KINETICS OF ELECTRODE PROCESSES ON THE IRON ELECTRODE

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The behaviour of the iron electrode in alkaline solutions is characterised by the complexity of the electrode processes due to the diversity of compounds which iron forms with oxygen. The interest of investigators was early attracted by this problem. Faraday was the first to state that the presence of oxygen on the surface of iron hinders its dissolution in acids and this has been repeatedly confirmed in later investigations. In the case of the anodic dissolution of platinum in acids Ershler [1] succeeded in determining the least amount of oxygen necessary to retard appreciably the kinetics of the reaction. It is considerably less than that needed to form a monolayer.

In the experiments reported in the present paper we determined the amount of oxygen needed to passivate an iron electrode under various conditions and showed that it, too, may be very small.

I. Influence of an Oxide Film on the Anodic Passivation of Iron in Alkaline Solutions.

The process of anodic oxidation and cathodic reduction of iron in alkaline solutions was studied by Förster and others [2] especially in connection with the problem of the nickel-iron cell. In his experiments with powdered iron electrodes, Förster established that iron which has been preliminarily subjected to cathodic reduction forms $Fe(OH)_2$ upon anodic polarisation. This process comes to an end due to passivation of the iron after a certain amount of electricity has passed through the electrode. The mechanism of such anodic passivation of iron in alkaline solutions has been but sparingly studied so far.

It was shown by a number of investigators that the oxide film formed when iron is exposed to gaseous oxygen passivates the surface of the

[1] Ershler, *Acta Physicochim.*, 1944, **19**, 139.

[2] Förster, *Z. Elektrochem.*, 1910, **16**, 461 ; Faust, *ibid.*, 1907, **13**, 161 ; Krassa, *ibid.*, 1909, **15**, 490 ; Grube and Gmelin, *ibid.*, 1920, **26**, 459.

...on electrode.[3] However, the least amount of oxygen necessary for passivation was not determined. We undertook some experiments to clear up this point. The method used in these experiments has been described in details elsewhere.[4, 5]

The experiments were carried out with smooth iron electrodes made of Hilger spectroscopically-pure iron rods or wire from the same material. The true surface of the electrode was 2-3·5 times greater than the apparent surface depending on the previous treatment and was determined from the amount of oxygen taken up by activated adsorption.[4] On smooth iron at room temperature, polarisation curves similar to Förster's had not been obtained so far due to the fact that even after cathodic polarisation the electrode surface did not become active. In order to obtain a smooth electrode in the active state it is necessary to remove oxygen from the electrode surface; this was accomplished by heating the iron in hydrogen at 600° C. and then transferring it to a solution saturated with hydrogen without exposure to air.[5]

The anodic polarisation curves obtained after this treatment have two arrests corresponding to processes which take place at constant potentials. The potentials in this paper if the contrary is not stated, are referred to the hydrogen potential in the same solution. The electrode does not change outwardly during the first arrest but then gradually turns brown after the second begins. The first arrest corresponds to the process, $Fe \rightarrow Fe(OH)_2$, the second, which is half as long, to the oxidation of $Fe(OH)_2$ to ferric hydroxide, which contains probably less water than $Fe(OH)_3$. Upon cathodic polarisation there appears an arrest equal in length to the second anodic arrest and corresponding to reduction of the ferric hydroxide to $Fe(OH)_2$. These conclusions respecting the stoichiometry of processes on the iron electrode are based on polarisation measurements and on the values of the potentials determined on interruption of the current; they differ somewhat from Förster's views.[2]

The yield of the first electrochemical process on the iron electrode * depends, as shown by our experiments, on a number of factors, in particular on the state of the surface. If the electrode surface is oxygen-free the yield on it is great. For example, in 2N. NaOH at a c.d. of 1×10^{-5} amp./cm.^{2} it is equal to 8×10^{-2} coulomb/cm.^{2} of true surface. After brief exposure to the air the electrode in the same solution is completely passive, i.e. the polarisation curve shows no arrests. The amount of oxygen adsorbed on the iron upon brief exposure to the air is, however, equivalent to only $2{\cdot}5 \times 10^{-3}$ coulomb/cm.^{2}. The yield increases with the concentration of the alkali.

In a recent paper [4] we have reported data on the influence of definite amounts of adsorbed oxygen on the passivation of the iron electrode. Prior to this, the kinetics of oxygen adsorption on iron at temperatures ranging from 90° K. to 500° K. were investigated and it was shown that a definite amount of oxygen, depending on the temperature, is adsorbed rapidly, whereafter a second slow stage of adsorption follows. These results agree in part with those found by other authors.[6]

The apparatus used in these experiments allowed of combining the

[3] Freundlich, Patcheke and Zocher, *Z. physik. Chem., A*, 1927, **128**, 321; 1927, **130**, 289; Evans, *Trans. Faraday Soc.*, 1923, **18**, 1; Tamann, *Z. anorg. Chem.*, 1919, **107**, 104; Kistiakovsky, *J. Physic. Chem. Soc.* (*Russ.*), 1925, **57**, 97

[4] Burstein, Shumilova and Golbert, *Acta Physicochim.*, 1946, **21**, 785.

[5] Kabanov and Leikis, *ibid.*, 1946, **21**, 769.

[6] Langmuir, *J. Amer. Chem. Soc.*, 1918, **39**, 1380; Gulbranson, *Trans. Electrochem. Soc.*, 1942, **81**, 327; 1942, **82**, 375; 1943, **83**, 301; Kochetkov, *Bull.* (*Isvestja*) *Acad. Sci. U.R.S.S.*, 1944, 320.

* The measure of the activity of iron, i.e. of its capacity to pass from the metallic state to $Fe(OH)_2$ upon anodic polarisation, is the quantity of electricity consumed in the process up to the passivation of the metal. This quantity will be called hereafter, " yield " of the electrochemical process.

gas adsorption technique with that used in electrochemical investigations. An iron wire 2·5 m. long and 0·2 mm. in diameter was reduced in hydrogen at 600° C. and outgassed at 850° at 1×10^{-5} mm. Hg; it was then allowed to adsorb oxygen and after being brought into contact with the outgassed solution was polarised anodically. The anodic polarisation curve of the outgassed, oxygen-free electrode is shown in Fig. 1 (curve 1).

These experiments showed that when oxygen is adsorbed to the amount of 2×10^{15} molecules per cm.² of true surface * i.e. to an amount corresponding to the stage of rapid adsorption at room temperature, the

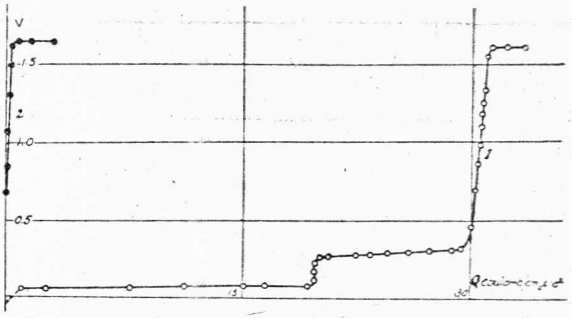

FIG. 1. — Dependence of the potential of an iron electrode on the quantity of electricity transmitted upon anodic polarisation (20°). Electrolyte 1·2 N. KOH. c.d. $1{\cdot}3 \times 10^{-5}$ amp./cm.². (1) Outgassed iron; (2) After adsorption of 4×10^{15} molecules of oxygen per cm.².

iron electrode retains its electrochemical activity at 20° C. In this case, too, the anodic polarisation curve obtained has two arrests. Entirely different is the behaviour of an iron electrode after adsorption of 4×10^{15} oxygen molecules per cm.² of true surface (Fig. 1, curve 2). In this case the electrode becomes completely passive at 20° C., i.e. the anodic polarisation curve had no characteristic arrest. The amount of oxygen corresponding to the stage of rapid adsorption on iron at room temperature is thus not sufficient to passivate the electrode.

It appeared that the amount of oxygen necessary to effect passivation could be reduced by carrying out the polarisation at — 15° C.[7] These

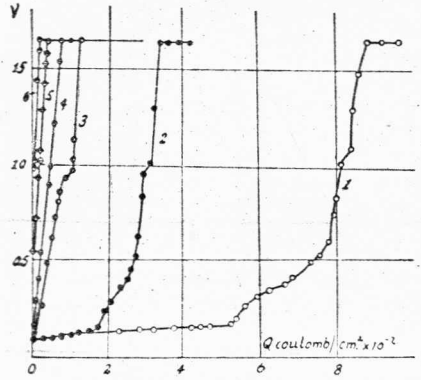

FIG. 2.—Dependence of the potential of an iron electrode on the quantity of electricity transmitted upon anodic polarisation (— 15° C.). Electrolyte 2·8 N. KOH. C.d. $1{\cdot}3 \times 10^{-5}$ amp./cm.².

(1) Outgassed iron;
(2) After adsorption of $0{\cdot}78 \times 10^{15}$
(3) " " $1{\cdot}5 \times 10^{15}$
(4) " " $1{\cdot}72 \times 10^{15}$
(5) " " $3{\cdot}5 \times 10^{15}$
(6) " " $7{\cdot}0 \times 10^{15}$

molecules of oxygen per cm.².

experiments showed that, in this case, upon the adsorption on iron of $0{\cdot}78 \times 10^{15}$ molecules of oxygen per cm.² of true surface, the yield of the electrochemical process on the iron electrode is reduced by a factor of three. Upon adsorption of $1{\cdot}72 \times 10^{15}$ oxygen molecules per cm.² of

* According to Emmett and Brunauer's data, the number of nitrogen molecules adsorbed per cm.² of true surface necessary to form a monolayer is 6×10^{14}.

[7] Burstein and Shumilova (unpublished data).

true surface, i.e. of the amount corresponding to the rapid stage of adsorption at −15° c., the iron electrode becomes passive (Fig. 2). With such an electrode the arrests on the charging curve corresponding to the formation of bivalent and trivalent iron compounds are no longer observed. Upon anodic polarisation at −15° c. there appears an arrest at 0·95 v. corresponding probably to the formation of an oxide of a higher degree of oxidation. We shall return to this question further on. These data show that the normal electrochemical process in strong alkaline solution at −15° c. ceases when the number of adsorbed oxygen molecules is approximately three times as large as Emmett and Brunauer's figure for the number of nitrogen molecules needed to form a monolayer. It is known from electronographic investigations[8] that when oxygen is adsorbed on iron Fe_3O_4 or γ—Fe_2O_3 is formed; hence when $1{\cdot}72 \times 10^{15}$ oxygen molecules are adsorbed per cm.² of true surface, the resultant oxide film, if it were homogeneous, should be ca. 5·3 A. thick. This value is less than that corresponding to a unit cell of γ—Fe_2O_3.

It should be observed that in order to shift in the anodic direction the potential of an iron electrode rendered passive through deposition of oxygen, a comparatively large amount of electricity must be still expended. Experiments have shown in this case that the sum of the amount of oxygen deposited from the gas phase and the amount of oxygen which must be deposited in the process of anodic polarisation in a KOH solution to bring the potential up to e.g. 0·9 v., is approximately constant and equal to about 7×10^{15} molecules per cm.² of true surface, which corresponds to $4{\cdot}3 \times 10^{-3}$ coulombs (Fig. 3).

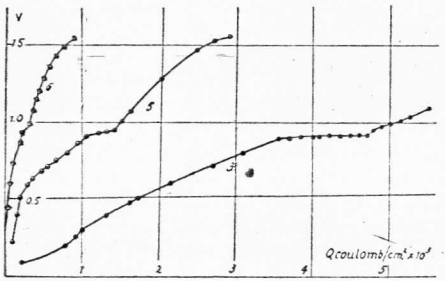

FIG. 3.—Curves 3, 5 and 6 of Fig. 2 on a different scale.

There is an essential difference between the course of the anodic polarisation of iron in dilute and in concentrated alkaline solutions.[9] If an electrode pre-heated in hydrogen is polarised anodically in a dilute solution of NaOH with sufficiently high c.d. then the iron behaves as if it were completely passive. In this case very small amounts of electricity are necessary to shift the potential of the iron electrode to the anodic side. For example, if $2\text{-}3 \times 10^{-4}$ coulomb is sent through 1 cm.² of true surface in 0·05 N. NaOH at a c.d. of 1×10^{-5} amp./cm.² the electrode potential is brought up to 0·2 v. After this treatment the electrode remains passive even if a more concentrated solution is substituted for the dilute one without exposing the electrode to the air.

The amount of electricity which passivates iron in dilute alkaline solution is therefore smaller than what is needed for the formation of an oxygen monolayer on the iron surface viz. *ca.* 4×10^{-4} coulomb/cm.².

A comparison of these data with the experiments on polarisation subsequent to the adsorption of oxygen from the gas phase leads to the conclusion that when oxygen is deposited from the gas phase the resulting film has a comparatively large number of vacant sites. This may perhaps be due to the bivalency of the oxygen molecules, which, as Langmuir has shown, makes it difficult to obtain a continuous layer. The vacant sites can interact with the ions of the solution.

[8] Nelson, *J. Chem. Physics*, 1937, **5**, 252; Winkel and Haul, *Z. Elektrochem.*, 1938, **44**, 611; Dankov and Shishakov, *Bull. (Isvestja) Acad. Sci. U.R.S.S.*, 1938, 1225.

[9] Kabanov and Leikis, *Acta Physicochim.* (in press).

2. The Mechanism of the Dissolution and Passivation of Iron in Alkaline Solution.

It has been shown in a number of experiments [9] that the yield of the electrochemical process $Fe \rightarrow Fe(OH)_2$ on an active electrode increases with increasing concentration of the alkali (Fig. 4) and decreasing c.d. The overvoltage of this electrochemical process is, however, almost independent of the concentration of the alkali and of the concentration of foreign anions (SO_4^{--}) and increases linearly with log c.d. The slope of the logarithmic curves at c.d.'s exceeding 10^{-6} amp./cm.^{2} equals 0·04 v., while at lower c.d.'s it is 0·02 v.

The capacity of the iron electrode as determined from the slope of the charging curves in dilute solutions or from the decay curves of the electrode potential when the polarising current is interrupted in the region of the first arrest in more concentrated solutions, is approximately 1500 μF/cm.^{2} of apparent surface.

On the basis of the experimental data reported above it is possible to advance a conception of the mechanism of the formation of $Fe(OH)_2$

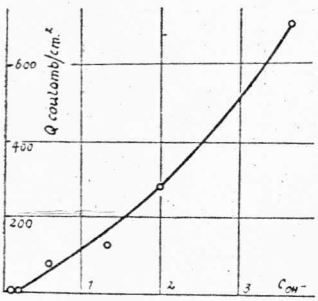

FIG. 4.—Dependence of the yield of the electrochemical process $Fe \rightarrow Fe(OH)_2$ on the concentration of the alkaline solution. The yield is given in coulomb/cm.^{2} of apparent surface.

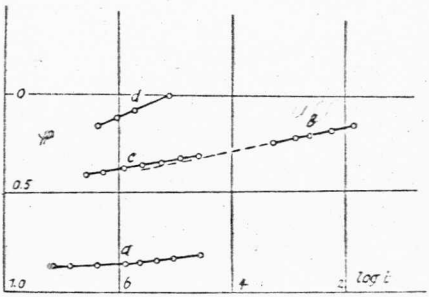

FIG. 5.—Potentials of the anodic dissolution of iron against log c.d. The potential is here referred to the standard hydrogen electrode.

(*a*) 2N. NaOH; (*b*) N. HCl; (*c*) 0·05 N. NaOH + 2N. NaCl; (*d*) 0·5 N. NaOH + 2N. NaCl.

and the passivation of iron in alkaline solutions. To this end it will be useful to compare the data on the anodic dissolution of iron in alkali with the data on the anodic dissolution of iron in acids.[10] The comparison was made by extrapolating the overvoltage curve of the anodic process $Fe \rightarrow Fe^{++}$ in acid solutions to the potentials of the anodic process $Fe \rightarrow Fe(OH)_2$ in the case of active iron electrode in an alkaline solution (Fig. 5). The comparison shows that at equal potentials the anodic dissolution of iron in alkaline solutions proceeds *ca.* 10^4 times as fast as in acids. On the other hand in alkaline solutions the anodic process on iron slows down greatly with time and is finally completely stopped due to passivation, a circumstance which does not occur in acid solutions. This indicates that the mechanism of the dissolution of iron is widely different in acids and in alkalies.

Both the greater rate of dissolution and the passivation observed in alkalies are evidently due to anodic deposition of oxygen on the iron surface which is stimulated in alkaline solutions by the large concentration of hydroxyl ions. Thus in alkaline solutions the oxygen on the iron surface plays a double role—on the one hand accelerating dissolution, on the other hand passivating the iron and bringing finally the dissolution to an end. These general considerations may be developed in somewhat greater detail.

Upon anodic polarisation of iron, $Fe(OH)_2$ is deposited in the form of

[10] Kusnezov, *J. Russ. Physic. Chem.*, 1947, **21**, 201.

a gelatinous porous precipitate weakly bound to the metal. This has been concluded from the failure to detect any ohmic resistance on an electrode covered with a deposit of $Fe(OH)_2$ although this compound is itself nonconducting. The structure of the ferrous hydroxide precipitate and its weak adhesion to the metal lead to the conclusion that it is deposited from a supersaturated solution and not formed directly from the metal. As was pointed out above, the reaction $Fe \rightarrow Fe^{++}$ is a slow process, at equal potentials, compared with the reaction $Fe \rightarrow Fe(OH)_2$, hence it cannot be an intermediate stage in the anodic formation of $Fe(OH)_2$ in alkaline solutions. As is known,[11] in alkaline solutions iron exists mainly in the form of $HFeO_2^-$ ions. Bearing in mind moreover that acceleration of the dissolution of iron in alkalies is connected with the adsorption of oxygen on iron, it is natural to assume that the intermediate product during the process of dissolution is a $HFeO_2^-$ ion which is formed on interaction of a surface iron oxide with the alkali :

$$(FeO)_{ads.} + OH^- \rightleftarrows HFeO_2^-.$$

Experiments show, however, that the potential of anodic dissolution of iron is not the reversible potential of the system $Fe/HFeO_2^-, OH^-$. A calculation of the increase in the concentration of $HFeO_2^-$ at the electrode surface on passing the current, based on the equations of non-steady diffusion (even assuming that in the initial stage of polarisation all the $HFeO_2^-$ ions formed remain in solution and precipitation of $Fe(OH)_2$ does not occur) shows that the experimentally-observed shift of the potential at the beginning of anodic polarisation of the active iron is considerably greater than what should correspond to an equilibrium potential of $Fe/HFeO_2, OH^-$.

It follows, on the other hand, from our data, that the process $Fe \rightarrow HFeO_2^-$ cannot be regarded as an irreversible reaction proceeding in one elementary act : $Fe + 3OH^- \rightarrow HFeO_2^- + H_2O + 2\ominus$. In fact, by computations similar to those used by Frumkin [12] in treating the kinetics of hydrogen overvoltage it can easily be shown that the anodic overvoltage of iron should decrease in this case by 0·12 v. when the concentration of alkali increases tenfold. This, however, does not take place. It should be noted that in computing the potential of the anodic process on iron we did not take into account the variation of the ζ-potential, as the introduction of SO_4^{--} ions into the solution does not affect the overvoltage of iron in dilute solutions.

Our data on the capacity of the iron electrode indicate that, in a certain potential range, an electrochemically-active oxygen adsorption layer is formed on the iron surface. The electrochemical deposition of oxygen may be assumed to be the first rapid stage of dissolution of iron in alkali. Judging by the magnitude of the capacity the amount of this oxygen at the potential of the first arrest comprises a fraction of a monolayer. This adsorbed labile oxygen can transform either in a surface oxide soluble in the alkali, or in a more firmly bound (passivating) surface oxide which retards further dissolution of the iron. Each of these processes requires addition of oxygen through an electrochemical reaction.

These considerations can be put in a more definite form by means of the following scheme. The first stage, which leads to the formation of an electrochemically-active layer of adsorbed oxygen is the discharge of OH^-

$$Fe + OH^- \rightleftarrows (FeOH)_{ads.} + \ominus \quad . \quad . \quad . \quad (1)$$

This is followed by the slow discharge of a second OH^- on the electrochemically-active surface oxide :

$$(FeOH)_{ads.} + OH^- \rightarrow (FeO)_{ads.} + H_2O + \ominus \quad . \quad . \quad (2)$$

The resulting surface ferrous oxide dissolves in alkali according to the equation

$$(FeO)_{ads.} + OH^- \rightleftarrows HFeO_2^- \quad . \quad . \quad . \quad (3)$$

[11] Schrager, *Chem. News*, 1929, **138**, 354.
[12] Frumkin, *Z. physik. Chem A*, 1933, **164**, 121.

On hydrolysis of the $HFeO_2^-$ ion a deposit of ferrous oxide if formed :

$$HFeO_2^- + H_2O \rightarrow Fe(OH)_2 + OH^- \quad . \quad . \quad . \quad (4)$$

It is easily seen that the rate of dissolution of iron upon anodic polarisation computed on the basis of this scheme (eqn. (2) and (1)) equals

$$i_A = K_1[FeOH]_{ads.}\,[OH^-]\,e^{\frac{\phi F}{2RT}} = K_2[OH^-]^2\,e^{\frac{2\phi F}{2RT}} \quad . \quad . \quad (5)$$

Let us denote by ϕ_r the reversible potential of the $Fe|Fe(OH)_2, OH'$ electrode. The overvoltage of the reaction η equals :

$$\eta = \phi - \phi_r = \frac{2RT}{3F}\ln i - \frac{RT}{3F}\ln [OH^-] + const.$$

In a first approximation this agrees with our experimental data.

A similar mechanism of anodic dissolution of a metal was suggested earlier by Ershler.[1] He showed that in the presence of Cl^- ions the dissolution of platinum proceeds, not by direct transition of hydrated metal ions into the solution, but by way of formation of an intermediate surface platinum chlorine complex. In our case the hydroxyl plays the part of the chlorine.

Let us now consider the transformation of the electrochemically-active oxide into the passivating surface compound. As was observed above, iron is passivated when very small quantities of passivating oxides are formed on the surface. Inasmuch as a considerable amount of iron is dissolved in the time necessary for passivation, the active surface oxide obviously goes over into the soluble form many times faster than into the passivating one. At the same time the passivation process is more accelerated with increasing potential than the process of dissolution, as appears from the decrease of the yield of the process $Fe \rightarrow Fe(OH)_2$ with increasing c.d. Such a relation can exist if, e.g., the passivating oxide is formed as a result of the discharge of OH^- accompanied by the transfer of two electrons :

$$(FeOH)_{ads.} + OH^- \underset{\text{slow discharge}}{\longrightarrow} \underset{\text{passivating oxide}}{(FeO.\,OH)_{ads.}} + H^+ + 2\ominus.$$

The rate of the process leading to the formation of the passivating oxide is then

$$i_p = K_3[FeOH]_{ads.}\,[OH^-]\,.\,e^{\frac{\phi F}{RT}} \quad . \quad . \quad . \quad (6)$$

The entire process of dissolution and passivation of iron in alkaline sclutions can thus be represented by the following scheme :

$$HFeO_2^- \xrightarrow{+H_2O} \underset{\text{dissolved}}{Fe(OH)_2} + OH^-$$

$$+OH^- \uparrow\downarrow$$

$$\underset{\substack{\text{soluble}\\ \text{surface}\\ \text{oxide}}}{(FeO)_{ads.}} + H_2O + \ominus$$

$$+OH^- \uparrow \text{ slow discharge.}$$

$$Fe + OH^- \rightleftarrows \underset{\substack{\text{electrochem.-}\\ \text{active surface}\\ \text{oxide}}}{(FeOH)_{ads.}} + \ominus$$

$$\text{slow discharge.} \downarrow +OH^-$$

$$(FeO.\,OH)_{ads.} + H^+ + 2\ominus$$

It cannot be claimed as yet that this scheme has been founded in all its details. We believe, however, that it renders satisfactorily the main features of the process.

We shall not consider here the kinetics of the passivation process in detail, observing merely that a considerable amount of iron is dissolved during passivation and hence the passivating oxide thereby formed must be partially removed from the surface. A complete theory should explain the progressive accumulation of passivating oxide despite its continuous removal, and take into account that the velocity of the reaction stages given by eqn. (1) and (2) decreases with increasing surface concentration of the passivating oxide. The process of accumulation of passivating oxides is probably to some extent analogous to the self-accelerating process of crystallisation. The yield of the reaction $Fe \rightarrow Fe(OH)_2$ at any rate should increase with the ratio of the initial rates of the active (eqn. (5)) and passivating (eqn. (6)) processes:

$$\theta = f\left(\frac{A}{i_p}\right) = f\left(\frac{[OH^-]^{\frac{3}{2}}}{i^{\frac{1}{2}}}\right) = f_1\left(\frac{[OH^-]}{i^{\frac{1}{3}}}\right) \quad . \quad . \quad . \quad (7)$$

where f_1 is, as yet an undetermined, increasing function of the argument $[OH^-]/i^{\frac{1}{3}}$. According to eqn. (7) the yield should fall with increasing anodic c.d. and rise with increasing concentration of the alkali, which is actually observed.

The study of the dissolution and passivation of iron in alkaline solutions and of the reduction of $Fe(OH)_2$ is being continued.

3. The Electrochemical Process at Potentials $\sim 0{\cdot}95$ v.

Upon polarisation of iron in alkaline solutions we observed in several cases an arrest of the potential at approximately 0·93-0·95 v. (with respect to the hydrogen electrode in the same solution). Small arrests near the indicated value of the potential are obtained when molecular oxygen is present in the alkaline solution during cathodic and anodic polarisation of iron electrodes. The length of these arrests corresponds to $10^{-5}-5\times10^{-3}$ coulomb which is equivalent to a quantity of oxygen ranging from a small fraction of a monolayer to a few monolayers.[13]

A similar arrest can be obtained when iron, after reduction in hydrogen and outgassing at high temperature, is anodically polarised in dilute KOH solution. In this case the length of the arrest may correspond to as much as 50×10^{-3} coulomb/cm.^{2}.[7]

A small arrest is also observed on an iron electrode partially covered with oxygen adsorbed from the gas phase ($1{\cdot}5 \times 10^{15}$ molecules/cm.^{2}), if the anodic polarisation is carried out at low temperature ($-15°$). With a larger adsorbed amount equal to 7×10^{15} molecules per unit area no arrest is observed. Hence adsorbed oxygen passivates this process too (Fig. 3).

If passive iron is treated with hydrogen peroxide which is then removed from the solution, a cathodic and an anodic arrest are also observed in the same region of potentials. The overvoltage of the process corresponding to these arrests is less than that of other processes on an iron electrode in alkaline solutions.[14] It has not been proved as yet that the arrests in all these cases correspond to the same process, nor is the question of the composition of the resultant oxide clear.

[13] Kabanov and Vanjukova (unpublished data).
[14] Kabanov and Derjaguina (unpublished data).

4. Anodic Oxidation of Iron in the Presence of Chlorine Ions.

If iron oxidised in air is anodically polarised in an alkaline solution containing sodium chloride (e.g. in 2 N. concentration), then at low concentration of the alkali the electrode potential does not rise to the potential of oxygen evolution, but reaches a maximum value and then gradually decreases. In order to explain the mechanism of this effect which was first described by Haber and Goldschmidt,[15] we investigated the processes taking place during this decrease and after a stationary potential was attained.[13]

The anodic process in this case, too, consists in metallic iron going over into $Fe(OH)_2$. However, in contradistinction to the similar process in pure alkaline solutions, in the presence of Cl^- ions it can continue indefinitely unaccompanied by passivation of the iron. The overvoltage of this process under certain conditions can reach high values, e.g. 1·4 V. and more; it increases linearly with log c.d., with a coefficient which varies from 0·04 to 0·12 V., depending on the composition of the solution. At constant c.d. the greater the concentration of Cl^- ions and the smaller the concentration of OH^- ions the lower will be the potential; the relation between the concentration of these ions and the potential is linear. However, as the ratio $[Cl^-]/[OH^-]$ is increased, the steady potential will decrease only down to a certain limit. This minimum value of the potential of anodic formation of $Fe(OH)_2$ in the presence of Cl^- ions coincides with the potential observed at the same c.d. in the case of the anodic dissolution of Fe in acids. The latter was found by extrapolating Kusnezov's [10] polarisation curve for the anodic dissolution of iron in HCl to the c.d.'s at which the iron electrode was polarised in alkaline solutions of chlorides (Fig. 5).

The difference between the dissolution of iron in alkaline solutions of chlorides and in pure alkalies and the similarity between the former process and the dissolution in acids leads us to believe that the first slow stage of the process $Fe \rightarrow Fe(OH)_2$ in alkaline solutions of chlorides is the ionization of iron $Fe \rightarrow Fe^{++}$. The second, fast stage, is the chemical reaction: $Fe^{++} + 2OH^- \rightarrow Fe(OH)_2$ with the possible intermediate formation of the cation $FeOH^+$.

The Cl^- ion allows Fe^{++} to be formed, but does not participate in the process itself. This is evident, for instance, from the fact that when the concentration of Cl^- ions in 0·01 N. NaOH solution is varied from 0·01 N. to 4 N. the rate of the process $Fe \rightarrow Fe(OH)_2$ remains unaffected and equal to the rate of the process $Fe \rightarrow Fe^{++}$ in acid at the same electrode potential. The accelerating effect of Cl^- ions on the corrosion of iron is thus due to the fact that it hinders the passivation of iron by adsorbed oxygen which otherwise would put an end to the dissolution of the iron.

As was observed above, the rate of the process takes off with increasing concentration of the alkali but not with time. This shows that a stationary concentration of the passivating agent establishes itself on the surface of the iron electrode, which increases with increasing concentration of the alkali. At sufficiently high concentrations of alkali and high c.d.'s the process $Fe \rightarrow Fe(OH)_2$ ceases completely, the iron becoming passive not gradually, as in pure alkali, but abruptly. A lowering of the c.d. reactivates the iron.

The following circumstance is essential for an understanding of the mechanism of this process. It was shown that in solutions containing Cl^- ions and OH^- ions in 2 N. concentration the charging curves of passive iron are twice as steep as in solutions devoid of chlorine ions. This means that the chlorine ions adsorbed on passive iron hinder the deposition of oxygen on the iron.

Ershler was the first to observe a decrease of the electrode capacity

[15] Haber and Goldschmidt, *Z. Elektrochem.*, 1906, **12**, 49; Britton and Evans, *J. Chem. Soc.*, 1930, 1780.

due to chlorine ions upon the polarisation of platinum in acid solutions (for references, see paper of Ershler in this issue). His explanation was that the adsorption of chlorine retards the deposition of oxygen on the platinum surface. In this case, however, the process is not a steady one, as oxygen is gradually accumulated on the surface and finally stops the dissolution of the metal. In the case of iron in the presence of Cl^- ions, if the concentration of OH^- ions is not too great, a steady process is observed.

It may be assumed that chlorine displaces the hydroxyl from the iron electrode surface and thus prevents the deposition of oxygen and consequently the formation of passivating oxides. This allows the process $Fe \rightarrow Fe^{++}$ to proceed indefinitely; on the other hand the adsorption of chlorine prevents the iron from being dissolved by way of intermediate oxygen adsorption.

An increase in the positive potential facilitates the displacement of adsorbed oxygen by chlorine ions. As a result of this, if an iron electrode becomes covered with very firmly adsorbed oxygen due to the action of air or to anodic polarisation, then upon anodic polarisation in the presence of chlorine the electrode potential first rises to a definite maximum and then gradually falls off to a steady value (Fig. 6). The anodic process in this case does not take place at first over the whole surface but only in microscopic pores of the oxide film; however, as the process continues

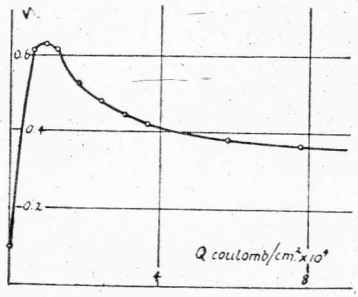

FIG. 6.—Dependence of the potential of iron previously passivated through contact with air on the quantity of electricity transmitted in

0·1 N. NaOH + 2N. KCl.

c.d. 10^{-6} amp. per cm.^{2}. Potential referred to hydrogen electrode in the same solution.

the oxide film previously formed gradually loses contact with the metal and disaggregates.

The above point of view is different from the interpretation given by Evans. It appears to us that the activating effect of anions like Cl^- is due to an adsorption effect, i.e. to the displacement of oxygen from the surface of iron, and not to a special ability for penetrating the oxide film.

The foregoing considerations on the mechanism of anodic dissolution of iron in the presence of Cl^- bear a preliminary character. Experimental facts like the linear increase of the overvoltage with concentration of the alkali and decrease with concentration of Cl^-, complete passivation upon increase in the c.d. and the accompanying periodic phenomena stand still in need of a more detailed study.

Summary.

It is shown that upon anodic polarisation in alkaline solutions at room temperature a smooth iron electrode from the surface of which oxygen was removed goes over into $Fe(OH)_2$ which is afterwards oxidised to trivalent iron. The electrochemical transition of iron to $Fe(OH)_2$ proceeds with a low overvoltage, but after some time the process ceases due to the formation of passivating surface oxides. The greater the concentration of OH^- ions the greater is the quantity of iron participating in the reaction. The iron does not go over into $Fe(OH)_2$ at room temperature if prior to anodic polarisation an amount of oxygen corresponding to $2{\cdot}5 \times 10^{-3}$ coulomb/cm^2 of true surface is deposited from the gas phase. If the anodic polarisation is carried out at $-15°$ c. the necessary quantity of

oxygen corresponded to $1 \cdot 1 \times 10^{-3}$ coulomb/cm.^{2}. Upon anodic polarisation in dilute alkali passivation sets in when the amount deposited is only 2×10^{-4} coulomb/cm.^{2} of true surface.

A mechanism is proposed to explain the relation between the formation of $Fe(OH)_2$ and the passivation of iron upon anodic oxidation. The mechanism of the anodic dissolution of iron in the presence of both Cl^- and OH^- ions in the solution is also discussed.

Résumé.

Une électrode de fer lisse, dont la surface a été débarrassée d'oxygène, est transformée en $Fe(OH)_2$ (qui est ensuite oxydé en fer trivalent) par polarisation anodique en solution alcaline à température ordinaire. Le phénomène a lieu à un faible survoltage, puis cesse par suite de la formation d'oxydes, qui rendent la surface passive. Il peut être complètement empêché, si, avant la polarisation, de petites quantités d'oxygène sont déposées en phase gazeuse sur l'électrode. On propose deux mécanismes pour rendre compte de ces faits, ainsi que de la dissolution anodique du fer, lorsque les deux ions Cl et OH sont présents dans la solution.

Zusammenfassung.

Eine glatte Eisenelektrode, von deren Oberfläche aller Sauerstoff entfernt ist, wird bei anodischer Polarisation in alkalischer Lösung bei Zimmertemperatur in $Fe(OH)_2$ verwandelt (das darauf zu dreiwertigem Eisen oxydiert wird). Diese elektrochemische Reaktion verläuft bei geringer Überspannung, aber wird nach einiger Zeit durch die Bildung von passivierenden Oberflächenoxyden aufgehalten. Sie kann verhindert werden, wenn vor der Polarisation geringe Sauerstoffmengen aus der Gasphase an der Elektrode abgeschieden werden. Es wird ein Mechanismus zur Erklärung dieser Vorgange vorgeschlagen, sowie auch einer, der die anodische Auflösung des Eisens, wenn Cl′ und OH′ zusammen in der Lösung vorhanden sind, zu erklären vermag.

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