Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1941. Volume XXXIII, № 7—8

PHYSICAL CHEMISTRY

THE DISSOLUTION OF NICKEL IN ACIDS

By J. KOLOTYRKIN and A. FRUMKIN, Member of the Academy

In a preceding paper(¹) treating the dissolution of lead in sulphuric and hydrochloric acids we have shown that not only for amalgams(²), but also for solid metals the mechanism of dissolution in acids can be interpreted on the basis of the laws of electrochemical kinetics, without having recourse to the assumption of local action processes existing on the surface of the dissolving metal. With the aim of extending these conclusions to other metals we carried out further investigations on nickel, this metal being particularly interesting because of the specific properties of the metals of the iron group.

In contradistinction to lead, the rate of the basic anodic processes, i. e. of the ionization of metallic atoms (F_1) and of the reverse reaction of ion discharge (F_2), is low in the case of nickel. For this reason and also because of the small value of hydrogen overvoltage on nickel, the rate of discharge of hydrogen ions (F_3) cannot be neglected. The potential established on a nickel electrode immersed in an acid in the absence of external polarisation will, therefore, be shifted towards more positive values as compared to the Ni, $Ni^{\cdot\cdot}$ equilibrium potential. This shift must lead to a further decrease of the rate of discharge of nickel ions, so that the latter process may be neglected at sufficiently low concentrations of nickel ions in the solution.

When a current flows through the system the following relation holds:

$$i = F_3 - (F_1 + F_4) \tag{1}$$

positive values of i corresponding to a cathodic current and F_4 being the rate of ionization of hydrogen.

When the potential established during the dissolution is markedly more negative than the reversible hydrogen potential, F_4 can be neglected, and equation (1) transforms into

$$i = F_3 - F_1. \tag{2}$$

Finally in the absence of an external polarisation there results

$$F_1 = F_3. \tag{3}$$

The stationary potential established in this case will be determined by two processes: ionization of the metal and discharge of hydrogen ions. This non-equilibrium potential depends both on the concentration of hydrogen ions and on the structure of the electrode surface. To determine the rate of dissolution of nickel it is necessary to know, besides the value of the hydrogen overvoltage, the value of the stationary potential, which varies with the experimental conditions. For a given potential F_3 may be found from Tafel's equation, if the latter is valid in the case of spontaneous evolution of hydrogen on the metal during its dissolution. If this relation holds, the rate of hydrogen evolution must correspond to the value obtained by extrapolating the hydrogen overvoltage curve to the stationary potential. The rate of all the processes on the nickel electrode in the neighbourhood of the stationary potential being small, the variations in the acid concentration may be neglected.

When the stationary potential of nickel electrodes is close to the reversible hydrogen potential, F_4 cannot be neglected and the rate of spontaneous dissolution can no longer be determined by mere extrapolation to the stationary potential of the hydrogen overvoltage curve measured at high current density, because under these conditions the kinetics of hydrogen evolution will not follow Tafel's equation in its usual form.

At high cathodic polarisation of the electrode, when the rate of transition of metallic atoms into ions can be neglected, equation (2) transforms into

$$i = F_3. \tag{4}$$

In this case the relation between the current and the overvoltage will follow Tafel's equation. However, for potentials which are close enough to the stationary potential, Tafel's relation holds no longer because the process of hydrogen evolution will be partly compensated by the dissolution of the metal. This was observed in an investigation by Lukovtzev, Levina and Frumkin(3) on the overvoltage of hydrogen on nickel electrodes in acid solutions. The hydrogen overvoltage curves obtained by these authors near the stationary potential are almost horizontal.

Equation (2) allows of determining the rate of nickel dissolution at different potentials F_1 if the rate of hydrogen evolution and the current density are known.

The experimental procedure consisted in obtaining an accurate hydrogen overvoltage curve and in measuring simultaneously the volume of hydrogen evolved during fixed intervals of time, both in presence and in absence of an external polarisation. The rate of dissolution was expressed in electric units.

The measurements were carried out in an atmosphere of hydrogen, in order to exclude depolarisation by oxygen. The hydrochloric acid solutions of various concentrations were prepared by diluting with conductivity water Kahlbaum's concentrated acid, redistilled twice in an atmosphere of hydrogen. The sulphuric acid solutions were prepared similarly from c. p. sulphuric acid redistilled twice in vacuo. All the experiments were carried out with Hilger's spectroscopically pure nickel which from its outward appearance might be supposed to have been prepared by decomposition of a gaseous compound in a heated tube. Experiments in which less pure Kahlbaum nickel was used gave similar results. The treatment of the nickel electrode was throughout the same, so that the structure of its surface remained unchanged during all the series of experiments. Before each measurement the electrode was washed with a warm solution of alkali and thoroughly rinsed with water.

The whole set-up can be seen in Fig. 1.

The acid solution was purified in cell *B* by cathodic polarisation, the auxiliary cathode being made of the same material as the basic nickel cathode and carefully cleaned. The polarisation was pursued during 6—10 hours, the solution being stirred with a current of hydrogen. The purified solution was introduced in cell *A* containing the electrode *K* under investigation, after the latter had been heated in hydrogen for 4—5 hours at 430° C in order to remove the oxides from its surface, and then cooled in a current of hydrogen. To prevent the introduction of air in cell *A* the ground joint *L* was protected with water. To measure the volume of evolved hydrogen, the electrode *R* was placed in a glass cylinder *M* joined to a burette. The nickel wire connected with the electrode was scaled in a glass capillary *g* so that no hydrogen could evolve on it and the whole amount of gas liberated by the current was gathered in the burette. The acid solution was transferred from cell *A* to cell *B* by hydrogen pressure.

The electrode *C* made of platinized platinum was used as anode both for the purification of the solution and for the polarisation of electrode *R*. The anode liquid was separated from the cathode liquid by two taps, which excluded the possibility of oxygen and traces of platinum being carried over from the anode to the cathode. A platinized platinum electrode placed in *D* was used as reference electrode.

We have found that the overvoltage curve obtained, when starting from high current densities after a prolonged preliminary cathodic polarisation of the electrode at high current density, is situated higher and has a steeper slope than the same curve measured in the reverse direction, i. e. from low current densities to high ones. If after the latter treatment the electrode is not subjected again to a prolonged cathodic polarisation, the last curve can be fairly well reproduced in both directions. The state of high overvoltage observed after the abovementioned cathodic treatment is unstable. All the results given further in this paper were obtained beginning with low current densities.

The stationary potential of spontaneous dissolution is not established immediately after the current is cut off; the overvoltage η falls at first rapidly and then slowly increases (Fig. 2). The rate at which a constant value is attained depends on the concentration of the acid; it is higher in more concentrated solutions. This phenomenon remains as yet unexplained. Every point of the overvoltage curve plotted with reference to the rate of hydrogen evolution is an average of several concording values. The time necessary for the establishment of a stationary rate after changing the potential did not exceed 30 min.

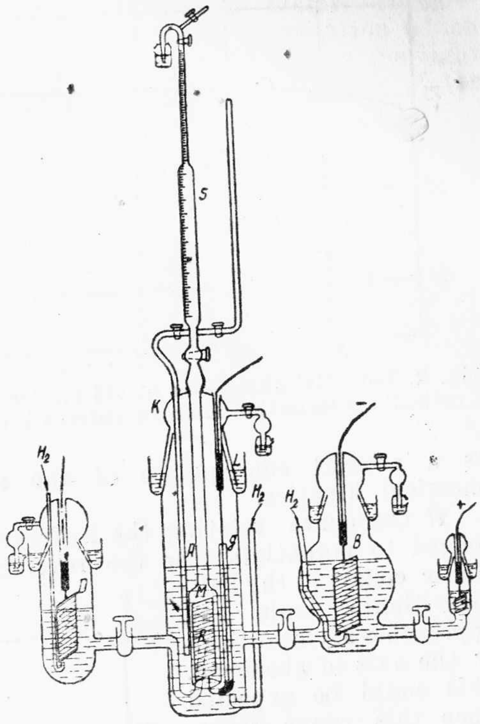

Fig. 1.

The hydrogen overvoltage curves in a half-logarithmic scale obtained in the usual way by measuring the current density and those obtained from the rate of hydrogen evolution in a norm H_2SO_4 are given in Fig. 3 (curves *1* and *2*). The point corresponding to the evolution of hydrogen in the absence of current lies at the intersection of curves *2* and *4*. It can be seen from this figure that in contrast to the current density curve, the curve obtained from hydrogen volume measurements strictly follows Tafel's equation remaining rectilinear down to the potential of spontaneous dissolution. The logarithm of the current density corresponding to the rate of hydrogen evolution in the absence of an external polarisation is exactly given by the extrapolation to the stationary potential of the overvoltage curve obtained from current density measurements. The law of hydrogen evolution expressed by Tafel's equation is therefore observed for nickel as well as for lead in the case, when there is no external polarisation, so that the rate of spontaneous dissolution of nickel may be determined from the value of hydrogen overvoltage and from the stationary potential.

The rate of hydrogen evolution was measured also at potentials more positive than the stationary potential, under anodic polarisation of the electrode, the current density corresponding to a given anodic polarisation (curve *3*) being measured along with the rate of hydrogen evolution.

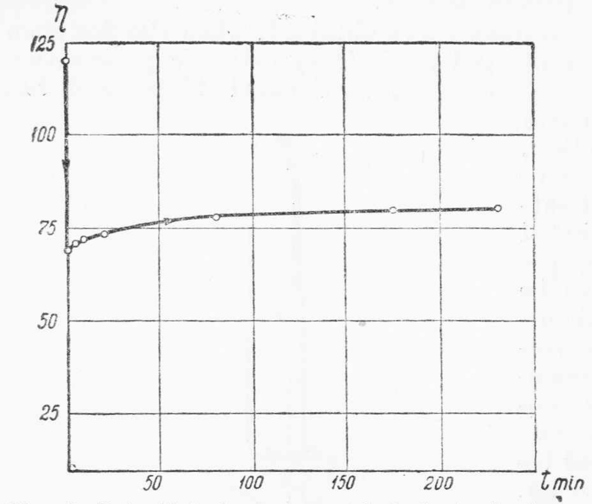

Fig. 2. Potential change on nickel electrode during cathodic polarisation after the current is cut off.

It can be seen from curve *3* that so long as the potential referred to the reversible hydrogen potential is sufficiently negative, the anodic polarisation exerts no influence on the law of hydrogen evolution which still obeys Tafel's equation *.

The decrease in the velocity of hydrogen evolution on a dissolving metal with increasing anodic polarisation, which in the literature on corrosion is known by the name of «differenz-effekt», is obtained here as a natural consequence of the application of the laws of electrochemical kinetics.

If the curve relating the hydrogen evolution to the potential is prolonged to potentials near the reversible hydrogen potential, it loses its linear course in the half-logarithmic scale and approaches asymptotically the axis of abscissae. This could be expected since this curve represents the value F_3-F_4, and F_4 cannot be neglected as compared to F_3 in the neighbourhood of the reversible hydrogen potential. At the reversible hydrogen potential, the value of F_3-F_4 must become zero if the processes related to the hydrogen evolution are independent of the process of metal ionization, as required by the electrochemical theory of metal dissolution.

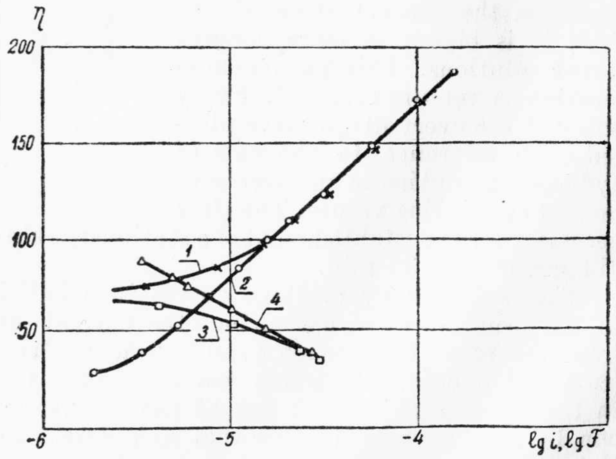

Fig. 3. Overvoltage change as related to the logarithm of the current density during cathodic and anodic polarisation (*1* and *3*), to the logarithm of the rate of hydrogen evolution (*2*), to the logarithm of the rate of dissolution of nickel (*4*).

---

* It must be kept in mind that the good conformance of experimental data with the theoretical surmises reported in this case is a consequence of the high purity of the nickel used. In other cases the anodic polarisation must lead to changes in the electrode surface, and consequently to a variation of the overvoltage.

The results obtained allowed us by using equation (2) to calculate the rate of dissolution of nickel (F_1) at different potentials * (curve *4*).

It can be seen from Fig. 3, that in this case, as well as in that of hydrogen evolution, the curve obtained in a half-logarithmic scale is almost a straight line.

The rate of spontaneous dissolution of nickel is given by the intersection of two curves corresponding to independent processes: the discharge of hydrogen ions and the ionization of metallic atoms. The decrease in the rate of metal dissolution during cathodic polarisation which required a special explanation in the theory of local action, is in the light of the present theory a direct consequence of the cathodic shift of the metal potential.

Karpov Institute of Physical
Chemistry.

Received
17. XI. 1941.

REFERENCES

[1] J. Kolotyrkin and A. Frumkin, Acta Physicochimica URSS, **14**, 469 (1941). [2] A. Frumkin. Z. physikal. Chem., (A), **160**, 116 (1932); Wagner und Traud, Z. Elektrochem., **44**, 391 (1938). [3] P. Lukovtzev, S. Levina and A. Frumkin, Acta Physicochimica URSS, **11**, 21 (1939); A. Legran and S. Levina, Journ. Phys. Chem. (Russ.), **14**, 211 (1940).

---

* In an investigation carried out by A. Sindiukov in the Laboratory of Electrochemistry of the Moscow State University it was shown by direct analytical measurements, that the values of the rate of dissolution of nickel calculated in this way are corroborated by experimental data.