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INFLUENCE OF ACID CONCENTRATION AND OF THE ADDITION OF PLATINUM ON THE DISSOLUTION OF NICKEL

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

The influence of acid concentration on the dissolution of nickel was studied by means of the method described in the preceding paper.

The overvoltage of hydrogen on nickel and the rate of dissolution of the latter were measured in 0.01, 0.1 and 1.0 *N* HCl (Fig. 1);

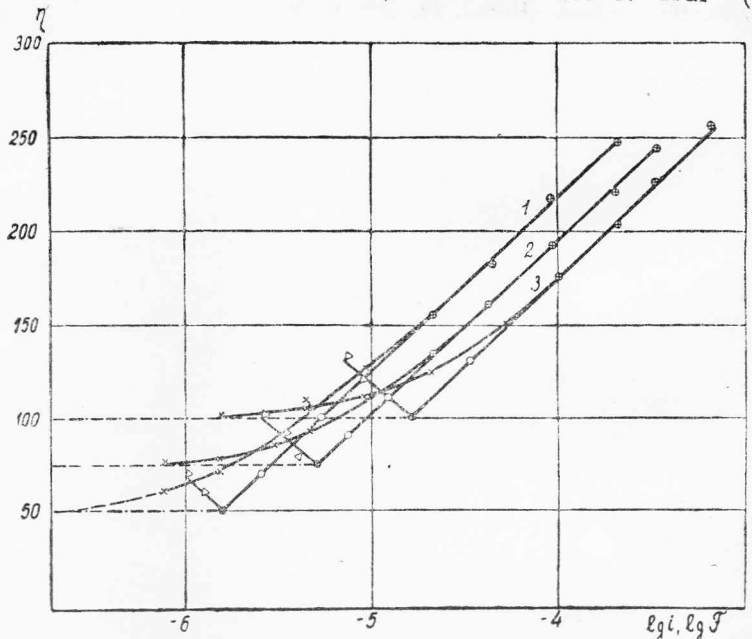

Fig. 1. Hydrogen overvoltage on nickel and dissolution of the latter in HCl of various concentrations: *1* — 0.01 *N* HCl; *2* — 0.1 *N* HCl; *3* — 0.94 *N* HCl; × — overvoltage in relation to current density; ○ — to the rate of hydrogen evolution; ▽ — to the rate of nickel dissolution.

and in 0.01, 0.1, 1.0 and 10 *N* H_2SO_4. The data obtained in HCl solutions of different concentration are referred in Fig. 2 to the same potential, viz., to the standard hydrogen potential, the activity of the H^+ ion being taken equal to the mean activity of the acid. For more concentrated solutions this assumption is certainly somewhat arbitrary.

The potentials being thus recalculated, the curves relating the logarithm of the dissolution rate of nickel to the potential obtained for different concentrations coincide forming a straight line. In other words,

the velocity of anodic dissolution of nickel at a given potential does not depend on the concentration of acid. In this respect nickel differs substantially from platinum, the latter's rate of dissolution being proportional at a given potential to the Cl′-ion concentration, as shown by B. Ershler in this laboratory (unpublished data). Similar results were obtained for sulphuric acid, the slope of the anodic dissolution curves of nickel obtained in H_2SO_4 differing, however, somewhat from that in HCl. This slight discrepancy may be due to the use of different electrodes in the two series of measurements.

It can be seen from Fig. 2 that the relation between the rate of spontaneous dissolution of nickel and the concentration is determined by the hydrogen overvoltage and the slope of the dissolution curve. When the acid concentration increases, the rate of hydrogen discharge increases (F_3); the overvoltage curve is shifted downwards; the course of the dissolution curve remains unchanged. The rate of spontaneous dissolution increases

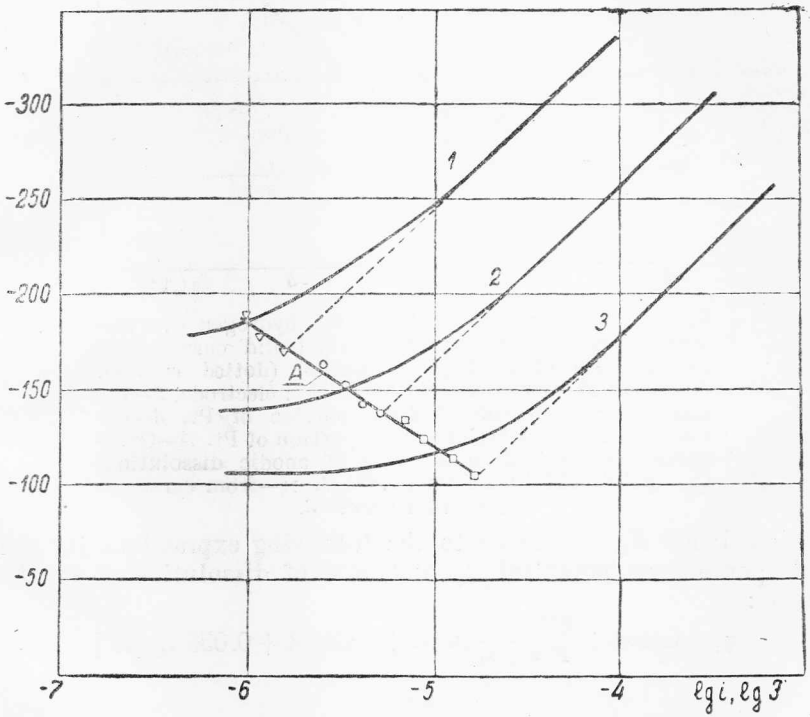

Fig. 2. Potential φ of a nickel electrode in HCl of various concentrations in relation to current density (solid curves) and to the rate of hydrogen discharge (dotted curves): *1* — 0.01 *N* HCl; *2* — 0.1 *N* HCl; *3* — 0.94 *N* HCl; *A* — potential in relation to the rate of anodic dissolution. ▽—points obtained from curves *1*, ○ — from curves *2*, ◇ — from curves *3*.

owing to the fact that the new overvoltage curve intersects the dissolution curve at a more positive potential.

Quantitatively these relations can be expressed as follows:

$$F_1 = ke^{\frac{\alpha_1 \varphi F}{RT}}, \tag{1}$$

where φ is the potential of the nickel electrode. It results from our data that α_1 is equal to 0.76 for the nickel electrode (average value). Accor-

ding to the theory of hydrogen overvoltage, the kinetics of the hydrogen ion discharge are governed by the relation

$$F_3 = K_1 [H\cdot]^{\beta} e^{-\frac{-\alpha\varphi F}{RT}}. \qquad (2)$$

In the overvoltage theory the value of β varies between 0.5 and 1 according to different assumptions. Empirically we found the following average values: $\beta = 0.77$ and $\alpha = 0.54$.

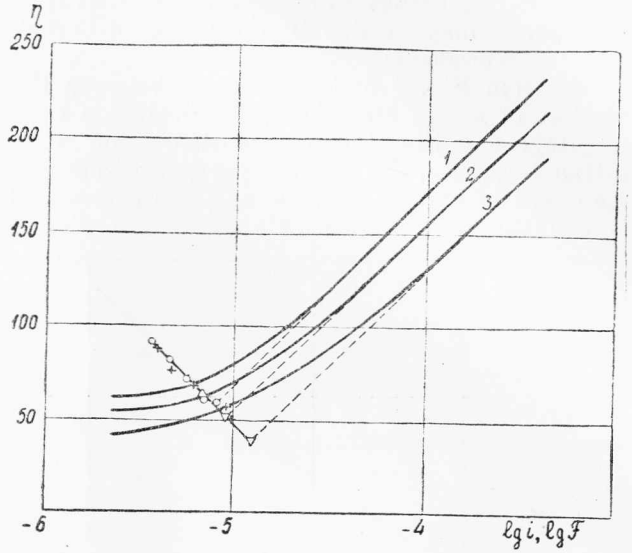

Fig. 3. Influence of platinum on hydrogen overvoltage in relation to current density (solid curves) and to the rate of hydrogen evolution (dotted curves). *1*—curves obtained with a pure nickel electrode, *2*—the same after deposition of first portion of Pt, *3*—the same after deposition of second portion of Pt. *A*—Overvoltage in relation to the rate of anodic dissolution; ○ – points obtained from curves *1*, ×—from curves *2*, ▽ — from curves *3*.

The condition $F_1 = F_3$ leads to the following expressions for the relation of spontaneous potential φ_s and rate of dissolution v to the concentration:

$$\varphi_s = \text{Const} + \frac{RT}{F}\frac{\beta}{\alpha + \alpha_1} \ln [H\cdot] = \text{Const} + 0.035 \lg [H\cdot] \qquad (3)$$

and

$$v = \text{Const}' [H\cdot]^{\frac{\alpha_1\beta}{\alpha_1+\alpha}} = \text{Const}' [H\cdot]^{0.45} \qquad (4)$$

If φ_s and v are known for one concentration, the corresponding values can be calculated for other concentrations by means of these equations. The results of such calculations are given in the following table.

Acid	Concentration	Spontaneous dissolution potential referred to the standard hydrogen electrode		Rate of dissolution in amp. per sec.	
		Measured	Calculated according to equ. (3)	Measured	Calculated according to equ. (4)
HCl	0.96 *N*	0.105	0.105	1.66×10^{-5}	1.56×10^{-5}
»	0.1 *N*	0.138	(0.138)	5.6×10^{-6}	(5.6×10^{-6})
»	0.01 *N*	0.170	1.171	1.62×10^{-6}	1.80×10^{-6}

It can be seen from these data that the agreement between the calculated and experimental data is satisfactory *.

Fig. 3 shows the influence of small quantities of platinum on the overvoltage of hydrogen and on the dissolution of nickel. Curve *1* is obtained on a pure nickel electrode, curves *2* and *3* are obtained with the same electrode after the deposition of platinum in small quantities on its surface. The quantity of platinum on the surface of the electrode was five times as large in the case of curve *3* as in the case of curve *2*. The platinum was introduced in the electrolyte in the form of a solution of $PtCl_4$ saturated with hydrogen by means of a special device in the apparatus, the platinum being subsequently deposited on the nickel surface by cathode polarisation. It is seen from Fig. 3 that all the points corresponding to the rate of dissolution of nickel calculated from these data form a straight line. Covering a small part of the electrode surface with platinum does not influence the rate of dissolution at a given potential, but strongly influences its rate of spontaneous dissolution. This may be due to the fact that traces of platinum deposited on the surface of the electrode act as centers of lowered hydrogen overvoltage. The latter's rate of evolution is, therefore, strongly increased whereas the rate of dissolution of nickel at a given potential remains unaltered. As to the rate of spontaneous dissolution, it increases owing to the shift of stationary potential in the anodic direction in consequence of the increase in rate of discharge of hydrogen ions.

Karpov Institute
of Physical Chemistry.

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* A similar treatment of the conditions of metal dissolution has already been proposed, as we know, by A. Shutin, Journ. Phys. Chem. (in press).