THE EFFECT OF RADIOLYSIS ON THE POTENTIAL OF A NICKEL ELECTRODE IN AN ALKALINE SOLUTION AS A FUNCTION OF THE COMPOSITION OF THE GAS PHASE

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Abstract

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THE EFFECT OF RADIOLYSIS ON THE POTENTIAL OF A NICKEL ELECTRODE IN AN ALKALINE SOLUTION AS A FUNCTION OF THE COMPOSITION OF THE GAS PHASE

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As is known, on a nickel electrode in alkaline solutions in an atmosphere of hydrogen, the potential of a reversible hydrogen electrode is established. The authors of the present communication have shown that, under the action of atomic hydrogen (^{1}), a potential is established on nickel in an alkaline solution that is more negative than the reversible hydrogen potential (by 45-70 mV)*. In connection with these experiments, it seemed of interest to clarify the behavior of a nickel electrode under conditions in which, simultaneously with the supply of hydrogen atoms to the electrode, oxygen atoms or OH radicals are brought to it.

To realize such conditions, we chose the method of radiolysis of aqueous solutions. According to numerous data in the literature (^{2}), the primary products of water radiolysis are hydrogen atoms, free OH radicals, as well as hydrogen molecules and hydrogen peroxide molecules, formed according to the reaction

$$H_2O \sim H_2,\ H_2O_2,\ H,\ OH,\ HO_2$$

with yields (g) per 100 eV

$$g_H = 2.8, \quad g_{OH} = 2.2, \quad g_{H_2O_2} = 0.8, \quad g_{H_2} = 0.42.$$

As was shown by Zalkind and Veselovskii (^{3}, ^{4}), under the action of γ-radiation on the system Pt electrode–sulfuric acid, the potential of this electrode (+800 mV), under the influence of radiolysis, shifts in the negative direction and, within 10-15 min, reaches the potential of a reversible hydrogen electrode, which is maintained during irradiation. These authors explain such an effect by the ability of platinum selectively to adsorb hydrogen and assume that the observed shift in potential is caused and maintained by the action of free hydrogen atoms formed during radiolysis.

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

In the present work, the course of the change in the potential of nickel in an alkaline solution under the action of X-radiation was studied at various hydrogen pressures, as well as in the absence of gases and in an atmosphere of an inert gas (neon).

The nickel electrode—a plate measuring 1.5 × 1.5 cm (A)—was reduced in an atmosphere of hydrogen at 400° and stored in hydrogen until the experiment. Before the experiment, the electrode was quickly transferred into the apparatus shown in Fig. 1. The electrode was placed at the shortest possible distance from the horizontal bottom of the apparatus (B) and parallel to it. A mercury oxide electrode (V), separated by a glass filter (G) from the rest of the apparatus, served as the reference electrode. A previously degassed alkaline solution was in the ampoule (D). Radiolysis of the solution was carried out by irradiation generated in an X-ray tube operating at a voltage of 80 kV and an anode current of 200 mA. Under these conditions the amount of energy absorbed by 1 cm^3 of solution was $6.8 \cdot 10^{16}$ eV/sec. Irradiation was carried out through the bottom of the apparatus (B), which was placed as close as possible to the radiation source.

Fig. 1. Apparatus for studying the course of the electrode potential in an electrolyte solution under the influence of radiation

Before the start of an experiment a vacuum (10^{-6} mm Hg) was created in the apparatus; then gas was introduced to the desired pressure, and the apparatus was sealed off from the rest of the system (I). By means of the electromagnetic striker (Zh), the bottom of the ampoule was broken, and the solution (0.68 *N* NaOH) filled the apparatus, after which measurement of the electrode potential was begun.

Figure 2 presents the change in the potential of the nickel electrode with time under the influence of radiation in the absence of gases. As can be seen from Fig. 2, the initial potential of the nickel electrode, owing to the presence on it of an oxygen film formed as a result of transferring it through air, has a value approximately 250 mV more positive than that of the reversible hydrogen electrode. As shown in the work of Shurmovskaya and Burshtein[5], on the surface of nickel, upon contact with air, a limiting oxygen film is formed, corresponding to the adsorption of $1.3 \cdot 10^{15}$ oxygen atoms per 1 cm^2 of true surface. Under the action of radiation the potential begins to shift in the negative direction, and after 10–12 min this shift

* Relative to reversible hydrogen at atmospheric pressure.

Fig. 2. Change in the potential of the nickel electrode with time under the influence of radiation in the absence of gases: *a*—radiation on; *b*—radiation off

amounts to about 200 mV, i.e., the potential falls short by approximately 50 mV of the potential of the reversible hydrogen electrode at atmospheric pressure. With continued radiation this potential is maintained for several minutes, after which it gradually shifts in the positive direction. If irradiation is stopped, the potential again shifts in the negative direction and again reaches the greatest negative value. The described effect of the potential shift in the positive direction during continued radiation and in the negative direction when it is switched off can be observed many times in succession on the same electrode. The effect ceases in the case when, under the influence of prolonged radiation, the electrode is oxidized to a value,

approximately 500 mV more positive than the reversible hydrogen potential, i.e., when a stable phase oxide film has time to form on the nickel. From examination of the curves in Fig. 2 it is clear that in the first stage of radiation hydrogen is adsorbed on the nickel. This is what causes the shift of the potential in the negative direction. However, as oxidizing agents accumulate in the solution, the nickel potential shifts in the positive direction. From the course of the curves the following conclusions may be drawn. Judging from the comparatively slow shift in the positive direction under the influence of radiation, a certain role in this process must be played by the gradual accumulation of H_2O_2 in the solution. On the other hand, the very rapid return of the potential to a negative value when irradiation is stopped is apparently associated with the disappearance from the solution of short-lived radicals having an oxidizing action. At the same time decomposition of H_2O_2, which is unstable in alkaline solution, must also occur; however, this process does not proceed so rapidly. The mechanism of the phenomenon described is thus not yet entirely clear and will be studied in greater detail subsequently. The curves obtained in neon (pressure of the order of 6–10 mm) have the same course as the curves in the absence of gases.

According to the studies of Scheuble (^{6}), adsorption of hydrogen from the gas phase occurs much more rapidly if it is adsorbed not on the surface of pure nickel but on nickel on which oxygen has been adsorbed beforehand. In our experiments the adsorbing hydrogen is deposited on a nickel surface already covered with oxygen. If one proceeds from the analogy with the cited data on the adsorption of hydrogen on nickel from the gas phase, it is possible to explain why, in the absence of gases and in an atmosphere of neon, under the action of radiation the potential first shifts in the negative direction.

Figure 3 shows the change in the potential of nickel in the same solution at a hydrogen pressure equal to 80 mm (*I*), 6 mm (*II*), and also in a mixture of hydrogen with neon, about 1 mm hydrogen and 6 mm neon (*III*). When the radiation is switched on, the nickel potential shifts toward more negative values and, after

Fig. 3. Change in the potential of a nickel electrode with time under the

Fig. 3

Figure 3: Fig. 3

influence of radiation at different hydrogen pressures. The dashed lines are the reversible hydrogen potential: **A**—at atmospheric pressure, —at 80 mm hydrogen, —at 6 mm, —at 1 mm hydrogen + 6 mm Ne. **a**—radiation switched on, —radiation switched off.

4-5 min, the shift reaches its maximum value. In contrast to experiments in the absence of gases and in neon, in these cases the potential changes only slightly in connection with the switching on and off of the radiation. The initial potential of nickel is close to the potential of the reversible hydrogen electrode at the corresponding pressure. In the case of curve *I* it differs by 5 mV, curve *II* by 15 mV, and curve *III* practically coincides with it.

The action of radiation at a pressure of 80 mm hydrogen shifts the potential in the negative direction by a maximum of 5-10 mV. Switching off the radiation is accompanied by a return of the potential to the initial value. At a pressure of 1 mm hydrogen + 6 mm neon, the potential shifts in the negative direction on average by 30-35 mV. The concentration of molecular hydrogen in the solution as a result of radiolysis, at an absorption of $6.8 \cdot 10^{16}$ eV/sec per 1 cm^3 of so-

4 min (the time required for establishment of the potential) may reach values on the order of 10^{-4} mole/liter*. Hence it is clear why the hydrogen liberated during radiolysis has no appreciable effect on the potential at a pressure of 80 mm, at which the hydrogen concentration is $0.75 \cdot 10^{-4}$ mole/liter. On the other hand, since at a hydrogen pressure of 1 mm its solubility is only on the order of 10^{-6} mole/liter, the molecular hydrogen formed during radiolysis should noticeably shift the potential in the negative direction. An exact allowance for this shift is difficult, since hydrogen is distributed between the solution and the gas phase. In addition, part of the hydrogen formed reacts with oxygen on the nickel surface. In any case, a shift of 30-35 mV in the negative direction under the influence of radiation at a hydrogen pressure of 1 mm can be explained by an increase in the amount of molecular hydrogen in the solution. Thus, under the conditions of our experiments, in order to explain the shift of the nickel potential to values more negative than the reversible hydrogen potential, it is not necessary to assume the action of atomic hydrogen.

For the results obtained both at 1 mm hydrogen and at higher pressures, in contrast to experiments in the absence of gases, it is characteristic that the electrode potential changes little during irradiation. The small observed fluctuations of the potential may be attributed either to temperature effects or to the competing action of reducing agents and oxidizing agents. During the first few minutes after the radiation is switched on, the strongest shift of the potential in the negative direction occurs, and the maximum negative value of the potential reached is maintained for some time. After the radiation is switched off, as can be seen from the curves in Fig. 3, a very small shift of the potential is also observed, the nature of which is not yet entirely clear.

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* The amount of molecular hydrogen at a radiation dose rate of $6.8 \cdot 10^{16}$ eV/sec$\cdot$cm^3, with a yield of 0.42 per 100 eV, in 4 min is:

$$\frac{6.8 \cdot 10^{16} \cdot 0.42 \cdot 240 \cdot 1000}{100 \cdot 6.03 \cdot 10^{23}} = 1.12 \cdot 10^{-4} \text{ mole/liter.}$$

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

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