

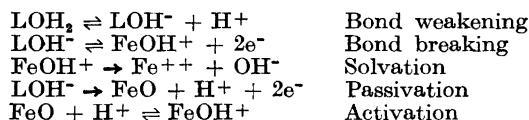
Anodic Dissolution of Iron

I. General Mechanism

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It is suggested that the kinetics of the anodic dissolution of iron is essentially governed by a mechanism in which the pH dependent and potential dependent dissociation of chemisorbed water plays a dominating role. The steps in this mechanism are



LOH_2 is a surface iron atom, still belonging to the metal lattice, with a chemisorbed watermolecule. LOH^- is a surface iron atom with a chemisorbed hydroxyl ion. FeOH^+ and FeO are adsorbed oxidized forms and Fe^{++} the solvated ferrous ion.

The system of differential equations for this mechanism is derived and solved for steady state conditions. The resulting kinetic expression is

$$s = \frac{N}{A + B \cdot h + C/h}$$

where s is the rate of dissolution and N the number of sites on the surface, able to accommodate water molecules and hence to go through the series of steps described above. A , B and C are functions of potential dependent rate constants and h is the concentration of proton donor in the solution. Experiments illustrating the qualitative validity of this expression are described.

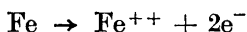
A more thorough analysis of the mechanism, both for steady state and for non steady state experimental conditions, is given, and compared with experimental results, quantitative as well as qualitative. It is shown that the general mechanism given above is in good agreement, both with new experimental findings of the present paper and with results from other laboratories.

An interesting consequence of the above is that the mechanism of passivity is the electrostatic repulsion of hydrogen ions, necessary for the dissolution of surface oxide layers. The striking influence of oxygen, dissolved in the aqueous phase, and of hydrogen, dissolved in the metal phase, is discussed on the basis of new experiments.

The apparent complexity of the anodic dissolution of iron, a process which has long been a problem of major interest, is well illustrated by the observed effects of increasing positive (anodic) potential and of the addition of hydrogen ions. When iron dissolves as an anode under conditions where the Tafel equation¹

$$E = a + b \log i \quad \text{I}$$

is obeyed, it has been reported that b (the voltage change which changes the anodic current by a factor of ten) may have values from well above 100 mV² to below 20 mV³. As current theories of electrode kinetics would suggest a value around 58 mV^{4,5} for the simple reaction



it has hitherto not been possible to give any theoretical explanation for either of these extreme values. Some workers⁶⁻⁹ maintain that 29 mV is the typical value of b in acid solution and ascribe this value to a mechanism with a "transition complex" containing two iron atoms about to dissolve, or to a mechanism in which each sequence of steps containing one rate determining step, involves the dissolution of two iron atoms.

One interesting feature of the behaviour of iron is its dissolution (no applied potential) in strong non-oxidizing acid. Stern^{10a} has found that the velocity of the process



is very nearly independent of acid concentration in the range $4 \geq \text{pH} \geq 1$ in agreement with the work of Bonhoeffer and Heusler⁸ and others. At the same time the potential of this corroding iron electrode decreases nearly 58 mV per pH unit.

In spite of the above agreement between different experimentalists some doubt nevertheless remains as yet other workers^{7,11} have found some increase in corrosion rate with increasing acidity, and a change of potential somewhat less than 58 mV/pH unit. It may be relevant that Stern^{10b} has also found that his results quoted above are valid for pure iron only and that small amounts of phosphorus or sulphur in the iron change the picture drastically. In this connection it is also important that Hoar and Hurlen⁶ found that while the Tafel line for the anodic dissolution of iron is nearly independent of impurities in the iron the Tafel lines for cathodic production of hydrogen show the highest "hydrogen overvoltage" for the purest iron. Thus it may be that the results obtained by Stern and by Bonhoeffer and Heusler are very nearly correct and that the other workers used less pure conditions. If this is not so it is still certain that a change in acidity gives an opposing change of potential so the actual rate of spontaneous dissolution of iron in strong acid is rather insensitive to change in acid concentration.

This striking feature has provoked the senior author of the present paper¹² to suggest that a rate determining step in this process is independent of potential. A change in acidity causes a corresponding change in potential so the actual "equilibrium" concentration of a "transition complex" containing the catalyzing hydroxyl ion^{13,14} is nearly independent of acidity within the limits of pH

quoted above. The transformation of this species into the final corrosion product, the ferrous ion, would then occur according to a potential independent rate law. The hydrogen evolution must then occur according to a similar pattern. These points of view will be amplified in the following and some experimental evidence for their validity presented.

The complexity of the corroding iron electrode is also reflected in the existence of the passivity phenomena. It is well known that the practical corrosionist to a certain extent protects iron from corrosion in an aqueous medium by rendering this medium alkaline. According to some of the authors mentioned above hydroxyl ions catalyze anodic dissolution of iron, as does positive potentials. Yet alkaline environments and high potentials are features generally associated with the passive state, in which the corrosion of iron is strongly inhibited. There is general agreement in the literature that the passive state of iron is due to some kind of oxide layer on iron, but at the same time there is strong controversy about the nature of this layer as far as thickness and composition is concerned. Though interesting in itself this controversy seems to be somewhat irrelevant at the present time; it seems to us that one is still faced with the problem of how an oxide layer is able to protect iron from corrosion; why it will not dissolve away under strongly oxidizing conditions but does so under more reducing conditions. It is generally assumed that the transition between the active and the passive state of iron is discontinuous, a definite potential, the so called Flade potential¹⁵ governed at 25°C by the equation¹⁶

$$E_{\text{r}} = 0.590 - 0.058 \text{ pH}$$

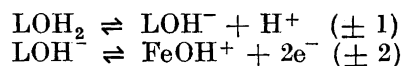
separating a negative potential region where iron is active and a positive region in which iron is passive. It is shown in the present paper that this relationship is an artefact, that the transition between a fully passive state and a fully active state is smooth and continuous, both in neutral and in strongly acid environment. It is proposed, that the mechanism of passivity is electrostatic repulsion from the oxide layer of hydrogen ions necessary for the dissolution of the oxide layer.

THE MECHANISM

The model of the iron electrode on which the following is based is a very simple one. Water is chemisorbed to the surface in a such way that there is a constant potential difference between the interior of the iron phase and the surface of chemisorbed water. Any change of potential between the iron electrode and the liquid is essentially restricted to the region outside this layer of water. A change of iron potential in a positive direction will increase the tendency of the adsorbed water to transfer hydrogen ions to the solution, *i.e.* the adsorbed water is behaving as an acid the strength of which is potential dependent. The degree of ionization of this adsorbed "acid" water is thus determined both by the pH of the bulk solution and also by the electrode potential.

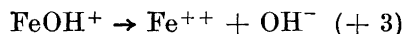
It is now suggested that the bond between a surface iron atom still belonging to the metal lattice is stable when the iron atom is accommodating an

adsorbed water molecule, but has a certain probability of breaking when a hydroxyl ion is adsorbed. This would give the following sequence of reactions:



where LOH_2 represents a surface iron atom with a chemisorbed water molecule, the iron atom still belonging to the metal lattice. LOH^- is an iron atom, also belonging to the lattice, with a hydroxyl ion, and FeOH^+ is a hydroxy ferrous ions which still belongs to the surface but no longer to the metal lattice.

The anodic dissolution of an iron atom is finally completed by a solvation step:



When anodic dissolution is proceeding at a potential far from the equilibrium potential of the Fe/Fe^{++} electrode, *i.e.* when the anodic dissolution is independent of the ferrous concentration in the solution, it should not be necessary to take a step (— 3) into consideration.

The potential dependence of the rate constants corresponding to these steps might possibly be derived in the following way:

Step 1. The quotient k_{+1}/k_{-1} , where k_{+1} and k_{-1} are

rate constants for the first step forwards and backwards, respectively, should be the equilibrium constant for the protolytic reaction (± 1). According to the picture given above a change of potential (η) between metal phase and solution (iron electrode and reference electrode) would involve an identical change between the region in which the hydrogen ion is situated when belonging to the LOH_2 acid and the phase where there is free hydrogen ion. This may of course be a somewhat crude picture of the actual (unknown) situation but seems nevertheless to give a very satisfactory working hypothesis. According to this hypothesis the equilibrium constant for this reaction shall have the form

$$K_{1,\eta} = K_{1,0} \exp (F \cdot \eta / RT) \quad \text{II}$$

where $K_{1,0}$ is the value of K_1 at an arbitrary reference potential ($\eta = 0$). This is a simple consequence of Boltzmann's distribution law. We then have

$$\frac{k_{1,\eta}}{k_{-1,\eta}} = \frac{k_{1,0}}{k_{-1,0}} \cdot \frac{\exp (\alpha \cdot F \cdot \eta / RT)}{\exp (-(1-\alpha) F \cdot \eta / RT)} \quad \text{III}$$

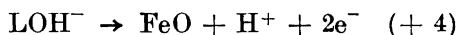
This equation is valid for any value of α as far as the formal relationship between rate constants and equilibrium constants is concerned. There are however good reasons for giving the value 0.50 to α . The exponential factors in nominator and denominator governs the influence of electrical forces on the transport of the hydrogen ion in either direction through the diffuse part of the electrical double layer at the iron surface. According to the picture given above potential changes between metal interior and liquid interior are restricted to this part of the double layer. It is true that the thickness of this layer, like the radius of the ionic atmosphere in the Debye-Hückel theory of

ionic solutions, is strongly influenced by, *e.g.*, concentration and charge type of electrolytes in the solution, but the part of the total potential drop found in the diffuse part of the double layer is hardly changed very much. Probably electrode kinetics will in the future turn out to be the best source of information about the actual double layer structure.

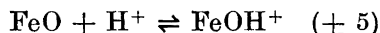
Step 2. The second step in the mechanism suggested above does not involve transference of charged species between two phases. Therefore the rate constants of this step should not directly be functions of potential. They might be functions of, *e.g.*, availability of electrons and hence may be linear functions of potential and double layer capacity, but for the present it seems adequate simply to regard k_2 and k_{-2} as potential independent.

Step 3. k_3 is a little more obscure as the fate of the hydroxyl ion is unpredictable. If the solvation process were transference of FeOH^+ through the double layer the potential dependence of k_3 should be the same as for k_1 . There is experimental evidence which could mean that the constant k_3 depends on potential according to the law expected for transfer of a double charged particle and this will be maintained throughout in the following discussion.

The water molecules, of course, are to be considered as a two basic acid. As we shall see later the process (+ 2) is probably fairly slow, so that at high potentials or at high pH values, (+ 2) must compete with

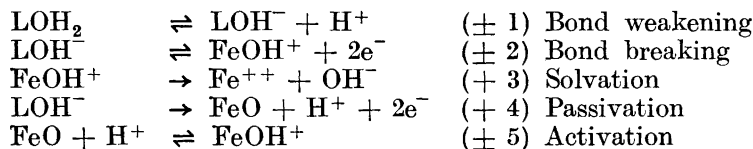


We suppose that this splitting off of the second proton leads to immediate bond breaking between surface iron atom and lattice, and that the FeO formed remains on the surface as a constituent of the passivity oxide layer. It will not solvate unless a hydrogen ion is taken up:



It seems reasonable to believe that if the bonding between surface iron and lattice is indefinitely stable when water is adsorbed and is less stable when one hydrogen is split off, then the bond will break immediately when both hydrogen ions are split off. The constants k_4 , k_5 , and k_{-5} will all have potential dependence corresponding to transference of one hydrogen ion. There is no reason to believe that the back reaction (—4) will play any significant part in the mechanism of the iron electrode.

To summarise, the proposed mechanism is:



with the corresponding rate constants (η in mV)

$$\begin{aligned}
 \log k_{1,\eta} &= \log k_{1,0} + \eta/116 \\
 \log k_{-1,\eta} &= \log k_{-1,0} - \eta/116 \\
 \log k_{2,\eta} &= \log k_{2,0} \\
 \log k_{-2,\eta} &= \log k_{-2,0} \\
 \log k_{3,\eta} &= \log k_{3,0} + \eta/58 \\
 \log k_{4,\eta} &= \log k_{4,0} + \eta/116 \\
 \log k_{5,\eta} &= \log k_{5,0} - \eta/116 \\
 \log k_{-5,\eta} &= \log k_{-5,0} + \eta/116
 \end{aligned}
 \tag{IV}$$

OVERALL STEADY STATE KINETICS

The mechanism outlined above gives the following overall steady state kinetic expression:

$$s = \frac{N}{A + B h + C/h} \tag{V}$$

In this expression s is the velocity of iron dissolution per unit of anode area. N is the number of iron atoms per unit anode area which are able to accommodate a water molecule and hence to go through the sequence of events described above. A , B and C are functions of the rate constants given above. h is the hydrogen ion concentration.

The definition of the parameters of V is deliberately crude. In the calculation of the actual number of sites on the iron surface it is of course necessary also to take into account the fact that other species than water can, and will, adsorb on to the iron surface. Some foreign adsorbed species may promote corrosion, others may protect the host iron atom from oxidation or at least from solvation. The protolytic reactions must be highly dependent on the availability of acid-base systems in the solution apart from water molecules. Therefore the above mechanism can, even if it turns out to be essentially correct, only represent a fairly crude picture of the complete mechanism of the iron electrode. With these reservations V is derived as follows:

The surface concentrations of the forms LOH_2 , LOH^- , FeOH^+ , and FeO are, respectively, a_2 , a_1 , b_1 , and b_0 . Hence

$$a_2 + a_1 + b_1 + b_0 = N \tag{VI}$$

According to the mechanism these surface concentrations obey the differential equations

$$\left. \begin{aligned}
 \frac{da_2}{dt} &= -k_1 a_2 + k_{-1} h a_1 + k_3 b_1 \\
 \frac{da_1}{dt} &= k_1 a_2 - k_{-1} h a_1 - k_2 a_1 + k_{-2} b_1 - k_4 a_1 \\
 \frac{db_1}{dt} &= k_2 a_1 - k_{-2} b_1 - k_3 b_1 + k_5 h b_0 - k_{-5} b_1 \\
 \frac{db_0}{dt} &= k_4 a_1 - k_5 h b_0 + k_{-5} b_1
 \end{aligned} \right\} \tag{VII}$$

The term k_3b_1 in the expression for a_2 indicates that LOH_2 is reformed by immediate adsorption of a new water molecule at the surface iron atom exposed after solvation of the ferrous ion. As the four equations of VII through VI are interrelated we have four independent equations with four unknowns, *viz.* the four surface concentrations. The dependent parameter of greatest interest is the corrosion rate introduced by the equation

$$s = k_3b_1 \quad \text{VIII}$$

It is of course a hopeless task to attempt to give general solutions for this system of differential equations when the potential dependence of the rate constants is considered, although it would not be difficult to investigate the properties of the system on an analogue computer and to compare its behaviour with that of the actual iron electrode. Here, however we can only give the steady state solution, obtained by equating the differential quotients of VII to zero, eliminating the surface concentrations and thus determining s .

The result is

$$\begin{aligned} \frac{N}{s} = & \frac{1}{k_1} + \frac{1}{k_3} + \frac{1}{k_2 + k_4} + \frac{k_{-2}}{k_3(k_2 + k_4)} + \frac{\frac{k_{-1}}{k_1} + \frac{k_{-1}k_{-2}}{k_1k_3}}{k_2 + k_4} \cdot h \\ & + \frac{\frac{k_{-2}k_4}{k_3k_5} + \frac{k_4k_{-5}}{k_3k_5} + \frac{k_4}{k_5} + \frac{k_2k_{-5}}{k_3k_5}}{k_2 + k_4} \cdot \frac{1}{h} \end{aligned} \quad \text{IX}$$

which is seen to be of the same form as V.

The following experiments are meant to illustrate the most general applicability of this expression.

Fig. 1 shows examples of the dependence of the velocity of anodic dissolution on pH as measured by the anodic current at constant potential. The curves have maxima in accordance with V and IX, proving that the hydrogen ions both catalyze and inhibit the anodic dissolution. A complete quantitative analysis of these experiments would seem to be of little value at present; the system is too complicated. Thus comparison of the three curves for three acetate concentrations shows immediately that not only pH, but also sodium acetate or acetic acid concentration has influence on the integral behavior of the iron electrode.

Fig. 2 shows the influence of potential on the corrosion rate at three fixed pH values. It is seen that the influence of increasing potential is very similar to that of increasing pH as shown in Fig. 1. The accordance between IX and the experiments of Fig. 2 follows from the potential dependence of the terms of the denominator of V (IX):

$$A = 1/k_1 + 1/k_3 + 1/(k_2 + k_4) + k_{-2}/k_3(k_2 + k_4)$$

If $k_4 \ll k_2$ the numbers $-1, -2, 0, -2$ give the factor of 10 by which these terms are changed when the potential of the iron electrode is changed 116 mV

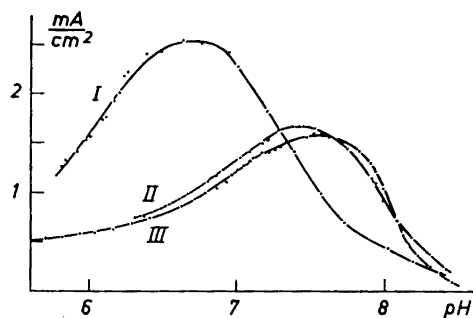


Fig. 1. Rate of anodic dissolution vs. pH;

Temp. 25.0°C;

Potential: $E_h = -210$ mV;

Electrode area: 2.40 cm²

Medium: I 0.100 M sodium acetate

II 0.500 M sodium acetate

III 1.000 M sodium acetate

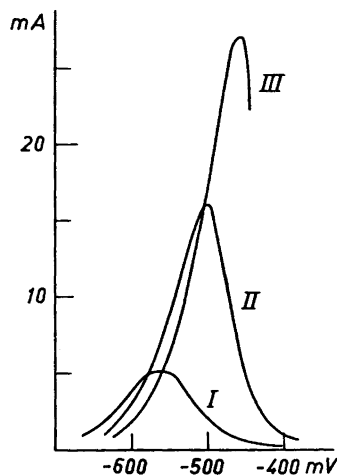


Fig. 2. Rate of anodic dissolution vs. potential;

Temp. 25.0°C:

Reference electrode: Ag/AgCl; 0.1 M HCl;

Medium: 1 M sodium acetate, 2×10^{-3} M

o-phenanthroline;

Scanning rate: 5 mV/sec;

Electrode area: 2.40 cm²;

pH: I 7.65

II 7.07

III 6.76

in anodic direction. It is seen that A decreases with increasing positive potential. Hence the A term is most significant at negative potentials.

$$B = [k_{-1}/k_1 + k_{-1}k_{-2}/k_1k_3]/(k_2 + k_4)$$

Again, provided $k_4 \ll k_2$ the numbers -2 and -4 give the factor of ten by which the two terms in the square brackets are changed when the potential is changed 116 mV. Also the term $B \cdot h$ decreases with increasing potential.

$$C = (k_{-2}k_4/k_3k_5 + k_4k_{-5}/k_3k_5 + k_4/k_5 + k_2k_{-5}/k_3k_5)/(k_2 + k_4)$$

Still retaining the assumption $k_4 \ll k_2$ which may be reasonable at not too positive potentials the exponents are 0, +1, +2, and 0, respectively. Hence the term C/h must increase with increasing anodic potential.

This means, that at fixed pH the denominator of V must go through a minimum, and therefore the steady state corrosion rate must go through a maximum when measured as a function of potential. The two functions of potential $B \cdot h$ and C/h must be shifted with increasing h in such a way, that the maximum at lower pH values occurs at potentials where the potential function A is greater. Hence the value of the maximum corrosion rate must decrease with increasing pH, as in fact seen on Fig. 2. This result is of course of

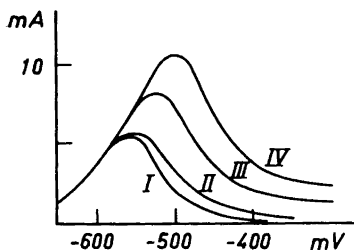


Fig. 3. Rate of anodic dissolution vs. potential;

Temperature: 25.0°C;

Reference electrode: Ag/AgCl; 0.1 M HCl;

Medium: as Fig. 2. I;

Rate of scanning: I 5 mV/sec

II 20 mV/sec

III 100 mV/sec

IV 200 mV/sec

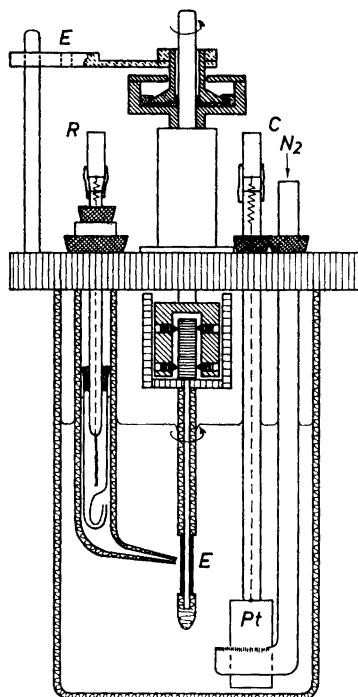


Fig. 4. Reaction vessel with electrode system. Volume: 400 ml, R, reference electrode; E, Experimental electrode (iron); C, counter electrode (platinum).

practical interest as it shows that the highest possible value of iron corrosion rate decreases strongly with increasing pH. It is on the other hand clear from Fig. 2 that when rather negative potentials only are considered the rate of corrosion at constant potential now increases with increasing pH. Fig. 3 shows the influence of increase of scanning rate. It is clear, that when the steady state condition is not fulfilled IX will not be the solution of VI, VII and VIII. It is seen that the corrosion rate shoots up to higher maximum values when the potential is changed at a rather fast rate. It should be emphasized that the measured anodic current under non steady state conditions comprises both anodic dissolution and change of charge of double layer, *e.g.* by change in the degree of acid dissolution of the adsorbed water molecules. It is of course hopeless to attempt a quantitative analytical theory for the

Fig. 5. Simple potentiostat:

E, experimental electrode;
 R, reference electrode;
 C, counter electrode;
 P₁, potential selector;
 MA, current measuring device;
 K₁, DC amplifier. Usually Kintel BFO 111.
 (gain: ca -10^6 . bandwidth: DC-40KC,
 zero point stability: ca $2 \mu\text{V}$).

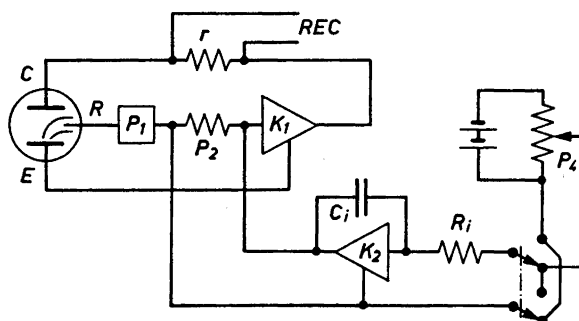
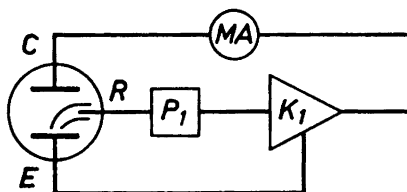
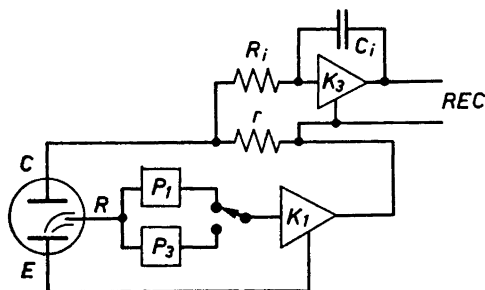


Fig. 6. Fully electronic polarograph. Details of potentiostat part as Fig. 5. Sliding potential provided by the integrator consisting of the amplifier K₂, the condenser C_i and the resistance R_i. Direction and rate of scanning determined by choice of C_i, R_i and of sign and magnitude of the potential P₄. Example: C_i = 1 μF , R_i = 1 M Ω gives scanning rate = P₄ mV/sec. Current measuring device generally an X-Y recorder (Moseley Autograph 2 S. 10" \times 15"), the X position of which is controlled by the sliding potential.

Fig. 7. Potentiostat with coulombmeter. Details of the potentiostat as for Fig. 5. The amplifier K₂ forms together with R_i and C_i an integrator, the output of which is proportional to the amount of electricity passed through the resistance r during the time elapsed since C_i was last short-circuited. Recorder: Moseley Autograph X-Y recorder 10" \times 15".



experiments of Fig. 3. A numerical solution of the system of differential equations governing the iron electrode for such conditions would on the other hand be of great value for assigning definite values to the numerous rate constants of the iron electrode.

EXPERIMENTAL PROCEDURES

The experiments described in this paper were all carried out at 25°C. The electrolysis system had three electrodes (Fig. 4): the iron electrode, the reference electrode with Luggin capillary and a platinum counter electrode. The iron was supplied by Vacuum Schmelz, Hanau, Germany, as 4 mm rods, described as "Rein Eisen, gasfrei". The

limits of impurities are fairly generous (*e.g.*, C 0.02 %; Ni 0.1 %) but the quality was considered satisfactory for the experiments described in this paper (see remarks on the paper by Hoar and Hurlen⁶, p. 301). The rods were cut in 20 mm length and a 2 mm hole drilled through the whole length. The cylinders were suspended in a lathe, ground with suitable grades of emery paper and finished with diamond powder polishing. They were mounted in an electrode holder of glass as seen on Fig. 4 so that only the outer cylindrical area was exposed (apparent area: *ca* 2.4 cm²). The electrode holder was designed so that the electrode could be rotated and easily well centered. The cylindrical electrode form was chosen because all points on the electrode can be regarded identical, both electrically and hydrodynamically. The stirring rate was generally about 1 000 revolutions/min and none of the phenomena discussed in this paper were changed appreciably by change of rate of stirring, *i.e.* there was no transport control.

The reference electrodes were in most cases silver/silver chloride electrodes, 0.1 M HCl, which are about 290 mV more positive than the normal hydrogen electrode.

The platinum counter electrodes were generally screened from the bulk of solution in such a way that they were placed in a glass tube, connected with the rest of the system through a sintered glass plate. Nitrogen, freed from oxygen by means of a Meyer-Ronge apparatus¹⁷ was bubbled through the solutions, unless otherwise stated. Most of the electrolysis experiments were carried out at controlled potential. The active elements of the potentiostats were analogue computer amplifiers, either those from a small Donner computer or KINTEL B F O 111 amplifiers. These latter amplifiers are especially attractive for electrode kinetic purposes as they are floating, thus making it possible to choose freely the point of the electrolysis system to be earthed. Fig. 5 shows the basic wiring for a potentiostat. In Fig. 6 is shown the system used for experiments of the type shown in Figs. 2 and 3, a second amplifier connected as integrator providing the scanning potential. Fig. 7 shows a setup in which a second amplifier is used as an integrator to record the number of coulombs passed through the electrode rather than the current.

Solutions were made up with doubly distilled water and materials of analytical reagent grade. Most solutions contained 2–4 mmole of *o*-phenanthroline to keep the ferrous ion produced on the "polarographically inert" *o*-phenanthroline complex form. This measure was found to increase the reproducibility of experiments enormously, without changing the nature of the results obtained. Experiments have shown, that the adsorption of *o*-phenanthroline is too slow to compete with adsorption of water or other solution constituents, provided the electrode is continuously corroding.

INFLUENCE OF HYDROGEN

Fig. 8 demonstrates the reproducibility attained by the experimental procedure outlined above, and also one of the pitfalls which had to be overcome before high reproducibility was obtained. The experiments were carried out with the circuit of Fig. 5. The bellshaped curve I represents two identical experimental runs with the same electrode, which had never been polarized

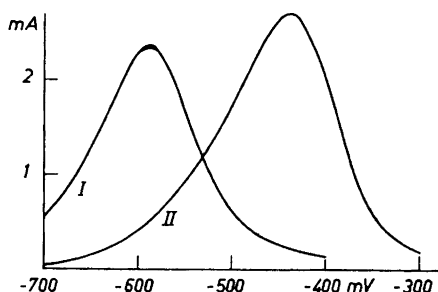


Fig. 8. Rate of anodic dissolution vs. potential;

Medium: 0.5 M sodium acetate, 0.002 M *o*-phenanthroline. pH: 7.95;

Temp. 25.0°C; Reference electrode: Ag/AgCl, 0.1 M HCl;

Rate of scanning: 4 mV/sec.

Electrode area: 2.36 cm².

I Two identical runs with nonhydrogenated electrode.

II Same experiment after cathodic polarization.

cathodically. Curve II represents a similar run with the same electrode after the electrode had been held at a more negative potential with hydrogen evolution for some time (a few minutes). The shift towards more positive potentials cannot possibly be attributed to an adsorption phenomenon, as something like 100 atomic layers of iron are stripped off in each run. The almost identical shape of the two curves indicates, that the rate-determining phenomena in the two cases are also the same, *i.e.* that the "zero charge potential", the potential at which the electrode acts on the hydrogen ions of the chemisorbed water with zero coulombic force, is shifted by diffusion of hydrogen into the electrode. The shift persists for about half an hour after the cathodic treatment.

Hoar and Hurlen⁶ have found that their potential dependent rate laws for anodic dissolution and cathodic deposition of iron combine to give the accepted standard potential of the iron/ferrous ion electrode. The drastic influence of hydrogen on the iron electrode, which we have found in acid solution also, suggests that this relationship cannot be expected to hold under all conditions. We have found that there is no shift when the solution contains nitrate ion. The explanation given here seems to be the only one reasonable, and supports the point of view that the influence of change of potential is essentially electrostatic as suggested in the discussion above.

THE ACTIVE IRON ELECTRODE

The expression IX is too complicated to warrant a detailed analysis at present. It is however a promising feature that most of the terms of IX are strongly potential dependent. This means that when the potential of the iron electrode is changed it can be expected that the various terms change in relative significance to an extent which makes it possible to isolate the influence on the overall kinetics of at least some of the terms. In this way it may be possible to identify such terms and hence to prove more directly the correctness or not of some of the aspects of the mechanism given above. It may be reasonable to assume that the surface species FeO, which according to the mechanism suggested in this paper is at least a precursor of the passive layer of the iron electrode, is absent from the electrode mechanism when the potential is sufficiently negative. Under such conditions IX is reduced to

$$\frac{N}{s} = \frac{1}{k_1} + \frac{1}{k_2} + \frac{1}{k_3} + \frac{k_{-2}}{k_2 k_3} + \left[\frac{k_{-1}}{k_1 k_2} + \frac{k_{-1} k_{-2}}{k_1 k_2 k_3} \right] \cdot h \quad \text{X}$$

When this relationship holds, a plot of the inverse corrosion rate against acidity at constant potential should be a straight line with intercept on ordinate

$$A = \frac{1}{k_1} + \frac{1}{k_2} + \frac{1}{k_3} + \frac{k_{-2}}{k_2 k_3} \quad \text{XI}$$

and slope

$$B = \frac{k_{-1}}{k_1 k_2} + \frac{k_{-1} k_{-2}}{k_1 k_2 k_3} \quad \text{XII}$$

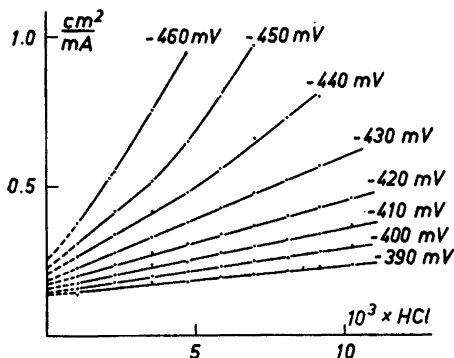


Fig. 9. Reciprocal rate of anodic dissolution against concentration of hydrochloric acid. Medium: 1 M sodium chloride, 0.004 M *o*-phenanthroline.

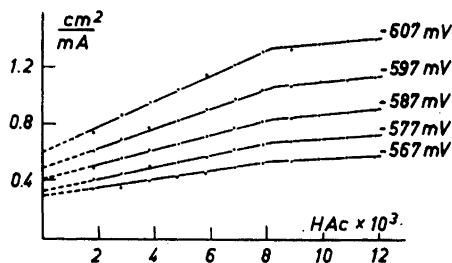


Fig. 10. Reciprocal rate of anodic dissolution against acetic acid concentration. Medium: 1 M sodium acetate, 0.004 M *o*-phenanthroline.

We have, in disagreement with some earlier workers, found, that it is generally not possible to obtain a Tafel line for the overall corrosion rate of the iron electrode. This should be possible if only one term of IX is significant for the overall kinetics. We have, however, found that X often reproduces data of experiments at lower potentials (where the electrode is active) reasonably well. Examples are shown in Figs. 9 and 10, which are for a hydrochloric

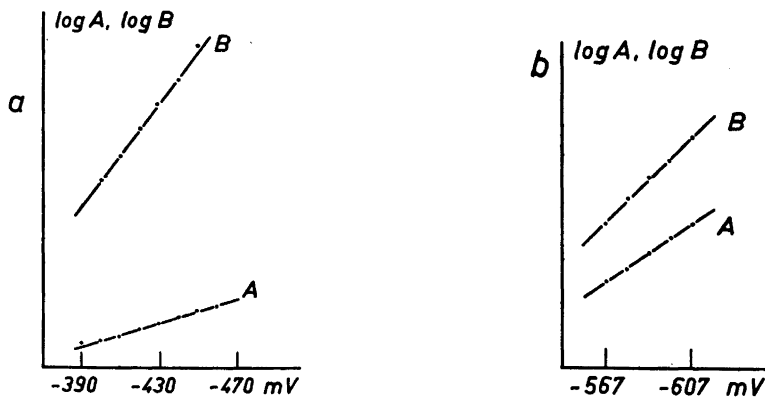


Fig. 11. Tafel lines for intercepts (*A*) and slopes (*B*) from the experiments on Figs. 9. and 10, respectively.

a) the hydrochloric acid experiment

$$\frac{d \eta}{d \log A} = 170 \text{ mV}; \quad \frac{d \eta}{d \log B} = 61 \text{ mV}$$

b) the acetic acid experiment

$$\frac{d \eta}{d \log A} = 116 \text{ mV}; \quad \frac{d \eta}{d \log B} = 86 \text{ mV}$$

acid and an acetate/acetic acid system, respectively. Fig. 9 shows very good agreement with X at a number of potentials. The curvature of the upper curves undoubtedly reflects the fact that when acidity is high and potential low the hydrogen evolution on the electrode is not fully suppressed; hence the electrode is changed as described above. Both the slopes and the intercepts of Fig. 9 give good Tafel lines as shown on Fig. 11. The slope of the line for *B* corresponds to a factor of ten change for 61 mV, not much different from the 58 mV slope expected if only the first term of XII were significant (*cf.* p. 307). The slope of the line for *A* is near 170 mV suggesting that both the term $1/k_1$ (corresponding to $b = 116$ mV) and the term $1/k_2$ (with no potential dependence) are significant. The experimental data for *A* from Fig. 9 fit a Tafel line with slope 116 mV after subtraction of a suitable contribution from the term $1/k_2$.

Fig. 10 shows also good agreement with X at lower acidities. At high acidities the inverse rate is too low, *i.e.* the rate too high, for the simple expression. Other experiments with the acetic acid system have shown that a plateau is reached on which the electrode seems to be fully covered with adsorbed acetic acid and where the rate follows a 116 mV slope Tafel law. In this state the rate of corrosion seems to be governed by splitting off of one proton from adsorbed acetic acid. The *B* values from the steep parts of Fig. 10 obey, as again seen on Fig. 11, a Tafel equation with $b = 80$ mV whereas the *A* values from Fig. 10 give a b value close to 116 mV. It is seen that these findings are in substantial agreement with the general picture given in the present paper.

In the introduction we have mentioned the papers by Hoar and Hurlen ^{6,7} and by Bonhoeffer and Heusler ^{8,9}, in which it was found, that the overall kinetics of the anodic dissolution obeys a Tafel type equation with $b = \text{ca. } 29$ mV. It is seen, again from the discussion on p. 307, that this is the b value corresponding to the second term of XII. This would be the leading term of XII if

$$k_{-2} \ll k_3 \quad \text{XIII}$$

It is reasonable to postulate, that a major difference between the experimental conditions of the workers mentioned above and ours is the validity of XIII. In their case, iron electrodes were heated in hydrogen flames before experiments and hydrogen gas was thoroughly bubbled through solutions during experiments. In our case, no such pretreatment of electrodes was performed, and nitrogen was used to keep oxygen away from the electrode system during experiments. It is not unlikely that the probability of the reaction (—2), which is a reduction, is strongly influenced by hydrogen dissolved in the iron phase. The validity for the hydrogen treated electrode of our mechanism in connection with the assumption XIII is in Heuslers ⁹ case strongly supported by his own experiments. Heusler changed the potential of an iron electrode suddenly from a steady state condition at a constant potential to another constant potential and found that the rate of anodic dissolution changed, immediately according to a $b = 58$ mV law, and after a slower transition, to a new steady state corrosion rate, related to the original steady state rate according to a $b = 29$ mV law. Considering that the measured rate is governed by VIII this result is understandable; the immediate response to a change of

potential would be a change of k_3 according to a 58 mV law, followed by a slow change of the concentration of the surface species b_1 , also increased by a factor of 10 when the potential is changed 58 mV, provided the dominating species on the surface is adsorbed, undissociated water. That would give

1) a fast change of dissociation of water when potential is changed so

$$a_1 = a_2 \frac{k_1}{k_{-1}} = NK_1 \quad \text{XIV}$$

2) slow equilibrium adjustment of b_1 according to

$$b_1 = a_1 \frac{k_2}{k_{-2}} \quad \text{XV}$$

and therefore an overall change of two factors of ten for 58 mV change of potential. This explanation of the 29 mV Tafel lines for anodic dissolution of iron is amplified, still with reference to Heuslers interesting experiments, when the differential equation for b_1 is considered:

$$\frac{db_1}{dt} = k_2 a_1 - k_{-2} b_1 - k_3 b_1 \quad \text{XVI}$$

The solution of XVI, when from an arbitrary steady state condition a_1 is suddenly changed to a new value a'_1 , is:

$$b_1 = a'_1 \frac{k_2}{k_{-2} + k_3} - (a'_1 - a_1) \frac{k_2}{k_{-2} + k_3} \exp [-(k_{-2} + k_3)t] \quad \text{XVII}$$

If the steady state velocities according to VIII, based on a'_1 and a_1 , but both with the new value of k_3 , are called s_{st} and s_{min} , respectively, we have:

$$s = s_{st} - (s_{st} - s_{min}) \exp (-t/\tau) \quad \text{XVIII}$$

where $1/\tau = k_{-2} + k_3$.

XVIII is identical with eqn. (1) of Heusler's paper. τ is in his experiments independent of potential and is about 0.3 sec. It is strongly suggested that this is the potential independent value of $1/k_{-2}$. We have found similar time constants in our experiments, but of much higher values (several seconds). It is therefore suggested, that one of the differences between the hydrogen treated iron electrode and our non treated electrodes is, that for the hydrogen treated electrode the assumption XIII is valid, and hence the term with $b = 29$ mV of XII the leading one, whereas in our case the first term of XII was the dominating one.

It is of course possible to investigate a differential equation of the form XVI for experimental conditions other than those mentioned above. An analogue to XVI is valid for the acid dissociation of the adsorbed water:

$$\frac{da_1}{dt} = k_1 a_2 - k_{-1} h a_1 - k_2 a_1 \quad \text{XIX}$$

This may be solved analytically for small changes of potential as linear functions of time. If we neglect both oxidized forms in VI, we have

$$\frac{da_1}{dt} = k_1 N - (k_1 + h k_{-1} + k_2) \cdot a_1 \quad \text{XX}$$

We want to solve this equation for the condition

$$\eta = \eta_0 + at \quad \text{XXI}$$

where $at \ll 116$ mV. The initial condition is

$$0 = k_{1,0}N - (k_{1,0} + k_{-1,0}h + k_2) \cdot a_{1,0} \quad \text{XXII}$$

where the indices 0 refer to a steady state at the potential η_0 . We define, introducing XXI

$$\left. \begin{aligned} k_1 &= k_{1,0} \exp\left(\frac{1}{2} \cdot \frac{zF}{RT} \cdot a \cdot t\right) \sim k_{1,0}(1 + \beta \cdot t) \\ k_{-1} &= k_{-1,0}(1 - \beta \cdot t) \\ a_1 &= a_{1,0} + \Delta a_1 \end{aligned} \right\} \quad \text{XXIII}$$

k_2 is potential independent.

Introduction of these expressions in XX and combination with XXII gives:

$$\begin{aligned} \frac{da_1}{dt} = \frac{d \Delta a_1}{dt} &= [k_{1,0}N - (k_{1,0} - k_{-1,0}h)a_{1,0}]\beta t \\ &\quad - [k_{1,0} + k_{-1,0}h + k_2]\Delta a_1 \\ &\quad + \text{terms of higher order} \end{aligned} \quad \text{XXIV}$$

which we write

$$\frac{d \Delta a_1}{dt} = Kt - L \cdot \Delta a_1 \quad \text{XXV}$$

As $\Delta a_1 = 0$ for $t = 0$ we have

$$\Delta a_1 = \frac{K}{L} \cdot t - \frac{K}{L^2} (1 - \exp(-Lt)) \quad \text{XXVI}$$

An increase of a_1 is seen experimentally as an anodic current:

$$\Delta a_1 = \frac{1}{F} \cdot \Delta q = \frac{1}{F} \cdot C \cdot \Delta \eta = \frac{1}{F} \cdot C \cdot a \cdot t$$

where C is a formal capacity.

For large t the exponential term of XXVI vanishes, so

$$\frac{d \Delta a_1}{dt} = \frac{K}{L} \text{ and } C = F \cdot \frac{K}{L}$$

or

$$C = \frac{N(2hk_{-1}k_1 + k_1k_2) \cdot z \cdot F^2}{(k_1 + k_{-1}h + k_2)^2 RT} \quad \text{XXVII}$$

The potential dependencies of the kinetic constants imply that C is small at extreme potential values and has a maximum somewhere in the potential region where corrosion is significant. We have determined the total double layer capacities of iron electrodes by an impulse method, details of which will be reported in a later paper: a result is seen in Fig. 12. It is seen that the

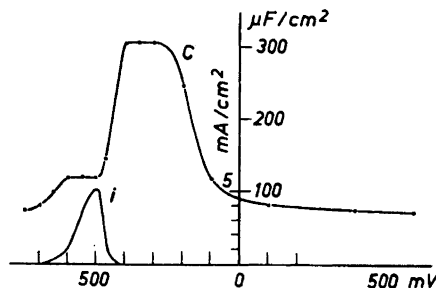


Fig. 12. C , capacity of iron electrode vs. potential;

i , anodic dissolution rate vs. potential;

Medium: 1.00 M sodium acetate, 0.002 M *o*-phenanthroline. pH 7.05; Temp. 25.0°C.

double layer capacity has high values at intermediate potentials as expected from the theory. The integral

$$\int \frac{C}{F} d\eta = 10^{-9} \text{ mole/cm}^2$$

taken over the potential region where C is high, should be an expression for the amount of hydrogen ion given off by the electrode going from fully active to fully passive electrode state. The estimated experimental value given is reasonable for a monomolecular layer of water.

It is seen from XXVI that a transition phenomenon should be shown by such capacity measurements. The values of $L = k_1 + k_{-1}h + k_2$ actually observed were about 10^3 – 10^4 sec^{-1} , nearly independent of h and with the higher values at the more positive potentials. It appears that the observed values essentially represent k_1 . It has not however hitherto been possible to obtain very accurate data for capacities and time constants because of inherent noise. We intend to return to these phenomena in future work.

Fig. 13 shows the result of some experiments, which typify the behaviour of the iron electrode. A potentiostat was programmed to change the potential of an iron electrode in a triangular way. The total change of potential was 59 mV the scanning time was 10 sec. for a full period. It is seen that the measured corrosion current was throughout lower for increasing potentials than for decreasing potentials.

Very similar hysteresis phenomena were, as seen on Fig. 14, observed when an analogue computer solved a differential equation of the type XIX for the condition that k_1 and $k_{-1}h$ were exponential functions of time. There is a striking resemblance between the behaviour of the electrode system and of the analogue computer. A quantitative agreement was not obtained, as the three first steps of the general mechanism must have had an influence on the overall kinetics, but only two steps were actually incorporated in the "mechanism" of the computer. The computer at our disposal was too small to accommodate a more correct representation of the corroding iron electrode. The comparison of Figs. 13 and 14 does, however, illustrate that the various hysteresis phenomena, so typical for the kinetic behaviour of solid electrodes, often do reflect quite simple aspects of the electrode reaction studied. Hence the investigation of such phenomena should be worth while if appropriate means of calculation are at disposal.

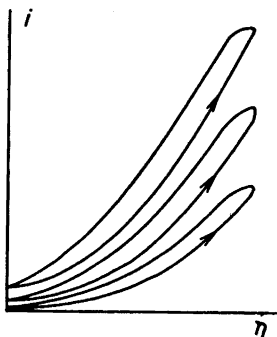


Fig. 13. See text. Medium: 0.5 M sulphuric acid.



Fig. 14. See text.

THE PASSIVE STATE

The mechanism for the iron electrode suggested in this paper would seem to involve that the passive layer is of monomolecular thickness. It is well known from many investigations, that this is not so. The surface species FeO occurring in our mechanism must therefore essentially be regarded a precursor for the passive layer as this is described in the literature⁴. We have on the other hand found that both the passivation of iron and the reactivation necessitate much less exchange of electricity than generally assumed. In neutral or weakly alkaline solutions we have been able to passivate rotating iron electrodes, suddenly raised to a potential in the passive region, with a few millicoulombs/cm². Fig. 15 shows a direct recording of the amount of electricity passed through an iron electrode the first few seconds after a sudden potentiostatic reactivation. It is seen that there is an immediate demand for cathodic current amounting to about one millicoulomb/cm², followed by a slower anodic corrosion current. Whether the cathodic current represents a reduction of the passive layer or not it is still certain, that some mechanism for the transport of electricity between electrode surface and solution must exist. As the solution does not contain reducible matter we can think of no better explanation than that the cathodic current is a manifestation of a transport of hydrogen ion from the solution to the passive layer. That would also explain why both the electrode potential and the pH of the solution are so important for the state of the iron electrode.

The mechanism of passivity given here is *not* in accordance with the existence of a sharp transition between a passive and an active state of the iron electrode. Fig. 16 shows that when the potential of a passive iron electrode is carefully changed to more negative values, it is possible to obtain a smooth increase in anodic current with decreasing potential. It is seen that two of the Tafel lines have slopes of 58 mV, and one of them somewhat less. These values are in reasonable accordance with the discussion on p. 302; whether or not they are actually determined exactly by the terms of the factor C they do

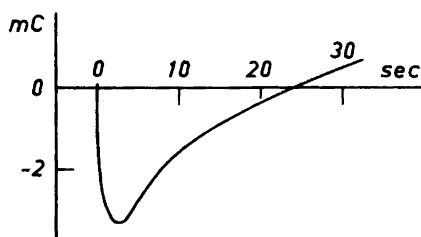


Fig. 15. Direct recording of amount of electricity passed through an iron electrode after change of potential at time zero. Medium: 1 M sodium hydrogen carbonate. 10% CO₂ in gasphase. Temp. 25.0°C. Electrode area, 2.41 cm².

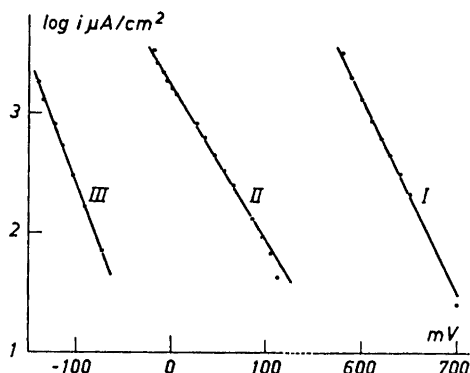


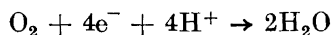
Fig. 16. Tafel lines for reactivation of passive electrodes.

- I 0.5 M sulphuric acid
- II 1.0 M sodium acetate + acetic acid, pH 5.75
- III 0.5 M sodium chloride + 0.5 M sodium acetate + acetic acid, pH 6.75.

support the point of view of a catalytic influence of hydrogen ion, taken up by the passive layer, as the mechanism of the effect demonstrated in Fig. 16. Inversely; the mechanism of passivity must be the electrostatic repulsion of hydrogen ions, in the absence of which the solvation step, which completes the anodic dissolution of iron, is impossible.

INFLUENCE OF DISSOLVED OXYGEN

A passive iron electrode will, according to our experience, not reduce dissolved oxygen at potentials, where oxygen is reduced readily on, *e.g.*, a silver electrode. At somewhat more negative potentials, where iron becomes active it will reduce oxygen. It is of great interest that an electrode which according to a potential-anodic dissolution diagram for oxygenfree solution should be slightly active, will not corrode at that potential in the presence of oxygen. It seems, that the difference between the active iron electrode and the silver electrode on one hand, and the passive iron electrode on the other hand, might very well be the availability of hydrogen for a reaction such as



The slightly active electrode would then become passive because this reaction removes the hydrogen ion from the surface of the iron electrode. In accordance with this point of view oxygen is found to catalyse the anodic dissolution at more negative potentials, *i.e.* at the ascending branch of the potential-corrosion rate diagram. It seems that presence of oxygen causes a change of

behaviour of the iron electrode corresponding to a change of potential towards more positive values, *i.e.* towards conditions with lower steady state surface concentration of hydrogen.

CONCLUDING REMARKS

The mechanism of the anodic dissolution of iron given in this paper is obviously very crude. It seems however, that all known features of the behaviour of the iron electrode are reasonably well explained by this mechanism and there should be every reason to study its implications more closely, as we intend to do in coming papers.

A question which must arise in this connection is the power of resolution of kinetic methods altogether. The mathematical image of the mechanism is the differential equations of VIII; once their validity is established the mechanism is also proved valid. In this sense, the word mechanism only means the sequence of events an iron atom must go through from the time it belongs to the metal lattice till it is solvated or till it is embedded into a passive layer in a more or less oxidized form. In a wider sense the mechanism is not understood until not only the sequence of events, but also the nature of each event is more precisely understood. To obtain such understanding it is essential that the numerous rate constants of the electrode are ascribed absolute values in their dependence on thermodynamic parameters such as temperature, potential and properties of solvent. It is interesting, that the velocity and the parameter N are inseparable according to the steady state solution of the kinetic equations, and also that, however accurate are the data for the experimentally accessible parameters of IX or X, it will not be possible to separate the various rate constants without auxiliary assumptions, *e.g.* those of IV. Even so can IX and X only provide the rate constants multiplied by N . That this is a special feature of the steady state solutions of the kinetic equations is seen from the solutions for non steady state conditions. In these solutions the exponential terms involved contain naked rate constants. This opens up a way of determining the important parameter N . Future work may thus disclose whether the active corrosion process is confined to special active sites, *e.g.* lattice defects, to all iron atoms in a monomolecular surface layer or may be to a spongy layer of a thickness corresponding to several atomic layers.

REFERENCES

1. Tafel, J. *Z. physik. Chem.* **50** (1905) 641.
2. Okamoto, G., Nagayama, M. and Sato, N. *CITCE* **8** (1958) 72.
3. Hoar, T. P. *Private communication*.
4. Hoar, T. P. *Modern Aspects of Electrochemistry* No. 2 (Ed. J. O'M. Bockris) (1959) 262 (This excellent review contains 351 references).
5. Bockris, J. O'M. *Modern Aspects of Electrochemistry* (Ed. J. O'M. Bockris) (1954) 180.
6. Hoar, T. P. and Hurlen, T. *CITCE* **8** (1958) 445.
7. Hurlen, T. *Teknisk Ukeblad* **1958** 95, 119.
8. Bonhoeffer, K. F. and Heusler, K. E. *Z. physik. Chem. N. F.* **8** (1956) 390.

9. Heusler, K. E. *Z. Electrochem.* **62** (1958) 582.
10. Stern, M. *J. Electrochem. Soc.* **102** (1955) a. 609; b. 663.
11. Makrides, A. C., Komodromos, N. M. and Hackerman, N. *Ibid.* 363.
12. Nord, H. *Ingeniøren* **1958** 261.
13. Kabanov, B., Burstein, R. and Frumkin, A. *Discussions Faraday Soc.* **1** (1947) 259.
14. Bonhoeffer, K. F. and Heusler, K. E. *Z. Electrochem.* **61** (1957) 122.
15. Flade, F. *Z. physik. Chem.* **76** (1911) 513.
16. Frank, U. F. *Z. Naturforsch.* **4a** (1949) 378.
17. Meyer, F. R. and Ronge, G. *Angew. Chem.* **52** (1939) 637.

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