HYDROGEN OVERVOLTAGE. II. APPLICATIONS OF ITS VARIATION WITH PRESSURE TO REDUCTION, METAL SOLUTION AND DEPOSITION.

BY D. A. MACINNES AND A. W. CONTIERI.

1. The Variation of Hydrogen Overvoltage with Pressure.

In a previous article[1] it was shown that, for low current densities, hydrogen overvoltage, E, is related to the radius r, of the bubbles formed on an electrode, the pressure p, and the surface tension γ, by the expression

$$2FE = \frac{3RT}{pr}\, \gamma. \qquad (1)$$

For platinized platinum electrodes, at one atm. pressure, the agreement of observed overvoltages, and those calculated from determinations of r, was found to be quantitative. Also, it will be recalled, the variation of the overvoltage with pressure, for mercury, lead and nickel electrodes, was shown to be in the direction predicted by Equation 1. The nearly quantitative nature of this agreement was, however, not pointed out. If Equation 1 is valid, a plot of the varia-
tion of the overvoltage with the pressure should be a hyperbola, provided that the bubble radius r is a constant. In Fig. 1, where overvoltages are plotted as ordinates and pressures as abcissas, the continuous line represents the measurements of Goodwin and Wilson on a nickel electrode, and the dotted line shows the calculated values, the overvoltage at one atm. having been used in obtaining the values at the lower pressures. Although these curves have nearly the same form, the overvoltage changes with pressure somewhat more slowly than is predicted by the theory. This small
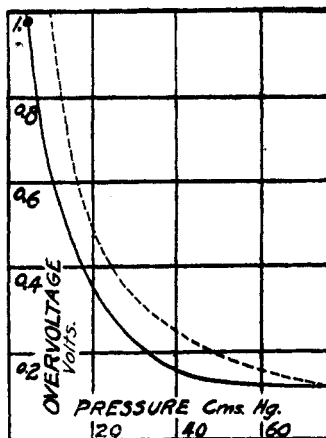

Fig. 1.

difference may be due to a slight increase in the size of the bubbles as the pressure decreases or, more probably, to an increased stirring effect, due to the larger number of bubbles formed at the lower pressures from a given weight of gas. It is interesting to observe that this theory of overvoltage, which was based mainly on observations, at atmospheric pressure, on platinized platinum electrodes, can be used to explain phenomena obtained with electrodes having much higher overvoltages, and at widely varying pressures.

[1] THIS JOURNAL, 41, 194 (1919).

2. Applications of the Variation of Hydrogen Overvoltage with Pressure.

The variation of overvoltage with pressure being established, theoretically and experimentally, it becomes important to study the effect of pressure on chemical processes involving the evolution of hydrogen in order to observe whether, in each case, changes in these processes can be predicted from the variation of the overvoltage. Three such chemical processes are: (a) the solution of metals in electrolytes, (b) reduction, in acid solutions, by metals, and (c) the electro-deposition of metals.

(a) **The Role of Hydrogen Overvoltage in the Solution of Metals. The Variation of the Rate of Solution with Pressure.**—When a piece of a metal is placed in a solution of an electrolyte there is a tendency for the metal to form ions, i. e., to split into ions and electrons. With metallic iron, for instance, the following reaction tends to take place:

$$Fe = Fe^{++} + 2\epsilon \qquad (2)$$

However, no chemical action will follow unless another reaction, involving the absorption of the electrons, can also occur. In the absence of oxidizing agents the only possible reaction is

$$2H^+ + 2\epsilon = H_2 \qquad (3)$$

and this will take place only when the potential between the metal and the electrolyte is greater than the lowest potential at which Reaction 3 can proceed in the system. Any factor which tends to decrease the velocity of Reaction 3, i. e., which increases the overvoltage, will, of course, decrease the rate of solution of the metal.

Watts and Whipple[1] have found that, contrary to statements in the chemical literature, a decrease of the gaseous pressure will produce a reduction of the rate of solution of metals in acids. These workers, however, attribute the decreased corrosion in the acid solutions which were under reduced pressure, to the absence of oxygen. As it seemed probable to us that this effect is, largely at least, due to an increase of the overvoltage with decreased pressure, we repeated the experiments on zinc, cadmium and iron, taking care to exclude oxygen from all the solutions. In these experiments two test pieces of each metal were cut so as to expose very nearly the same area, and weighed. The pieces were then placed in separate test-tubes containing the same volume of acid from which the air had been removed by boiling under reduced pressure. One of these tubes was then connected to a vacuum pump, and a stream of hydrogen at atmospheric pressure was passed through the other tube. After the reaction had proceeded for some hours the test pieces were removed, dried, and again weighed. A few typical results of such experiments are given in Table I.

[1] *Trans. Am. Electrochem. Soc.*, 32, 257 (1917).

TABLE I.

The Solution of Metals in Normal Sulfuric Acid.

Metal.	Time. Hours.	Loss in wt. per sq. cm. area. Mg.	
		At. atm. pressure.	At 8 cms. Hg.
Zn................	6	15.4	9.90
Fe................	4	11.01	6.52
Cd................	7	0.42	0.42

Since, at the lower pressures, a given mass of gas occupies a larger volume than at atmospheric pressure, the agitation of the solutions was greater when under partial vacuum, but, at least in the cases of zinc and iron, the rate of solution was much decreased. Cadmium was, however, but slowly acted upon by the acid and no bubbles were observed to leave its surface, the liberated hydrogen evidently dissolving and diffusing away. Under these conditions no change of the overvoltage with pressure is to be expected, as no (liquid-gas) surface energy is involved. On comparing our results with those of Watts and Whipple it seems probable that, although the effect described is responsible for the greater portion of the change of the rate of solution with pressure, oxygen also aided in the solution of the metals in the experiments they carried out at atmospheric pressure.

If a piece of platinum is attached to a sample of cadmium the latter will enter solution rapidly enough to cause an evolution of gaseous hydrogen. In this case we found that the rate of solution of the metal was decreased from 4 mg. to 1.4 mg. per sq. cm. in 23 hours by decreasing the pressure from atmospheric to 11 cm. Hg. The test pieces were prepared by soldering a given length of platinum wire to each sample of cadmium. The soldered joint was covered with paraffin while in the acid.

Copper, although normally below hydrogen in the electromotive series, will dissolve with an evolution of hydrogen when placed in a strong potassium cyanide solution. As is well known, this is due to a very low copper ion concentration in the solution, caused by the formation of complex ions. In this case also the rate of solution was greatly decreased by lowering the pressure. At atmospheric pressure 1.7 mg. per sq. cm. dissolved in 5 hours. This was decreased to 1.0 mg. per sq. cm. in the same time by reducing the pressure to 11 cm. of Hg.

It also follows from the theory that an increase of pressure above that of the atmosphere will result in a decrease in overvoltage. The rate of solution of a metal, when the reaction is accompanied by a liberation of hydrogen, should thus be increased by an increase of pressure. To test this point two nearly identical samples of sheet iron were placed into tubes, A and B, containing the same volume of 0.5 N hydrochloric acid. The air was pumped out of Tube A and the reaction was allowed to proceed at ordinary pressure in an atmosphere of hydrogen. In Tube B was

placed a simple pressure indicator consisting of a capillary tube closed at one end and with a drop of mercury initially near the other end. After replacing the air in Tube B with hydrogen it was sealed up, and the gas generated by the progress of the reaction caused a rise of pressure to nearly 10 atmospheres. After 16 hours, the losses in weight of the pieces of iron in Tubes A and B, were respectively, 18.1 and 34.2 mg. per sq. cm., the latter figure being, of course, the result of pressures varying from 1 to 10 atm. It was interesting to note that, throughout the experiment, there was no apparent change in the rate of the reaction as judged by the rate of evolution of hydrogen bubbles, although when the pressure in the Tube B reached its maximum, a bubble of a given size in the latter Tube represented 10 times the mass of hydrogen that it did in the Tube A. As nearly as could be estimated, the bubbles were of the same size in both tubes.

(b) **The Variation, with the Pressure, of the Efficiency of Reductions by Metals.**—When the reduction of a compound is carried out in aqueous solution with the aid of a metal above hydrogen in the electromotive series, the efficiency of the reduction is usually decreased because of the evolution of hydrogen. For example, when a piece of iron is placed into a slightly acidified solution of ferric chloride the metal dissolves according to the reaction

$$Fe = Fe^{++} + 2\epsilon. \qquad (2)$$

The two reactions that compete for the liberated electrons are

$$Fe^{+++} + \epsilon = Fe^{++} \qquad (3)$$

and

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

Here we can predict that a decrease of pressure will, by increasing the over-voltage, reduce the velocity of Reaction 1, with the result that the efficiency of the reduction represented by Reaction 3 will be increased. Several series of experiments were carried out in which pieces of iron, of constant area, were placed in contact with acidified ferric chloride solutions at a series of pressures. The results of one series are given in Table II.

TABLE II.

Pressure. (Cm. Hg.)	Equivalents of $FeCl_3$ reduced in 90 minutes.
8.0	0.415
8.5	0.400
17.0	0.363
20.2	0.259
22.0	0.280
25.6	0.240
32.0	0.220
36.8	0.095
76.0	0.078

The solution contained 0.625 mole per liter of ferric chloride and 0.17 mole per liter of hydrogen chloride, 20 cc. being used in each experiment. The pieces of iron exposed 3.08 sq. cm. area to the solution. The amount of ferric iron remaining after each reduction was determined with the help of a colorimeter. The figures on Table II are also plotted in Fig. 2 in which ordinates represent ferric iron reduced and abscissas pressures in cms. Hg. Although the points are scattered the drift is clearly very similar to that of the overvoltage-pressure curve given in Section 1. The continuous line in the figure is a hyperbola. A number of attempts were made to secure data that would yield smoother curves, but without success, the difficulty being, in all probability, the variability of the surface of the iron. As suggested, the rapidity and efficiency of the reduction
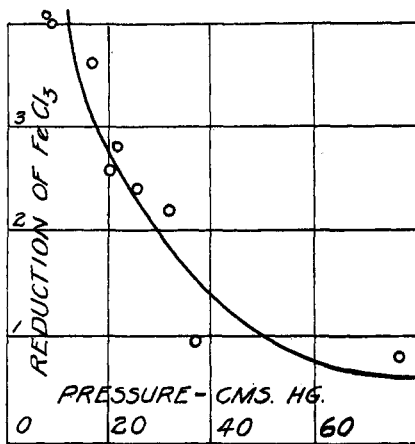

Fig. 2.

appears to be closely related to the overvoltage of the iron. Very similar results to the above were obtained with zinc as the reducing metal.

It appears probable that the speed and efficiency of a large class of reductions can be increased by carrying out the reactions under diminished pressure. Further work on this subject will be carried out in this laboratory.

(c) **The Effect of Variation of Hydrogen Overvoltage on the Efficiency of the Electrolytic Deposition of Metals.**—If hydrogen were evolved at a cathode at its reversible potential, under all conditions, no metal higher than hydrogen in the electromotive series could be deposited electrolytically from aqueous solutions. The fact that metals as high in the series as zinc can be obtained in this way is due, of course, to the fact that the overvoltages of the metals are of the same order of magnitude as the potentials between the metals and the electrolytes from which they are deposited. In all such depositions, however, the current efficiencies are decreased because of the evolution of hydrogen. It is to be expected, therefore, that any factor which tends to increase hydrogen overvoltage will increase the efficiency of the deposition of a metal above hydrogen in the electromotive series.

To determine whether the effect of reduction of pressure is in the direction predicted, a study was made of the deposition of zinc from ($1/_2$ molar) zinc sulfate solution. Two cells, each containing an anode and cathode of zinc, were placed in series in a circuit containing a copper coulometer.

One of the cells was arranged so that the electrolysis could be carried out under reduced pressure. The two cathodes, which were made as nearly alike as possible, were weighed before and after each electrolysis. The current density was kept at 3 milliamperes per sq. cm. Table III gives the efficiencies at a series of pressures.

TABLE III.

The Effect of Pressure on the Efficiency of the Deposition of Zinc.

Pressure, cm. Hg........................	76	13	11	7	6
Efficiency, %........................	75	81.0	92.4	94.5	97.5

The efficiency at atmospheric pressure is the mean of 4 values differing by several per cent. As in the case of reductions at the surfaces of metals, it is difficult to obtain reproducible results. The increase of efficiency with a decrease of pressure is, however, unmistakable. A similar, although smaller, effect with decrease of pressure, was found in the deposition of iron.

It should be emphasized here that the effects described in this paper are obtainable only for comparatively slow reactions and for low current densities. A violent evolution of hydrogen gas apparently breaks down the layer of supersaturated hydrogen solution which is responsible for the overvoltage.

3. Further Discussion of Overvoltage Fluctuations.

A topic that deserves more consideration than was accorded it in the previous communication is the somewhat puzzling observation that the formation of a single minute bubble can determine the potential at an electrode with an area several thousand times the surface covered by the
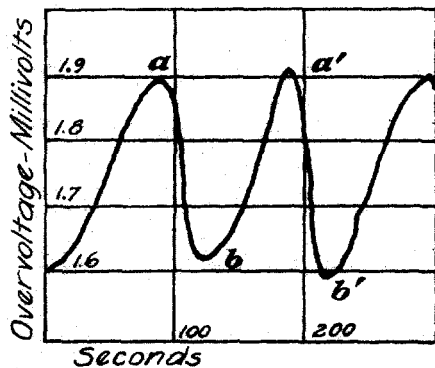

Fig. 3.

bubble, as was the case in the experiments described. Fig. 3 represents a typical fluctuation of the overvoltage with time. As explained in the former article, at point b a bubble has separated, leaving a nucleus attached to the electrode, which is surrounded by a solution of hydrogen in equilibrium with bubbles the size of the one which has just separated. At a', however, a concentration is reached at which the nucleus can grow, after which a very rapid drop in the potential is observed. This drop is due, in all probability, to an ionization of a portion of the dissolved hydrogen (according to the reaction $H_2 = 2H + 2\epsilon$) and the reappearance of an equivalent amount of hydrogen in the bubble. It will be recalled that as the bubble grows the equilibrium concentration of dissolved hy-

drogen decreases, since the "solubility" of small bubbles is greater than that of larger ones. The electrolyte immediately surrounding the growing bubble is, therefore, less concentrated than at points on the surface of the electrode removed from the bubble. These differences of concentration produce short-circuited concentration cells, the operation of which results in the formation of hydrogen ion from dissolved molecular hydrogen at points where the latter is more concentrated, and the reverse reaction at the bubble or in the adjacent electrolyte.

4. Summary.

The increase of hydrogen overvoltage with diminished pressure is shown to follow, in a nearly quantitative manner, from the theory advanced by MacInnes and Adler.

A study has been made of the effect of change of gaseous pressure on several chemical processes involving the evolution of hydrogen. The changes in rates of reaction and in reaction efficiencies were found in each case to be in the directions which follow from the change of hydrogen over-voltage with pressure, *i. e.*, a decrease of gaseous pressure produces (*a*) a decrease of the rate of solution of metals in electrolytes, (*b*) an increase in the efficiency of reductions by metals, and (*c*) an increased efficiency of metal deposition.

The theory explaining the fluctuation of overvoltage accompanying the evolution of a single bubble from a platinum electrode is more fully discussed.

CAMBRIDGE, MASS.

THE EFFECT OF PRESSURE, AND OF DISSOLVED AIR AND WATER ON THE MELTING POINT OF BENZENE.

BY THEODORE W. RICHARDS, EMMETT K. CARVER AND WALTER C. SCHUMB.

The need of a large number of accurately determined fixed points for standardizing thermometers is too well understood to need comment. The transition temperatures of the hydrated salts seem to be the points best suited for this purpose, although the freezing points of pure liquids are also convenient. To give a useful fixed point the liquid adopted must not only be one that may be easily and surely purified, but it must also have a high latent heat of fusion. This last is important for two reasons: because such a substance sooner compensates for loss of heat through the walls of the container or gain from stirring, and because the effect of impurities on the freezing point is inversely proportional to the latent heat of fusion.