constant after the current was turned off. The potential change was produced by a current of $7.5 \cdot 10^{-6}$ A. Taking the charging curve under these conditions took 450 hours. This choice of current strength was determined by the fact that preliminary experiments had shown that with a more rapid change in electrode potential it was not possible to establish equilibrium between the hydrogen and oxygen adsorbed on the carbon surface on the one hand, and the solution on the other, with the result that a lowering in the electrode capacity was observed. The charging curve was first varied to a cathode potential of 0.25 V. The rate of molecular hydrogen evolution at this potential, although it already lies in the hydrogen over voltage range, is so small that the current consumed in this reaction may still be neglected in comparison with the current consumed in charging the electrode. Then, the carbon potential was returned by means of anode polarization to its initial value of + 0.13 V, after which the anode charging curve was measured up to a potential of + 0.74 V.

The electrode was then given a cathode polarization to a steady state potential of +0.13 V, after which the acid solution was removed by N_2 pressure and replaced by 0.01 N KOH solution. When the acid solution was replaced by alkaline solution in a nitrogen atmosphere, the potential of the carbon electrode jumped in the negative direction to a potential of -0.08 V, which is nearly the same as the potential of degased carbon in 0.01 N KOH solution (-0.05 V) [3]. In 0.01 N KOH solution, using the same current strength $7.5 \cdot 10^{-6}$ A, a cathode charging curve was taken, which was carried up to a potential of -0.55 V, after which the electrode was returned by anode polarization to the steady state potential of -0.08 V, and an anode charging curve was taken up to +0.28 V. The resulting charging curves are shown in Fig. 3.

The abscissas are the total charge Q expended in measuring the charging curve, from an initial potential of +0.13 V for acid solutions (curve 1) and from -0.08 V for alkaline solutions (curve 2). It is obvious that with this choice of initial values of φ correspond into equal amounts of charge Q given to the electrode in acid and alkaline solution respectively will be equal to the potential shift $\Delta\varphi$ on going from acid to alkaline solution under isoelectric conditions. The dotted line in Fig. 2 gives $\Delta\varphi$ as a function of φ in 0.1 N H_2SO_4, as determined in this way from the charging curves. It may be seen that the $\Delta\varphi$ vs. φ curve calculated from the charging curves gives a good approach to the $\Delta\varphi$ vs. φ curve found directly by experiment, although the minimum is somewhat less clearly pronounced.

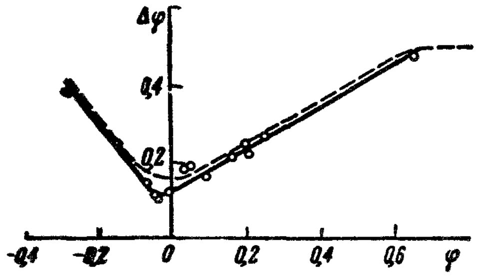

Fig. 2. Negative potential shift Δφ of a carbon electrode on going from 0.01 N H_2SO_4 to 0.01 N KOH, as a function of the initial potential φ: —) experimental data; ----) curve found from charging curves.

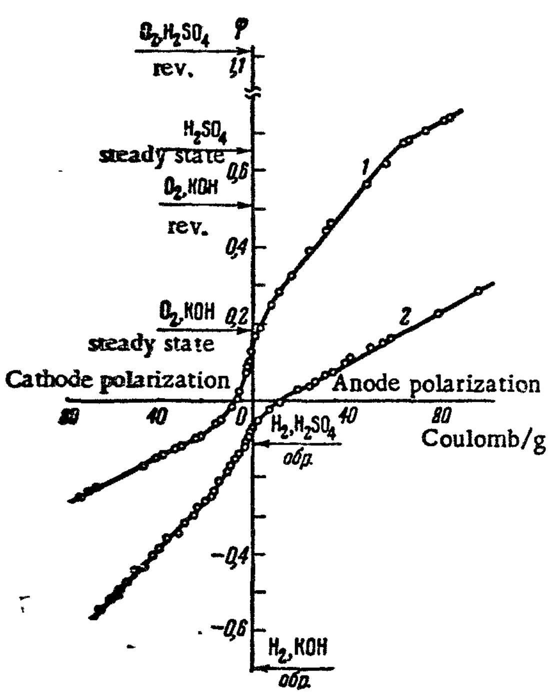

Fig. 3. Charging curves for an activated carbon electrode in 0.01 N H_2SO_4 (1), and in 0.01 N KOH (2).

DISCUSSION OF EXPERIMENTAL RESULTS

The charge curves of Fig. 3 have segments with a large slope between segments of less slope lying at the more negative potentials. In acid solution, the high slope segment lies between $\varphi = 0.0$ and $\varphi = 0.25$, and in alkaline solution, where it is less clearly pronounced, it is close to and somewhat more negative than $\varphi = 0.1$. By analogy with the behavior of the platinum electrode [1,5], it may be assumed that on these segments, on which the capacity of the carbon electrode $dQ/d\varphi$ is a minimum, there is also a minimum in the concentration of adsorbed gases, and at more positive potentials the electrode has excess oxygen adsorbed on it, while at more negative potentials it has excess hydrogen. We shall refine these ideas somewhat later on. The surface of the carbon with which these measurements were made, measured by the BET method from low temperature argon adsorption, was ~500 m^2/g, and the capacities calculated from this value are equal, in acid solution, to 67, 6, and 27 $\mu F/cm^2$ respectively for the hydrogen, the double layer, and the oxygen parts of the charging curve. For $\varphi > 0.65$, the capacity increases to 61 $\mu F/cm^2$. In alkaline solution, the capacities for the same three parts of the charging curve are equal to 30, 13, and 58 $\mu F/cm^2$. The values of the capacities for a carbon electrode are much less than the corresponding values for a platinum electrode. The small capacity in the double layer region in acid solution is partly due to the fact that this part of the charging curve lies near the zero charge point [3], with the result that the double layer has a diffuse structure. It is impossible that the diffuseness of the double layer shows up more sharply in the case of a porous carbon electrode, as the result of the molecular dimensions of the pores in the carbon, which make if difficult for hydrated ions to penetrate [5].

In order to use the values of the total capacity found from the charging curves to find the amount of adsorbed gases, it is necessary to determine the amount of charge which goes into charging the double layer. To this end, the amounts of H_2SO_4 and KOH were determined which are adsorbed respectively on positively and negatively charged carbon at two different potentials. These measurements gave the following results: adsorption of acid from 0.01 N H_2SO_4 on positively charged carbon was 0.40 mequiv/g for $\varphi = 0.65$ V, and 0.069 mequiv/g for $\varphi = 0.250$ V, while the adsorption of alkali on negatively charged carbon was 0.30 mequiv/g for $\varphi = -0.69$, and 0.005 mequiv/g for $\varphi = 0.220$. From these data, we find for the capacity of a double layer with positive surface charge, the value 17 $\mu F/cm^2$, and for negative charge, the value of 14 $\mu F/cm^2$. A comparison of these values with those given above for the total capacity of the carbon electrode makes it possible to find the amounts of chemisorbed gases. Thus, for the pseudocapacity from the adsorbed oxygen in acid solution at $\varphi < 0.65$, we find ~ $(27-17) \mu F/cm^2$, i.e., ~10 $\mu F/cm^2$. Thus, the concentration of chemisorbed oxygen in this range of potentials is small.* The amount of chemisorbed oxygen at $\varphi = 0.65$ is, for orientational purposes, only 0.20 mequiv/g, and only with further increase in φ does it increase appreciably.

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*Judging from the slope of the charging curve, the chemisorbed oxygen is present on the surface at $\varphi > 0.25$, in spite of the fact that in experiments with degased carbon it only occurs at values of $\varphi > 0.32$ [3]. This small difference is possibly due to difference in preparation of the carbon surface in the two cases. In calculating the amount of chemisorbed oxygen, we have assumed that the oxygen branch of the charging curve in 0.01 N H_2SO_4 begins at $\varphi = 0.25$ V, while in 0.01 N KOH, it begins at $\varphi = -0.05$ V.

The large (up to 67 $\mu F/cm^2$) increase in electrode capacity at potentials more negative than $\varphi = 0.0$, with a double layer capacity of 14 $\mu F/cm^2$, indicates that atomic hydrogen is being adsorbed on the surface, as was to be expected, considering that equilibrium with hydrogen at atmospheric pressure has already been reached at $\varphi = -0.11$. At potentials more negative than $\varphi = -0.25$, it is impossible for the charging curve to change, since at these potentials large amounts of charge are already being consumed in the evolution of molecular H_2 Making an orientational correction for the amount of charge consumed in charging the double layer, and assuming that the hydrogen branch of the charging curve in 0.01 N H_2SO_4 begins at $\varphi = -0.02$, it is possible to make an approximate estimate of the amount of the hydrogen chemisorbed at the most negative potential reached when measuring the $\varphi = -0.25$ charging curve. The value is ~0.55 mequiv/g. Thus, in acid solution, the amount of chemisorbed hydrogen that can be fastened to the carbon surface with cathode polarization, is considerably greater than the amount of oxygen present on the surface at air potential. A different picture is observed in alkaline solutions. The potential of -0.03 V, which is taken on in a solution with pH = 12 by carbon depolarized to the zero charge potential in acid solutions [3], is only 0.21 V more cathodic than the air potential of carbon (0.18), and 0.54 V more cathodic than the reversible oxygen potential in the same alkaline solution. At the same time, in acid solution, the potential of degased carbon, $\varphi = 0.16$, is 0.49 more cathodic than the air potential, and 0.95 V more cathodic than the reversible oxygen potential in the same solution. In accordance with this, the amount of oxygen that can be sorbed on the carbon surface at the initial point in the charging curve, and at more positive values of φ, will be considerably greater for an alkaline solution than an acid solution. Actually, at the value of $\varphi = 0.28$, to which the charging curve was taken in our measurements in alkaline solution, the amount of oxygen on the electrode surface is ~0.68 mequiv g,* which is considerably in excess of the amount of calculated for an acid solution. The inverse of these relations occur in the hydrogen part of the charging curves. While the potential of degased carbon at 0.01 N H_2SO_4 is only 0.28 V more positive than the reversible hydrogen potential in the same solution, the potential of the same carbon in the solution with pH ~12 differs from the reversible hydrogen potanila by 0.65 V. In accordance with this, the concentration of adsorbed hydrogen on the carbon surface over the whole hydrogen part of the charging curve in alkaline solution is small, and even at the highest negative potentials that we were able to reach ($\varphi = -0.55$ V), the amount of adsorbed hydrogen, calculated in the same way as shown above, assuming that the hydrogen branch of the charging curve in 0.01 N KOH lies at $\varphi = -0.16$, is only ~0.31 mequiv/g. Although the calculation of the amounts of O and H adsorbed are inaccurate because of the unreliability of the correction for the double layer charge ε and because of a certain amount of arbitrariness in the selection of the initial points on the oxygen and hydrogen parts of the charging curves, no doubts are raised about having more O adsorption in alkaline solutions and more H adsorption in acid solutions under isoelectric conditions. Thus, going from acid to alkaline solution and the more positive potential range is accompanied by an increase in the amount of adsorbed hydrogen in accordance with the reaction

$$C_x + 2OH^- \rightarrow C_xO + H_2O + 2e^-$$

or

$$C_x + OH^- \rightarrow C_x(OH) + e^-$$

while in the more negative potential range, the amount of adsorbed oxygen decreased in accordance with the reaction

$$C_xH + OH^- \rightarrow C_x + H_2O + e^-$$

The above reactions lead to a potential shift in a negative direction, since the liberated electrons remain on the electrode surface. The minimum potential shift will occur under conditions where the amount of oxygen and hydrogen adsorbed is as small as possible in both the initial and final state of the electrode. It may be seen from Fig. 3 that this condition is realized for an initial potential somewhat more negative than $\varphi = 0.0$, since this case both the initial and final state fall in the "double layer" range of the charging curves. This agrees with the position of the minimum on the curve of Fig. 2. The potential shift in the negative direction will increase with increase in the amount of O_{ads}

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*This is in good agreement with the data for the irreversible adsorption of oxygen on sugar charcoal from the gaseous phase, obtained by Juza and Langheim [6].

in the final state of the electrode and H_{ads} in the initial state, i.e., on both sides of the potential corresponding to the minimum displacement, which serves to explain the form of the curve in Fig. 2. With increase in φ, the value of $\Delta \varphi$ increases, but for $\varphi > 0.65$, growth of $\Delta \varphi$ is held down even without $\Delta \varphi$ approaching the value 0.58 which should be observed for a reversible oxygen electrode when the pH changes by 10 units. This discrepancy comes from the essentially irreversible nature of the oxygen carbon electrode, which is more clearly pronounced in acid than in alkaline solutions. A consideration of the causes of the irreversibility is beyond the range of the present work.

The calculations given above make it possible to compare the values of $|AF|$ and $|\delta|$ for an electrode made of activated charcoal. The value of $|AF|$ in the range of potentials from 0.65 in acid to - 0.55 V in alkaline solution, investigated in the present paper, are not greater than 14 $\mu C/cm^2$, while the largest value of $|\delta|$ in this same range is 7 $\mu C/cm^2$. Thus, these quantities are not of the same order of magnitude, in contrast with both the platinum electrode, where $|AF|$ reaches hundreds of $\mu C/cm^2$, and the mercury electrode, where $|AF|$ may be neglected. The surface filling of the carbon electrode with chemisorbed gases reaches several per cent of the total surface.

Garten and Weiss [7,8] relate the adsorption of cations on negatively charged carbon with transition of the quinone groups existing, in their opinion, on the carbon surface, to hydroquinone groups with ionization of the hydrogen. It may be seen from the charging curves given Fig. 3 that the concentration of ionized hydrogen on the carbon surface as a function of potential is not in accord with an equilibrium between two groups, changing into one another with addition of two electrons and two H^+ ions, and the explanation proposed by Garten and Weiss for the adsorption of alkali by high temperature activated charcoal is in just as poor agreement with the experimental data as the corresponding explanation for the adsorption of acids on positively charged carbon [3]. Garten and Weiss derive, from their theory, a formula, which, in their opinion, agrees with the experimental data on the adsorption of alkali on carbon with cathode polarization, obtained in [4], but the agreement can only be reached if the coefficient RT/F ln 10 is given the value of 0.3-0.4 instead of the theorectical value 0.029.

SUMMARY

1. A discussion is given of the change in electrode potential with change in solution pH under conditions where the electrode surface has oxygen or hydrogen adsorbed on it.

2. The magnitude of the potential change depends on the relation between the amount of electrochemically active gases adsorbed and the surface charge in the initial and final states of the electrodes.

3. The changes in potential of a carbon electrode on going from 0.01 N H_2SO_4 to 0.01 N KOH as a function of the initial value of the potential, found from experiment, are in agreement with theory. The minimum potential shift in the negative direction (0.1-0.15 V) is observed for an initial potential in 0.01 N H_2SO_4 of ~ -0.03 V, at which the amounts of adsorbed gases are a minimum in both the initial and final states.

4. It follows from the charging curves that at equal distances from the zero charge point, the amount of hydrogen chemisorbed on the surface is greater in acid, and the amount of chemisorbed oxygen is greater in alkaline solutions.

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