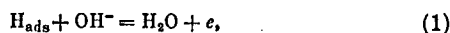


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passes should be less than 10^{-4} cm thick³. We solved the problem of producing extremely thin layers of solution between the gas phase and the electrode by forcing the gas through the liquid in the form of large bubbles on to the electrode surface. This method has been described in detail elsewhere¹.

Experiments were carried out in a mixture of hydrogen and neon (1 mm H₂ and 6–7 mm Ne).^{1–3} The hydrogen atoms were obtained in a discharge tube usually at 2500–3000 V and 250 mA.¹ Nickel and mercury were selected for investigation, each having a quite specific mechanism of hydrogen overpotential. The hydrogen overpotential of nickel and mercury has been previously studied in our laboratory, in the absence of extraneous gas, over a wide pH range and with different pretreatments of the electrode^{4–7}. The results obtained in this work can serve as a criterion for assessing the new experimental results obtained under somewhat special conditions. In fact, since the hydrogen atoms were generated in a discharge tube with aluminium electrodes, there could be no complete certainty that impurities were absent from the system.

When the alkaline solution is saturated with molecular hydrogen, nickel functions as a hydrogen electrode. Introduction of hydrogen atoms into the gas phase is accompanied by their ionisation at the nickel surface according to the equation



which should make the potential more negative. We have in fact shown^{1,2} that, under the influence of atomic hydrogen, the potential of the nickel becomes 40–70 mV more negative than the reversible hydrogen electrode at atmospheric pressure. The effect of atomic hydrogen on a polarised nickel electrode is of considerable interest. Fig. 1 shows curves for the hydrogen overpotential on nickel in alkali both without the introduction of atomic hydrogen (curve 1) and in its presence (curve 2). The curves were obtained over a comparatively wide range of current densities (10^{-7} – 10^{-4} A cm⁻²). It can be seen from Fig. 1† that curves 1 and 2 intersect. At low values of the

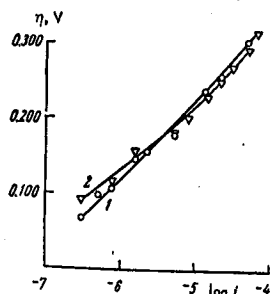


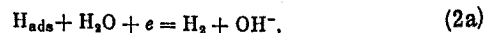
Fig. 1. Hydrogen overpotential of nickel as a function of the logarithm of current density: 1) in the absence of atomic hydrogen; 2) in the presence of atomic hydrogen.

† The curves in Fig. 1 have already been published². We reproduce them in the present paper for comparison with the new experimental results.

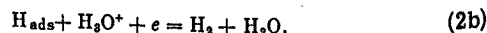
polarising current density, the passage of hydrogen atoms still produces, as with the steady-state potential, some negative shift in the potential. The upper parts of the curves show that the effect of hydrogen atoms is to lower the overpotential [make it more positive (Ed. of Translation)] by about 5–6 mV.

It can be concluded from this that, at low overpotentials, reaction (1), *i.e.* the ionisation of hydrogen, takes place at an appreciable rate on nickel and has an effect on the electrode potential. At higher overpotentials the ionisation of atomic hydrogen takes place so slowly that its effect is insignificant. Over this part of the curve a diminution in overpotential is observed: *i.e.* the atomic hydrogen exerts an oxidising effect.

Such an "oxidising" action of atomic hydrogen is explained by the fact that removal of hydrogen from the electrode can take place at least partly by an electrochemical desorption mechanism, as suggested earlier by several authors⁸. In alkaline solution this reaction takes place according to the equation



and in acid solution according to



Since our experiments were carried out in the presence of water vapour, we thought it necessary to determine whether our observed "oxidising" action of hydrogen atoms might be due to the presence of oxidising radicals produced by the action of the discharge on the water vapour†. Such a hypothesis seemed improbable because at low cathodic polarisations the nickel potential was shifted to more negative values [as a result of the introduction of atomic hydrogen? (Ed. of Translation)], and it was only at higher polarisations that it became more positive. In order, however, to settle this question finally, a series of experiments was carried out in an atmosphere of pure neon, and at the end of an experiment hydrogen was introduced as well. These experiments showed that the electrode potential always shifts in a negative direction when the discharge takes place in pure neon. Addition of hydrogen to the neon at the end of the experiment makes this change in potential still greater. Fig. 2 shows the curve obtained with an electrode having an initial potential 225 mV more positive than the reversible hydrogen potential at atmospheric pressure⁸. Discharge in pure neon (6 mm) yielded a potential which was 30 mV more negative than the hydrogen potential at atmospheric pressure, and after addition of hydrogen the potential became 60 mV more negative than the hydrogen potential.

Thus the experiments in pure neon show that, of the hydrogen atoms and oxidising radicals simultaneously formed by the action of a discharge on water vapour, it is the hydrogen atoms which have the greater effect on the potential of the nickel electrode, making it more negative. We have confirmed this still more convincingly in experiments on the effect of γ -rays on the potential of a nickel electrode in an alkaline solution both in the absence of gases and in the presence of neon and hydrogen⁷. In spite

† In spite of various precautions, such as a low reaction temperature (0° and below) and thorough drying of the circulating gas leaving the solution, there could have been an effect of the discharge on water vapour.

§ In several experiments the electrode potential became somewhat more positive when gas started to bubble through the solution. The nature of this effect still remains obscure.

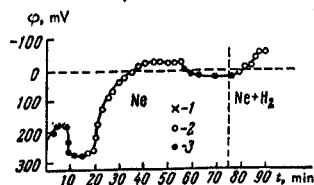


Fig. 2. Variation in the potential of a nickel electrode with time under the influence of a gas discharge. The zero on the ordinate axis corresponds to the potential of the reversible hydrogen electrode at atmospheric pressure: 1) start of passage of gaseous mixture through liquid; 2) curve during gas discharge; 3) curve in the absence of gas discharge.

of the presence of a high concentration of oxidising agents, the nickel potential was in all cases shifted towards more negative values at the start of irradiation. In the absence of gases or in neon a marked negative shift (200 mV) is followed after 12–15 min of irradiation by the potential beginning to move in a positive direction, probably owing to the accumulation of H_2O_2 in the solution. When hydrogen is present in the gas phase (for example 1 mm H_2 and 6 mm Ne), further intermittent application of irradiation after the limiting negative displacement has been reached has practically no effect on the potential of the nickel electrode. It follows from the above that oxidising radicals formed from water vapour in the discharge are not responsible for the effect which we have described, and that our observed decrease in the hydrogen overpotential of nickel in alkali is caused by the atomic hydrogen introduced into the reaction sphere.

The removal of hydrogen atoms from a mercury surface in acid solution undoubtedly⁸ goes by an "electrochemical desorption" mechanism. Indeed, removal of hydrogen atoms by their combining to form molecules is improbable under these conditions because of their extremely low concentration on the surface. Further introduction of hydrogen atoms should accelerate the evolution of hydrogen, owing to the occurrence of reaction (2b), and cause a shift in potential to more positive values at constant current density⁹.

Our initial experiments were carried out on a drop of mercury of diameter 6–10 mm,¹ which was not completely covered with electrolyte. In several experiments the effect of atomic hydrogen was to lower the overpotential by 20–35 mV. However, the results obtained by the above method showed poor reproducibility, and great difficulties were involved in setting up the experiments. Furthermore, when the electrode is not completely covered with liquid, there is no certainty that the diminution in overpotential is not due to heating of the electrode surface by the recombination of hydrogen atoms.

For these reasons, we designed an apparatus similar to that described for nickel¹. After the apparatus (Fig. 3) had been evacuated and filled with a mixture of hydrogen and neon, a tube of mercury was smashed by an electromagnetic striker, and the mercury fell into the apparatus. The mercury, after careful purification, had been kept under a high vacuum in sealed tubes. The surface of the

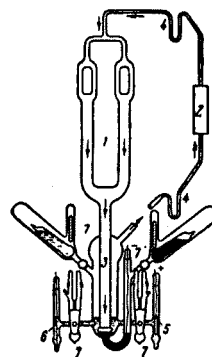


Fig. 3. Apparatus for measuring the overpotential of a mercury electrode during a gas discharge.

mercury cathode was $\sim 8 \text{ cm}^2$, and could be renewed during an experiment by running off mercury into a special reservoir by means of tap 7'. Traces of oxygen were removed from the neon and hydrogen by pumping them through a trap, the walls of which were covered with a layer of sublimed metallic potassium, for a long period before they were admitted to the system. Both in the apparatus described here and in the work with nickel the mercury surface was covered with a layer of electrolyte 1–1.5 cm thick. By means of the circulating pump 2, the mixture of gases was forced through tube 3 in the form of large bubbles, which settled on the surface of the mercury and thus formed a thin liquid film in which the hydrogen atoms fed to the mercury were unable to combine to form molecules.

The measurements were carried out by determining the overpotential at a particular current density, then switching on the discharge, and again measuring the overpotential at the same current density. When the discharge was switched off, the potential regained its original value. After this, another current density was applied to the electrode, and the above procedure repeated. The series of points obtained in this way, representing the potentials of the mercury electrode at a given current density, both in the absence and in the presence of a discharge, were joined together by curves (Fig. 4). These show that the electrode potential is more positive in the presence of a discharge, the maximum effect being 10–15 mV, which is less than in the experiments with an incompletely covered drop (20–35 mV). This is probably associated with the greater size of the electrode (by a factor of about 15), i.e. with the decrease in the quantity of atomic hydrogen per unit surface of the mercury.

It is clear from the shape of the curves obtained in the absence and in the presence of a discharge that the effect of atomic hydrogen decreases with increase in current density. At current densities of the order of $10^{-4} \text{ A cm}^{-2}$ and below atomic hydrogen decreases the overpotential (Fig. 4). At higher current densities the curves run together. As Frumkin has shown⁹, this phenomenon can be explained when it is recalled that the ratio of the number of hydrogen atoms arriving from the gas phase to the number evolved

† The design of the taps has already been described^{1, 8}.

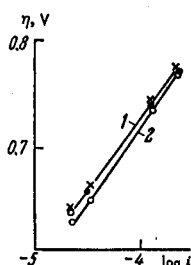


Fig. 4. Hydrogen overpotential of mercury as a function of the logarithm of current density: 1) in the absence of atomic hydrogen; 2) in the presence of atomic hydrogen.

by cathodic polarisation falls as the current density increases. In order to make sure that the decrease in the overpotential of mercury is caused by hydrogen atoms and not by any other products formed in the discharge, the relation between η and $\log i$ was first determined in neon both with and without a discharge present. Fig. 5 shows that the shift in potential towards more positive values observed during a discharge at certain current densities in the presence of hydrogen was not observed in pure neon at these densities. The quantity of atomic hydrogen formed from water vapour by the action of the discharge is probably insufficient to affect the value of the hydrogen overpotential at these current densities. On the other hand, it does suffice, as has been shown above, to make the nickel potential (in the absence of current) 200–300 mV more negative (Fig. 2), and in some experiments still more negative.

In order to check the effect of neon, experiments were also carried out with hydrogen at 7 mm pressure in the absence of a discharge. Under these conditions the measured overpotentials were practically the same as those in the mixture of neon and hydrogen. Our curves give almost normal values of 120–130 mV for the coefficient b in the Tafel equation: $\eta = a + b \log i$. The constant a remains ~150 mV below the correct value, i.e. it is approximately 1.25 V, even after correcting for the specific conditions

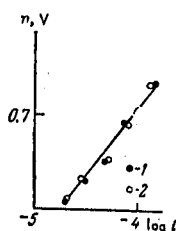


Fig. 5. Hydrogen overpotential of mercury as a function of the logarithm of current density in an atmosphere of neon: 1) in the absence of a gas discharge; 2) in the presence of a gas discharge.

in the experiments (for example change in the electrode surface during intense bubbling, etc.). The low value of a may perhaps be due to the effect of impurities which had not been completely eliminated by the conditioning of the discharge tube in a high vacuum with the discharge being switched on and off. This conditioning, which was undertaken for every experiment, was intended to clean the electrodes of the discharge tube. Evacuation of the system was continued until the pressure in the system ceased to increase after the discharge had been switched on. It was also possible that, in spite of the conditioning, a certain amount of the substances which had been removed remained on the walls of the apparatus. The same conditioning of the apparatus was carried out in the experiments with nickel, but the values obtained for the overpotential were close to those obtained by Lukovtsev *et al.*⁴ The coefficient a in the Tafel equation was ~700 mV, and the coefficient b was 0.10 V.

The fact that the overpotential of mercury was underestimated [in the absence of a discharge? (Ed. of Translation)] in these experiments makes it necessary to exercise care in drawing conclusions. Nevertheless, we think it correct to conclude, from an analysis of the experimental results described above, that the decrease in the overpotential, of both nickel and mercury, is caused by the "oxidising" action of atomic hydrogen. This is supported by our control experiments in neon (in the absence of hydrogen), in which no decrease in overpotential was observed during the discharge. It is also significant that, when the gas discharge is switched off, the overpotential returns to its initial value.

We express our thanks to Academician A. N. Frumkin for his interest in the work and for discussing the results.

SUMMARY

1. In the absence of current and at low cathodic polarisations, the introduction of atomic hydrogen into the reaction zone shifts the potential of a nickel electrode in an alkaline solution towards more negative values. At higher cathodic polarisations the atomic hydrogen exerts an "oxidising" action, shifting the electrode potential to more positive values, and this can be explained by its facilitating electrochemical desorption. Atomic hydrogen has a similar effect on a mercury cathode in an acid solution at not too high cathodic polarisations.
2. Experiments in an atmosphere of neon and in a mixture of neon and hydrogen, as well as in the presence of radiolysis in the case of nickel, have confirmed that with both nickel and mercury the observed effect is due to the presence of atomic hydrogen and is not caused by oxidising radicals which might be formed by the action of a glow discharge on water vapour. The results obtained with mercury are to be regarded as preliminary, since it is not clear why the value obtained for the constant a in the Tafel equation was too low.

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Institute of Electrochemistry,
USSR Academy of Sciences,
Moscow

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KINETICS OF DECOMPOSITION OF PEROXO-SALTS IN SOLUTION

G.A. Bogdanov and I.K. Prokhorova

Previous investigations¹⁻³ dealt with the kinetics of the catalytic decomposition of H_2O_2 under the combined action of $Na_2WO_4 + BaCl_2$, $Na_2WO_4 + SrCl_2$, and $Na_2MoO_4 + BaCl_2$. Nikolaev's experiments⁴, in which water as solvent was partly replaced by benzene or methyl methacrylate, showed that the catalysis of hydrogen peroxide decomposition by molybdates or tungstates does not take place by a radical-chain mechanism. The above findings led to the hypothesis that intermediates responsible for the catalysis are formed in these processes: peroxo molybdates and peroxotungstates of barium or strontium. We synthesised the substances, most of which have not been described in the literature. Their constitution includes water†.

The present paper describes an investigation of the kinetics of decomposition of the intermediates in aqueous solution; the electrical conductance of the hydrate of the white product $SrWO_6$ in solution, during its decomposition, was investigated.

† The nature of the water and of the bond joining the peroxo-oxygen in these compounds will be discussed in the next communication. It has been established that some of these compounds are peroxohydroxo-compounds.

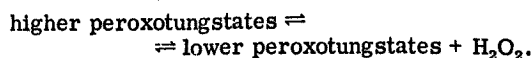
EXPERIMENTAL

Peroxo-salts containing water of crystallisation and hygroscopic water have been investigated by a method described previously^{5,6}. Hydrochloric acid and sodium hydroxide were used to provide the acid and alkaline media respectively. The weight of the peroxo-compound was the same in all the experiments, amounting to ~1 g. The volume of the reaction mixture was 36 ml.

The rate of decomposition of the peroxo-salts v was determined gas-volumetrically and expressed in mole $\times$ litre⁻¹ min⁻¹, the concentration of the peroxo-salts c was expressed as moles of H_2O_2 per litre, and the electrical conductance of the solution κ was expressed in Ω^{-1} . The rate of the reaction and the electrical conductance were measured simultaneously after the evolution of each 2 ml of oxygen.

Fig.1 shows the kinetic (1-3) and conductance (1'-3') curves for strontium peroxotungstate, $SrWO_6$, at 35° and various values of the pH. Curves 1 and 1' correspond to a neutral medium (the peroxo-salt dissolved in twice-distilled water), curves 2 and 2' correspond to $c_{H^+} = 0.016$ M, and curves 3 and 3' to $c_{OH^-} = 0.016$ M. Fig.1 shows a maximum in the conductance and breaks in the kinetic curves. The electrical conductance at first increases, reaches a maximum, and then falls continuously until the substrate is completely decomposed. Therefore in the course of the transformation of the peroxo-salt in the solution at any pH highly conducting species are formed, which in the subsequent stages gradually disappear.

Hence it follows that the peroxotungstates of strontium, and obviously of all the alkaline-earth metals, undergo stepwise changes in solution. Initially the higher strontium peroxotungstates lose hydrogen peroxide and are converted to lower peroxo-compounds. Thus if the breakdown of the higher peroxo-compound is not too rapid, equilibrium is established in solution:



In the present case the species in equilibrium are $SrWO_6$, $SrWO_5$, and H_2O_2 . The peroxotungstate $SrWO_5$ is readily soluble and has high electrical conductance.

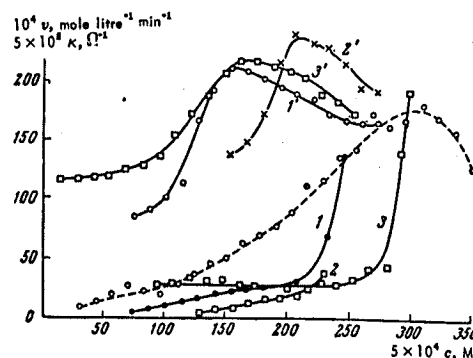


Fig.1.