ACTA PHYSICOCHIMICA U.R.S.S.

1944 Vol. XIX. No. 1

Theory of Hydrogen Ion Discharge. III. Palladium*

By. *A. Frumkin* and *N. Aladjalova*

I. Introduction

Phenomena occurring in the hydrogen ion discharge on palladium electrodes contrast sharply with those observed on mercury electrodes. In the latter case only ions of the double layer and the ultimate products of reaction *viz.* molecular hydrogen but neither adsorbed hydrogen nor hydrogen dissolved in the metal are observed. At palladium electrodes phenomena bound with the change of concentration of dissolved hydrogen, which, at least for certain definite conditions, must be in equilibrium with absorbed hydrogen, become, on the contrary, prominent. Owing to its capacity for dissolving great amounts of hydrogen, palladium presents a very convenient object for measurements in non-stationary conditions. Under such conditions the alterations in the state of the palladium surface are very considerably slowed down owing to a complete or partial equilibrium setting-in between the surface of the electrode and its volume. Moreover, in case of a thin palladium electrode polarized on one side, the high rate of hydrogen diffusion through palladium at room temperature permits to establish a connection between the states of the surface on the diffusion and polarization sides [1], thus giving additional information on the state of the surface.

---

* Part I. A. Frumkin, Acta Phys. Chim. URSS, **18**, 23 (1943); part II. S. Jofa and A. Frumkin, Acta Phys. Chim. URSS, **18**, 183 (1943).

[1] Nernst u. Lessing, Nachr. Gött. Ges. Wiss., **154**, (1902); Köhler, Z. physik. Chem., **134**, 376 (1928). The transfer of potentials more negative than the reversible hydrogen potential through palladium was first descried probably by Drucker, Z. Elektrochem., **33**, 504 (1927). The electrodiffusion of hydrogen through Pd under various conditions was investigated by Kobosev and Monblanova (Acta Phys. Chim. URSS, 1. 611. 1934).

Unfortunately, experimenting with a palladium electrode presents specific difficulties, since the properties of the surface and the kinetics of dissolution of hydrogen in palladium are in a high degree influenced by the previous treatment of the electrode and not easily reproducible.

The data obtained are therefore far less reliable than those referring to mercury electrodes. The results stated further on were obtained before 1941, and in part still earlier, but were not published at the time, additional information being thought necessary. However, in this connection, the importance for the overvoltage theory of the potential transfer to the diffusion side of the electrode was pointed out by one of us[2]. Owing to war circumstances further investigation was suspended and we considered it desirable to publish the results obtained so far, allowance being made for their preliminary character.

We are much indebted to J. Siver, Mendeleev Institute of Chemical Technology, Moscow, from whose graduation paper the experimental data for Part II,2 are mainly taken, as well as to A. Fedorova, Moscow University, for data concerning the palladized electrode in Part II, 7.

II. Experimental part

1. Preparation of electrodes, purification of solutions, measurements technique

As already mentioned the properties of the palladium electrode depend in a high degree on the state of its surface. The electrodes used in the present investigation were prepared as follows.

Smooth palladium electrodes were cut from 20, 40 and 50 μ thick palladium foil of 99.98% purity and platinum wires welded to them. The electrodes were heated in air in an electric furnace, washed with hydrochloric acid (1 : 1), then with conductivity water and again heated for 2—3 hours at 600—700° C. On heating the surface of the electrode assumed a dark bluish-green colour and lost some of its brightness. After this treatment the electrode was activated.

---

[2] Frumkin, Acta Phys. Chim. URSS, **7**, 480 (1937). See also in this connection Bennet and Polanyi, Trans. Farad. Soc., **36**, 377 (1940). Hickling and Salt seem, however, to have overlooked these publications, as in a paper of theirs (Trans. Farad. Soc., **38**, 480, 1942), which came lately to our knowledge, the importance of the potential transfer for the understanding of the overvoltage phenomena is stated to have passed hitherto unnoticed.

The diffusion electrodes, which will be described lower, were first welded into a platinum frame and after this fused into glass. Direct sealing into glass is to be avoided, the volume of metal being altered on cathodic polarization, which results in the cracking of glass. After being sealed into glass the surface of the electrode was cleaned with sulphuric and hydrochloric acids (1 : 1). The platinum frame protruding somewhat from under the glass, all the surface of the electrode which was not protected with glass was covered with a thin (1—2 μ) coating of smooth palladium electodeposited from an ammonia solution of palladous dichlorodiamine and then again cleaned with warm sulphuric acid and water. The diffusion electrodes were likewise activated on both sides.

The activation consisted in anodic polarization with a 0.002—0.003 A/cm.^{2} current until the beginning of visible oxygen evolution, after this a prolonged cathodic polarization was set in with a 0.02 A/cm.^{2} current. This resulted generally in establishing of an overvoltage of 0.04—0.11 V at the electrode.

The method of surface activation by means of anodic polarization is long known and has been recently applied by Knorr[3] and others. In our investigation the anodic polarization of palladium cleaned in the manner described above in conjunction with a subsequent intensive cathodic polarization resulted in a surface of moderate and fairly definite activity, which permitted to reproduce all the measurements made with different electrodes with a sufficient degree of accuracy. In some cases results obtained with non-activated electrodes were likewise used, despite their much lesser reproducibility, if presenting some particular interest.

The activity of the surface was checked measuring the overvoltage with a cathodic current of 0.01 A/cm.^{2} density. The activity of an electrode, however, can be fully estimated only in observing its behaviour in various measurements. Thus, for instance, the degree of activity, besides being expressed by the position and course of the overvoltage curve, reveals itself in the different rate with which a definite potential is attained by the electrode on pola-

---

[3] Kandler, Knorr, Schwitzer, Z. physik. Chem., (A) **180**, 281 (1937). Judging from the results of their measurements the electrodes used were more active than ours, owing probably to anodic polarization not being followed by prolonged cathodic treatment.

rization. Likewise the activity of a sample influences the kinetics of hydrogen diffusion through palladium.

Palladized electrodes were obtained by electrodeposition of palladium on smooth platinum foil from an acidulated $PdCl_2$ solution at a current density of 0.002 A/cm.^{2}. The amount of Pd was 0.008—0.017 g. per cm.^{2} of visible surface of the electrode. The colour of the latter was dark-gray. After palladizing, the electrodes were cleaned by cathodic polarization and afterwards washed with water under bubbling of hydrogen.

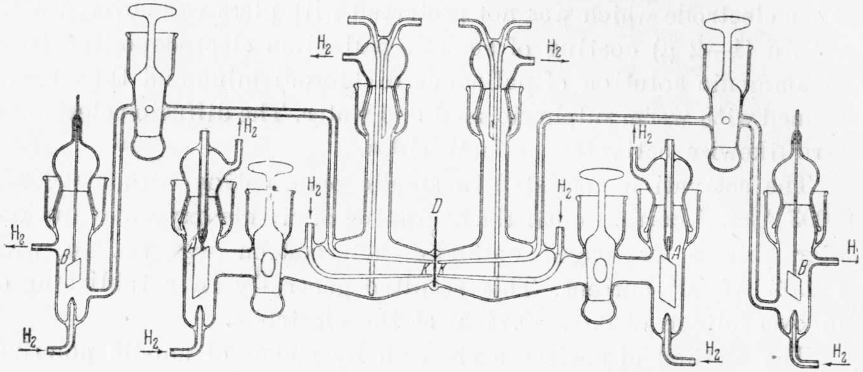

Fig. 1. The diffusion electrode cell.

The electrolytes used in the present investigation were purified in addition to usual proceedings (redistillation of sulphuric acid, calcination and recrystallization of salts) by the method of Aten[4]. According to the latter, the solutions are brought for many hours in contact with a large palladium electrode (2—3 g. of palladium black per litre of solution). During the purification the solutions were stirred by a stream of hydrogen. In some cases prior to experiment the solutions were polarized with auxiliary electrodes.

In the solutions thus purified and in an atmosphere of hydrogen the potential of the smooth palladium electrode kept a constant value equal to that of the reversible hydrogen electrode. The cell for the diffusion electrode in many respects similar to that of Kobosev and Monblanova is shown in Fig. 1. A palladium diaphragm *D* sealed into the glass by means of a platinum ring divided the apparatus into two parts excluding any contact between the electrolytes on the right and left. The parts of the apparatus *K* adjoining the diaphragm were connected by means of stop cocks with the anodic space *A*. Owing to the presence of electrodes on both sides of the diaphragm, the latter may be polarized and activated on either side at will. The potential of the polarization as well as that of the reverse (diffusion) side may be measured by means of hydrogen electrodes *BB* disposed on the right and left of the metallic diaphragm. The volume of the electrolyte on either side of the apparatus was 18—25 cm.^{3}.

All the ground joints, stop cocks and connections in the apparatus were made of glass and kept under water.

The measurements of cathodic overvoltage were carried out in an atmosphere of hydrogen, which was streamed through the apparatus for 10—20 hours before the beginning of the experiment, thus ensuring the removal of oxygen and the setting-in of equilibrium between the palladium electrode and hydrogen at 1 atm. During the measurements the electrolyte was stirred by bubbling hydrogen through it. The measurements described in Part II, 7 were carried out in an atmosphere of purified nitrogen.

All measurements were carried out at room temperature (17—20° C). All values of the potential are referred to the potential of the reversible hydrogen electrode in the same solution. Experiments on the same electrode were reproducible without additional activation within 0.005 V even after the electrolytes were repeatedly renewed. Experiments carried out with different but similarly activated electrodes gave qualitatively reproducible curves; diffefrences between the absolute values of overvoltage ranging up to 0.05 V.

2. Variation of the overvoltage with time

Measurements of overvoltage on palladium showed that the value of hydrogen overvoltage η on a palladium electrode is attained on passing a constant current in two stages. As may be seen rom Fig. 2, the potential is first abruptly shifted to a certain value η_1; after which for a considerable time the increase of overvoltage proceeds more slowly and in a definite interval almost linearly with time. Since the method of measurement adopted in the present investigation comprised measurements of the overvoltage taken at intervals approximating one minute; the course of the change of overvoltage could be followed only during the second stage of the process. Nevertheless, the discrimination between the

---

[4] Aten u. Zieren, Rec. Trav. Chim. Pays-Bas, 48, 944 (1929).

two stages could be made with sufficient accuracy owing to the almost linear relation between potential and time at the beginning of the second stage (probable error 0.001 for low current densities, and 0.001—0.002 for stronger currents). The values of the «slow» change of overvoltage η_2 given below were measured from the value obtained by extrapolation of the observed values to the moment the current was switched on. Slow changes of overvoltage with time have frequently been observed and described in the literature. In the case of a palladium electrode they are, undoubtedly, bound with the increase in the concentration of hydrogen dissolved in palladium in excess to the amount corresponding to the equilibrium with gaseous hydrogen at atmospheric pressure. The increase in the concentration of hydrogen dissolved in palladium on cathodic polarization is further substantiated by the fact that an appreciable evolution of gas bubbles occurs only a considerable time after the current has been switched on.

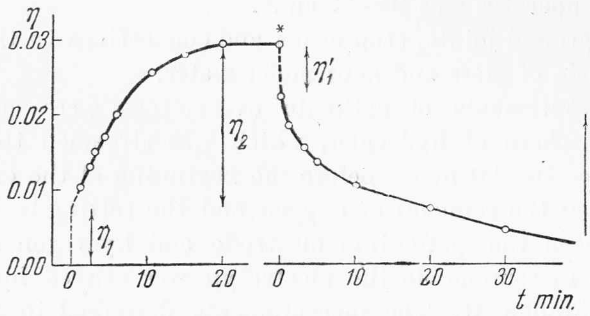

Fig. 2. Change of overvoltage at a palladium electrode with time. Current density 0.001, * —the moment of interruption of the current.

The stopping of the polarizing current is followed by an abrupt decrease of overvoltage by a certain value η_1' with subsequent slow change; the value of the latter is denoted by η_2'. This value was determined by extrapolating to the moment of interruption the values of overvoltage measured after the current had been switched off. In Fig. 2 the moment the polarizing current has been stopped is marked by *. The right hand side of the curve in Fig. 2 represents the course of the potential decrease. After stopping the current the evolution of gas bubbles from the surface of the electrode proceeds for some minutes. The supersaturation of the electrode with occluded hydrogen in amounts exceeding the equilibrium value, which

can be retained only when the current is passing, must be considered as the main cause delaying the return of the potential to the reversible value.

Comparison of the slow rise of overvoltage η_2 with the residual overvoltage η_2', measured after interrupting the current, shows them to be equal at any definite current density. In Table 1 are listed typical results of a series of measurements made at various current densities with an electrode of medium activity.

Table 1

0.6 *N* HCl

I	II	III	IV	V
Current density	Overvoltage			η_2 calcul. acc. eq. $\eta_2 = 0.029 \times \lg(5 \times 10^3 i + 1)$
	η	η_2	η_2'	
0.0001	0.004	0.0035	0.0035	0.0051
0.0003	0.013	0.009	0.0105	0.0116
0.0005	0.018	0.0135	0.015	0.0157
0.001	0.029	0.0225	0.0225	0.0225
0.002	0.045	0.0335	0.035	0.0302
0.003	0.053	0.0365	0.039	0.035
0.005	0.0665	0.041	0.041	0.041

The values of the third and fourth columns coincide within the limits of experimental error. Obviously, η and η_1', coincide with the same accuracy. The absolute values of overvoltage vary somewhat from one electrode to another as well as the ratio $\eta_2 : \eta$[5], but η_2 and η_2' remain equal under all conditions.

An investigation was also started on the dependence of the value of the residual overvoltage on time. Preliminary results show that after a lapse of time t after stopping of the current the value η is equal to $\eta_2' - K\lg\left(\frac{t}{B}+1\right)$ where the constant K does not depend upon i (~ 0.016), and B is approximately inversely proportional to i.

3. Overvoltage transfer to the diffusion side of the electrode

Important data may be obtained by comparing observations on

---

[5] For electrodes with high overvoltage, *i. e.* less active ones, this ratio is considerably less.

the establishment of a stationary potential on an ordinary electrode with the results of experiments on the polarization of diffusion electrodes.

The results of the polarization of a diffusion electrode with 0.01 A/cm.^{2} current density are shown in Fig. 3. The curves *I* and *II* refer to the polarization and the diffusion surfaces, respectively (* represents the moment the current is switched off). In its initial state the electrode was in equilibrium with hydrogen at one atmosphere, and the potential on both sides was equal to the reversible hydrogen potential. Normal sulphuric acid was used as electrolyte on both sides.

A stationary potential on the polarization side of the diffusion electrode sets in in the same way as at an ordinary electrode. The value of the slow rise η_2 approximates 0.030—0.040 V. On the diffusion side the switching-on of the current is similarly followed by a rise of overvoltage, which, however, proceeds slowly. After a certain lapse of time a definite value of overvoltage is established, which we shall denote by η_D and which for the given case equals 0.040 V. On switching-off the current the overvoltage of the polarized side becomes, after passing the first more rapid stage of decrease, equal to the overvoltage value on the diffusion side, so hereafter both sides of the electrode regain the equilibrium value at an equal rate. On the diffusion side of the electrode no rapid changes of overvoltage following the switching-on and -off of the current are observed.

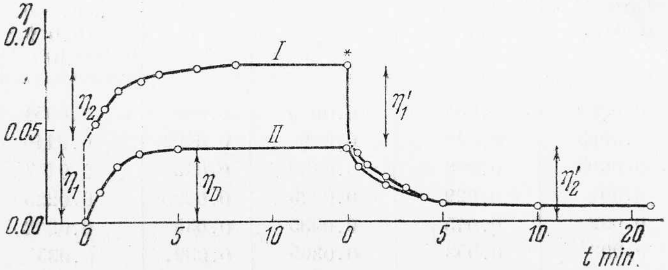

Fig. 3. Change of overvoltage with time on the polarization (*I*) and the diffusion (*II*) sides of a palladium electrode. Current density 0.01, * — moment of interruption of the current.

Two conclusions may be drawn from this experiment: 1) the polarization of membrane electrodes gives rise on the diffusion side to an overvoltage not related directly to the process of ion discharge, since the latter does not occur on this side; 2) the value of this overvoltage is approximately equal to that part of the total overvoltage on the polarization side of the membrane, which corresponds to the slow increase of overvoltage and which does not immediately disappear when the current is stopped. This shows that the excess of hydrogen, accumulating on the electrode when the current passes, diffuses through the metal and saturates all the volume of the electrode.

Table 2 shows the results of comparative measurements of the potential on the diffusion side of the electrode and of the part of the overvoltage on the polarization side which slowly decreases after the current is stopped, carried out at different current densities. With the exception of the last line, the values of columns 3 and 4 coincide very nearly.

Table 2

1 N H_2SO_4

Current density	Overvoltage on the polarized side		Overvoltage on the diffusion side η_D
	η	η'_2	
0.0004	0.011	0.009	0.009
0.001	0.019	0.014	0.013
0.002	0.035	0.022	0.021
0.004	0.054	0.026	0.027
0.01	0.085	0.027	0.033

There was so far no clarity in the literature as to the possibility of the transfer of a potential more negative than the equilibrium one to the diffusion side of a palladium electrode. The shift of potential described by some authors is accounted for by Ferguson[6] as due to porosity.

In the light of our experiments such an explanation seems scarcely probable. Measurements described below, in which different solutions were used on both sides of the electrode, definitely prove its non-validity.

---

[6] Ferguson and Dubpernell, Trans. Electrochem. Soc., **64**, 221 (1933). In the discussion of this paper Aten denied the reality of this shift altogether.

The magnitude of the overvoltage transfer to the diffusion side depends on the activity of the polarized surface. The low activity of a surface, revealing itself by higher values of the overvoltage, is generally accompanied by a low value of the potential shift on the diffusion side.

Variations in the thickness of the membrane electrode ranging from 20 to 40 μ do not affect markedly the value of the potential shift observed on the diffusion side.

Comparison between the amounts of hydrogen evolved on the polarization and the diffusion sides of a membrane electrode would be of great interest but, unfortunately, the corresponding experiments had to be suspended. According preliminary data, at a density of polarizing current equal to 0.003 A/cm.^{2} the amounts of hydrogen evolved on each side did not greatly differ. In these experiments the electrolyte was 0.1 *N* H_2SO_4 or 0.1 *N* HCl on both sides of the electrode. Our experiments are not quite comparable with usual diffusion experiments in so far as the evolution of hydrogen on the diffusion side proceeds generally *in vacuo*, and the state of the electrode surface not in contact with the electrolyte and, consequently, non-activated, considerably differs from that on the polarization side.

4. Relation between the equilibrium potential of hydrogen dissolved in palladium and its concentration

As it will be shown in the theoretical part of this paper the part of the overvoltage, which is transferred to the diffusion side of the electrode and which decreases slowly after the current is interrupted, may be considered as representing the equilibrium potential of hydrogen dissolved in palladium.

It appeared very desirable to determine the relation between this potential and the concentration of hydrogen dissolved in the metal; accordingly a series of experiments was carried out in this direction also. As it will be seen further on for potentials more anodic than the reversible hydrogen potential this relation may be determined directly by taking a charging curve, *i. e.* by measuring the change in the electrode potential accompanying the passage trough it of definite amounts of electricity, provided the current density to be sufficiently low. It appears that up to electrode potentials of *ca.* 0.05 the relation between the hydrogen content in the electrode, calculated from the amount of electricity passed, *Q*, and its potential remains approximately linear but then the growth of the potential is slowed down.

In the determination of the dependence between potential and hydrogen content for potentials more cathodic than the reversible hydrogen potential, it must be borne in mind that a part of the electricity passed, which in reaching the stationary potential amounts to 100 per cent, is required for the evolution of molecular hydrogen. Therefore, the determination of the relation between potential and hydrogen content in the electrode would necessitate a measurement of the volume of hydrogen, evolved at the electrode during the period from the beginning of polarization up to the establishment of the stationary potential, and a corresponding correction of the measured amount of electricity. Until now these experiments were not carried out and the correction was made according to calculations, assuming the rate of hydrogen evolution for each moment to be determined by the value η_2. The physical meaning of this assumption will be made clear in the theoretical part of the paper. The relation between η_2 and the rate of hydrogen evolution may be determined from observations on the stationary values of overvoltage. Basing on such a calculation which was carried out for overvoltages up to ~ 0.04V we were able to show that the linear relation between potential and hydrogen content holds approximately in this region.

In passing from the reversible hydrogen potential to 0.040 V the atomic ratio H/Pd is increased by 0.07, *viz.* on the average by 1.75×10^{-3} per mV.

The linear relationship between hydrogen content and potential is equivalent to a linear relationship between hydrogen content and the logarithm of pressure. A logarithmical equation of the isotherm for hydrogen, dissolved in palladium in the region of the β-phase, was proposed by Samson-Himmelstjerna[7] on the basis of experimental data obtained by Hoitsema and Roozeboom[8]. The isotherm, proposed in a more recent theore-

---

[7] Samson-Himmelstjerna, Z. anorg. allg. Chem., **186**, 355 (1930).

[8] Hoitsema, Z. physik. Chem., **17**, 1 (1895). Roozeboom, Z. physik. Chem., **17**, 23 (1895).

tical paper by Lacher[9] in good accordance with data by Sieverts[10] and Gillespie[11], contains no region where the hydrogen concentration would increase linearly with the logarithm of pressure. The conclusions of Lacher cannot, however, be applied to ratios exceeding 0.59, as in our case. A linear relation between the content of dissolved hydrogen and the overvoltage was obtained by Laue and Masing[12] when polarizing platinum in alkaline solutions. In former publications from our laboratory the existence of a linear relationship between the amount of hydrogen adsorbed on platinum and the potential was repeatedly pointed out.

5. Relation of overvoltage to concentration and nature of the acid

The overvoltage of hydrogen in acid solutions on active electropes, obtained in the manner described above, is small. No clearly definite relationship between overvoltage and concentration of the acid or any change of its value in going over from HCl to H_2SO_4 could be observed. In this case an addition of lantanum salts did not bring about any change of overvoltage. On non-active electrodes the dilution of the acid produced a considerable increase of overvoltage; the values of the overvoltage are, however, not sufficiently stable and reproducible to permit for any quantitative conclusions to be drawn.

For active electrodes, as seen from Table 1, the relation $\eta_2 = 0.029 \lg(\mathrm{const} \cdot i + 1)$ holds with sufficient approximation.

6. Overvoltage in alkaline solutions

Palladium electrodes exhibit a considerably higher overvoltage in alkaline solutions. This cannot be considered as resulting from a poisoning of the electrode, low values of overvoltage being again observed after substitution of an acid solution for the alkaline.

Knorr, Kandler and Schwitzer[3], who account for all the overvoltage on palladium by the slow diffusion of the evolved hydrogen into the solution, have nevertheless also observed a higher overvoltage in alkaline solutions. Fig. 4 shows a $\varphi - \lg i$ curve for a palladized electrode (0.016 g. Pd per cm.^{2}) in $1N$ KOH and Fig. 5 the same curve for a smooth electrode.

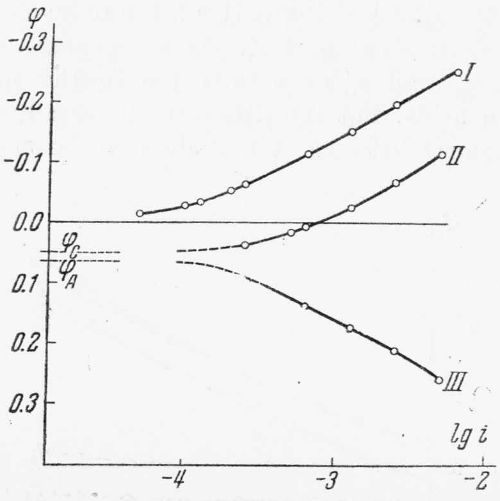

Fig. 4. Relation between potential and logarithm of current density in electrode processes at a palladized electrode in $1N$ KOH solution.

I — overvoltage on evolution of H_2. *II* — overvoltage in the transition from the α- to the β-phase. *III* — overvoltage in the transition from the β- to the α-phase (according to Fedorova).

Table 3

Current density	η_2 0.6 N HCl	η_2 1.1 N KOH
0.0003	0.009	0.013
0.0005	0.0135	0.016
0.001	0.0225	0.027
0.002	0.0335	0.031
0.003	0.0365	0.0475
0.005	0.041	0.045

As may be seen, in this case a linear dependence between φ and $\lg i$ with a coefficient b about 0.13 is observed within a considerable current density interval.

---

[9] Lacher, Proc. Roy. Soc., (A) **161**, 525 (1937).

[10] Sieverts u. Zapf, Z. physik. Chem., (A) **174**, 359 (1935). Sieverts u. Hagen, Z. physik. Chem., (A) **174**, 247 (1936).

[11] Gillespie and Galstaun, J. Am. Chem. Soc., **58**, 2565 (1936); Gillespie and Downs, ibid., **61**, 2496 (1939).

[12] Laue u. Masing, Z. physik. Chem., (A) **178**, 1 (1937).

On switching-on and -off the polarizing current the same phenomena as in acids are observed in alkalis. In alkaline as well as in acid solutions the slowly rising part of the overvoltage η_2 is equal to its slowly decreasing part η_2'. As it appears from Table 3, the values of η_2 and η_2' in alkalis are in the mean somewhat higher than in acids, but the difference is small, and the considerable discrepancy between the values of overvoltage in acid and alkaline solutions, observed on palladium electrodes, is due almost totally to different values of η_1. It may be seen in Fig. 5 that after correcting for the value of residual overvoltage the rectilinear dependence between overvoltage and $\lg i$ becomes still better. The overvoltage in alkaline solutions increases with decreasing concentration. In 0.01 N KOH the overvoltage is about 0.1 V higher than in 1 N KOH.

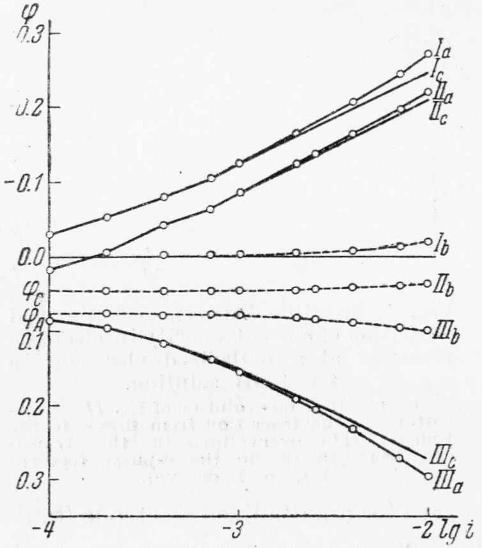

Fig. 5. Relation between potential and logarithm of current density in electrode processes at a smooth Pd- electrode in a 1.1 N KOH solution.

I_a—overvoltage during evolution of H_2. I_b—potent al after interrupting the current. I_c—corrected overvoltage on evolution of H_2. II_a, II_b, II_c — corresponding curves for the process of transition from the α- to the β-phase. III_a, III_b, III_c — corresponding curves for the process of transition from the β- to the α-phase.

The value of the overvoltage, which is transferred to the diffusion side of the membrane electrode, is practically the same in acid and alkaline solutions, as is shown in Fig. 6. Despite a high increase of overvoltage on the polarization side (in this experiment the values of overvoltage and the shape of the curve seem to indicate that a poisoning of the electrode has taken place), the potential on the diffusion side remained constant. If an alkaline solution be placed on the diffusion side of a membrane electrode the value of overvoltage on this side still remains the same as in the acid solution. In one of our experiments at $i = 0.01$ the overvoltage on the polarization side in a 1 N HCl solution was equal to 0.071. When a 1N HCl solution was placed on the diffusion side the overvoltage on this side amounted to 0.042, while it was 0.044 in presence of 1N KOH. Since in this last instance the potential on the diffusion side is much more negative than on the polarization side, the experiment may be also considered as unambiguously demonstrating that the polarization is not transmitted to the diffusion side of the electrode by means of the electrolyte penetrating its pores.

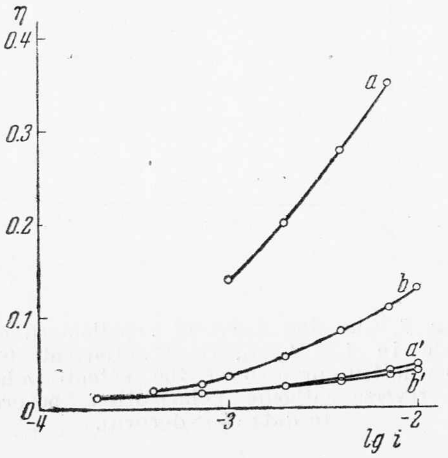

Fig. 6. Transfer of overvoltage to the diffusion side of a membrane electrode for acid and alkaline solutions, a and b—overvoltage on the polarization side in 1N KOH and 1N HCl. a' and b'—overvoltage on the diffusion side in the same solutions.

7. Overvoltage on phase transition in the palladium-hydrogen system

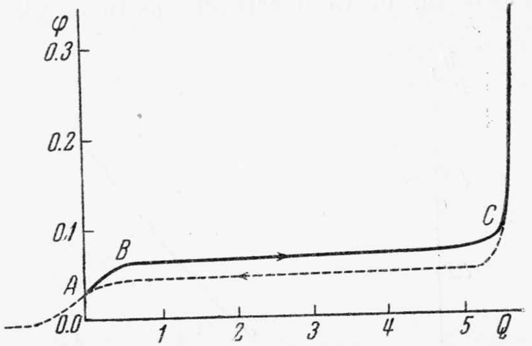

Fig. 7. Charging curve of a palladized electrode in $1N$ H_2SO_4, $t=20°$. Current—0.002. The dotted curve shows the potential change at reverse cathodic polarization (according to data of Fedorova).

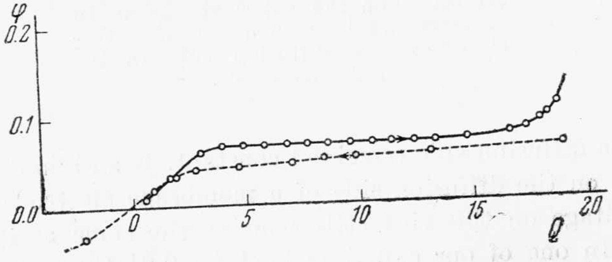

Fig. 8. Charging curve of a smooth Pd electrode in $1N$ H_2SO_4; thickness—50 μ, weight—0.03 g. Current density 0.0025. Potential measured after stopping the current. Dotted curve shows the potential change at reverse cathodic polarization.

The study of electrochemical phenomena at potentials more positive than the reversible hydrogen potential is of the greatest importance for the elucidation of the mechanism of electrode reactions on the surface of a palladium electrode. If a palladium electrode immersed in a solution is saturated with hydrogen at atmospheric pressure and then most of the dissolved hydrogen is removed by passing nitrogen through the cell, the potential of the electrode is shifted to the anodic side by 0.025—0.03 V. At room temperature, owing to the decrease of the equilibrium pressure of hydrogen on the Pd electrode, further change of the potential becomes very slow. On subsequent anodic polarization with current in a solution saturated with nitrogen (bubbling of the gas being suspended) the change of the electrode potential with the amount of electricity expressed in coulombs Q passed through the cell may be investigated. Fig. 7 shows the charging curve of a palladium electrode (0.0094 g. Pd) in $N\,H_2SO_4$ obtained in this manner. Similar curves were obtained for electrodes made of Pd foil (Fig. 8). In this case the potential was measured in each point of the curve after stopping the polarizing current. As already mentioned above, the initial portion of the charging curve AB (Fig. 7) has an almost linear course. In the vicinity of point B a deviation from the linear course and an approach to a constant value of the potential are observed. The medium almost horizontal portion BC of the curve corresponds to the phase transition from the β-phase of high hydrogen content to the α-phase, which has been repeatedly described in the literature [9,11]. Similar curves of the potential change of a Pd electrode with time under the action of oxidizing agents have already been obtained by Nylen[13].

It must, however, be emphasized that the states of the electrode resulting from polarization by current do not entirely satisfy the conditions of two-phase equilibrium, as may be observed from the following. The potential on the BC portion of the charging curve does not remain strictly constant, but increases with anodic polarization. This effect is much more pronounced in alkaline solutions than in acid ones. The charging curve, which is obtained on reverse cathodic polarization (dotted lines in Figs. 7 and 8) does not quite coincide with the anodic polarization curve even in the case of measurements being taken after stopping the current. In the medium portion of the curve the discrepancy ranged for different cases from 0.006 to 0.03. The potentials, corresponding to the middle of the AB section on the charging curve after anodic and cathodic polarization shall be denoted by φ_A and φ_C. Finally the transition from the region of the two-phase system to regions, corresponding to one of the phases on the charging curves, is not abrupt but gradual, especially in alkaline solutions. The deviations from the equilib-

---

[13] Nylen, Z. Elektrochem., **43**, 915 (1937).

rium conditions are more pronounced for smooth than for palladized electrodes.

We shall not discuss here the causes of these deviations, although they are undoubtedly of great interest, our objective being primarily the kinetics of phase transition. We shall only point out that the mean of the values of φ_A and φ_C, measured in H_2SO_4 solutions, is in good agreement with the equilibrium values of hydrogen pressure in the two phase region, according to Gillespie and others [11]. Further, as the mean from a great number of experiments it appears that the hydrogen content in palladium in equilibrium with hydrogen at atmospheric pressure corresponds to the relation $H/Pd=0.68$, and the hydrogen content in the β-phase in equilibrium with the α-phase — to the atomic ratio $H/Pd=0.57$. The determination of the latter ratio is not very reliable, owing to the somewhat arbitrary choice of the location of point B on the charging curve. The equilibrium potential of the β-phase at $t=18°$ being according to our data ~ 0.058, the mean increase of the ratio H/Pd when the potential is changed by one millivolt towards the cathodic side amounts to $1 \cdot 9 \times 10^{-3}$, which is in a satisfactory agreement with the value found above from measurements in the region of cathodic overvoltage.

We have studied the kinetics of the β-phase $\rightleftarrows$ α-phase transition in acid and alkaline solutions both for palladized and smooth electrodes. For alkaline solutions particularly the transition potential from one phase to another is very markedly influenced by the current density, as already pointed out by Nylen [13]. In acid solutions this dependence is much less marked. To determine the relation between phase transition potential and current density we measured the potential shift at a hydrogen content corresponding approximately to the middle of section BC on the charging curve and at various densities of the polarizing current. The amount of electricity passed was selected so as to ensure a not too great deviation from the initial degree of saturation of the electrode. In other experiments charging curves were taken at various current densities, and were afterwards used for the determination of potentials corresponding to a definite degree of saturation of the electrode. We shall define the value of the potential shift during the phase transition, as compared with the value observed in the absence of current, as the overvoltage during phase transition, by analogy with the overvoltage during the evolution of molecular hydrogen. The value of the overvoltage during phase transition was determined both for anodic and cathodic polarization. The results of such determinations in an alkaline solution both for a palladized and a smooth electrode are represented in Fig. 4 (curves *II* and *III*) and Fig. 5 (curves *II* and *III*), respectively. These figures show the relation between overvoltage and current density during phase transition from the α- to the β-phase to be the same as for molecular hydrogen evolution, and Tafel's formula with the coefficient $b \sim 0.13$ was found to apply equally to this case. As seen, in particular from Fig. 5, the difference between the values of overvoltage for the evolution of molecular hydrogen and for the transition from the α- to the β-phase is but slight. After correction for the value of the residual shift of potential the curves φ—$\lg i$ appear to run almost parallelly for the two processes.

Owing to the comparatively high values of overvoltage for the transition from the α- to the β-phase in alkaline solutions, potentials more negative than the reversible hydrogen potential may be reached even at small current densities during the cathodic polarization of the α-phase, despite the hydrogen content in the electrode being smaller than that corresponding to the equilibrium β-phase and the evolution of molecular hydrogen not taking place. The relation between potential and current density may also be determined for the case of anodic polarization of the β-phase (Figs. 4 and 5, curves *III*). The curve obtained is almost symmetrical to the cathodic polarization curve of the α-phase (curves *II*). On anodic polarization of the β-phase much higher values of current density may be attained than with an usual hydrogen electrode, the current density of the latter being limited by concentration polarization.

The kinetics of phase transition, like the process of molecular hydrogen evolution, is very sensitive to poisoning. The effect of As_2O_3, $HgCl_2$ and KCN admixtures was studied by A. Šlygin at the Moscow University [14]. These substances cause a sharp rise of overvoltage during phase transition; in the case of As and Hg a decrease in the capacity of hydrogen absorption by the electrode has moreover been observed. An addition of 1.2×10^{-3}g. of Hg to

---

[14] Unpublished data.

the palladized electrode, on which 0.1 g. Pd had been deposited, lowers its absorption capacity towards H_2 down to 10% of its initial value.

III. Theoretical discussion

Although our experimental data are incomplete and partly wanting in accuracy the following two conclusions may still be considered as established.

1. The overvoltage on palladium during hydrogen evolution may be considered as consisting of two parts. One of them (η_2) is almost independent from the nature of the solution, is slowly attained after the switching-on of the current, disappears slowly after its interruption and can be transmitted to the diffusion side of the palladium electrode. The independence of the overvoltage observed on the diffusion side from the nature of the solution in contact with the electrode permits to consider the potential measured as an equilibrium potential of hydrogen dissolved in the metal.

2. The remaining part of the overvoltage (η_1), which may attain high values in alkaline solutions, is not related to the evolution of molecular hydrogen, but depends only on the electrochemical reaction itself, since this overvoltage may equally be observed during the electrochemical transition of the α-phase into the β-phase, which is not accompanied by the evolution of molecular hydrogen. The quantitative coincidence between the value of overvoltage during cathodic evolution of hydrogen and that during transition of the α- into the β-phase shows the value of this part of the overvoltage to be independent from the degree of covering of the metal surface by hydrogen. The existence of considerable overvoltages in the electrochemical reaction of hydride formation without evolution of molecular hydrogen is probably the most direct evidence in support of the assumption of the slow rate of the electrochemical reaction itself.

Let us now deduce from the theory of slow discharge that the total value of overvoltage must be in fact additively composed of two parts, possessing the above mentioned properties. In order to do this, we shall consider the relation between overvoltage and covering of the surface. Since the palladium electrode easily gives up its molecular hydrogen into the gas phase at room temperature, the rate of the recombination reaction at its surface must be considerable. We shall first assume the formation of H_2 to proceed only by way of recombination, *i. e.* without taking into account the reaction of hydrogen ions discharge on already occupied sites of the surface with direct formation of hydrogen molecules $H^{\bullet} + H_{ads.} + \ominus \rightarrow H_2$ or molecular ions $H^{\bullet} + H \rightarrow H^{\bullet}_2$ (electrochemical mechanism of removal). If we consider hydrogen ions to be discharged only on unoccupied sites, it follows from the equations of electrochemical kinetics, that the density of the cathodic current in an acid solution equals

$$i = k_1 [H^{\bullet}] (1 - \theta)\, e^{-\frac{\alpha\varphi F}{RT}} - k_2\, \theta\, e^{\frac{\beta\varphi F}{RT}} \qquad (1)$$

where θ is the degree of covering of the surface with hydrogen, $\alpha + \beta = 1$ and k_1 and k_2 are constants. We do not take into account the difference between the surface and the volume concentration of hydrogen ions in the solution $[H^{\bullet}]$ and consider the Langmuir adsorption isotherm to apply to adsorbed hydrogen, *i. e.* its activity to be directly proportional to $\frac{\theta}{1-\theta}$.

In applying equation (1) to non-stationary processes the non-faradaic current expended in charging the double layer should also be considered. For the palladium electrode the amount of electricity, used in the charging of the double layer, owing to the small value of the overvoltage and the high solubility of hydrogen in palladium is, except in the case of very rapid potential changes, small as compared with the amounts consumed in the evolution of hydrogen or in the change of concentration of hydrogen dissolved in palladium. We shall further return to this question in more detail. Let us now introduce the quantity φ_θ, which we shall call the potential of adsorbed hydrogen and which satisfies the condition $i = 0$ for given values of θ and $[H^{\bullet}]$, and let us assume, for the sake of simplicity, that $\alpha = \beta = {}^1/_2$. Then

$$\varphi_\vartheta = \frac{RT}{F} \ln \frac{k_1 [H^{\bullet}] (1 - \theta)}{k_2\, \theta}, \qquad (2)$$

$$i = -2 \{k_1 k_2 [H^{\bullet}]\, \theta (1 - \theta)\}^{1/2} \operatorname{sh} \frac{(\varphi - \varphi_\theta) F}{2RT},$$

$$\varphi = \varphi_\theta - \frac{2RT}{F} \operatorname{arg\,sh} \frac{\{k_1 k_2 [H^{\bullet}]\, \theta (1 - \theta)\}^{1/2}}{2} \cdot i\,. \qquad (3)$$

In the vicinity of $\theta = {}^1/_2$ the variation of $\theta(1 - \theta)$ with the degree of covering is small and this quantity may, in the first approximation, be considered constant. In this case the value of the cathodic potential may be considered as a sum of two terms, *viz.* the potential of adsorbed hydrogen and a term depending only upon the current intensity. In the case of an adsorbed layer possessing the above mentioned properties this assumption is only approximately exact. For θ ranging from 0.3 to 0.7 the error may amount to 0.005, and in the interval between 0.2 and 0.8 to 0.011.

It has been shown by Frumkin and Šlygin[15] for hydrogen layers adsorbed on a metallic electrode that in the case of medium covering of the surface the best approximation is to assume the activity of the adsorbed hydrogen to be directly proportional in a wide interval to the quantity $e^{f\theta}$, where f is a constant. Kinetic relations compatible with such termodynamic properties have been derived by Temkin[16]. They have already been used in the papers of Dolin, Ershler and Frumkin[17, 18] for the interpretation of the kinetics of transition of ions into adsorbed atoms on the surface of platinum. We give lower a brief derivation of the fundamental relationships referred to the case under examination, assuming θ to be not too near zero or unity (medium covering). Instead of (1) there obtains

$$i = k_1 [\mathrm{H}^\cdot]\, e^{-\alpha f\theta}\, e^{-\frac{\alpha\varphi F}{RT}} - k_1 e^{\beta f\theta} e^{\frac{\beta\varphi F}{RT}} =$$

$$= k_1^\beta [\mathrm{H}^\cdot]^\beta k_2^\alpha \left\{ e^{\frac{-\alpha(\varphi-\varphi_\theta)F}{RT}} - e^{\frac{\beta(\varphi-\varphi_\theta)F}{RT}} \right\} \tag{4}$$

where

$$\varphi_\theta = \frac{RT}{F} \left\{ \ln \frac{k_1 [\mathrm{H}^\cdot]}{k_2} - f\theta \right\}. \tag{5}$$

The quantity φ_θ has here again the value of the equilibrium potential of adsorbed hydrogen, since for $\varphi = \varphi_\theta$ and with given θ and $[\mathrm{H}^\cdot]$ $i = 0$.

With $\varphi - \varphi_\theta \ll \frac{RT}{F}$ equation (4) transforms into

$$i = k_1^\beta [\mathrm{H}^\cdot]^\beta k_2^\alpha \frac{F}{RT} (\varphi - \varphi_\theta) = \frac{1}{A} (\varphi - \varphi_\theta)$$

---

[15] Frumkin and Šlygin, Acta Phys. Chim. URSS, **3**, 781 (1935); **5**, 819 (1936).

[16] Temkin, J. Phys. Chem. (Russ.), **15**, 296 (1941); ibidem, **14**, 1153 (1940). See also Love and Emmet, J. Am. Chem. Soc., **63**, 3297 (1941).

[17] Dolin and Ershler, Acta Phys. Chim. URSS, **13**, 747 (1940).

[18] Dolin, Ershler and Frumkin, ibidem, **13**, 779 (1940).

where

$$A = k_1^{-\beta} [\mathrm{H}^\cdot]^{-\beta} k_2^{-\alpha} \frac{RT}{F}. \tag{4a}$$

From equation (4) it follows that $\varphi = \varphi_\theta + \xi(i)$ where $\xi(i)$ depends only upon i, but not upon θ.

If $\alpha = \beta = \frac{1}{2}$

$$\varphi = \varphi_\theta - \frac{2RT}{F} \operatorname{arg\,sh} \frac{\{k_1 k_2 [\mathrm{H}^\cdot]\}^{-1/2}}{2} \cdot i, \tag{6}$$

and, finally, if $-\frac{(\varphi-\varphi_\theta)F}{RT} \gg 1$ and $i > 0$

$$\varphi = \varphi_\theta - \frac{2RT}{F} \ln i + \frac{RT}{F} \ln k_1 k_2 [\mathrm{H}^\cdot]. \tag{6a}$$

Replacing potentials by overvoltages we obtain instead of (6)

$$\eta = \varphi_0 - \varphi = \eta_\theta + \frac{2RT}{F} \operatorname{arg\,sh} \frac{\{k_1 k_2 [\mathrm{H}^\cdot]\}^{-1/2}}{2} \cdot i, \tag{6b}$$

and instead of (6a)

$$\eta = \eta_\theta + \frac{2RT}{F} \ln i - \frac{RT}{F} \ln k_1 k_2 [\mathrm{H}^\cdot] \tag{6c}$$

where φ_0 is the equilibrium potential at an initial (*e. g.* atmospheric) hydrogen pressure, and $\eta_\theta = \varphi_0 - \varphi_\theta$.

Equations (6b) and (6c) show the overvoltage to be additively composed of two parts, one of which depends only upon the intensity of the current, this dependence being the same as usually derived in the theory of slow discharge, while the other is determined by the equilibrium potential of adsorbed hydrogen. Let us assume now the existence of an equilibrium between hydrogen adsorbed on the palladium surface and hydrogen dissolved in the layers of the volume phase adjacent to the surface. Such an equilibrium must necessarily set in in stationary conditions if the whole surface of the electrode is polarized. In case of a diffusion electrode or in non-stationary conditions the above assumption holds only if the activation energy of the transition from adsorbed to dissolved hydrogen is low. This assumption is also made by Farkas[19] whereas Kobozev and Monblanova[20] as well as Melville

---

[19] Farkas, Trans. Farad. Soc., **33**, 552 (1937); **32**, 1667 (1936).

[20] Kobosev and Monblanova, Acta Phys. Chim. URSS, **1**, 611 (1934).

and Rideal[21] consider this activation energy to play an important rôle. It seems probable that for an electrode with an activated surface our assumption will not result in too great an error. Under these conditions the quantity φ_θ or η_θ may be determined from observations on non-stationary processes using equations (6) and (6b). In fact, the value η_1, *viz.* the initial value of the overvoltage η observed when the current is being passed through an electrode in equilibrium with gaseous hydrogen under atmospheric pressure, obviously corresponds to $\eta_\theta = 0$, since the change of hydrogen concentration in the metal requires a considerable lapse of time as compared with that required for the charging of the double layer (see below). There follows that for stationary values of η

$$\eta = \eta_1 + \eta_\theta \,, \tag{7}$$

which means that η_θ corresponds to the «slowly» attained component of the overvoltage, which was denoted in the experimental part of this paper by η_2. Let us now consider the case when the initial state of the electrode is in the region of phase transition. According to our assumption of an equilibrium between the surface and the volume of the electrode θ must remain constant as long as both volume phases are present[22], φ_θ being obviously nothing else than the equilibrium potential of the phase transition. If we suppose further the adsorbed hydrogen to retain its thermodynamic properties expressed in equation (5) also in the vicinity of the phase transition region, there follows directly from equations (6) and (6b) the relationship between the overvoltage in phase transition and in the evolution of molecular hydrogen already established experimentally.

We shall now suppose the rate of hydrogen diffusion to be so high and the thickness of the electrode so small as to make it possible to apply the assumption of equilibrium between the adsorbed and dissolved hydrogen throughout the bulk of the diffusion electrode. In this case the hydrogen on the diffusion side of the electrode surface will also be in equilibrium with the dissolved hydrogen and, consequently, with the hydrogen adsorbed on the polarization side. Since on the diffusion side $i = 0$ it follows from (6) and (6b) that the overvoltage established on this side must equal η_θ as already demonstrated in the experimental part.

Let us further consider the change of potential observed after the current has been switched off and examine more in detail the rôle played by the double layer charges in non-stationary processes. Taking into account the presence of charges in the double layer, the capacity of which we will denote by C, equation (4), expressing the balance of the hydrogen ions discharge, must be written

$$i + C\frac{\partial\varphi}{\partial t} = k_1^\beta [\mathrm{H}^\cdot]^\beta k_2^\alpha \left\{ e^{-\frac{\alpha(\varphi-\varphi_\theta)F}{RT}} - e^{\frac{\beta(\varphi-\varphi_\theta)F}{RT}} \right\}. \tag{8}$$

For the given particular case, before stopping the current we have $\frac{\partial\varphi}{\partial t} = 0$, after stopping it $i = 0$, and, consequently:

$$C\frac{\partial\varphi}{\partial t} = k_1^\beta [\mathrm{H}^\cdot]^\beta k_2^\alpha \left\{ e^{-\frac{\alpha(\varphi-\varphi_\theta)F}{RT}} - e^{\frac{\beta(\varphi-\varphi_\theta)F}{RT}} \right\}. \tag{8a}$$

In order to integrate this equation, knowledge of the relation between φ_θ and t is necessary. This relation is determined by the law of molecular hydrogen evolution, *viz.*:

$$NF\frac{\partial\theta}{\partial t} = -\omega(\theta) + C\frac{\partial\varphi}{\partial t} + i \tag{9}$$

where $\omega(\theta)$ is the rate of evolution (in coulombs per second) of molecular hydrogen from the metal for a covering θ, and $Nd\theta$ — the variation in the number of gramm-equivalents of hydrogen in the electrode, corresponding to a variation of θ by $d\theta$.

In order that equation (9) may still hold the dissolved hydrogen in the region of hydrogen overvoltage must possess the same thermodynamic properties as the adsorbed hydrogen, *viz.* the relation between concentration and potential must be linear, as it has actually been confirmed by our experimental data. In point of fact, in the general case the left hand side of equation (9) should have the form $N_1F\frac{\partial\theta_1}{\partial t} + N_2F\frac{\partial\theta_2}{\partial t}$, the subscripts 1 and 2 referring to the adsorbed and dissolved hydrogen, respectively. If the above supposition is made $\frac{d\theta_2}{dt} = \mathrm{const}\,\frac{d\theta_1}{dt}$ and the left hand side of equation (9)

---

[21] Melville and Rideal, Proc. Roy. Soc. (A), **153**, 89, 103 (1935).

[22] Towards the end of the phase transition, *i. e.* when the amount of one of the phases becomes small, the rate of phase transition must decrease and this condition is invalidated which is manifested by the increase of overvoltage. In a similar manner, at high current densities the relationship between the amounts of both phases in layers adjacent to the surface may considerably differ from that within the bulk of the metal, even up to the total disappearance of one of the phases. This explains the occurrence of slowly decreasing potential shifts likewise in the region of phase transition (Fig. 5, curves *IIb*, *IIIb*).

transforms into $NF\frac{d\theta}{dt}$. After the current has been cut off, $i=0$, and

$$NF\frac{\partial\theta}{\partial t}=-\omega(\theta)+C\frac{\partial\varphi}{\partial t}. \tag{9a}$$

From equations (5) and (9a) it follows that

$$\frac{NF^2}{RTf}\cdot\frac{\partial\varphi_\theta}{\partial t}=+\omega(\theta)-C\frac{\partial\varphi}{\partial t}. \tag{10}$$

An exact solution of the system of simultaneous equations (8a) and (10) presents some difficulties. For the palladium electrode, however, the problem may be solved in the first approximation in a much simpler way. At the moment $t=0$ immediately following the interruption of the current the quantities $\omega(\theta)$ and $C\frac{\partial\varphi}{\partial t}$ equal each other, since they are both equal to the density of the stationary current before the interruption. On the other hand, the coefficient $\frac{NF^2}{RTf}$ in equation (10) represents a quantity, which may be called the capacity of the electrode referred to hydrogen, since the reciprocal value $\frac{RTf}{NF^2}$ is equal to the change of the potential φ_θ corresponding to the introduction into the electrode of an amount of hydrogen equivalent to one coulomb. This capacity is high as compared with the capacity of the double layer. Thus, for a $10\,\mu$ thick electrode the ratio between the two values is $\sim 10^{-6}$ and, consequently, in the initial period after stopping the current $\frac{\partial\varphi_\theta}{\partial t}\ll\frac{\partial\varphi}{\partial t}$. In this case, equation (8a) may be approximately solved, considering φ_θ constant. The solution is of the form (for $\alpha=\beta={}^1/_2$):

$$t=-\frac{RTC}{F}\{k_1k_2[\mathrm{H}^\cdot]\}^{-1/2}\ln\left\{\mathrm{th}\frac{(\varphi-\varphi_\theta)F}{4RT}\,\mathrm{cth}\frac{(\varphi_i-\varphi_\theta)F}{4RT}\right\}=$$

$$=-AC\ln\mathrm{th}\frac{(\varphi-\varphi_\theta)F}{4RT}\,\mathrm{cth}\frac{(\varphi_i-\varphi_\theta)F}{4RT}, \tag{11}$$

where φ_i is the initial potential at the moment the current has been stopped. It is seen from equation (11) that with $\frac{t}{AC}\gg 1$, $\varphi\sim\varphi_\theta$. From equation (4a) and data given in Table 1 it follows that in acid and alkaline solutions $A\sim 5\,\Omega$ and $A\sim 300\,\Omega$, respectively. Since $C\sim 2\times 10^{-5}$ farad/cm.^{2} the condition $\frac{t}{AC}\gg 1$ will be satisfied if $t>10^{-2}$, as it was always the case in our experiments. The time required for the setting-in of an equilibrium between the double layer and hydrogen adsorbed or dissolved in the metal is determined by the condition $\frac{t}{AC}\gg 1$. Thus, the decay of the overvoltage with time in case of a Pd electrode may comprise two stages: the rapid falling-off of that part of the overvoltage, which depends upon the absence of equilibrium between the double layer and the adsorbed atoms, and a slow change depending upon the decomposition of the surface and volume hydrides followed by the evolution of molecular hydrogen[23]. The occurrence of two stages in the process of overvoltage decay has already been pointed out in the literature[24]. The interpretation advanced in the present paper will be confronted lower with explanations proposed by other authors. The kinetics of the slow change of overvoltage is determined by equation (10). If $\frac{t}{AC}\gg 1$ equation (10) transforms into $\left(\frac{NF^2}{RTf}+C\right)\frac{\partial\varphi_\theta}{\partial t}=\omega(\theta)$ or, since $C\ll\frac{NF^2}{RTf}$, into

$$\frac{NF^2}{RTf}\frac{\partial\varphi_\theta}{\partial t}=-NF\frac{\partial\theta}{\partial t}=\omega(\theta). \tag{12}$$

In order to solve this equation, definite assumptions must be made referring to the character of the function $\omega(\theta)$. Let us at first assume the delay in the evolution of hydrogen to be determined by the low rate of H_2 formation from two H atoms. Since, according to Temkin, with the above thermodynamic properties of the adsorbed hydrogen the rate of desorption of molecular hydrogen will be $k_d e^{2\beta' f\theta}$ and the rate of adsorption $k_a c_{\mathrm{H}_2} e^{-2\alpha' f\theta}$ there obtains

$$NF\frac{\partial\theta}{\partial t}=k_a c_{H_2} e^{-2\alpha' f\theta}-k_d e^{2\beta' f\theta} \tag{12a}$$

where c_{H_2} is the concentration of H_2 in the solution and $\alpha'+\beta'=1$. The occurrence of the coefficient 2 in the exponent is due to the fact that two atoms of adsorbed hydrogen are involved in the process. Taking into account equation (5), equation (12a) may also be written:

$$\frac{NF^2}{RTf}\frac{\partial\varphi_\theta}{\partial t}=-k_a^{\beta'}c_{H_2}^{\beta'}k_d^{\alpha'}\left\{e^{+\frac{2\alpha'(\varphi_\theta-\varphi_0)F}{RT}}-e^{\frac{2\beta'(\varphi_\theta-\varphi_0)F}{RT}}\right\}. \tag{12b}$$

---

[23] It must be emphasized that this conclusion does not depend on any assumptions on the equation of state for the adsorbed hydrogen, but depends solely upon the ratio between the capacity of the electrode referring to hydrogen and that of the double layer.

[24] Ferguson and Kleinheksel, J. Phys. Chem., **42**, 171 (1938); Ferguson, Trans. Am. Electrochem. Soc., **76**, 29 (1939). Hickling and Salt, Trans. Farad. Soc., **37**, 450 (1941).

This equation is similar in form to equation (8a), in other words, although the change of φ_θ is much slower than that of $(\varphi - \varphi_\theta)$ both are governed by the same law[25]. In solving equation (12a), we shall limit ourselves to the case of sufficient remoteness from equilibrium with gaseous hydrogen, when the rate of adsorption is relatively small as compared with the rate of desorption. We have then from (12a)

$$\theta = -\frac{1}{2\beta' f} \ln\left(\frac{2tk_d\beta' f}{NF} + e^{-2\beta' f\theta^i}\right)$$

where θ_i is the value of θ before the switching-off of the current whence, with equation (5) and considering that $k_d e^{2\beta' f\theta_i} = i$, we obtain

$$\varphi_\theta = (\varphi_\theta)_i + \frac{RT}{2F\beta'} \ln\left(\frac{2t\beta' fi}{NF} + 1\right), \tag{13}$$

where $(\varphi_\theta)_i$ is the value of φ_θ before interrupting the current. As already mentioned in the experimental part, equation (13) accurately depicts the character of the dependence of φ_θ on time, the value of the constant before the logarithm being, however, less than should be expected according to equation (13). Thus we are compelled to question the correctness of our assumption of a considerable departure from equilibrium between the adsorbed molecular hydrogen and the same dissolved in the electrolyte. The determination of the relationship between the intensity of the stationary current i and the value φ_θ leads to the same conclusion. Indeed, if the processes of desorption and adsorption of molecular hydrogen are sufficiently slow, then at some distance from the equilibrium potential, as referred to gaseous hydrogen, we have obviously

$$i = k_d e^{2\beta' f\theta} = \text{const} \cdot e^{-\frac{2\beta' F\varphi_\theta}{RT}}$$

or

$$\varphi_\theta = \text{const} - \frac{RT}{2\beta' F} \ln i \sim \text{const} - \frac{RT}{F} \ln i. \tag{14}$$

In this case also the experimental value of the coefficient before $\ln i$ is smaller than should be expected from equation (14). All this leads to suppose that the rate of molecular hydrogen evolution is not expressed by the quantity $k_d e^{2\beta' f\theta}$.

In investigating the polarization of activated palladium electrodes Knorr and co-workers[3] came to the conclusion that it is due solely to the slow rate of removal from the solution of the evolved molecular hydrogen. For acid solutions the explanation of his data as advanced by Knorr is, undoubtedly, correct. In this case the relation between overvoltage and current is expressed by the relation

$$\eta = 0.029 \lg\left(\frac{i}{i_0} + 1\right)$$

the constant i_0 being equal to $\frac{2DF}{\delta}(c_{H_2})_0$, where δ is the thickness of the Nernst diffusion layer, $(c_{H_2})_0$—the concentration of hydrogen dissolved in the electrolyte in equilibrium with gaseous hydrogen at atmospheric pressure, and D its coefficient of diffusion. According to our data, the same relationship may be applied to the value of η_2. The magnitude of i_0 was in our experiments by one order less than in Knorr's, this being, however, possibly due to more intense stirring of the solutions in his experiments. According to his data, the solution was stirred by means of an intense hydrogen stream and, which is especially important, the electrode was made of a fine wire, thus creating much more favourable conditions for stirring than in our experiments, where palladium foil of 2 cm.^{2} area was used as electrode. It seems, therefore, probable that in our experiments likewise the hydrogen dissolved in palladium or adsorbed on it had come in equilibrium with the hydrogen dissolved in the electrolyte and that the total overvoltage observed is composed of two parts, the first depending upon the slowness of the discharge and the second—upon the delay in the removal of hydrogen from the solution. It is possible, however, that equilibrium between the hydrogen in palladium and in the solution

---

[25] Just as the rate of the $(\varphi - \varphi_\theta)$ change is governed by the ratio of $k_1^{\beta}[H^{\cdot}]^{\beta} k_2^{\alpha}$ to C the rate of variation of φ_θ is determined by the ratio $k_a^{\beta'} c_{H_2}^{\beta'} k_d^{\alpha'}$ to $\frac{NF^2}{RTf}$.

The character of the whole process of the φ change depends upon the relationship between these two quantities. If the second ratio is high as compared with the first one, the value of $\varphi - \varphi_\theta$ will become zero before the change of φ_θ attains an appreciable value, as it was actually assumed in the case of a Pd eletrode. If the values of both ratios are comparable—the two stages of the discharge process are mutually overlapping.

is not completely attained and that the slowness of the recombination process may exert some influence on the value of the overvoltage. At any rate, this possibility must not be overlooked in applying the above theory to other kinds of electrodes. Whether hydrogen adsorbed or dissolved in the metal comes in equilibrium with hydrogen dissolved in the electrolyte or not, *i. e.* whether the occurrence of that part of the overvoltage which we denoted by η_2 or η_θ, is due to slownness of diffusion or recombination, our conclusions concerning the properties of this quantity remain valid. The quantitative relations between η_θ and i in stationary conditions of polarization and between η_θ and t after the current has been interrupted only are affected. In considering the phenomena of overvoltage on activated palladium electrodes Knorr takes into account only the influence of hydrogen dissolved in the electrolyte. Owing, however, to the much higher concentration of hydrogen dissolved in palladium itself, the properties of η_θ are to a greater extent determined by the latter, even in case of equilibrium between molecular hydrogen in the electrolyte and hydrogen in the metal being established.

Besides the term, which we regard as the potential of adsorbed hydrogen, the overvoltage on the palladium electrode comprises another part η_1, determined directly by the electrochemical reaction. In acid solutions it is small, and with more active electrodes it practically disappears, as may be seen from Knorr's data, in the measurable interval of current density. In our experiments the value of η_1 was directly proportional to i within the limits of experimental error; for the observed values of η_1 this was in agreement with equation (6b). A more detailed study of its dependence on other factors met with difficulties, owing to its value being very small It must, however, be pointed out that we failed to observe the influence of the $H^{\cdot}$-ion concentration on η_1 required by the theory [*cf.* equation (6c)]. In alkaline solutions the value of η_1 is substantially higher and, as already mentioned, the Tafel equation with the usual value of the coefficient 0.12—0.13 is found to be valid. The overvoltage in KOH increases with dilution. Thus, here as in the case of nickel, the primary act of the electrochemical reaction is apparently not the hydrogen ion discharge, but the discharge of a water molecule with formation of an OH' ion. In the reverse process it is the formation of a water molecule from OH' and an adsorbed hydrogen atom [26]. In this case

$$i = k_1 e^{-\alpha f\theta} e^{-\frac{\alpha'\varphi F}{RT}} - k_2 [OH'] e^{\beta f\theta} e^{\frac{\beta\varphi F}{RT}} =$$

$$= k_1^{\beta} k_2^{\alpha} [OH']^{\alpha} \left\{ e^{-\frac{\alpha(\varphi-\varphi_\theta)F}{RT}} - e^{\frac{\beta(\varphi-\varphi_\theta)F}{RT}} \right\},$$

$$\varphi_\theta = \frac{RT}{F} \ln \left\{ \frac{k_1}{k_2 [OH']} - f\theta \right\},$$

and instead of equations (6b) and (6c), we have

$$\eta = \eta_\theta + \frac{2RT}{F} \operatorname{arg\,sh} \frac{\{k_1 k_2 [OH']\}^{1/2}}{2} i, \tag{6d}$$

$$\eta = \eta_\theta + \frac{2RT}{F} \ln i - \frac{RT}{F} \ln k_1 k_2 \, [OH']. \tag{6e}$$

These equations give a correct description of the behaviour of a palladium electrode in an alkaline solution with the accuracy corresponding to our experimental data.

Our conclusions concerning the relative rate of the different stages of the electrochemical evolution of hydrogen on a palladium electrode do not concord with those of Farkas [19]. The latter regards the measurements of the separation coefficient of hydrogen and deuterium between solution, metallic phase and gas in the process of electrolysis as corroborating the existence of equilibrium between hydrogen dissolved in palladium, and, consequently, also of that adsorbed on palladium, and the ions in the electrolyte solution. The slow stage is, according to Farkas, the process of recombination of the adsorbed atoms. With the exception of one incomplete measurement permitting no conclusions to be drawn made with 0.1 *N* NaOH, all Farkas' data refer to 2 *N* H_2SO_4 and a current density not exceeding 0.002. In these conditions, according to Table 1, we may expect a value of $\eta_2 \sim 0.01$ and a ratio between the rates of the direct and reverse reactions of hydrogen ion discharge with formation of an atom ~ 1.5; *i. e.* the departure from the equilibrium conditions is actually comparatively small. A correct control of Farkas' conclusions as to the absence of equilibrium between hydrogen dissolved in the metal (as well as adsorbed), on one hand, and evolved molecular hydrogen, on the other, is impossible without data on the equilibrium distribution of H and D between the β-phase of

---

[26] Lukowzew, Lewina and Frumkin, Acta Phys. Chim. URSS, **11**, 21 (1939).

palladium and the gas phase. Such data, however, are not available. According to Farkas, when molecular hydrogen is evolved from a Pd electrode supersaturated with pure H in a solution containing 39—69% D the gas obtained contains only traces of D. This experiment which Farkas tries to explain by the assumption made *ad hoc* of the solution being separated from the electrode by the gas bubbles formed, presents in fact direct evidence in support of a high rate of the reaction of hydrogen evolution as compared with the reaction of interchange between electrode and solution.

Thus far, we have discussed only the recombination mechanism of hydrogen removal, without considering the possibility of its [17, 2] proceeding by an electrochemical mechanism. In the latter case we must substitute for equation (4) the more complicated expression

$$i = k_1 [\mathrm{H}^{\bullet}]\, e^{-\alpha f\theta} e^{-\frac{\alpha\varphi F}{RT}} - k_2 [\mathrm{H}^{\bullet}]\, e^{\alpha' f\theta} e^{-\frac{\alpha'\varphi F}{RT}} - \\ - k_3 e^{\beta f\theta} e^{\frac{\beta\varphi F}{RT}} - k_4 [\mathrm{H}_2]\, e^{-\beta' f\theta}\, e^{\frac{\beta'\varphi F}{RT}} \qquad (15)$$

where the terms with coefficients k_2 and k_4 refer to reactions, corresponding to the formation or disappearance of molecular hydrogen. Consideration of equation (15) shows that in the electrochemical mechanism of H_2 formation the overvoltage in the general case cannot be represented as a sum of two terms, the one dependent only upon i and the other — only upon θ. However, this possibility remains, as it was already shown in one of our previous papers, if in equation (15) we may limit ourselves to the first and third terms, *i. e.* if the reaction rate of molecular hydrogen formation or disappearance is not high.

While in the recombination mechanism the rate of molecular hydrogen formation depends both for stationary and non-stationary conditions and whatever the composition of the solution only on θ (or, which is the same, on $\eta_\theta = \eta_2$) this conclusion does not hold for the electrochemical mechanism. A direct experimental investigation of the rôle played by the electrochemical mechanism in H_2 formation on the Pd electrode could be most easily made by observing the decay of overvoltage at given hydrogen content in the metal in acid and alkaline solutions. In case of an electrochemical mechanism a slower rate of H_2 evolution is to be expected in the latter. In preliminary experiments made with this aim no such effects were observed but the experiments are to be repeated. Farkas' experiment, described above, concerning the evolution of hydrogen on an electrode supersaturated by H in a solution containing D ions seems also to point against the assumption of an electrochemical mechanism.

The possibility, however, is not excluded that at high current densities the electrochemical mechanism must be taken into account along with the recombination mechanism of hydrogen removal. This assumption is supported by the fact that neither on palladium nor on any other electrode the limiting values of the cathodic current required by the recombination theory are observed. However the recombination theory may be altered so as not to conclude to the existence of a limiting cathodic current. Thus, this important problem still remains open to discussion both from the theoretical and from the experimental standpoint. It must be pointed out that in the recombination process the increase of current density is accompanied by an illimited increase of the value $\eta_D = \eta_\theta$ while in the recombination process it inevitably tends to a certain limit since the covering of the surface itself tends to a limit. The problem of the recombination and electrochemical mechanisms of hydrogen removal was recently discussed in a paper by Hickling and Salt[27]. These authors deny the existence of slow discharge and assume the electrode potential to be determined by the pressure of atomic hydrogen in equilibrium with hydrogen adsorbed on the electrode[28] whilst the removal of hydrogen from the electrode is due partly to recombination and partly to the interaction between hydrogen ions and adsorbed atoms; the probability of a discharge on the occupied and the unoccupied sites of the surface being assumed equal. On this assumption the covering of the surface by adsorbed atoms cannot, obviously, exceed a limiting value equal to one half. Since, according to the authors, the total potential measured is an equilibrium potential with respect to the adsorbed hydrogen, the total overvoltage of the electrode with increasing current density must tend to a certain limit, whereas, according to our interpretation of the electrochemical mechanism, this refers only to η_θ.

---

[27] Hickling and Salt, Trans. Farad. Soc., **38**, 474 (1942).

[28] The physical meaning of introducing this pressure, which according to Hickling and Salt may be for instance $10^{-25.5}$ atm. for $\eta = 0.50$ remains somewhat obscure.

Hickling and Salt consider their conclusion to be corroborated by experimental data.

However, as it was shown for the mercury electrode in the first paper of this series [29], this overvoltage limit is, in fact, due only to an incorrect interpolation of the curves of overvoltage decay [30].

In studying the relation between overvoltage and time after the stopping of the current Hickling and Salt are lead to consider the curves of the overvoltage decay as composed of two parts: a more rapid and a slower decay. Being expressed in form of a relation between η and lg t they show different slopes. But whereas we consider the initial rapid decay as a process of establishment of equilibrium between the ions of the double layer and adsorbed (or dissolved) hydrogen. Hickling and Salt, assuming the electrode potential to be always governed only by the concentration of the adsorbed hydrogen, consider this initial part to be also determined by the process of hydrogen removal proceeding, however, by another mechanism, which we have called electrochemical. As shown above, the simultaneous assumption of Hickling and Salt, referring to the occurrence of an electrochemical mechanism of removal at high current densities and to the possibility of interpreting the total overvoltage as an equilibrium potential of the adsorbed hydrogen, leads to the conclusion that a limiting value of overvoltage must exist which, in contradiction with the opinion of these authors, finds no confirmation in experimental data.

In considering the poisoning of palladium electrodes from the standpoint expressed in this paper, the following cases may be encountered. If the poison delays the process of hydrogen ion discharge without affecting the process of recombination, its admixture will call forth an increase of overvoltage not followed, however, by penetration of hydrogen into the bulk of the metal. A poison delaying the recombination process, but not affecting the process of discharge (at the cost of an increase of η_0), will similarly

rise the overvoltage but will simultaneously increase the penetration of hydrogen into the metal. Kobozev and Monblanova [20], assuming the existence of equilibrium between the adsorbed hydrogen atoms and the hydrogen ions in the solution, account for the action of the poison by a decrease of the activation energy of dissolution of the adsorbed hydrogen in the bulk of the metal. If we admit the existence of a marked activation energy in the process of solution, we may assume that poisons delaying only the process of discharge also increase the dissolution of hydrogen, *i. e.* the excess energy, contained in the discharged atoms and which increases with increasing potential drop in the double layer, may be partly used to overcome the potential barrier in the process of solution. Thus, the simple relations between the amount of diffused hydrogen and the overvoltage on poisoned electrodes given in the interesting paper by Kobozev and Monblanova are possible but not necessary. Further detailed experimental investigations of the whole problem of poison action is desirable.

---

[29] Frumkin, Acta Phys. Chim. URSS, **18**, 29 (1943).

[30] While there is no doubt about the continuous increase of cathodic overvoltage with the rise of current density, the covering of the surface in case the electrochemical mechanism of removal may, in point of fact, tend to a limit and even decrease as shown above. In the latter case the overvoltage, measured some time after the interruption of the current, may pass through a maximum at a certain current density, as it was apparently observed by Hickling and Salt for some cathodes, for instance copper cathodes.

Summary

The fundamental conclusions drawn from experimental data are given in the beginning of the theoretical part of this paper. The results are interpreted from the viewpoint of the slow discharge theory, assuming the rate of discharge and ionization on a partly covered surface to be expressed by equations (4) and (5).

In case of the palladium electrodes, used in our investigation, there exists probably an equlibrium between hydrogen, adsorbed or dissolved in the metal, and molecular hydrogen, dissolved in the electrolyte. Consequently, all the observed overvoltage may be considered as summed up of two parts: the first depending upon the slowness of the electrochemical reaction itself, and the second — upon the slowness of hydrogen removal from the solution. In a more general case the latter value must depend also on the slowness of the recombination process

Karpov Institute of Physical Chemistry,
Moscow.

Received
October 2, 1943.