The larger part of the experimental portion of this investigation was carried out by Mr. S. P. Sweetser.

SCHENECTADY, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

HYDROGEN OVERVOLTAGE.

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Hydrogen overvoltage will be defined, for the purpose of this paper, as the difference of potential that exists between a reversible hydrogen electrode and an electrode, in the same solution, at which molecular hydrogen, H_2, is being formed from hydrogen ions. A reversible hydrogen electrode is, of course, one at which the reaction

$$2H^+ + 2\epsilon = H_2 \qquad (1)$$

(ϵ = electron) has reached equilibrium. This equilibrium is attained, and maintained during the passage of very small currents, only on electrodes covered with a dispersed "noble" metal, such as platinum, palladium, or iridium. If a stronger current is passed across such a metal-electrolyte boundary, or if other electrodes are used, the reaction does not take place under equilibrium conditions, and an overvoltage appears.

A number of theories have been advanced to account for overvoltage. The one proposed by Nernst,[1] discussed by Lewis and Jackson,[2] and lately championed by Bennett and Thompson,[3] assumes that Reaction 1 occurs in the two stages

$$2H^+ + 2\epsilon = 2H_1 \quad (2), \qquad \text{and} \qquad 2H_1 = H_2, \quad (3)$$

that Reaction 3 is slower than Reaction 2 and that the excess potential is due to an accumulation, above the equilibrium concentration, of H_1. Möller,[4] on the other hand, finds a relation between the overvoltage of an electrode, and its "randwinkel," *i. e.*, the angle between the surface of an electrode and the edge of a large bubble attached to it. Newbury,[5] in his later papers, considers that hydrogen overvoltage is principally due to the formation, during electrolysis, of metallic hydrides with higher solution tensions than that of hydrogen. However, it is not our purpose to review all of the theories of overvoltage. It is noteworthy, nevertheless, that none of the published theories, with the exception of that of Möller, attempts an explanation of the great influence the physical condition of the electrode may have on the overvoltage. For instance, a polished platinum electrode may show an overvoltage as high as 0.1 volt,

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[1] *Ber.*, **30**, 1547 (1897).

[2] *Z. physik. Chem.*, **56**, 193 (1906).

[3] *Trans. Am. Electrochem. Soc.*, **29**, 24 (1916) and *J. Phys. Chem.*, **20**, 296 (1916).

[4] *Z. physik. Chem.*, **65**, 226 (1909).

[5] *J. Chem. Soc.*, **109**, 1359 (1916).

whereas for platinized platinum it is nearly zero. The surface concentration of H_1 or of hydrides should not differ greatly on two such electrodes.

It is believed by the authors that the results of the present investigation throw light on this difficulty, and form the basis of a theory which will account for the major portion of the phenomena relating to hydrogen overvoltage.

2. The Apparatus and Method of Measurement.

The apparatus resembled, in many particulars, that used by Thiel and Breuning.[1] A number of differences in details will, however, be noticed. As shown in Fig. 1, the cell consisted of 3 cylindrical compartments, G_1, G_2, and G_3, each 4 cm. diameter and 10 cm. long. Compartments G_1 and G_2 were connected by a tube of 8 mm. bore, G_2 and G_3 by a tube of 2 mm. bore. The electrode E of the metal whose overvoltage was to be determined was inserted through a rubber stopper which closed compartment G_2. Through this stopper was also passed a tube with a capillary outlet from which flowed a stream of hydrogen bubbles, and also an outlet for hydrogen. In compartment G_1 a rod of amalgamated zinc passed through a glass tube, which was in turn inserted through the stopper closing the compartment. Gaseous hydrogen could be made to pass between the zinc rod and the tube, as shown. Compartment G_3 contained the reference hydrogen electrodes, a capillary inlet, and an outlet for hydrogen. The flow of gas into the several compartments was controlled by means of the stopcocks C_1, C_2 and C_3. To equalize the hydrogen pressure the outlet tubes were connected to a common tube, which was provided with

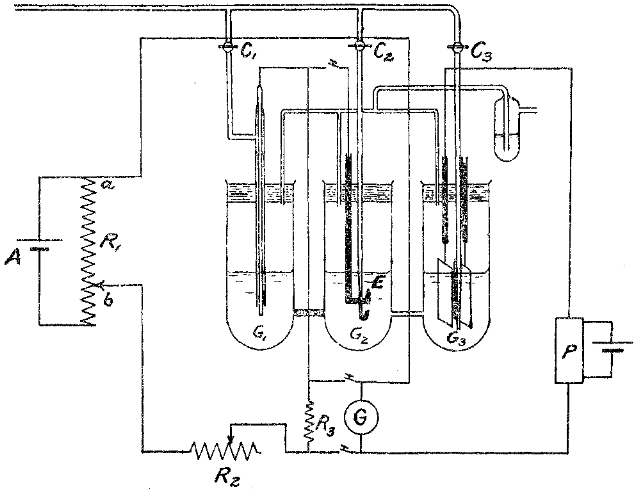

Fig. 1.

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[1] *Z. anorg. Chem.*, 83, 329 (1913).

a water seal to prevent the entrance of air. In order to diminish the diffusion into G_2 of the zinc salt that formed in G_1, a cotton plug was placed in the tube connecting the two vessels.

The platinum electrodes on which overvoltage measurements were made consisted of fine platinum wire sealed into glass tubing, bent as shown in the figure in order that the hydrogen bubbles could escape readily. A low power microscope was arranged so that the evolution of bubbles could be observed. The reference hydrogen electrodes in compartment G_3 consisted of sheets of platinum, 2 by 3.5 cm., welded to platinum wires which were sealed into glass tubes; these electrodes were platinized in chloroplatinic acid, following the directions and precautions given by Ellis.[1] The smaller platinum electrodes were treated in a similar manner. The cell was kept in a thermostat at 25.00 ± 0.01°.

As the minimum overvoltage, in most cases, was desired, a suitable method for regulating and measuring small currents had to be developed. The first attempt was to interpose a sufficiently large resistance between the zinc electrode and the electrode E. Resistances of the order of several million ohms were necessary, and were prepared, but it was not found possible to make them sufficiently adjustable. An arrangement, the electric connections of which are shown on the left side of Fig. 1, was found to be very satisfactory. A dry cell, A, was connected to the large adjustable resistance R_1. The connections *a* and *b* were placed at points such that the potential between them was in opposition to, and slightly less than, the voltage between the zinc electrode and the electrode E. The final adjustments could be made by means of the resistance box R_2 of 100,000 ohms' capacity. The small currents could be readily measured by connecting the galvanometer G across the terminals of the resistance R_3. A calibration of the galvanometer was, of course, necessary. The galvanometer, which was of the Leeds and Northrup "High Sensitivity" type, served also for the potentiometer P. The use of this sensitive galvanometer may account for the observation of some phenomena overlooked by other workers in this field.

The overvoltage, which is the difference of potential between the hydrogen electrode in G_3 and the electrode E, was measured on a potentiometer while the exciting current from the zinc electrode was flowing. Newbury[2] and others have used a method for measuring overvoltages in which the exciting current is cut off momentarily while the potential measurements are made. Newbury's objections to the method used in our experiments are: first, that a film of hydrogen over the electrode will raise the resistance of the metal-electrolyte boundary; and, second, that some of the

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[1] THIS JOURNAL, 38, 737 (1916).

[2] *J. Chem. Soc.*, 105, 2429 (1914).

"current lines" of the exciting current will pass through the reference electrodes. Since very small currents are used in the exciting circuit, and the reference electrodes were connected, as shown, with the rest of the apparatus by means of a capillary tube, the second of the objections does not apply to our measurements, and as a very small fraction of the surface of the electrode was covered with bubbles at any time, the potential could hardly be influenced as suggested in his first objection.

For each electrode on which measurements were made the cell was cleaned thoroughly, fresh cotton was placed in the tube connecting G_1 and G_2, the cell was partly filled with 2 *N* sulfuric acid, and the assembling of the apparatus was completed. A current of hydrogen was then passed into all of the chambers for at least 12 hours. During the measurements the gas current was usually stopped in chambers G_1 and G_2, but was continued in the chamber containing the reference electrodes.

A supply of very pure hydrogen was obtained from a generator consisting of a two-liter bottle, the bottom of which was covered with a layer of mercury containing pieces of zinc. This formed one electrode of a galvanic cell, the cathode of which was a cylinder of platinized platinum. The electrolyte consisted of 25% sulfuric acid. Connection with the mercury-zinc layer was made by means of a glass tube, filled with mercury, with a platinum wire sealed into the lower end. The stopper through which the connections passed also had an outlet for hydrogen. The flow of hydrogen could be regulated by means of an adjustable resistance connected across the two electrodes. After running a short time the oxygen originally in the electrolyte was either displaced by the hydrogen or reduced at one of the electrodes. The evolved gas was, however, bubbled through alkaline pyrogallol.

3. Overvoltage Measurements on Platinized Platinum Electrodes.

If a connection was made between the zinc electrode and a platinized platinum electrode (E of Fig. 1), allowing a small current to flow, bubbles formed instantly on the latter electrode. By increasing the potential drop between *a* and *b* or by increasing R_2 the current and the rate of evolution of bubbles could be decreased. When the current was lowered to a value such that one bubble appeared in one or more minutes, fluctuations in the overvoltage were observed. Table I, which contains the figures obtained in one set of measurements, is one of many such sets of observations taken with different electrodes. The asterisks indicate the points at which, in this experiment, a bubble left the electrode. In Fig. 2 the voltages are plotted as ordinates against time as abscissas, the places on the curve at which the bubbles were evolved being shown by small circles.

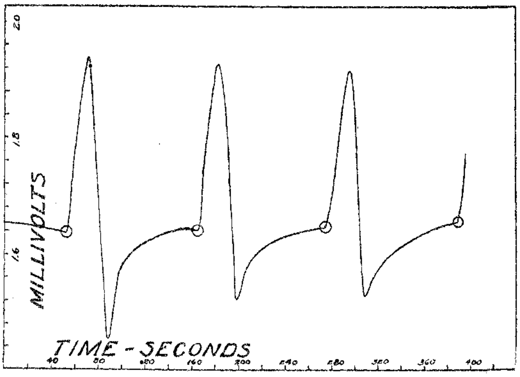

Fig. 2.

TABLE I.

Seconds.	Overvoltage, millivolts.
0	1.655
53	1.637*
70	1.940
88	1.450
100	1.609
120	1.675
165	1.639*
182	1.925
198	1.520
210	1.596
275	1.646*
295	1.913
308	1.524
322	1.587
390	1.655*

Current = 8.0×10^{-7} amperes.

The currents involved are, unfortunately, too small to operate an oscillograph, so the curves were followed from point to point with the potentiometer. The shape of the curve was undoubtedly influenced by small currents from the potentiometer, which could not always be in exact balance. Curves of somewhat different form were obtained, but the sharp break after the highest voltage was always observed. In other experiments the bubbles did not always come off at points corresponding to those given on the curve in Fig. 2, but there was always one bubble for each cycle or fluctuation. The current in amperes was constant in every experiment. At low current densities the bubbles came off at one point on the electrode and continued to do so no matter how long the observations were continued. It thus appears probable that the bubbles leave a nucleus behind when detaching. Other experiments supporting this supposition will be described below.

A theory which explains these interesting fluctuations, and, we believe, most of the phenomena of overvoltage, will now be outlined. Other experiments which were undertaken for the purpose of testing this theory will be described in later paragraphs.

A plausible assumption, and one that simplifies the following discussion, is that molecular hydrogen, H_2, when formed from hydrogen ion by the reaction

$$2H^+ + 2\epsilon = H_2,$$

goes directly into solution in the electrolyte immediately surrounding the electrode. Unless it is carried away by diffusion, stirring, or other means, the concentration of the hydrogen in immediate contact with the electrode will tend to rise, and produce a supersaturated solution. However, if a nucleus of *gaseous* hydrogen is present on the electrode a portion of the liberated hydrogen will enter this gaseous phase, either directly from the electrode or by being absorbed from the electrolyte. The gaseous nucleus will thus play a similar role to that of a small crystal in a supersaturated salt solution. It is evident that hydrogen gas in the form of small bubbles must have a larger energy content per mol of gas than the same volume of undispersed gas, as energy must be expended in overcoming the surface tension in the formation of the small bubbles. Such bubbles will be more soluble (*i. e.*, remain at equilibrium with more concentrated dissolved hydrogen) than the undispersed gas. This is, of course, analogous to the increase of solubility produced by the fine grinding of solids. Since the potential at a hydrogen electrode depends primarily upon the concentration of the dissolved hydrogen (other factors being kept constant) an electrode in equilibrium with the small bubbles will reach a potential higher than a similar electrode in equilibrium with the undispersed gas.

With the foregoing in mind, we can now proceed to an explanation of the voltage fluctuations. Let *a*, *b*, *a′*, *b′*, of Fig. 3, represent a typical fluctuation, the ordinates and abscissas being the same as in Fig. 2. At the point *a* bubble has separated from the electrode, leaving a nucleus behind. As electrolysis proceeds this nucleus will grow, obtaining hydrogen from the electrode or from the supersaturated solution surrounding it. However, as the nucleus increases in size, the energy necessary to produce further increases in volume must decrease, as the ratio

$$\frac{\text{increase in surface}}{\text{increase in volume}}$$

is continually decreasing. If the bubble is growing slowing the hydrogen-bearing solution surrounding the electrode will tend to get into equilibrium with the bubble. This accounts for the decrease in overvoltage from *a* to *b*. At *b* the buoyant effect of the solution is sufficient to overcome the attraction of the electrode for the bubble, which breaks away, leaving a nucleus behind. From *b* to *a′* the concentration of dissolved hydrogen is increasing to a value such that the nucleus can again grow, when the processes described above are repeated. As the bubbles are not always evolved at points corresponding to *b* it seems probable that, since the nuclei tend to form in depressions in the electrode, the bubbles that separate from the nuclei remain in these depressions until forced out by the growth of the following bubbles.

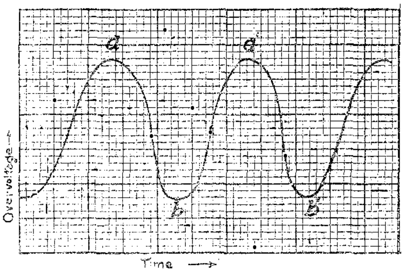

Fig. 3.

Such fluctuations were observed only with electrodes made from very fine platinum wires (B. and S. No. 30 or smaller), heavily platinized. On such electrodes the formation of a single minute bubble will absorb a large portion of the current passing from the electrolyte. If the solution is stirred the overvoltage drops, and, at these low current densities, the gas evolution ceases.

Two questions naturally occur to the reader. Do these gas nuclei actually exist? And is the surface energy of the bubbles sufficient to account for the absorption, indicated by the overvoltage, of electrical energy?

To aid in answering the first question, experiments were made in which very small and slowly increasing currents were applied to electrodes from which gas had not been evolved for some time. Briefly summarized, these experiments showed that, without stirring, the overvoltage, with an ascending current, can rise to 16 millivolts, or about 10 times the values given in Table I, before any bubbles will appear. With stirring, the overvoltage may rise as high as 88 millivolts before the gas phase appears. Also, it was found that if, while taking a series of measurements such as is given in Table I, the current is stopped for a few minutes, it is necessary to apply a large current and slowly decrease it again before the slow evolution of bubbles could be regained. These experiments, together with the observation that bubbles come off from definite points on the electrodes, make the existence of nuclei, which take a comparatively large voltage to form, and, which, because of their high energy content, tend to dissolve as soon as the supersaturated layer of hydrogen is removed, seem certain. From thermodynamic considerations it is evident that it makes no difference, in so far as the absorption of energy is concerned, whether small bubbles are evolved, or a solution of hydrogen in equilibrium with the bubbles is formed. In the following paragraph, in which the relation between the overvoltage and the surface energy is investigated, the assumption will be made that all of the hydrogen goes into the form of bubbles.

The number of bubbles of radius r that can be formed from a mol of hydrogen of volume V is $3V/4\pi r^3$. To obtain the surface energy of such a system this must be multiplied by $4\pi r^2$ and by the surface tension γ. Substituting RT/p for V (R, T, and p are the gas constant, the absolute temperature and the pressure, respectively) and equating the surface energy with the electrical energy $2FE$ in which F is the faraday equivalent and E the overvoltage, we obtain:

$$2FE = \frac{4\pi r^2 RT}{{}^4/_3 \pi r^3 p}\,\gamma = \frac{3RT}{pr}\,\gamma \qquad (4)$$

Substituting 75.6 dynes per square centimeter for γ and appropriate values for the other terms, Equation 4 becomes, for 25°,

$$E = \frac{2.87 \times 10^{-2}}{r}. \qquad (5)$$

Interesting confirmation of this equation was obtained by actual measurement of the size of the evolved bubbles, by means of a calibrated scale in the microscope. The bubbles given off during the measurements given in Table I had radii of 0.017 mm., which corresponds to an overvoltage of 1.6 millivolt. The measured voltage fluctuated between 1.6 and 1.9, the lower voltage, according to the theory, being that of the fully formed bubble. In another case the bubbles had radii of 0.023, corresponding to 1.25 mv. overvoltage. The voltage measurements fluctuated between 1.25 and 1.84 mv. Similar measurements with other electrodes than platinum were unsuccessful for reasons that will be given below.

If Equation 4 is true for the whole range of overvoltage, the upper limit of that quantity will be determined by the lower limit of the size of bubbles. A simple calculation shows that bubbles of the size corresponding to one volt contain 2,450 hydrogen molecules. Few overvoltage measurements higher than this are recorded. It is quite improbable, however, that the unmodified theory is sufficient for these high overvoltage values, since, with the very sharp curvatures involved in these minute globules, the surface tension must certainly differ in value rom that determined for nearly flat surfaces.

4. Overvoltage and Adsorption.

The supposition now seems reasonable that the factor determining the overvoltage of a metal is the size of the gaseous nuclei that can cling to it. Several observers have noticed that metal surfaces with great adsorptive powers have low overvoltages. Such surfaces can probably adsorb, among other things, gaseous nuclei. The metals that form these adsorbing surfaces are low in the electromotive series, and, in consequence of their small chemical activity, they can remain in the amorphous, highly dispersed condition, such as that of the "platinizing" of a hydrogen electrode. These surfaces also favor the retention of large nuclei by providing depressions in which the nuclei are more or less completely surrounded.

In order to test, with another metal, whether the amorphous, highly dispersed state is accompanied by a low overvoltage, the attempt was made to produce metallic silver in that state. The results were very interesting and suggestive. Black amorphous silver can be obtained by reducing a silver halide electrochemically. As it was found that the resulting material changed to silvery white shortly after all the halide was reduced, it was decided to form the silver from the halide in the cell and to determine the overvoltage immediately after the reduction was complete. Accordingly a cup-shaped electrode, filled with silver chloride, and with a silver wire for electrical connection at the bottom of the depression, was put in the place of electrode E of Fig. 1. The reduced silver, which was black while the halide was still present, turned to gray as soon as hydrogen bubbles were seen. The overvoltage measured during the first evolution of gas was 0.095 volt; this, however, rose in the course of two hours to 0.165, the silver meanwhile becoming whiter and gaining a metallic luster. This experiment suggests the idea that the tendency of a metal surface to adsorb decreases as the surface becomes more crystalline, the adsorption, in all probability, being due to crystallizing forces that are unsaturated in the amorphous material.

The fact that large bubbles occasionally cling to the electrodes caused us to doubt, for a time, the theory as outlined. Such bubbles, which remain stationary in size even when much smaller ones are being formed on the same electrode, are the result of the union of many smaller ones. The phenomenon is particularly evident when hydrogen is evolved from mercury and zinc. It is probable that these bubbles are not in immediate contact with the electrode, but are adsorbed through an intermediate layer of electrolyte, or are attached to a superficial oxide film.

5. Zero Overvoltage and "Undervoltage."

With electrodes of platinum and palladium, Thiel and Breuning[1] found 0.00000 ± 0.00001 for the overvoltage, which they define as the minimum potential necessary to yield bubbles. We were unable to repeat this result for either metal for electrodes from which hydrogen *gas* was being evolved. To test the effect of the purity of the platinum, electrodes were made from Heraeus wire and platinized with platinic chloride prepared from the same metal. With these electrodes overvoltages of the same order as those given in Table I were observed. The authors mentioned have anticipated the foregoing theory in a number of particulars, but have discarded it on account of their observation of zero overvoltage, and also because of their measurements in solutions containing "bathotonic" substances, *i. e.*, substances which lower the surface tension. If the electrode surface remains unchanged, such substances should, by Equation 4, produce a decrease of the overvoltage. An increase in this quantity, was, however, always observed. By the Gibbs-Thompson law, substances that lower the surface tension are those which are adsorbed. For this reason it appears probable that the addition of these "bathotonic" substances modifies the nature of the electrode, as well as the gas-electrolyte, surface. It is significant also that very small bubbles were observed to leave electrodes immersed in the solutions with the lower surface tensions.

Phenomena that may explain the discrepancy between our results and those of the authors mentioned, appeared when we were trying to repeat

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[1] *Z. anorg. Chem.*, 83, 329 (1913).

their work. If the exciting current is gradually decreased below the amount necessary for the evolution of gaseous hydrogen, the overvoltage will fall to zero and then assume negative values. In other words, the overvoltage becomes an "undervoltage." It is probable that this is an effect produced by local heating, as the potential, even when a small current is flowing, slowly returns to zero.

The reversibility of the reference hydrogen electrodes (in G_3 of Fig. 1) was investigated by approaching the equilibrium from both sides. One of the electrodes was supersaturated with hydrogen by closing the circuit between it and the zinc electrode in G_1. The other electrode in G_3 had, presumably, reached equilibrium from undersaturation. The voltage measurements changed with time in the same manner as those described in the preceding paragraph: the initial overvoltage (of the supersaturated electrode when compared with the other) dropped, in the course of several hours, through zero; the undervoltages, however, disappeared in several more hours, and the two electrodes, without having been connected, assumed the same potential within 0.01 millivolt. The reference electrodes were evidently in true equilibrium under normal conditions.

6. Microscopic Examination of Various Electrodes when Evolving Hydrogen.[1]

In order to determine the sizes of bubbles from various electrodes, a simple cell was devised by which an electrode could be put into the field of a low power microscope, the eyepiece of which carried a scale of 60 divisions to a millimeter. The cell also contained a zinc electrode. The electrical connections, which were similar to those of Fig. 1, made it possible to evolve bubbles at any desired rate. No attempt was made to determine the overvoltages as their relative magnitudes are sufficiently well known.

From platinized platinum the bubbles came off, at low current densities, from one spot on the electrode, their radii varying from 0.025 to 0.02 mm. From smooth platinum, which has a higher overvoltage, the bubbles were distinctly smaller (0.008 mm. and less). With a silver (overvoltage about 0.15) wire sealed into glass the bubbles came from far down in the junction of the two substances. If, however, the wire was fastened into the glass with cement, the bubbles were evolved on the surface of the wire from several favored spots, probably minute crevasses in the material; they were of 0.015 to 0.025 mm. radius, and evidently formed by the union of a number of smaller ones, since the growth was a series of jerks. By lightly tapping the cell much smaller bubbles left the electrode. Nothing equivalent to the last two phenomena could be ob-

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[1] With the exceptions given in the text, the experiments described in Parts 6 and 7 were carried out, by the senior author, in the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology.

tained from platinum electrodes. The observations on copper (overvoltage about 0.25) were similar to those on silver. With these two metals small bubbles evidently form in the pores of the metal and combine on the way to the surface. The mercury electrode consisted of a small cup of the liquid with a platinum connector at the bottom; from this, at low current densities, the hydrogen bubbles formed at the glass surface, far below the upper meniscus of the mercury. This effect has been noted by Lewis and Jackson,[1] who found widely varying values for the overvoltage of this element. The very high overvoltage of mercury is undoubtedly due to the fact that nuclei cannot remain on its constantly shifting surface, and unless held between the glass and the mercury, they have to be constantly re-formed.

7. Overvoltage and Pressure.

Since the pressure p occurs in the denominator of the equation

$$FE = \frac{3RT}{2pr}\gamma \tag{4}$$

the overvoltage should increase with a decrease of p, and *vice versa*, provided the bubble radius r is a constant. The only published experiments dealing with this matter are those of Newbery,[2] who determined the overvoltage of oxygen on platinum, and of zinc on zinc,[3] the experiments were, however, made at high current densities. In the former case there was a decrease of 0.02 volt when the pressure was changed from 1 to 100 atmospheres; in the deposition of zinc there was no change in the voltage observed under the same conditions, as is to be expected, since but little volume change occurs during the reaction.

Since the preceding experiments were carried out the attention of one of the authors has been called to some unpublished work by H. M. Goodwin and L. A. Wilson, of the Massachusetts Institute of Technology, who have very kindly given permission to outline in this article some of the conclusions of their investigation. Careful measurements were made by these workers on the overvoltage of hydrogen from mercury, lead, and nickel, at pressures from one atmosphere down to the vapor pressure of the electrolyte. In each case the change of overvoltage was in the direction predicted by the foregoing theory, *i. e., the overvoltage rose as the pressure decreased.* Fig. 4, shows the magnitude of the effect when hydrogen is evolved from nickel.

To determine whether the bubble radius r is a function of the pressure p the cell shown in Fig. 5 was constructed. The electrode A of zinc was soldered to a platinum wire, which was in turn sealed through the glass

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[1] *Z. physik. Chem.*, **56**, 193 (1906).

[2] *J. Chem. Soc.*, **105**, 2429 (1914).

[3] In the article mentioned, "zinc overvoltage" refers, not, as we at first supposed, to the evolution of hydrogen from the metal, but to the deposition of zinc.

wall of the cell. B is a closed manometer with which pressures were measured from the position of the mercury thread C. The evolution of hydrogen bubbles was observed, with a microscope, from the fine platinized platinum wire E. The current was regulated by placing a counter E. M. F. between the electrodes A and E in the manner described in Part 2. The pressure was increased by causing the evolution of hydrogen from the platinum spiral F, by connecting it with the zinc electrode A. A preliminary experiment showed that this additional electrode was necessary, as the surface of E changed after prolonged evolution of gas. Observations made while the pressure changed from 1 to 16 atmospheres showed no change in the radius of the bubbles.

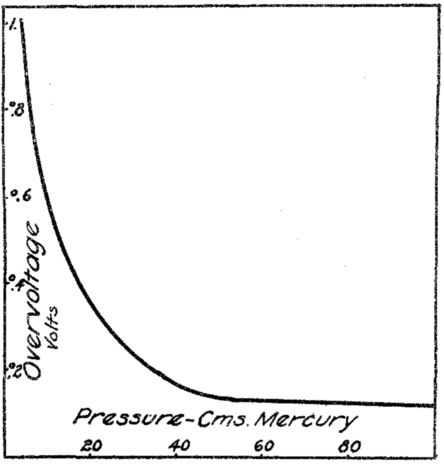

Fig. 4.

This radius is probably determined by a balance of the attraction of the electrode for, and the buoyant effect of the electrolyte on, the bubbles. Since the density of gaseous hydrogen, even at the higher pressures, is far removed from that of the electrolyte, the buoyant effect of the latter would hardly be expected to change with the pressure. The origin of the attraction of the electrode for the bubble is more obscure, but this experiment shows that it is determined more by the size than by the mass of the bubble.

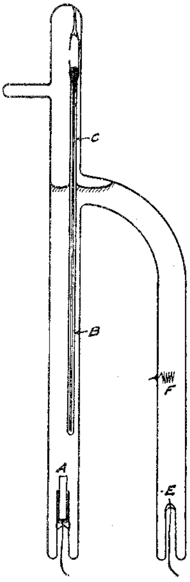

Fig. 5.

A factor, which probably explains the slow change of oxygen overvoltage with pressure, as observed by Newbery, and which must have influenced Goodwin and Wilson's work to a certain extent, is the change in the number of bubbles when the pressure is varied. As the size of the bubbles is apparently constant, or nearly so, the number of bubbles must be greater in the case of pressures lower than one atmosphere, and smaller for higher pressures. Stirring has a marked effect in lowering the overvoltage since it tends to remove the supersaturated hydrogen layer near the electrode, and the liberated bubbles have a decided stirring action. This stirring effect will decrease when the pressure is raised, and *vice versa.* That stirring by the evolved bubbles can lower the overvoltage is indicated by Newbery's[1] observation that at extremely high current densities the overvoltage drops almost to zero.

8. Discussion.

It seems desirable to consider, at this point, the theory in which overvoltage is explained by means of the assumption of the formation of the intermediate product H_1, or "nascent" hydrogen. An idea of the concentration of H_1 at equilibrium at room temperature can be obtained from the experiments of Langmuir,[2] and the free energy calculations of Lewis and Randall.[3] The latter give $\Delta F_{298} = -RT \ln K = 61{,}100$, in which ΔF_{298} is the free energy of the reaction $H_2 = 2H_1$ at 25°, K is the equilibrium constant of the reaction, and the other terms have their usual significance. From these figures the pressure of H_1 in equilibrium with H_2 at 1 atm. pressure is 7×10^{-23}, or about two atoms to a liter. A hundredfold increase of this concentration would account for an overvoltage of 0.12. These calculations undoubtedly involve an unwarranted extrapolation, and furthermore, the figures apply only to the gaseous phase, but it seems hardly possible that concentrations of any such magnitude can be the determining influence at an electrode, upon which, for instance, at the low current densities used in this investigation, at least 10^{11} molecules are liberated per sec. per cm^2.

It is quite significant, also, that although intermediate products are possible in many electrode reactions, large overvoltages are observed only for reactions in which gases are evolved. For example, intermediate products can be present in the liberation of iodine from iodide solutions, and in the deposition of copper from solutions of cupric ions, and but little or no overvoltage effects are found. Large overvoltages are, however, associated with the formation, by electrolysis, of the gases hydrogen, oxygen, and chlorine. The explanation is, of course, that no (liquid-gas) surface energy is involved in the first two reactions mentioned.

An electrode from which hydrogen is being liberated is a three-phase system not in equilibrium, and the hydrogen will tend to distribute itself in all the phases. This accounts, in part, for the complexity of the phenomena observed, especially at high current densities. A certain portion of the hydrogen will enter the metal of the electrode, the greater amounts corresponding to large concentrations of hydrogen in the electrolyte. Since the hydrogen concentration of the latter is subject to fluctuations, hydrogen will tend alternatively to enter and leave the electrode. As high "fugacities" of hydrogen are involved, this accounts

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[1] *J. Chem. Soc.*, **109**, 1066 (1916).

[2] THIS JOURNAL, **34**, 860 (1912).

[3] *Ibid.*, **36**, 1971 (1914).

readily for the pittings observed in the electrodes, by Newbery[1] and others.

9. Summary.

Hydrogen overvoltage is due, primarily, to a layer of supersaturated dissolved hydrogen in the electrolyte surrounding an electrode. If, however, the electrode can adsorb large hydrogen gas nuclei to start bubble formation the supersaturation cannot rise to high values, and the electrode will have a low overvoltage. Metals with small adsorptive powers hold small nuclei and have high overvoltages. This explanation is supported by: (*a*) experimental evidence as to the presence of nuclei, (*b*) by observations on fluctuations of the voltage during the evolution of a single minute bubble, (*c*) by a quantitative relation between the size of the bubbles from, and the overvoltage of, platinized platinum electrodes, (*d*) observations on the sizes of bubbles from electrodes of various metals, (*e*) by the agreement, with the prediction of the theory, of the direction of the variation of the overvoltage with the pressure.

URBANA, ILL., AND CAMBRIDGE, MASS.

NOTE.

"A Study of the Test for Tartrates Depending upon the Formation of the Copper-Tartrate Complex."—In a previous communication[2] on the same subject, the authors made the statement[3] that comparatively small amounts of phosphates or borates when treated by Böttger's procedure[4] respond in the same way as tartrates. Recent work along this line has shown this statement to be incorrect. A large number of experiments has demonstrated that neither of these anions, even in amounts as high as 500 mg. when subjected to the Böttger procedure gives a blue filtrate. The tests obtained were invariably negative. Efforts to account for the data originally obtained and reported were unsuccessful.

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[1] *Loc. cit.*

[2] THIS JOURNAL, 39, 2623–2630 (1917).

[3] *Loc. cit.*, p. 2629.

[4] "The Principles of Qualitative Analysis," Smeaton's translation, 1906, p. 159.