

XXVI.—*The Effect of Hydrogen-ion Concentration on the Electrode Potential of Iron.*

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CORROSION of iron in practical cases is almost entirely due to the electrolytic effect of currents flowing between points on its surface which are in different electrical conditions. A trace of moisture on the surface is sufficient to permit corrosion to take place in this manner. The existence of such differences in electrode potential is known to be caused to a great extent by differences in exposure to oxygen of adjoining regions in the corroding iron. It is also known that the electrode potential of iron varies greatly with other external conditions, and it is important to know what effect the variation of some of these conditions will produce. The two most powerful factors in determining the behaviour of a corroding iron surface are (i) exposure to oxygen, and (ii) the hydrogen-ion concentration of the electrolyte causing corrosion.

It was thought that an investigation of the electrical behaviour of iron surfaces under varying conditions of p_{H} would give information of fundamental importance, provided that the initial difficulties in the realisation of a standard reproducible state could be overcome. It was further hoped that, with rigorously simplified conditions, results of theoretical interest might be obtained which would throw light on the general mechanism of the production of electrode potentials.

A previous investigation (McAulay and Bastow, J., 1929, 85) led to the recognition of a standard condition in neutral solutions, and gave the results of varying the degree of exposure to oxygen of a surface brought to this standard state. The present paper is mainly concerned with an investigation of the effect of varying hydrogen-ion concentration on electrode potential in an air-free solution. The results differed according to the anion present, but

were completely reproducible with the two anions (chloride and phosphate) investigated. Further experiments were carried out in solutions in a normal state of aeration; here no attempt was made to obtain accurate quantitative reproducibility, but certain large-scale effects are described which were qualitatively reproducible. In particular, conditions were observed where, with an extremely small change in p_H , a very great change in electrode potential was brought about.

EXPERIMENTAL.

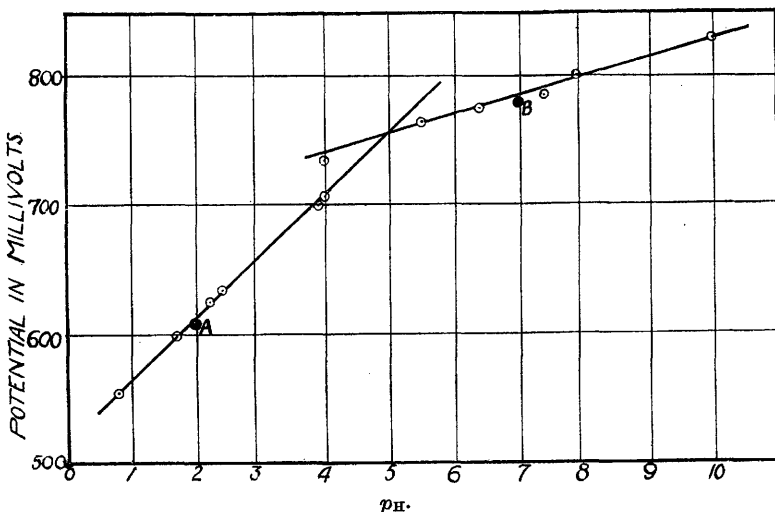
The apparatus and experimental technique for obtaining an iron electrode in an air-free solution and for measuring its potential were the same as in the previous paper (*loc. cit.*). $M/5$ -Solutions of potassium chloride and potassium phosphate were used, and the p_H was lowered by adding to each its appropriate acid, or raised by adding sodium hydroxide. The p_H naturally altered when the unbuffered solutions in the neighbourhood of neutrality were boiled; and it also changed, when on the acid side, owing to dissolution of oxide from the electrode. The solution was tapped and the p_H measured when equilibrium had been reached and the electrode was at a steady potential. The p_H measurements were made by the use of appropriate indicators standardised by solutions of the B.D.H. Universal Buffer, which were in their turn standardised with a hydrogen electrode, as it was found that they changed considerably with time. Some difficulty was experienced in obtaining steady conditions when the electrolyte was alkaline, probably owing to a decreasing tendency for destruction of the oxide film formed on the electrode before immersion. Up to a p_H of about 10, this difficulty could be overcome by the passage of a quantity of electricity of the order of 100 millicoulombs to the electrode as cathode. The electrode would in these conditions polarise to a high negative potential (of the order of 1.0 volt on the saturated calomel scale) and, when this polarisation had disappeared, would be found to be in a steady reproducible condition. The inconsistency between this effect of current and that found in the case of neutral solutions described in the earlier paper is a real one, and it is intended to make this and certain other peculiarities the subject of further investigation.

At higher alkalinity than p_H 10, it was not possible to bring iron to an electrically reproducible state. The electrode then showed all the features associated with the presence of a film of oxide, gradually drifting to an indeterminate potential of the order of -0.4 on the standard calomel scale.

Results.

(a) *In air-free solutions.* Fig. 1 shows the relation between p_H and equilibrium electrode potential of pure iron* against the saturated calomel electrode. Fig. 1(a) represents points given by potassium chloride and Fig. 1(b) those given by potassium phosphate. The solution was $M/5$ in anion concentration, with the exception of the most acid point on the chloride curve and of the two check points *A* and *B* in Fig. 1(a).

FIG. 1 (a).



Equilibrium potentials (saturated calomel scale) in $N/5$ -KCl (point A, electrolyte = $N/100$ -Cl'; point B, electrolyte = $4.2N$ -Cl'.)

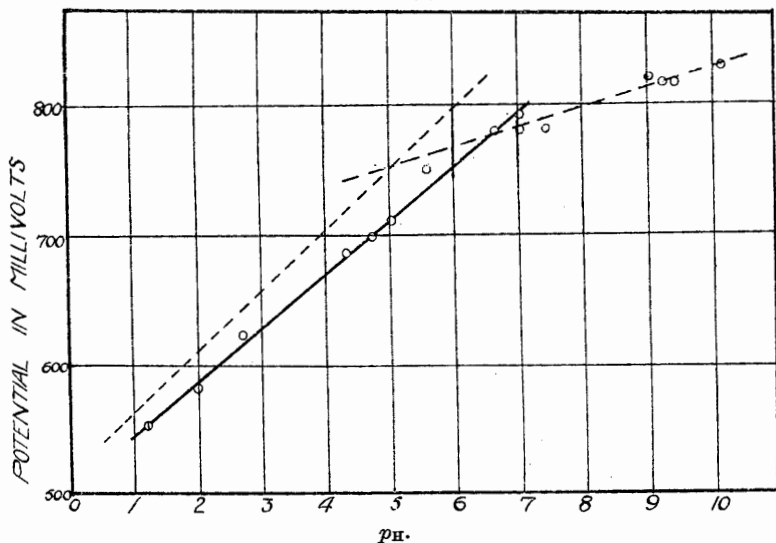
These final equilibrium potentials required very different times for their establishment. The rise in the extreme alkaline region was very slow indeed, and the slightest trace of oxygen would prevent an equilibrium potential being reached, presumably owing to the formation of an oxide film which caused the potential to drift to a more positive value than the equilibrium potential. Difficulties of a different sort were encountered in the acid region, where the potential tended to become unsteady at a higher value than the equilibrium potential. In the neutral region with chloride solutions, difficulty was experienced in maintaining the p_H constant and in measuring its true value in the cell. Occasionally, in

* The iron electrodes were supplied by Hilger and the following analysis given: Sn, 0.02; Pb, 0.001; As, 0.005; P, 0.010; Mn, 0.031; Mo, 0.05; Cu, 0.04; Ni, 0.007; Cr, 0.016%; Si and Sb, traces; Al, Mg, Ca, Ti, V, none; Co is not mentioned.

making check experiments, an indicator was introduced into the cell.

It will be seen that in each case the relation between p_H and equilibrium electrode potential is expressed fairly exactly by a pair of straight lines, the one of less slope in the alkaline region being the same for both anions, but that in the acid part being specific for each anion. A tentative explanation is attempted later.

FIG. 1 (b).



Equilibrium potentials (saturated calomel scale) in $M/5$ -phosphate solutions. [The broken lines are reproduced from Fig. 1 (a).]

In order to test whether the concentration of the anion had any effect on the potential at a given p_H , experiments were made with concentrations of $N/100$ - and of $4.2N$ -potassium chloride [points *A* and *B*, respectively, Fig. 1(a)]. In both cases the equilibrium values are seen to be practically on the curve, although peculiarities were noticeable in their establishment.

(b) *In solutions not rendered air-free.* The behaviour of electrodes in such solutions was so complicated that no standard quantitative work was attempted. Certain large-scale effects were observed, however, which seem to be of importance. In phosphate solutions, a definite critical p_H exists (between 7.5 and 8.5) on the alkaline side of which the equilibrium potential of a freshly-ground electrode starts at about -0.31 (saturated calomel scale) but falls in about 10 mins. to about -0.3 , at which it remains constant; on the acid

side, however, the potential rises rapidly to the neighbourhood of -0.8 and then remains constant. In chloride solutions no such critical p_H for equilibrium potentials exists: for solutions as alkaline as $p_H 9$ the potential very slowly drifts to a value near -0.7 .

Discussion of Results.

(a) *Air-free Experiments.*—The following tentative theory is advanced to explain the results shown in Fig. 1. The steeper straight line on the acid side of the curve represents the deposition of hydrogen by direct replacement of iron, the electrode in this region behaving directly as a hydrogen electrode with high negative potential due to overvoltage. This theory views the deposition of hydrogen as similar to its electrolytic deposition. The stream of ferrous ions leaving the metal and balancing the positive current caused by the hydrogen is thought to have no effect on the overpotential. Experiments on the simultaneous deposition of metal and hydrogen ions suggest that this should be the case (McAulay and Bowden, *Phil. Mag.*, 1926, **1**, 1282).

This theory immediately accounts for the fact that the slope of the line is less than 0.057 volt per p_H unit, for hydrogen evolution is more rapid the higher the concentration of the acid. It also accounts for the different lines obtained with chloride and phosphate. In the first case, deposition takes place at a clean iron surface, and in the second, at a surface of insoluble ferrous phosphate, and the overvoltage would be expected to have a different value.

There seems considerable difficulty in explaining the less steep straight line representing the more alkaline part of the curve, where evolution of bubbles does not take place. It is thought that it is determined by hydrogen overpotential and that the iron is effectively a hydrogen electrode. If the potential were determined by ferrous ions depositing on a clean iron surface, it would be at least 0.2 volt more negative than that observed; while ferric ions would be deposited till a concentration of less than $10^{-15}N$ was left in solution before they could be in equilibrium with an iron surface at this potential. The electrode cannot be acting as an oxidation-reduction electrode for ferrous and ferric ions, for the concentration of ferric ions at such a potential would have to be of the order 10^{-20} of that of the ferrous ions. It is impossible to conceive of such minute traces of an ion in the electrolyte determining the potential of the electrode when there is nothing to prevent the solution of ferrous ions from the iron. It appears probable, therefore, that hydrogen determines the electrode potential.

Another possibility is that the electrode surface throughout this part of the curve is in a different condition from that in which

there is direct replacement of iron by hydrogen, and that it has not the character of a clean iron surface. Possibly, the observed potential is characteristic of the equilibrium between ferrous ions in the solution and ferrous ions in some oxide lattice on the electrode surface. It is hoped that experiments with other metals will afford information as to the reason for this different slope.

(b) *Experiments in Solutions not rendered Air-free.*—The explanation of the qualitative results observed with these solutions is believed to be as follows. In the case of the phosphate, the definite positive potential obtained at p_H values greater than 8.5 is due to the formation of an oxide skin which the feeble disintegrating powers of the phosphate ion are unable to destroy. The negative potential obtained at smaller p_H values is believed to be due to the formation of a film of insoluble ferrous phosphate. The chloride ions, on the other hand, have a powerful disintegrating effect on the oxide film, and the final potential observed in aerated solutions is the result of the opposing effects of destruction of the film by chloride ions and its repair by dissolved air. Experiments with potassium sulphate indicated a much less energetic disintegration of the film by sulphate ions than by chloride ions.

Summary.

Examination of the electrode potentials of pure iron in air-free solutions of various p_H containing potassium chloride or phosphate has led to results of a standard and reproducible nature, which should provide a foundation for work of a more directly practical nature where conditions are necessarily more complicated. The curves showing the relation between p_H and equilibrium potential split up into two straight lines of different slope, and a discussion of these is attempted.

Experiments have also been made with solutions not rendered air-free, and a very marked discontinuity of the curves has been observed in the case of the phosphate solutions.

In conclusion, our best thanks are due to the Commonwealth Council for Scientific and Industrial Research for the generous grant that we have received from them which has made it possible to carry out the work described in this paper. In addition, attention is drawn to an oversight in a previous paper on this subject (J., 1929, 85), where it was intended to make a similar acknowledgment of an earlier grant made for the same purpose by the C.S.I.R.