Hydrogen Overvoltage on Nickel

By *P. Lukowzew, S. Lewina* and *A. Frumkin*

In recent years a number of papers[1–8] have provided material proving the correctness of the theory of hydrogen overvoltage based on the assumption that in hydrogen deposition the rate-determining step must be the discharge of hydrogen ions. Still some authors are inclined to see the cause of overvoltage in the process of hydrogen atoms recombination. Thus Horiuti and collaborators[9, 10] come to the conclusion that a mechanism of that kind ("catalytic" mechanism) is true for such metals as Ni, Au, Ag, Cu, Pt. As to Sn, Hg, Pb, on which the overvoltage is high, these authors consider the possibility of a mechanism similar to that suggested by Heyrowsky[11], according to which the slow reaction is the formation of the H_2 molecule from adsorbed hydrogen ions and already discharged hydrogen atoms adsorbed on the surface. This mechanism they call "electrochemical". Horiuti and Okamoto arrive at these conclusions using the transition state method for their calcu-

[1] Erdey-Gruz a. M. Volmer, Z. physik. Chem., **A 150,** 203 (1930).
[2] A. Frumkin, Z. physik. Chem., **A 164,** 121 (1933).
[3] I. Horiuti a. M. Polanyi, Acta Physicochimica URSS. **2,** 505 1935).
[4] Gurney, Proc. Roy. Soc., London, **A 134,** 137 (1932).
[5] M. Volmer a. Wick, Z. physik. Chem.. **A 172,** 429 (1935).
[6] L. Hammet, Trans. Farad. Soc., **29,** 770 (1933).
[7] S. Lewina a. M. Silberfarb, Acta Physicochimica URSS, **4,** 275 (1936).
[8] B. Kabanow, Acta Physicochimica URSS, **5,** 193 (1936).
[9] I. Horiuti a. G. Okamoto, Sc. pap. Inst. Phys. Chem. Res., **28,** 231 (1936).
[10] Okamoto, Horiuti a. Hirota, Sc. pap. Inst. Phys. Chem. Res., **29,** 223 (1936). See also [28].
[11] P. Herasymenko a. Šlendyk, Z. physik. Chem., **A 149,** 123 (1930).

lations[12]. As shown by Frumkin[13], from the standpoint of the recombination mechanism it is not possible to interpret the influence of the solution concentration upon the overvoltage nor the increase of the latter in the presence of neutral salts, *i. e.*, the effects caused by the dependence of the overvoltage on the structure of the double layer[2]. Most authors who studied the mechanism of overvoltage did not take into consideration the influence of solution concentration and only in some cases[11, 14] this dependence was investigated in a narrow range of concentrations.

The study of the dependence of overvoltage on concentration is, however, of no less importance than the study of the dependence of the reaction rate on pressure in the kinetics of gas reactions.

The effect of solution concentration and of neutral salt addition in the case of a mercury cathode[15, 16] has proved the correctness of the theory of the slow discharge of the hydrogen ion. It seemed essential to elucidate the rôle of these factors also in the case of metals capable of adsorbing hydrogen and which are referred by Horiuti and Okamoto to the first group. For such metals Frumkin[13], using the theory of the slow discharge, has shown that the surface concentration of hydrogen on the cathode with sufficiently high cathodic polarizations must always assume a value which causes the reactions of discharge of hydrogen ions and of interaction of hydrogen ions with the adsorbed atoms to proceed with equal velocities. Under these conditions, both reactions can be considered with equal right as the rate-determining step. The rate of ionization of the adsorbed hydrogen is thereby neglected. At lower polarizations this latter may become important and even surpass the rate of formation of H_2 molecules. In this case the mechanism discussed by Frumkin becomes qualitatively identical with the "electrochemical" mechanism of Horiuti.

12 Recently, Horiuti and Ikusima came to the conclusion that the "electrochemical" mechanism holds for platinum too (Proc. Imp. Akad. Tokyo, **15**, 39 1939), the rate-determining step is thereby considered to be the discharge of the molecule-ion $H-H^+$ adsorbed on Pt.

13 A. Frumkin, Acta Physicochimica URSS, **7**, 475 (1937).

14 F. Bowden, Trans. Farad. Soc., **24**, 473 (1928).

15 S. Lewina a. W. Sarinsky, Acta Physicochimica URSS, **6**, 491 (1937).

16 S. Lewina a. W. Sarinsky, Acta Physicochimica URSS, **7**, 485 (1937).

Experimental

As an object of investigation in the first place nickel was taken, being a metal which adsorbs hydrogen and strongly catalyses the recombination of hydrogen atoms. Moreover, on nickel, measurements of overvoltage in alkaline solutions are possible. The use of alkaline solutions enables us to carry out observations also at anodic polarizations, *i. e.*, to study not only the kinetics of hydrogen ion discharge but also that of the reverse reaction.

The measurements were carried out in solutions of hydrochloric acid and sodium hydroxide. The hydrochloric acid solutions were prepared by saturating twice distilled water with gaseous hydrogen chloride. The solutions of sodium hydroxide were prepared by decomposition of sodium amalgam with twice distilled water in a hydrogen atmosphere.

Fig. 1 shows an apparatus for producing sodium hydroxide solutions from sodium amalgam. The sodium amalgam produced by electrolysis of chemically pure alkali on a mercury cathode was kept in sealed ampoules in a hydrogen atmosphere. The ampoule with the amalgam was placed in tube *A*; the vessel *C* was filled with twice distilled water.

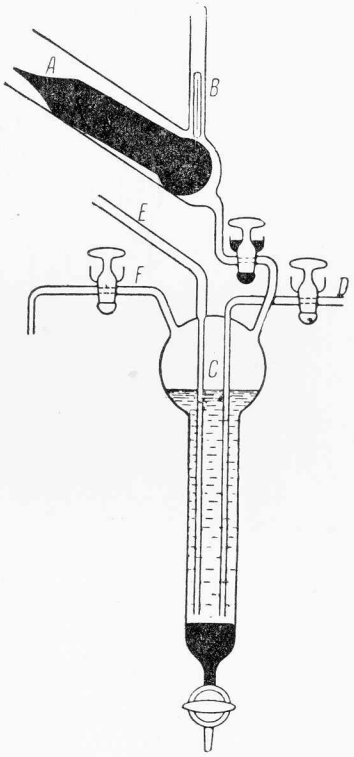

Fig. 1. Apparatus for producing alkali from amalgam.

The whole apparatus, as well as tube *A*, was then filled with hydrogen through tube *D*. With the aid of an electromagnetic arrangement *B* the ampoule was opened, and the amalgam entered in drops into the vessel where it was decomposed by water (in the absence of catalysts). Before the experiment the alkali was forced by the pressure of hydrogen along tube *E* into the measuring apparatus previously filled with hydrogen (Fig. 2).

Before each experiment the nickel[17] which served as cathode was washed with a hot KOH solution, after which it was carefully rinsed with water. The experimental procedure can be clearly seen from Fig. 2. The apparatus consisted of two parts: one of them served for a preliminary purification of the solution by electrolysis, and the other for making polarization measurements.

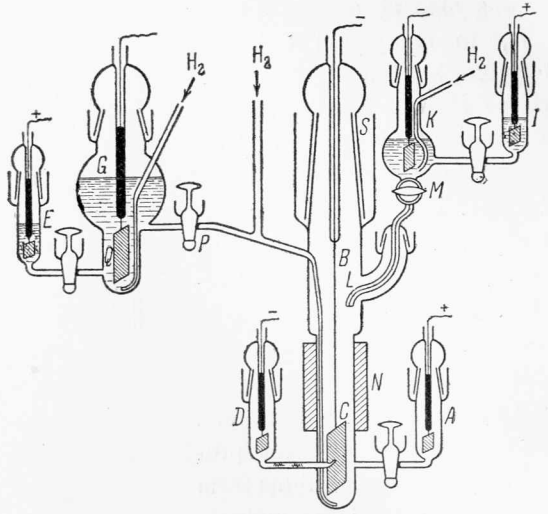

Fig. 2. Apparatus for measuring overvoltage on nickel.

For purification, the HCl solution was poured and the NaOH pressed through tube *E* (Fig. 1) into the electrolytic cell represented in Fig. 2; on the left *G* is the cathodic space, *Q* is the cathode of platinized platinum. The purification by electrolysis was usually carried out during 16—18 hours with continuous stirring (hydrogen bubbles). Prior to admitting the purified solution into the polarization apparatus, the nickel cathode *C* was heated in an atmosphere of hydrogen to 400—420° C to remove the oxides from the surface. For this purpose the cathode was raised to such a height as to get into the part of the apparatus located in an electric furnace. During this operation the air could not penetrate into the apparatus, since the ground joint *S* was immersed in water. The heating was continued for several hours after which the cathode was placed in its original position with the ground joint tightly closed. The cooling of nickel was also conducted in a stream of hydrogen. The HCl or NaOH solution was supplied to the polarization apparatus by turning the stop-cock *P*. As a reference electrode platinized platinum saturated with hydrogen placed in *D* and separated from the cathode space by a glass filter was used. The anode *A* was also made of platinized platinum. The anodic space was separated from the cathodic one by a stop-cock. For the addition of neutral salts ($LaCl_3$ in the case of acids, and NaCl in the case of alkalies) served a device shown in Fig. 2 on the right. The solution of $LaCl_3$ in hydrochloric acid, or correspondingly the solution of NaCl in alkali, previously purified by electrolysis, was added in drops through capillary *L*. The volume of the drops had been determined previously. All the stop-cocks and ground joints were wetted with water. It was noticed that immediately after the switching on of the current, the potential of the nickel electrode was not established at once, but continued to increase for some time[18]. This fact is probably due to slight oxidation of nickel before the immersion in the electrolyte at the expence of the oxygen of the water, since the cooling of nickel took place in an atmosphere of hydrogen saturated by water vapour.

During the polarization the increase of the potential of nickel ceases after some hours.

The measurements were begun after constant values of the cathode potentials had been attained.

[17] As cathode, both Kahlbaum's nickel in the form of a plate 1.5 × 4.5 cm. in size and Hilger's (spectroscopically pure) nickel in the form of a rod 0.5 cm. in diameter, 5 cm. in length, were used. In both cases the course of the curves remained the same, but the absolute value of the overvoltage on Hilger's nickel was 15 mV. lower than that on Kahlbaum's nickel. This discrepancy is probably associated with a difference in the true dimensions of the surface. The data given in Figs. 3 and 4 refer to Kahlbaum's nickel; those in Figs. 5, 6, 7, 8, 9 to Hilger's nickel.

[18] This fact has been observed already by Tafel [Z. physik. Chem., **34,** 200 (1900); **50,** 641 (1905)] who did not succeed in attaining constant values of potential on nickel. The same refers to some other authors [M. Reader a. I. Brun, Z. physik. Chem., **133,** 15 (1928); R. Hood a. Krauskopf, J. Phys. Chem., **31,** 786 (1931)], who worked after Tafel.

Experimental results and their discussion

1. Hydrogen overvoltage in acid solutions

The hydrogen overvoltage η on nickel in acids was studied in 0.15 N, 0.01 N, 0.001 N and 0.0003 N HCl solutions for the range of current densities i from 1×10^{-8} A/cm.^{2} to 5×10^{-4} A/cm.^{2} (Fig. 3) as calculated per cm.^{2} of apparent surface.

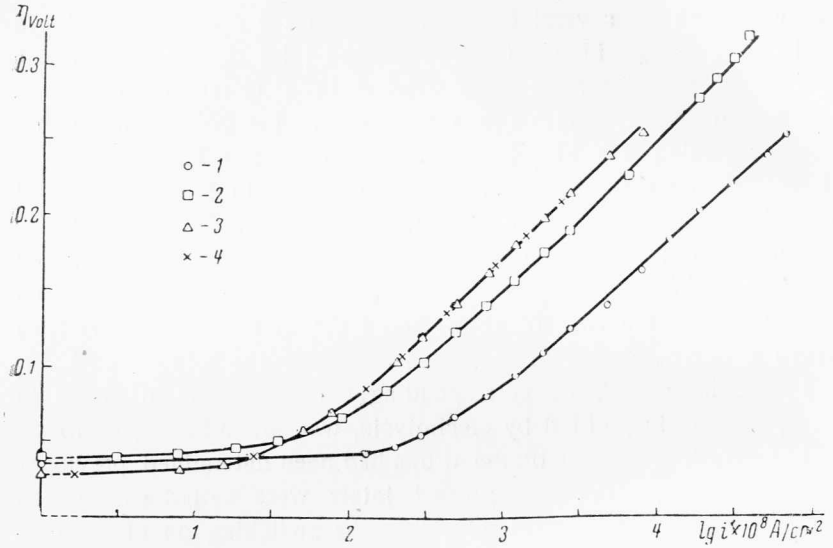

Fig. 3. Dependence of hydrogen overvoltage in acids upon the logarithm of current density: *1* — 0.15 N HCl; *2* — 0.013 N HCl; *3* — 0.0012 N HCl; *4* — 0.0003 N HCl .

As seen from Fig. 3, the initial portions of the η — lg$i$-curves for all concentrations are very close to each other and have a very small slope. Beginning from current densities of about 1×10^{-6}—1×10^{-5} A/cm.^{2} a very distinct linear course of the curves is observed; the coefficient b in Tafel's relation $\eta = a + b \lg i$ is equal to 0.10.

The initial course of the curves is accounted for by the fact that the stationary nickel potential in acid solutions is more negative than the potential of the reversible hydrogen electrode. The influence of the spontaneous interaction between the nickel and the acid is still noticeable with low polarization and disappears only in the region of comparatively high polarizations.

A similar course of the curves was observed also by Bowden[19] who studied the overvoltage on nickel in sulphuric acid.

From Fig. 3 it is seen that with increasing concentration of acid the overvoltage values are lowered. As the solution is diluted, the influence of concentration vanishes. Thus, for instance, with a current density of 1×10^{-5} A/cm.^{2} for 0.15 N HCl the overvoltage is 0.088 V.; for 0.013 N HCl — 0.152 V., and for 0.0012 N and 0.0003 N HCl — 0.172 V.

Fig. 4 (upper curves for 0.0012 N HCl) shows the influence of lanthanum chloride on the overvoltage. Curve *I* represents the dependence of overvoltage upon the logarithm of current density in pure acid; curve *II* shows the same dependence in the presence of 1.10^{-3} N $LaCl_3$. In the region of low current densities an addition of lanthanum chloride lowers the overvoltage, while in that of higher current densities an increase of overvoltage is observed.

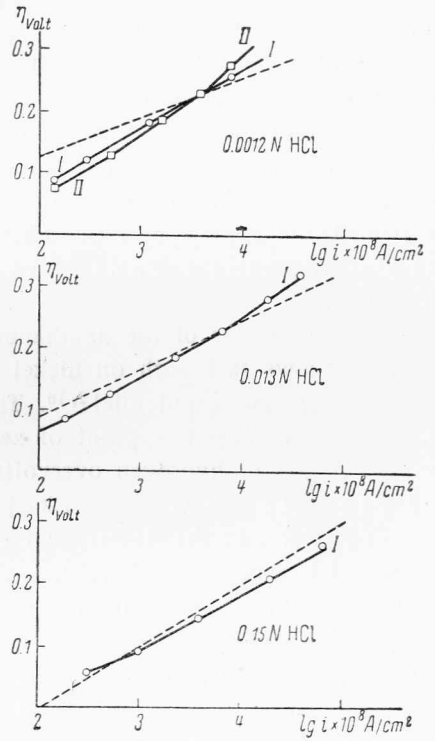

Fig. 4. Effect of lanthanum chloride on overvoltage in acids. Dotted curves — calculated for pure acid; curve *I* — experimental in pure acid; curve *II* — the same in the presence of lanthanum chloride.

The data obtained show a somewhat different dependence of overvoltage on the acid concentration on nickel as compared to the mercury cathode. On the latter, in the range of concentrations from 0.001 N to 0.1 N HCl, the overvoltage was independent on con-

[19] F. Bowden a. E. Rideal, Proc. Roy. Soc., London, **A 12,** 86 (1928).

centration. On nickel the independence on concentration is preserved only within the range from 0.001 N to 0.0003 N HCl. This is comprehensible, since the potential of nickel is considerably less negative than that of mercury, with the same current densities. Thus, for instance, for a current density of the order of 6×10^{-6} A/cm.^{2} on nickel in a 0.001 N solution the overvoltage is 0.15 V.; and on mercury under the same conditions — 0.80 V. As shown by Frumkin[13,15], the independence of overvoltage on concentration must be observed only with a negative charge on the cathode surface. If we compare the effect produced by the addition of lanthanum chloride upon the overvoltage on nickel with that observed in the case of a mercury cathode, it may be noted that in the former case there is a lowering of overvoltage for low current densities and a rise in the region of high current densities, while in the latter case throughout the whole curve only a rise of overvoltage was observed.

The character of the lanthanum chloride influence upon overvoltage shows that both on nickel and on mercury the overvoltage depends on the ζ-potential[2,16]. The case of nickel becomes clear if we assume that the point of zero surface charge of nickel lies in the region of hydrogen overvoltage, as it was shown for gallium by Frumkin and Gorodezkaja[20].

Therefore, in the lower part of the curves, where the surface of nickel is charged positively, lanthanum chloride lowers the overvoltage; while in the part of the curves where under the influence of polarization the charge of the surface becomes negative lanthanum ions cause an increase of overvoltage.

The dotted curves in Fig. 4 show the theoretical dependence of overvoltage on the current density as calculated according to the equation:

$$\varphi + \zeta = -\frac{2RT}{F} \ln i + \frac{2RT}{F} \ln [H^+] + \text{const.}$$

(which holds, provided the surface concentration of hydrogen has practically reached a constant limiting value independent of polarization[18]) and the Stern theory of the double layer[21] (φ — potential of the cathode).

The theoretical and experimental curves show a general agreement. The smaller slope of the theoretical curve for 0.0012 N HCl depends on the change of the ζ-potential near the zero point of surface charge. In the calculation the specific adsorption of anions was not considered. At present a special investigation is being carried out at this institute on the influence of different anions on the hydrogen overvoltage on nickel.

The experimental data obtained show that on nickel, as well as on mercury, in acid solutions the dependence of overvoltage on the concentration of the solution and on the structure of the double layer confirms the theory assuming that the limiting process in hydrogen deposition is the discharge of hydrogen ions. The data obtained in acids do not by themselves allow us to decide whether an equilibrium between adsorbed hydrogen and solution is established and to distinguish between different forms of the electrochemical mechanism. The data recently obtained by A. Legran in this institute seem to indicate that with very low concentrations of the acid (10^{-4} N and lower) when the discharge of hydrogen ions becomes very slow, a limit for the applicability of any electrochemical mechanism is probably reached. These data will be discussed in detail in a subsequent paper.

2. Hydrogen overvoltage in alkaline solutions

Hydrogen overvoltage on nickel was studied in the concentration range from 8.8 N NaOH to 0.001 N NaOH for current densities from 1×10^{-8} A/cm.^{2} to 5×10^{-4} A/cm.^{2}.

In Fig. 5 on the upper right-hand side, overvoltage curves are given for different concentrations of alkali. The initial parts of the curves for all the concentrations closely approach the potential of

[20] A. Frumkin a. A. Gorodezkaja, Z. physik. Chem., **136**, 451 (1928).

[21] See Frumkin[2]. The value of the double layer capacity used for calculating the ζ-potential according to Stern's theory was assumed to be equal to 50 μF. The zero of surface charge was supposed to correspond to the intersection of curves *I* and *II* (Fig. 4) in 0.0012 N HCl, the overvoltage being 0.234 V. The latter value was used to determine the magnitude of the constant term in our equation.

the hydrogen electrode in the same solution and have a very small slope. Beginning from current densities of about 1×10^{-8} — 1×10^{-5} A/cm.^{2} a linear course of the curves is observed, with the coefficient b equal to 0.108—0.115 V. Thus the course of the overvol-

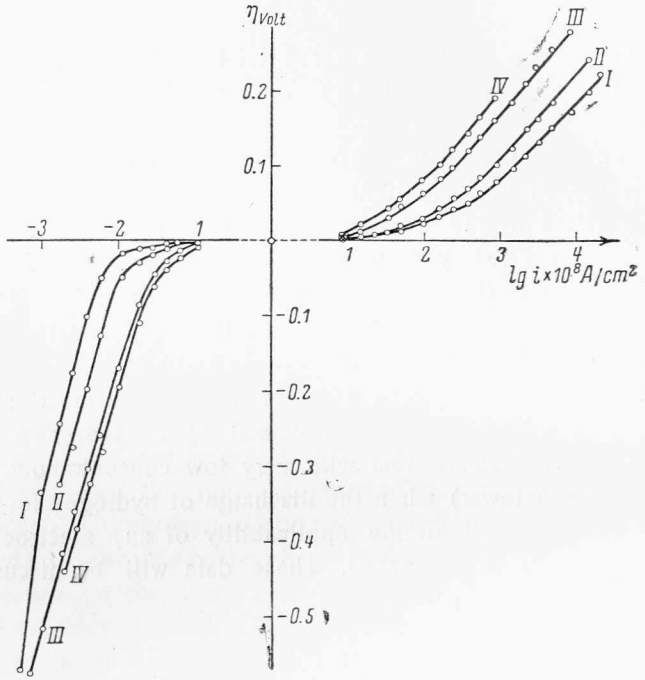

Fig. 5. Dependence of overvoltage and anodic polarization on the logarithm of current density in alkaline solutions: *I* — in 0.42 *N* NaOH; *II* — in 0.047 *N* NaOH; *III* — in 0.0075 *N* NaOH; *IV* — in 0.001 *N* NaOH.

tage-logarithm current density curves in alkalies is analogous to that in acids.

From Fig. 5 one can see that with an increase of the alkali concentration the overvoltage values are lowered; as the solution is diluted the influence of concentration becomes smaller. Thus, for the range of concentrations from 0.4 *N* to 0.0075 *N* NaOH, the overvoltage is increased by 0.058—0.060 V. with a tenfold decrease of NaOH concentration. This holds also for the range of concentrations from 0.4 *N* to 8.8 *N* NaOH. For concentrations from 0.0075

to 0.001 *N* NaOH the overvoltage increases only by 0.028 V. with the same dilution.

Fig. 6 shows the influence of sodium chloride on overvoltage. Curves *I* refer to pure alkali; curves *II*, the same in the presence of 0.10 *N* NaCl.

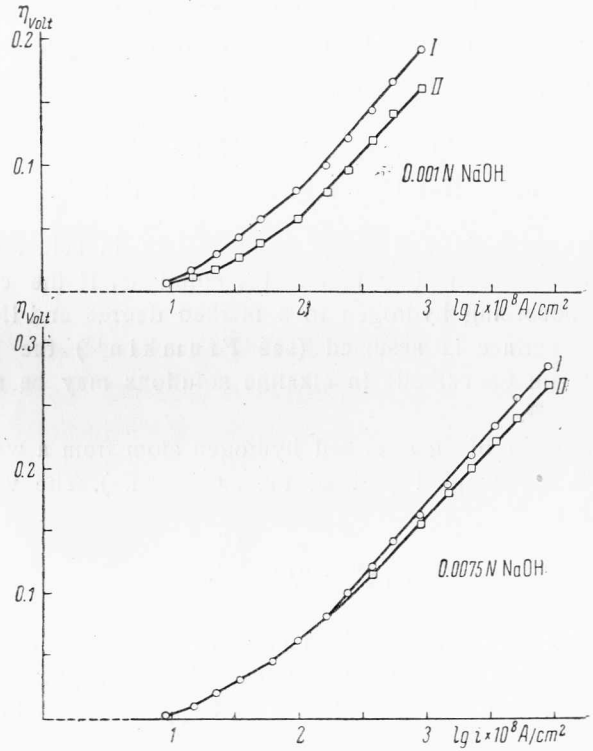

Fig. 6. Effect of sodium chloride on overvoltage in alkalies: curves *I* — in pure alkali: curves *II* — the same in the presence of 0.1 *N* NaCl.

As shown in Fig. 6, an addition of sodium chloride lowers the overvoltage, and the more so the greater the dilution of the alkali solution. Thus, for instance, with a current density of 1×10^{-5} A/cm.^{2} in 0.0075 *N* NaOH the lowering of overvoltage is 0.010 V.; and in 0.001 *N* NaOH — 0.031 V.

In stronger alkaline solutions the addition of sodium chloride of the same concentration does not affect the overvoltage.

The experimental results obtained for hydrogen overvoltage on nickel in alkaline solutions can be accounted for by the theory of the slow discharge, if we consider that on the cathode, along with the reactions

$$H_3O^+ + \ominus \rightleftarrows Me - H + H_2O, \qquad \text{I (a)}$$

$$Me - H + H_3O^+ + \ominus \rightleftarrows Me + H_2 + H_2O, \qquad \text{I (b)}$$

the following reactions are also possible:

$$H_2O + \ominus \rightleftarrows Me - H + OH', \qquad \text{II (a)}$$

$$Me - H + H_2O + \ominus \rightleftarrows Me + OH' + H_2. \qquad \text{II (b)}$$

The reactions Ia and Ib proceed mainly in acids, while the reactions IIa and IIb mainly in alkaline solutions. If the cathode is capable of adsorbing hydrogen to a marked degree and if homogeneity of the surface is assumed (see Frumkin[1,3]) the processes taking place on the cathode in alkaline solutions may be represented as follows[22].

1. Formation of an adsorbed hydrogen atom from a water molecule on the unoccupied part of the surface (IIa). The velocity of this process is

$$K_1 (1 - \theta) e^{-\frac{\varphi F}{2RT}}.$$

The H_2O concentration is included in the constants; θ represents the fraction of the surface occupied by hydrogen atoms. Tafel's constant α is assumed in a first approximation to be equal to 0.5.

2. Reaction between the water molecule and the adsorbed hydrogen atom with the formation of a hydrogen molecule (IIb). The velocity of this process is

$$K_2 \theta e^{-\frac{\varphi F}{2RT}}.$$

[22] Experiments carried out in this laboratory show that the strength of the Pt-H bond is markedly influenced by the constitution of the ionic double layer. In the following calculations we neglected this influence, since similar data for a nickel electrode are lacking.

3. Interaction of the adsorbed hydrogen atom with an OH′-ion and formation of a water molecule (IIa). The velocity of this process is

$$K_3 [OH'] \theta e^{\frac{\varphi F}{2RT}}.$$

4. Interaction of the hydrogen molecule on the unoccupied area of the surface with an OH′-ion with the formation of an adsorbed hydrogen atom and of a water molecule (IIb). The velocity of this process is

$$K_4 (1 - \theta) [OH'] [H_2] e^{\frac{\varphi F}{2RT}}.$$

For a stationary state,

$$K_1 (1 - \theta) e^{-\frac{\varphi F}{2RT}} - K_2 \theta e^{-\frac{\varphi F}{2RT}} - K_3 [OH'] \theta e^{\frac{\varphi F}{2RT}} + K_4 (1 - \theta) [OH'] [H_2] e^{\frac{\varphi F}{2RT}} = 0,$$

$$\theta = \frac{K_1 + K_4 [OH'] [H_2] e^{\frac{\varphi F}{RT}}}{(K_1 + K_2) + \{K_3 [OH'] + K_4 [OH'] [H_2]\} e^{\frac{\varphi F}{RT}}}. \qquad (1)$$

With comparatively large cathode polarizations the terms with $e^{\frac{\varphi F}{RT}}$ may be neglected; then

$$\theta = \frac{K_1}{K_1 + K_2}.$$

For the equilibrium state:

$$K_2 \theta' e^{-\frac{\varphi' F}{2RT}} - K_4 (1 - \theta') [OH'] [H_2] e^{-\frac{\varphi' F}{2RT}} = 0$$

and

$$K_1 (1 - \theta') e^{-\frac{\varphi' F}{2RT}} - K_3 \theta' [OH'] e^{\frac{\varphi' F}{2RT}} = 0,$$

where φ' is the reversible hydrogen potential; θ' is the fraction of the surface occupied by hydrogen atoms under equilibrium conditions.

Hence

$$\frac{\theta'}{1 - \theta'} = \sqrt{\frac{K_1 K_4}{K_2 K_3}} [H_2]^{1/2}$$

and

$$e^{\frac{\varphi' F}{RT}} = \sqrt{\frac{K_1 K_2}{K_4 K_3}} \frac{1}{[OH'] [H_2]^{1/2}}. \qquad (2)$$

For the cathodic current we obtain the expression:

$$i = 2F K_2 \theta e^{-\frac{\varphi F}{2RT}} = \frac{2F K_1 K_2}{K_1 + K_2} e^{-\frac{\varphi F}{2RT}}.$$

Hence $\varphi = -\frac{2RT}{F} \ln i + \text{const.}$ and the overvoltage in alkaline solutions is equal to:

$$\eta = \varphi' - \varphi = \frac{2RT}{F} \ln i - \frac{RT}{F} \ln [OH'] + \text{const.} \quad (3)$$

while for acid solutions

$$\eta = \frac{2RT}{F} \ln i - \frac{RT}{F} \ln [H^\cdot] + \text{const.} \quad (4)$$

For medium values of pH, both reactions I and II proceed with comparable velocities. In this case the cathodic current is equal to

$$i = 2F (K_2 + K_3' [H^\cdot]) \theta e^{-\frac{\varphi F}{2RT}},$$

where K'_3 is the constant of the discharge velocity of the hydrogen ion on the adsorbed hydrogen atom with the formation of a hydrogen molecule (Ib).

Hence, with sufficient cathodic polarization,

$$\varphi = \frac{2RT}{F} \ln [K_3' [H^\cdot] + K_2] - \frac{2RT}{F} \ln i + \text{const.}$$

Since

$$\varphi' = \frac{RT}{F} \ln [H^\cdot] + \text{const.} = \frac{2RT}{F} \ln [H^\cdot]^{\frac{1}{2}} + \text{const.},$$

the overvoltage will be

$$\eta = \varphi' - \varphi = \frac{2RT}{F} \ln i - \frac{2RT}{F} \ln \left\{ K_3' [H^\cdot]^{\frac{1}{2}} + K_2 [H^\cdot]^{-\frac{1}{2}} \right\} + \text{const.} \quad (5)$$

The expression $K_3' [H^\cdot]^{\frac{1}{2}} + K_2 [H^\cdot]^{-\frac{1}{2}}$ has its maximum at

$$[H^\cdot] = \frac{K_2}{K_3'}.$$

It is easily seen that with definitely acid and alkaline solutions equation (5) passes into (4) or (3)[23].

[23] It is interesting to compare the theoretical values of the overvoltage with equal concentrations of the OH' and $H^\cdot$-ions. From equations (3), (4) and (5) we obtain $\eta_{alc.} - \eta_{ac.} = \frac{2RT}{F} \ln \frac{K_3' K_{H_2O}^{1/2}}{K_2}$, where K_{H_2O} is the dissociation constant of water. As K_3 represents the kinetic constant of the H_3O^+-ion and K_2 that of the water molecule, there must exist, as is often observed in acid-base catalysis, a relation between K_2 and K_3 of the type $K_2 = K'_3 (K_{H_2O})^\beta$, where β lies between the limits 0 and 1. The possible difference between the strengths of one Ni-H bond in acid and alkaline solutions (see foot-note on page 32) is thereby neglected. We thus obtain $\eta_{alc.} - \eta_{ac.} = (1 - 2\beta) \frac{RT}{F} \ln K_{H_2O}$. In the case of hydrogen evolution on a nickel cathode, β seems to be fairly close to $1/2$, and the values of $\eta_{alc.}$ and $\eta_{ac.}$ nearly coincide.

The experimental results obtained for overvoltage in alkalies are in agreement with equation (3). Thus the experimental value for the coefficient b in alkalies, 0.108—0.115 V., approaches the theoretical value $\left(b = 2.3 \frac{2RT}{F} = 0.117 \text{ V.}\right)$.

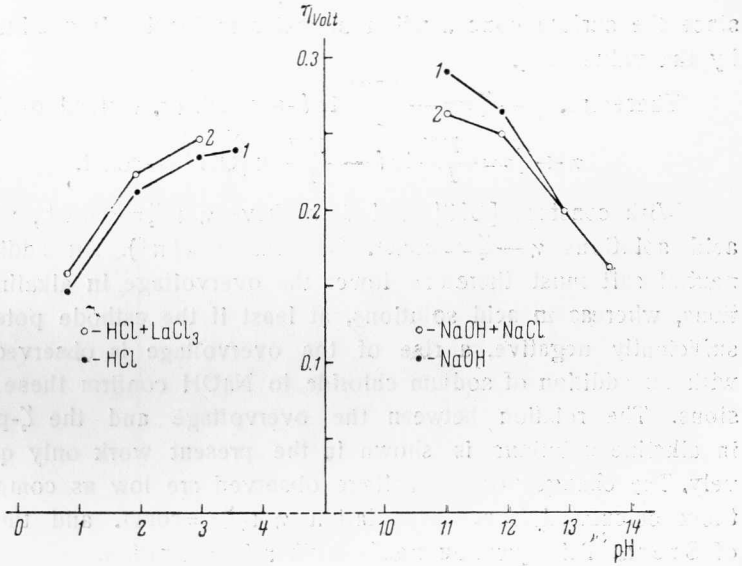

Fig. 7. Dependence of overvoltage on the pH of the solution at a current density of 1.6×10^{-4} A/cm.²: *1* — in pure HCl and NaOH; *2* — in HCl + 10^{-3} *N* $LaCl_3$ and in NaOH + 0.1 *N* NaCl.

The dependence of overvoltage on electrolyte concentration in HCl, beginning from 0.01 *N* and higher, as well as in NaOH from 0.001 *N* NaOH and higher, in general follows equations (3) and (4). This is illustrated in Fig. 7.

Equations (3) and (5) have been derived on the supposition of a non-diffuse double layer, *i. e.*, assuming that $\zeta = 0$.

If $\zeta \neq 0$, which is true for dilute solutions, then for cathodic polarization in alkaline solutions

$$i = 2FK_2\,\theta e^{-\frac{(\varphi-\zeta)F}{2RT}},$$

since the surface concentration of water molecules is not influenced by the value of ζ.

Therefore, $\varphi - \zeta = -\frac{2RT}{F} \ln i + \text{const.}$ or, instead of (3),

$$\eta + \zeta = \frac{2RT}{F} \ln i - \frac{RT}{F} \ln [OH'] + \text{const.}$$

With constant [OH'] and i we have $\eta + \zeta = \text{const.}$, while for acid solutions $\eta - \zeta = \text{const.}$ (see Frumkin[2]). An addition of neutral salt must therefore lower the overvoltage in alkaline solutions, whereas in acid solutions, at least if the cathode potential is sufficiently negative, a rise of the overvoltage is observed. Tests with an addition of sodium chloride to NaOH confirm these conclusions. The relation between the overvoltage and the ζ-potential in alkaline solutions is shown in the present work only qualitatively. The changes of overvoltage observed are low as compared to those calculated from the relation $\eta + \zeta = \text{const.}$ and the theory of Stern. This question needs further investigation.

Fig. 7 shows the dependence of the overvoltage on the pH of the solution in the presence as well as in the absence of neutral salt. With low concentrations of alkali, the dependence of the overvoltage on the concentration becomes less pronounced as we should expect from equations (3) or (5). Just as in the case of dilute acid solutions, one has the feeling that when the discharge of the H_2O molecule becomes very slow, another mechanism of the hydrogen removal from the electrode must be taken into account.

The behavior of the nickel electrode near the potential of the reversible hydrogen electrode was not the subject of a special study This is proposed to carry out in subsequent work. The theory outlined here must be considered as a rough approximation in so far as no account is taken of the possible inhomogeneity of the nickel surface and of the dependence of the Ni—H bond strength on the structure of the ionic double layer.

3. Anodic polarization of the nickel electrode in a hydrogen atmosphere

The measurements were made in the apparatus described above (Fig. 2), electrode *A* serving as the cathode, and *C* as the anode.

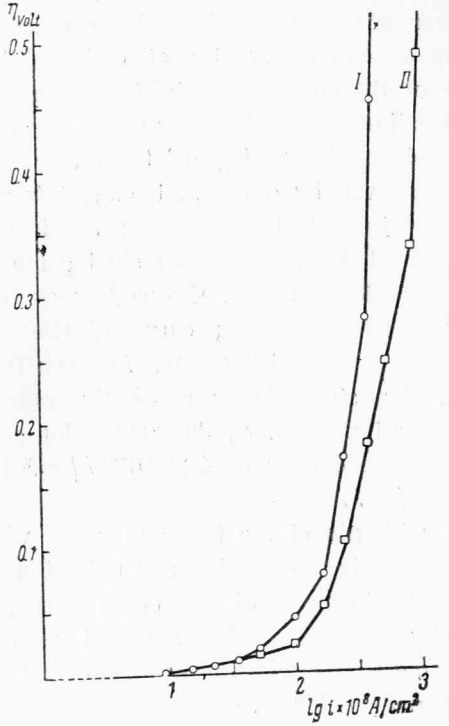

Fig. 8. Effect of stirring on the potential of the nickel anode in 0.42 *N* NaOH: Curve *I* — with slight stirring; curve *II* — with a threefold increase of stirring rate.

As the reference electrode platinized platinum was used, placed in the part *D* of the apparatus, *i. e.*, a hydrogen electrode in the same solution.

The anodic polarization of nickel was studied in the same solutions of alkali as used for the study of cathodic polarization. In Fig. 5, in the lower left-hand part the curves of the dependence of the nickel electrode potential on the logarithm of current density are given. As Fig. 5 shows, the initial parts of the curves have

a gentle slope. With higher current densities (5×10^{-7} A/cm.^{2} for 0.0075 and 0.001 N NaOH; 1×10^{-6} for 0.075 N NaOH; 2×10^{-6} for 0.42 N NaOH, etc.) the potential begins to increase rapidly and varies with the logarithm of current density with a slope $b = 0.324$—0.390 V.[24].

In the curves showing the dependence of anodic polarization on the logarithm of current density, at certain values of the latter a sharp increase of the anode potential is observed, which reminds one of the "saturation current" predicted by Horiuti and Okamoto on the basis of the "catalytic" theory.

However, as shown by our experiments, this rapid increase of the potential is not intrinsic to the process and is caused by secondary factors. Fig. 8 shows the effect of stirring the electrolyte upon the potential of the nickel anode. Curve *I* gives the variation of the potential with slight stirring; curve *II* shows the same with a threefold increase of the stirring rate. As seen from Fig. 8, with stronger stirring, the sharp increase of the potential occurs at a higher anode polarization, *i. e.*, the "saturation current" is observed not with a current density of 4×10^{-6} A/cm.^{2} but with a density of 1×10^{-5} A/cm.^{2}.

Experiments with nickel the true surface of which was increased by repeated successive oxidation and reduction showed that the beginning of a rapid increase of the potential depended only on the current density referred to the apparent surface. The curves obtained for two electrodes with the same apparent surface but with a different true surface coincide.

These data suggest that the "saturation current" observed is due to the concentration polarization of the hydrogen dissolved. This is confirmed by experiments carried out with 8.8 N NaOH. In 8.8 N NaOH after cathodic polarization of the electrode fine suspension of hydrogen bubbles is formed, and the solution appears turbid.

This is accounted for, first, by the fact that in strong alkali, as shown by Kabanov and Frumkin[25], the hydrogen bubbles

[24] It should be noted that with high current densities a strong increase of potential is observed in the course of time (the measurements were made in one minute after switching on the corresponding current).

[25] B. Kabanov a. A. Frumkin, Z. physik. Chem., **A 166**, 316 (1933).

are torn from the surface of the cathode with smaller contact angles and consequently have a smaller size; secondly, by the great viscosity of the solution. If under these conditions the anodic polarization curve is taken, it is found to be analogous to the cathodic curve, namely, at low current densities the potential is near to that of the

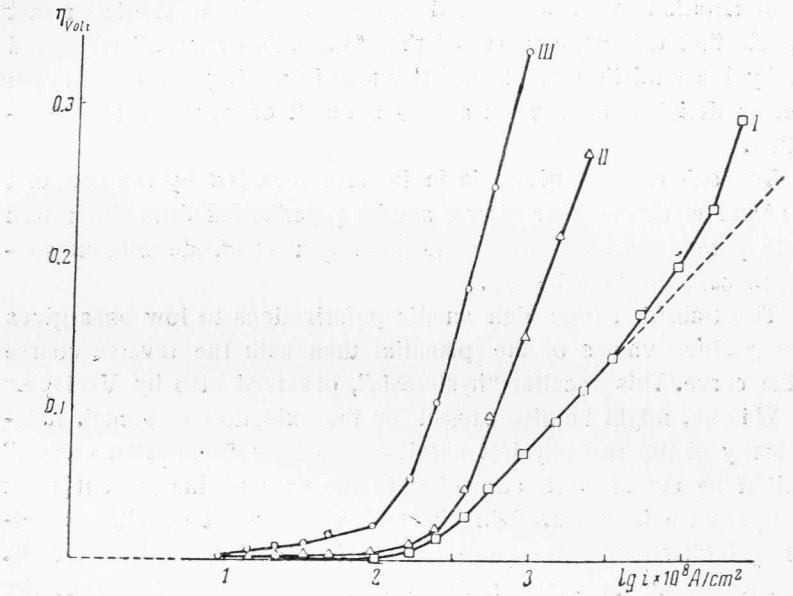

Fig. 9. Effect of suspended hydrogen bubbles upon the potential of the nickel anode. Curve *I* — in 8.8 N NaOH with hydrogen bubbles; curve *II* — in 8.8 N NaOH without bubbles; curve *III* — in 0.42 N NaOH.

hydrogen electrode in the same solution; at higher polarization a linear dependence on the logarithm of current density is observed, with the coefficient $b = 0.112$ V. At still higher current densities (1×10^{-4} A/cm.^{2}) deviations from this law appear. However, if the curve is taken after cathodic polarization, but when suspended hydrogen bubbles are absent, the polarization curve is similar to that obtained in weak alkalies, lying only lower than the latter. This is shown in Fig. 9, where curve *I* gives the dependence of the nickel anode potential in a 8.8 N NaOH solution containing hydrogen bubbles; curve *II* shows the same in a 8.8 N NaOH solution without bubbles; curve *III*, in a 0.42 N NaOH solution.

Thus in the case of a solution containing hydrogen bubbles the so-called "saturation current" is observed at a current density of 2×10^{-4} A/cm.^{2}; in a solution without bubbles already at 2×10^{-5} A/cm.^{2} and in a 0.72 N solution at 5×10^{-6} A/cm.^{2}. Moreover, it should be noted that in working with strong alkaline solutions the anode potentials were more stable in time. This is particularly true of solutions with suspended hydrogen bubbles. The latter fact suggests that the appearance of the "saturation current" is caused also by the oxidation of the nickel anode beginning when hydrogen becomes deficient on the surface as a result of concentration polarization.

The oxidatlon of nickel is in its turn revealed by the fact that the nickel electrode after strong anodic polarization does not return to the potential of the reversible hydrogen electrode without subsequent cathodic polarization.

The transition from high anodic polarizations to low ones gives more positive values of the potential than with the reverse course of the curve. This peculiar "hysteresis", observed also by Volmer and Wick[5], might be also caused by the oxidation of nickel. Independently of the real physical significance of the "saturation current" it might be stated that according to the data of the present work its appearance is observed in the region of current densities considerably higher than those predicted by Horiuti and Okamoto[10]. Thus, according to these authors, at a temperature of 50° C, the "saturation current" of anodic polarization is equal to 5×10^{-8} A/cm.^{2} which corresponds at a temperature of 20° C to 1×10^{-8} A/cm.^{2},[26] while from our data this "saturation current" is observed at 2×10^{-4} A/cm.^{2} ($t = 20°$ C).

On the basis of the conceptions developed above (see pp. 32—34) the anodic current in alkaline solutions is equal to

$$i = 2FK_3 [OH'] \theta e^{\frac{\varphi F}{2RT}}.$$

In a stationary state, with anodic polarization, from equation (1) it follows that $\theta = \frac{K_4 [H_2]}{K_3 + K_4 [H_2]}$, since K_1 and K_2 might be

[26] The calculation has been made by us using the temperature coefficient from the work of Horiuti and collaborators.

neglected in comparision with the terms containing $e^{\frac{\varphi F}{RT}}$; hence

$$i = \frac{2FK_3 K_4 [H_2]}{K_3 + K_4 [H_2]} [OH'] e^{\frac{\varphi F}{2RT}}. \quad (6)$$

A similar relation between i, [OH'] and φ may also be deduced assuming that the rate-determining step is the reaction between the adsorbed H-atoms and the OH'-ions, but that the adsorbed hydrogen is in equilibrium with hydrogen gas, which means that the velocity of hydrogen adsorption $Me + H_2 \rightarrow 2Me - H$ is great as compared to that of the reaction $Me - H + OH' \rightarrow Me + H_2O$. This is hardly likely to be true for strong anodic polarization and as it was shown above, equation (6) may be obtained without making such an assumption. From equation (6) it folows:

$$\varphi = \frac{2RT}{F} \ln i - \frac{2RT}{F} \ln [OH'] + \text{const.}$$

or

$$\eta_a = \varphi - \varphi' = \frac{2RT}{F} \ln i - \frac{RT}{F} \ln [OH'] + \text{const.} \quad (7)$$

The results obtained in the present work confirm equation (7) for anodic polarization. Thus, in 8.8 N NaOH (solution containing bubbles of hydrogen; Fig. 9, curve I) the coefficient b is equal to 0.112 V., approaching the theoretical value.

Fig. 5 shows that the dependence of η_a upon concentration is also in accordance with equation (7), namely, with an increase of the alkali concentration the values of η_a decrease.

It might be mentioned that the data obtained by N. Aladjalova[27] in this laboratory on the cathodic and anodic overvoltage of hygrogen on palladium in alkaline solutions are also in agreement with equations (5) and (7).

Conclusion

Summing up all the data obtained in the study of overvoltage on nickel in acids and alkalies within a wide range of concentrations and current densities the following conclusions may be made:

The nature of overvoltage changes depending on the concentration of the solution, the increase of overvoltage with addition of

[27] Unpublished.

neutral salts in acids and the decrease in alkalies are in agreement with the theory according to which the slow process is an ionic reaction influenced by the electric field of the double layer.

In contradistinction to acids, in alkaline solutions the process is accounted for by the kinetics of discharge of hydrogen from the water molecule. The mechanism of the process in very dilute alkaline and acid solutions needs further invesigation. The study of the influence of the concentration on the overvoltage does not by itself allow us to make definite conclusions about the state of the hydrogen film adsorbed on the electrode surface. The fact that both for the cathodic and anodic regions under suitable conditions (exclusion of concentration polarization) the Tafel relation $\eta = a + b \ln i$ holds good over wide ranges of current densities with b equal to $\frac{2RT}{F}$ seems to indicate that within the corresponding limits the surface concentration of hydrogen does not vary much with variation of potential. This is best explained assuming that in the cathodic region the surface concentration of hydrogen is controlled by the rate of the reactions $H^{\cdot}$ (or H_2O) $\rightarrow H_{ads.}$ ($H_{ads.} + OH'$) and $H_{ads.} + H^{\cdot}$ (or H_2O) $\rightarrow H_2$ ($H_2 + OH'$) and in the anodic region by the rate of the inverse reactions, the brackets referring to alkaline solutions.

From the standpoint of the recombination theory it is not possible to interpret either the influence of the concentration of the solution upon overvoltage or the effect of neutral salts.

Horiuti and Okamoto[9] on the basis of the recombination theory and the concept of a complete occupation of the surface by adsorbed hydrogen, predicted the appearance of a limiting "saturation current" with sufficient cathodic polarization. According to the calculations of these authors the "saturation current" in the cathodic region should be observed at an overvoltage of 0.4 V. and a current density of 10^{-4} A/cm.^{2} at a temperature of 50° C which corresponds to a current density of 2×10^{-5} A/cm.^{2} at 20° C. Experiments recently carried out in this laboratory by A. Legran showed that Tafel's relation holds up to current densities equal to 1.10^{-2} A/cm.^{2} (20° C). Under these conditions of experiment no change of the curve indicating the appearance of a "saturation current" was observed. The measurement of overvoltage at higher current densities was limited only by the design of the apparatus and the conductivity of the solutions.

In the anodic region a phenomenon similar to the "saturation current" took place, although at current densities considerably higher than those deduced by Horiuti and Okamoto. The experiments, however, establishing on the one hand that this effect is observed at higher current densities if the stirring of the solution is accelerated or if strongly concentrated alkali is taken, and on the other the identity of the effect both on smooth nickel and on nickel activated by alternate oxidation and reduction, suggest quite definitely that this effect is due to the concentration polarization of hydrogen and the oxidation of nickel and is not determined by the velocity of hydrogen adsorption[28].

Summary

1. A study has been made of hydrogen overvoltage on nickel in solutions of hydrochloric acid from 0.15 N to 0.0003 NHCl and in sodium hydroxide solutions from 8.8 N to 0.001 NNaOH for current densities from 1×10^{-8} A/cm.^{2} to 5×10^{-4} A/cm.^{2}.

2. The anodic polarization of nickel in a hydrogen atmosphere in the same sodium hydroxide solutions has been studied.

3. The results on overvoltage obtained are in agreement with Tafel's equation $\eta = a + b \lg i$ with $b = 0.100$ in acids and $b = 0.108 - 0.115$ in alkalies at $t = 20°$ C.

4. The effect of neutral salts upon hydrogen overvoltage has been studied both in acids and alkalies.

5. An explanation of the experimental results is given from the standpoint of the theory of the slow discharge.

[28] In two papers published recently (G. Okamoto, J. Fac. Sc. Hokkaido Univ., (3) **2**, 115, 1937; J. Horiuti a. G. Okamoto, Bull. Chem. Soc. Japan, **13**, 216, 1938) Horiuti and Okamoto present further arguments in favour of the catalytic theory of the overvoltage on nickel, which do not appear to us altogether conclusive. For instance, they find that the calculations of the number of catalytically active centers on the nickel surface effected (on the basis of this theory) starting from the rate of isotopic interchange and from the values of overvoltage with small current densities give approximately concordant results. This coincidence seems inconclusive as the theoretical relation between both quantities only slightly depends on the choice of the mechanism underlying the overvoltage. We hope to treat these questions, as well as the mechanism proposed by the Japanese authors for the overvoltage on a mercury cathode with more details in subsequent publications.

6. It has been shown that the potential of the nickel anode is greatly influenced by the concentration polarization of hydrogen and the oxidation of nickel, and that these are the causes producing the "saturation current".

7. The insufficiency of the recombination theory for an interpretation of all the effects connected with the cathodic and anodic polarization of nickel has been shown.

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