# Electrochemical Behaviour of Iron

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As part of a research programme on the kinetics of metal/metal-ion electrodes in aqueous solutions, investigations have been made on the anodic dissolution and cathodic deposition of iron in acid chloride solutions at 20°C by means of a slow amperostatic technique. The reactions are found to obey the Tafel relationship (except at higher current densities) and to have mutually symmetric Tafel lines with slopes of numerically 0.029 V $(2.303RT/2F)$. The rate of either reaction is moreover found to be proportional to the hydroxyl ion activity, and the rate of deposition to be proportional to the square of the ferrous ion activity. This indicates a mechanism covered by the equation:

$$2Fe + OH^- \rightleftharpoons 2Fe^{++} + OH^- + 4e^-$$
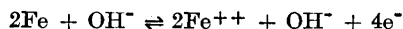
This mechanism is discussed, and a possible explanation is suggested.

For the exchange current (i_o) and the standard potential (E_o) of the Fe/Fe^{++}. aq-electrode, it is found:

$$\log i_o \ (A/cm^2) = 3.58 - pOH - pFe$$
$$E_o = -0.467 \ V$$

The latter value includes a (probably small) liquid junction potential, and both equations depend somewhat on the validity of the activity data applied.

Some measurements have also been made on the hydrogen evolution reaction at iron cathodes. The results indicate a Tafel slope of -0.116 V $(-2.303 \cdot 2RT/F)$ and an exchange current of

$$\log i_o(A/cm^2) = -5.36 - 0.5 \ pH$$

for this reaction in acid solutions. It is further found that the hydrogen evolution reaction is positively affected (stimulated) by the iron dissolution reaction and negatively affected (depressed) by the iron deposition reaction, and that it transforms from a pH-dependent to a pH-independent mechanism at a pH quite near to the neutral point. The Tafel slope is not affected by this change in reaction mechanism.

1.0 INTRODUCTION

A most important trend in recent studies of electrochemical kinetics is the development of theoretical equations for the rate of activation controlled electrode reactions [1-3]. These equations enable the identification of the rate

determining step and the determination of stoichiometric factors from suitable polarization measurements. The theory has so far mainly been used in elucidating the mechanism of hydrogen evolution at metal cathodes as this is by far the best known electrode reaction [1,2]. It has in this case apparently met with considerable success, making it a promising basis also for the study of other electrode reactions. On the other hand, such studies may also be of value in providing further data for testing the validity and applicability of the theory (see the criticism given by Horiuti [4] and Rüetschi [5]).

Metal deposition and dissolution constitute an important class of electrode reactions showing strong technological and practical implications (metal production, metal refining, electro-plating, corrosion, *etc.*). In spite of this, little seems to be known concerning their kinetics. This has been clearly demonstrated by Bockris [2] and Hoar [6], who have collected and discussed most of the relevant data available. These authors ascribe this state of affairs partly to experimental difficulties which have prevented many results being expressed in a form which allows theoretical analysis. Several of the results do also indicate that the polarization data to some extent depend on the method by which they have been obtained.

On this basis, it was assumed desirable to make renewed and extended investigations on a series of metal/metalion electrodes, using the same method for polarization measurements on all the metals. The metals which have been included in this programme, are *iron, cobalt, nickel, copper,* and *zinc.* The polarization method adopted, is a "slow" amperostatic method which allows the partial current density of the reactions to be estimated from the weight change of the electrodes. For checking the reliability of the method, parallel measurements have been made on the hydrogen evolution reaction at cathodes of the various metals involved. Other methods have also been applied.

This work will be presented in a series of papers of which this is the first. Experiments on *iron* in de-aerated acid chloride solutions at 20°C are here described and the kinetics of the anodic dissolution and cathodic deposition of this metal is discussed.

2.0 PREVIOUS WORK

Most of our present knowledge of the electrochemical behaviour of iron has come from the study of corrosion and allied processes. General reference may therefore be given to the corrosion monographs by Gatty and Spooner [7], Evans [8], Uhlig [9], Speller [10], Tödt [11], and Klas and Steinrath [12] and to the corrosion review by Grubitsch [13] where further references to original work — except the most recent — will be found. A general reference may also be given to the monograph by Fischer [14] on electrocrystallization of metals.

As already mentioned, most of the few data from this work which allow direct analysis on the basis of modern theory, have been collected and discussed by Bockris [2] and Hoar [6]. A great many of the additional data, however, may be used in testing the validity of the more direct ones by comparison with consequences deduced from these. Important data in this connection are for instance those on the relations between corrosion potential, corrosion rate

and pH. This will be discussed separately in a subsequent paper, and we will here only deal with the more direct results.

A complete analysis of the kinetics of an electrode reaction often requires data also for its reverse reaction [1,2]. This is especially the case for metal dissolution processes, as we here have no means of altering the activity of the main reactant, the solid metal itself. The work of Hoar and Hurlen [15-17] on iron and mild steel in acid sulphate solutions is the only work we are aware of in which the potential/rate relationship for anodic dissolution and cathodic deposition of iron has been studied under equivalent conditions. They found the Fe/Fe^{++}.aq-electrode to behave symmetrically and to have a Tafel slope of numerically 2.303 $RT/2F$ (0.029 V at 25°C) for either of its reactions. The rate of both reactions was moreover found to be proportional to the hydroxyl ion activity, the rate of deposition to be proportional to the square of the ferrous sulphate activity, and the rate of dissolution to be independent of the latter activity. The extrapolated Tafel curves gave reasonable values for the reversible potential and exchange current values directly proportional to both the above mentioned activities, e.g. —0.507 V (normal hydrogen scale) and 2.6 × 10^{-11} A/cm^2 in 0.1 M sodium hydrogen sulphate + 0.05 M ferrous sulphate at 25°C. This work includes experiments at 0, 25, and 50°C, and the method used was the same as in the present work.

Rojter, Juza, and Polujan [18] determined the exchange current of the Fe/Fe^{++}.aq-electrode in 1.25 M ferrous sulphate presumably at room temperature (not specified) from oscillographically determined charging curves and obtained approximately 10^{-8} A/cm^2. This is in reasonable agreement with the results of Hoar and Hurlen when the effect of ferrous ion activity and pH is considered.

Bonhoeffer and Heusler [19-21], from rapid oscillographic potential measurements, found a Tafel slope of 0.030 V for the stationary anodic dissolution of iron in acid sulphate and perchlorate solutions. They further found proportionality between the dissolution rate and the hydroxyl ion activity raised to a power of 1.55. Heusler [21] assumes 2 to be the correct value of this exponent. These results are only partly in accordance with those of Hoar and Hurlen.

Kabanow, Burstein, and Frumkin [22] found an anodic Tafel slope varying from 0.02 to 0.04 V for iron in 2 N sodium hydroxide. By comparing with corresponding results in 1 N hydrochloric acid (obtained by Kusnezov [23]), they further found indications that the dissolution at equal potentials was several orders of magnitude faster in alkaline than in acid solutions. These authors were thereby probably the first to draw attention to the effect of pH on the anodic dissolution of active iron. They also discussed the effect of chloride ions on the anodic dissolution reaction in alkaline solutions.

Values for the Tafel slope of anodic dissolution have been given also by a few other authors. Kaesche [24] found 0.03 V for iron in acid perchlorate solutions at 25°C. Makrides, Komodromos, and Hackerman [25] found 0.04 V for iron in 2 M hydrochlorid acid and Gatos [26] 0.06 V in 1 N sulphuric acid when the dissolution was caused by depolarizers. Hoar and Holliday [27] found 0.051 V for mild steel in 0.5 M sulphuric acid at 40°C, and Hoar and Farrer [28] 0.05 to 0.07 V for mild steel in 0.001 N solutions of various magnesium, calcium, and sodium salts at 25°C. Okamoto, Nagayama, and Sato [29] found about 0.1

V for iron in 0.3 N sulphuric acid when varying the current density be about twice every 0.1 sec. Stern and Roth [30] have moreover given an estimated value of 0.078 V for iron in an acid chloride solution.

According to Bockris [2], little relevant work has been done on the cathodic deposition of iron. A detailed discussion of results obtained up to 1954 has been given by Fischer [14]. A description of modern ideas on the mechanism of metal deposition reactions has more recently also been given by Conway [31]. Lyons [32] has described how the discharge process of cations may be visualized on the basis of electron configurations, and Conway and Bockris [33] have made a theoretical treatment of the mechanism of metal deposition. The most recent work we are aware of as to the deposition of iron, is that of Hoar and Hurlen [15-17] mentioned above.

A detailed description of the hydrogen evolution reaction at iron cathodes is outside the scope of the present work, and a few references will be given for comparison and checking purposes only. The most usual Tafel slope for hydrogen evolution at metal cathodes is $4.606\ RT/F$ (0.117 V at 25°C), a value also easily derivable by theory [1,2]. The results obtained for this reaction on iron in acid sulphate solutions by Hoar and Hurlen [15-17], in acid sulphate and perchlorate solutions by Bonhoeffer and Heusler [19,21], in acid perchlorate solutions by Kaesche [24], in acid chloride solutions by Stern [34,35], and by Fischer and Thoresen [35] (just to mention some of the most recent results) are partly in excellent agreement with this value. It is further to be expected that the rate of hydrogen evolution in this case should be proportional to the hydrogen ion activity provided the pH is not too high and excess indifferent salt is present [1,2]. The results of Hoar and Hurlen [16,17] show an effect of pH in accordance with this, while those of Stern [34,35] and of Bonhoeffer and Heusler [19,21] show a somewhat smaller pH effect. A modern analysis of the effect of the electrode material on the hydrogen evolution reaction is given by Parsons [37].

Stern [35] and Hoar and Hurlen [15-17] have recently studied the effect of impurities in iron on its electrode behaviour (the latter authors by comparing the behaviour of pure iron with that of a relatively clean mild steel). In both these investigations, a distinct stimulating effect especially of non-metallic impurities (as sulphur and phosphor) on the hydrogen evolution reaction was observed. Hoar and Hurlen found no differences in the pure dissolution and deposition characteristics of their iron and mild steel electrodes. Some earlier indications [38-40] that sulphur should promote also the anodic dissolution reaction were thereby not confirmed.

Most of the work on the electrochemical behaviour of iron has been performed with polycrystalline electrodes. Engell [41] and Buck and Leidheiser [42], however, have made some investigations on single crystals of α-iron. Engell found that the dissolution was nearly independent of the orientation of the crystal surfaces at low current densities (less than about 2 mA/cm²), whereas the (111) and (110) surfaces dissolved faster than the cube faces by a factor of about 2 at higher anodic loads. These investigations were performed in dilute sulphuric, perchloric, and nitric acid. Similarly, Buck and Leidheiser found that the rate of corrosion of the (321) face was approximately twice that of the (100) face in 0.2 M citric acid. The corrosion potential of the latter face was moreover more cathodic than that of the former face. This indicates that,

besides a possible difference in the cathodic hydrogen evolution reaction at these faces there is also a difference in the anodic dissolution reaction.

Buck and Leidheiser [42] further found that the rate of corrosion of the polycrystalline starting material from which the single crystals were prepared was several times greater than those of the single crystals, and that the conversion of the single crystals to polycrystalline material resulted in a considerably increased corrosion. They ascribe this to an effect of grain boundaries on the dissolution reaction. The effect of dislocation steps in the surface on the rate of dissolution and deposition has recently been treated theoretically by Vermilyea [43].

Reviews and dicussions of recent work of general interest to electrochemical kinetics are moreover presented by Grahame [44], Butler [45], Delahay [46,47], Breyer [48], Thirsk [49], Fleischmann and Oldham [50], and Frumkin [51].

The passivity of iron is not considered here as the present work solely deals with the electrochemistry of active iron.

3.0 MATERIALS AND METHODS

Electrodes of iron (0.03 % C, 0.01 % Si, 0.19 % Mn, 0.027 % P, 0.030 % S), presented by Domnarfvets Jernverk (Sweden), were used in the form of circular sheets (about 4.5 cm diameter and 0.5 mm thickness) punched out from cold-rolled strips. Prior to use, the electrodes were vacuum annealed for about one hour at about 700°C, polished with emery paper, etched in dilute nitric acid, washed in running water, distilled water, and acetone, dried, and weighed.

Electrolytes were prepared from A.R. quality ferrous chloride, potassium chloride, and hydrochloric acid in water distilled from a "pure" and soft fresh water. The solutions were presaturated with hydrogen which first was purified by passing a palladium catalyst at about 250°C. For the ferrous chloride solutions, the presaturation was performed in the presence of a large piece of platinized platinum. This reduced the ferric ion content to a very low level (as judged from the red-ox potential). The electrolytes were also stored under hydrogen and were further transferred to the test cell by hydrogen pressure. A sketch of the electrolyte preparation and storage unit is shown in Fig. 1.

The test cell was a cylindrical Pyrex glass cell (about 10 cm² internal cross section and about 15 cm long) carrying tubes for the ingress and egress of liquid and gas. Two
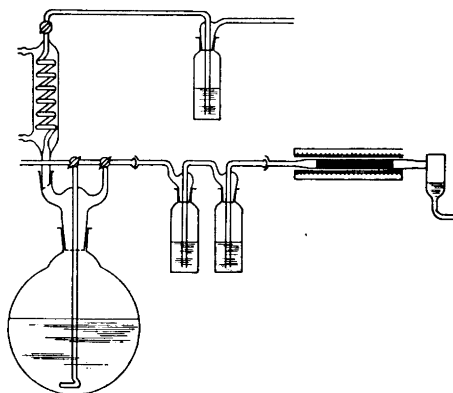

Fig. 1. The unit for preparation, pretreatment, and storage of electrolyte solutions.
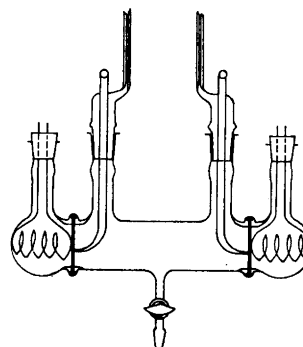

Fig. 2. The experimental cell.

electrodes could here be placed so as to form the two end walls of the cell. After having been clamped in position, the electrodes were covered around their outer edge with polystyrene (dissolved in chloroform) and paraffine wax. The cell further had two Haber-Luggin capillaries for electrolytic connections to two external reference electrodes, and copper wires for metallic connections to the potentiometer and to the current source. A sketch of the test cell, which could hold about 200 ml electrolyte, is shown in Fig. 2. In this cell, the electrolyte is exposed to the atmosphere only in two capillaries of about one millimeter diameter.

The experiments were performed galvanostatically. The current was supplied from an assembly of four 12 V accumulators connected in series. It was read on a calibrated Avo-meter and controlled by a number of variable resistances in series with the cell. The electrode potential of each electrode as a function of time was measured against a saturated calomel electrode by means of a Cambridge pH-meter.

The partial current density of the iron electrode reactions was estimated from the weight change of the electrodes over a considerable time at constant total current density. A Mettler semi-micro balance was used for these weighings. The duration of the runs varied from about one hour to two days, depending on the current applied ($10^{-6} - 10^{-2}$ A/cm^2). The experiments were performed in a thermostated room at $20 \pm 0.5°C$.

[4.0 THE ELECTROLYTE SOLUTIONS

The electrolyte solutions (I—IX) used in the present work, are described in Table 1. Data are there given for the composition and for the "molal ionic strength" defined by:

$$I(m) = \frac{1}{2} \sum_i m_i \cdot z_i^2$$

$I(m)$ is nearly equal to the ionic strength divided by the density of the solution (I/d). Values are moreover given for the mean molal activity coefficient (γ) of the solutes and for the activity (a) of the solvent (water). The dissociation constant of water (K_w) at 20°C is given by [52]

— log $K_w = 14.1666$

The mean molal activity coefficients of hydrochloric acid and of potassium chloride have been calculated from the recent results of Harned and Gancy [53] on mixtures of these two electrolytes. For the ferrous chloride containing solutions, it has been assumed as an approximation that γ_{HCl} and γ_{KCl} have the same values as in corresponding solutions in which the ferrous ions have been substituted by an equivalent amount of potassium ions. The mean molal activity coefficients of ferrous chloride have been estimated graphically, log γ *vs.* $I(m)$, from data tabulated by Robinson and Stokes [52].

The activity of water in the solutions I—IV has been calculated from the data given by Harned and Gancy [53] for the osmotic coefficient of such solutions. For solution V, in which ferrous chloride is the main electrolyte, the water activity has been calculated from the molal osmotic coefficient of 0.5 m ferrous chloride [52]. For the solutions VI—IX, a_{H_2O} has been estimated on the basis of data from the above mentioned sources.

All the data used in these calculations apply to 25°C. It will here be assumed, however, that the values in Table 1 are sufficiently valid also at 20°C.

Table 1. Composition, ionic strength, and thermodynamic activity data for the applied solutions (I—IX).

| | Molality | | | $I(m)$ | $-\log \gamma$ | | | $-\log a$ |
	HCl	KCl	FeCl$_2$	$(\approx I/d)$	HCl	KCl	FeCl$_2$	H$_2$O
I	1	0	0	1.0	0.0908	0.1502		0.016
II	0.1	0.9	0	1.0	0.1406	0.2119		0.014
III	0.01	0.99	0	1.0	0.1458	0.2176		0.014
IV	0.001	0.999	0	1.0	0.1462	0.2181		0.014
V	0.001	0	0.5	1.5	(0.146)		0.347	0.011
VI	0.001	0.6	0.2	1.2	(0.146)	(0.218)	(0.349)	(0.013)
VII	0.001	0.8	0.1	1.1	(0.146)	(0.218)	(0.348)	(0.013)
VIII	0.001	0.9	0.05	1.05	(0.146)	(0.218)	(0.347)	(0.014)
IX	0.0001	1.8	0.1	2.1	(0.120)	(0.240)	(0.334)	(0.014)

In electrode kinetics, we are interested in knowing single ion activities. These cannot be calculated from thermodynamic data (as those in Table 1) without the introduction of some non-thermodynamic (or extrathermodynamic) assumptions [52,54-57]. For solutions of single univalent chlorides, two approaches have often been used:

a) *The MacInnes assumption*, which states that the chloride ion activity in a solution of any chloride is the same as the mean ionic activity in a solution of potassium chloride at the same total concentration.

b) *The Guggenheim assumption*, which states that the activity of the chloride ion of any univalent chloride is equal to the mean ionic activity.

The first of these assumptions may directly and equally well be applied to mixed electrolytes, and this gives for the ferrous chloride free solutions (I—IV):

$$\log \gamma_H = 2 \log \gamma_{HCl} - \log \gamma_{KCl(o)} \tag{1}$$

where γ_H is the activity coefficient of the hydrogen ions in the mixed electrolyte, and $\gamma_{KCl(o)}$ is the mean activity coefficient of potassium chloride in a pure solution of this salt at the same total concentration. Results of calculations of pH $(= -\log a_H)$ on this basis are given in Table 2.

The Guggenheim assumption allows us to calculate the activity coefficent of hydrogen ions in a pure hydrochloric acid solution, $\gamma_{H(o)}$, as well as their limiting activity coefficient, $\gamma_{(o)H}$, in a mixed electrolyte of hydrochloric acid and potassium chloride by the relations:

$$\log \gamma_{H(o)} = \log \gamma_{HCl(o)} \tag{2a}$$

$$\log \gamma_{(o)H} = 2 \log \gamma_{(o)HCl} - \log \gamma_{KCl(o)} \tag{2b}$$

From the Guggenheim theory [52] of mixed electrolytes, one further has:

$$\log \gamma_H = \log \gamma_{(o)H} + x(\log \gamma_{H(o)} - \log \gamma_{(o)H}) \tag{3}$$

where x is the mole fraction of hydrochloric acid in the two component mixed electrolyte. Results of calculations of pH from these equations are also given in Table 2. As the *Guggenheim assumption* seems the thermodynamically most sound, the pH-values obtained on this assumption (together with the a_{H_2O}-values in Table 1) have been used in calculating the pOH-values given in Table 2.

For a pure ferrous chloride solution, the Debye-Hückel theory gives

$$\log \gamma_{Cl(Fe)} = \tfrac{1}{2}\log \gamma_{FeCl_2(o)} \tag{4}$$

when also the definition of the mean ionic activity coefficient is considered. On this basis and on the basis of the Guggenheim theory of mixed electrolytes, one may further assume the activity coefficient of chloride ions in a mixed solution of ferrous chloride and potassium chloride to be given by:

$$\log \gamma_{Cl(K,Fe)} = x_{KCl} \log \gamma_{KCl(o)} + \tfrac{1}{2}\, x_{FeCl_2} \log \gamma_{FeCl_2(o)} \tag{5}$$

where all the activity coefficients apply to the same ionic strength and x means the ionic strength fraction of the salts in the mixed solution. This equation has been used in calculating γ_{Cl} for the solutions V—IX (neglecting the possible effect of the small amount of hydrochloric acid present). γ_H and γ_{Fe} have then been calculated from the relationships:

$$\log \gamma_H = 2 \log \gamma_{HCl} - \log \gamma_{Cl} \tag{6a}$$

$$\log \gamma_{Fe} = 3 \log \gamma_{FeCl_2} - 2 \log \gamma_{Cl} \tag{6b}$$

where all the activity coefficients apply to the same solution. The ion activities thus obtained, are given in Table 2.

The values of γ_{FeCl_2} (see Table 1) needed in the just described calculations of γ_{Fe}, have been obtained on the assumption that the former coefficient is the same in any of the mixed solutions as in a pure ferrous chloride solution of the same $I(m)$-value. The ferrous ion activity coefficient may also be calculated on the assumption that this coefficient (instead of the mean ionic activity coefficient) obeys the above equality. This means, when eqn. 4 is considered, that

$$\log \gamma_{Fe} = 2 \log \gamma_{FeCl_2(o)} \tag{7}$$

where the two activity coefficients apply to solutions of the same ionic strength. The results of such calculations are also given in Table 2, and it will here be assumed that the thereby obtained activity values are the most correct ones.

Ferrous chloride has here been treated as a non-associated electrolyte. This may seem justified by the fact that its mean acitivity coefficient is well described by the Stokes-Robinson two-parameter equation [52] for this type of electrolytes. A possible hydrolysis of the ferrous ion has also been ignored, and this seems justified on the basis of the low value ($10^{-9.5}$) found by Hedström [58] for the hydrolysis constant of this ion.

Table 2. Estimated single ion activities of H^+, OH^-, and Fe^{++} in the applied solutions (I—IX).

	pH[1]	pH[2]	pOH[3]	Notes:		
				[1] MacInnes assumption		
I	−0.037	0.091	14.060	[2] Guggenheim assumption		
II	1.063	1.076	13.077	[3] From eqns. 5 and 6		
III	2.073	2.074	12.079	[4] From eqn. 7		
IV	3.074	3.074	11.079	pFe[3]	pFe[4]	a_{Fe}[4]
V		3.118	11.038	0.995	0.995	0.101
VI		3.091	11.063	1.345	1.397	0.040
VII		3.083	11.071	1.625	1.696	0.020
VII	(3.074)	3.081	11.072	1.920	1.995	0.010
IX	(4.000)	4.024	10.129	1.570	1.668	0.021

5.0 RESULTS AND INTERPRETATIONS

Examples of potential-time curves obtained for hydrogen evolution at iron cathodes and for anodic dissolution and cathodic deposition of iron, are given in Figs. 3, 4, and 5, respectively. The applied current density is given in A/cm^2 for the various curves in the diagrams. Due to corrosion and to simultaneously occurring hydrogen evolution and iron deposition, the partial current density of the reactions (as determined by weight change measurements) sometimes was quite different from the applied current density (see below). The former of these current densities and potential data from the potential-time curves have been used in constructing Tafel diagrams for the three reactions studied. The potentials most representative for the hydrogen evolution reaction at the initial pH of the solutions have been assumed to be those obtained by extrapolating the potential-time curves to zero time. For the dissolution and the deposition reaction, the stationary potentials (or in some cases the potential in the beginning of a period of nearly stationary potential) have been assumed the most representative ones. The Tafel diagrams obtained in this way are shown in Figs. 6—10.

In transforming the readings made against the saturated calomel electrode, to potentials on the normal hydrogen scale, a value of + 0.245 V has been used for the calomel electrode at 20°C (Potter [59]). No attempts have been made to correct for the possible liquid junction potentials between the test solutions and the saturated potassium chloride solution. On the basis of data tabulated by Milazzo [60], however, it is believed that these junction potentials are small.

Hydrogen evolution

The hydrogen evolution reaction has mainly been studied in the ferrous ion free solutions (I—IV), but partly (at low current densities) also in the solution of the lowest ferrous chloride content (VIII). The polarization data obtai-
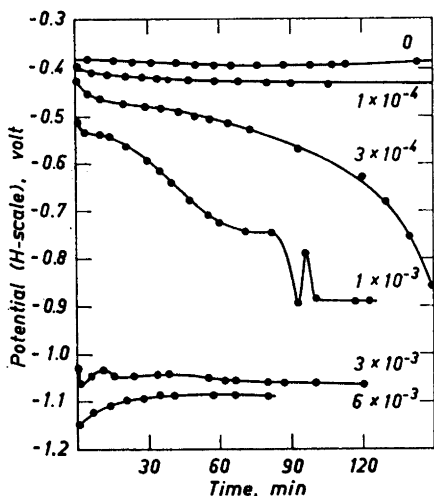
Fig. 3. Potential-time curves for hydrogen evolution at iron cathodes in solution III at various applied current densities (A/cm²).
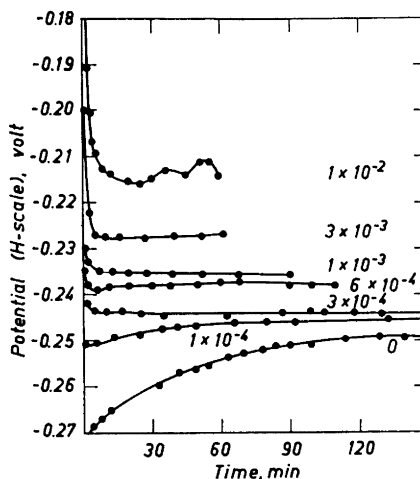
Fig. 4. Potential-time curves for anodic dissolution of iron in solution I at various applied current densities (A/cm²).

ned are given in Fig. 6, where the closed circles apply to cathodically polarized electrodes, the open circles to anodically polarized electrodes, and the centred circles to freely corroding electrodes. The terms *anodic* and *cathodic* are here used in reference to the corrosion potential so as to indicate the direction of the applied current.
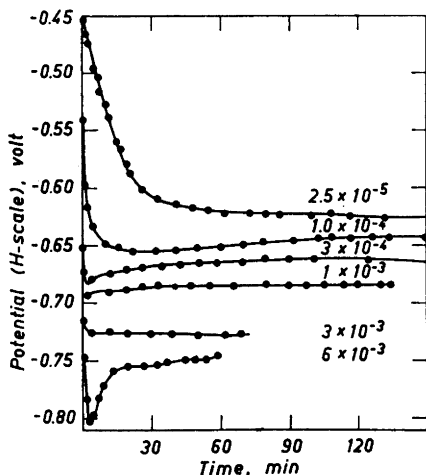

Fig. 5. Potential-time curves for cathodic deposition of iron in solution VII at various applied current densities (A/cm²).
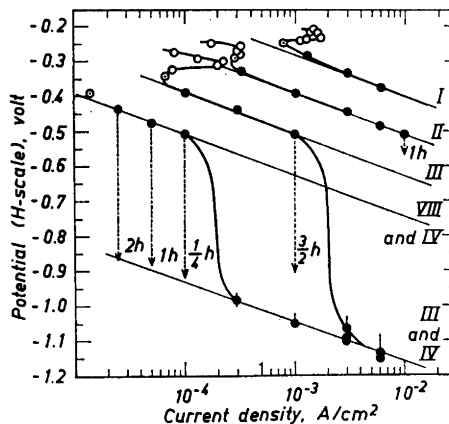
Fig. 6. Tafel diagram for hydrogen evolution at iron cathodes.

The partial current density of hydrogen evolution on anodically polarized electrodes has been estimated by the difference between the gravimetrically determined and the applied current density with corrections for the corrosion occurring prior to and after the application of current. On cathodically polarized electrodes, it has similarly been taken as the sum of the applied and the gravimetrically determined corrosion current. It is only at the lowest current densities in the two most acid solutions that a measurable corrosion occurred on electrodes of this kind, however.

The results (Fig. 6) clearly show that the hydrogen evolution reaction in these cases is strongly stimulated by a simultaneously occurring iron dissolution reaction when the rate of the latter approaches and exceeds that of the former (see the position of the corrosion points and the higher lying points in the diagram). This stimulating effect seems otherwise to be a complex function of the dissolution rate and possibly also of pH. It may here be of interest also to note that there both in the present work and especially in the previous work of Hoar and Hurlen [15,16] are indications that the hydrogen evolution reaction is affected in the opposite way by a simultaneously occurring iron deposition reaction.

The results further show that the hydrogen evolution reaction, when being the main or the only process occurring, follows the Tafel relationship with a Tafel slope (b) of very nearly -0.116 V. This indicates that

$$b = -2.303(2RT/F) \qquad (8)$$

which is in agreement with previous results (see above). The data in Fig. 6 and in Table 2 with very good approximation also give the following corresponding relationships for the effect of pH on this reaction in the acid chloride solutions (when the current density is not too high):

$$(\partial \log i / \partial \text{ pH})_V = -1 \qquad (9a)$$

$$(\partial V / \partial \text{pH})_i = -2.303(2RT/F) \qquad (9b)$$

This is the same as previously found by Hoar and Hurlen [15-17] in acid sulphate solutions.

At the higher current densities in the less acid solutions (III and IV) the polarization points fall on a much lower lying and apparently pH-independent Tafel line with the same slope as the other ones. Also at the lower current densities in the solution of the highest pH (IV) does the potential seem to reach this Tafel line after some time (as indicated in Fig. 6) and then to stabilize there. It may certainly be that the potential at the higher current densities also starts at the pH-dependent Tafel line, but falls so rapidly (in less than half a minute) down to the pH-independent line that this possible happening escapes observation by the technique used.

According to the present results and the data given in Table 2, the pH-independent Tafel line has a position corresponding to that to be expected for the pH-dependent lines at a pH of 6.8. This is not far from the neutral point in these solutions which is near to pH 7.07 at 20°C. It seems thus natural to assume that the pH-dependent and the pH-independent Tafel lines represent

a reduction of hydrogen ions and water molecules, respectively, and that the observed transition from the former to the latter of these lines is due to the pH-change accompanying the hydrogen evolution reaction. Such a transition has also been observed by Stern [34] for hydrogen evolution on iron in acid chloride solutions. The slope of the pH-independent Tafel line was by him found to be — 0.174 V at 25°C, however.

The values obtained for the exchange current (i_0) of the H_2/H^+.aq-electrode on iron by extrapolating the Tafel lines in Fig. 6 to the reversible potential of this electrode in the corresponding solutions are covered by the equation

$$-\log \ i_0 \ (20°C) = 5.36 + 0.5 \ pH \tag{10}$$

where the exchange current is given in A/cm^2. This equation tells that the exchange current is inversely proportional to the square root of the hydrogen ion activity, and that (at 20°C) it should be $10^{-5.36} \ A/cm^2$ when pH = 0. One should be aware of the fact, however, that the above results have been obtained mainly in the presence of excess neutral salt, and that divergences very well may occur in the absence of such salt [2]. On this basis, the results compare well with those tabulated by Parsons [60]: —log i_0 = 5.9, 6.29, and 6.19 in 1 M HCl (16°C), 0.01 M HCl (20°C), and 0.001 M HCl (20°C), respectively. Stern [34], however, found an essentially pH-indenpendent exchange current of the order of $10^{-4} \ A/cm^2$ in acidified 4 % sodium chloride solutions at 25°C. It may also be of interest to compare the present results with those of Hoar and Hurlen [15-17] in acid sulphate solutions at 25°C: — log i_0 = 5.9 and 6.3 at pH = 1.5 and 2.4, respectively. The difference in temperature taken into account, it may thus seem that the rate constant of the hydrogen evolution reaction at iron cathodes is very much the same in sulphate as in chloride solutions. In this respect, iron differs distinctly from nickel as electrode material [61,62]. This will be discussed in a subsequent paper.

Iron dissolution

The anodic dissolution reaction has been studied in all the solutions (I—IX) described above, and the polarization data obtained are given in Figs. 7 and 8. In the least acid solution (IX), the tendency of passivation was more marked and the reproducibility somewhat poorer than in the other solutions, and the anodic data obtained in this solution have therefore been omitted.

The results clearly show that the anodic dissolution reaction follows the Tafel relationship except at the higher current densities in the less acid solutions (IV—IX). The deviation from this relationship in the latter cases may be due to an initiation of passivation. The Tafel lines in Figs. 7 and 8 have been drawn with a slope of 0.029 V, and the reasonable fit of these lines to the experimental points (which apply to 20°C) indicates that the Tafel slope (b) of anodic dissolution of active iron is given by

$$b = 2.303(RT/2F) \tag{11}$$

This is in agreement with the previous results of Hoar and Hurlen [15-17] in acid sulphate solutions, of Bonhoeffer and Heusler [19-21] in acid perchlorate solutions, and also with some of the other results quoted above.
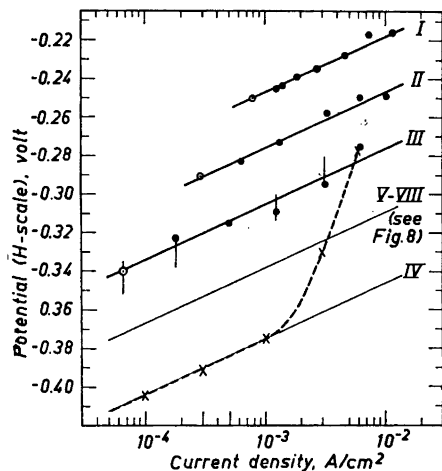
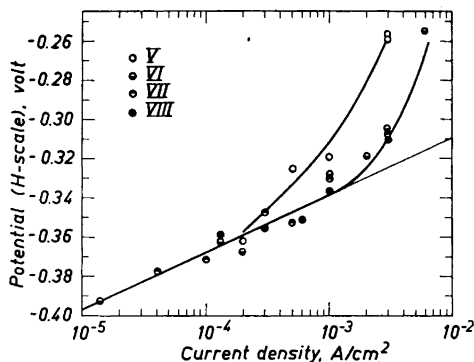*Fig. 7.* Tafel diagram for anodic dissolution of iron.

Fig. 8. Tafel diagram for anodic dissolution of iron in the ferrous ion containing solutions V−VIII.

The present data also agree with those of Hoar and Hurlen [15-17] and of Bonhoeffer and Heusler [19-21] in indicating a strong stimulating effect of hydroxyl ions on the dissolution reaction. Fig. 7 shows that the relationships

$$(\partial \log i / \partial \, \mathrm{pOH})_V = -\, 1 \tag{12a}$$

$$(\partial V / \partial \mathrm{pOH})_i = 2.303(RT/2F) \tag{12b}$$

with relatively good approximation apply to the results except for those obtained in solution IV. In this solution, the dissolution occurred much faster (by a factor of about twenty) than is to be expected from the above relationships and the results in the other solutions. This exception seemed so strange, especially when compared with the "normal" behaviour of the ferrous chloride containing solutions of very nearly the same pH (V—VIII), that three independent series of experiments were made with solutions of this type. As very nearly idential results were obtained in these series, this matter obviously needs further investigation. It may be that we here have some reason for the somewhat larger pOH-effect found by Bonhoeffer and Heusler [19-21].

The data in Fig. 8 further show that the rate of anodic dissolution reaction on active iron is essentially independent of the ferrous ion activity. Also in this connection, however, solution IV represents an exceptional, although extreme case.

There are no indications that a simultaneously occurring hydrogen evolution reaction does have any effect on the iron dissolution reaction comparable to that found for the opposite case (see above).
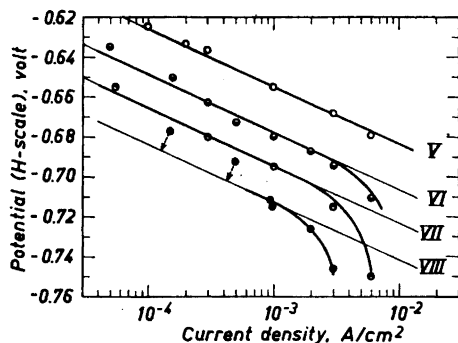
Fig. 9. Tafel diagram for cathodic deposition of iron (effect of ferrous ion activity).
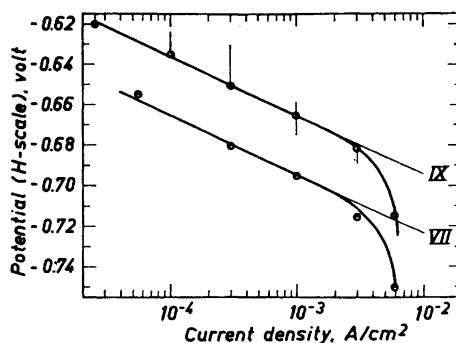
Fig. 10. Tafel diagram for cathodic deposition of iron (effect of pH).

Iron deposition

The polarization data obtained for the iron deposition reaction are given in Figs. 9 and 10. Also this reaction evidently follows the Tafel relationship except at the highest current densities applied. These deviations, however, are easily explained by the transition from activation control to diffusion control when approaching the limiting current. Especially in the solution of the lowest ferrous chloride content (VIII), there also are some distinct deviations at low current densities. In these cases, however, there was a relatively strong simultaneous evolution of hydrogen, and the deviations may very well be due to the pH-change accompanying this process (see below).

The Tafel lines in Figs 9 and 10 have been drawn with a slope of —0.029 V corresponding to

$$b = -2.303(RT/2F) \tag{13}$$

for the iron deposition reaction. This is numerically the same value as for the dissolution reaction, indicating that the Fe/Fe^{++}.aq-electrode behaves symmetrically. Also this is in agreement with the previous results of Hoar and Hurlen [15-17] for iron in acid sulphate solutions.

The results in Fig. 9 further show that the effect of the ferrous ion activity on the rate of the activation controlled deposition reaction is very nearly given by the following corresponding equations:

$$(\partial \log i/\partial pFe)_{V,\ pOH} = -2 \tag{14a}$$

$$(\partial V/\partial pFe)_{i,\ pOH} = -2.303(RT/F) \tag{14b}$$

This means that the deposition rate at any given potential and hydroxyl ion activity is proportional to the square of the ferrous ion activity, or, correspondingly, that the variation of the deposition potential with the ferrous ion activity at any given hydroxyl ion activity and deposition rate is twice that of the reversible potential of the Fe/Fe^{++}.aq-electrode. This, which also is in

accordance with the previous results of Hoar and Hurlen [16],[17], is simply what thermodynamics requires on the basis of the Tafel slope values and the independence of the anodic Tafel line on the ferrous ion activity.

On the further basis of the pOH-dependence of the anodic Tafel line, thermodynamics also requires that the relationships

$$(\partial \log i / \partial \, \text{pOH})_{V\,,\text{pFe}} = -1 \tag{15a}$$

$$(\partial \, V / \partial \text{pOH})_{i,\,\text{pFe}} = -2.303(RT/F) \tag{15b}$$

should apply to the deposition reaction. The results shown in Fig. 10 are in good agreement with these corresponding requirements.

The Fe/Fe^{++}.aq-Electrode

The values obtained for the reversible potential (E) and the exchange current (i_o) of the Fe/Fe^{++}.aq-electrode by extrapolating the Tafel lines for the dissolution and the deposition reaction (Figs. 8—10) to intersection, are covered by the following equations:

$$E(20°C) = -0.467 - 0.029 \, \text{pFe} \tag{16a}$$

$$\log i_o(20°C) = 3.58 - \text{pFe} - \text{pOH} \tag{16b}$$

when the activity data in Table 2 are applied, and E and i_o are given in V and A/cm^2, respectively.

Eqn. 16a apparently gives a value of —0.467 V for the standard potential of this electrode at 20°C. However, this value includes both the uncertainties attached to the single ion activities used for the ferrous ion, and the unknown liquid junction potentials between the test solutions and a saturated potassium chloride solution. The observed effects of the ion activities do suggest that these junction potentials are very much the same for all the solutions applied, and the data tabulated by Milazzo [63] for such potentials, do suggest that it should be very small, probably not more than 1—2 mV. The same data also show that the liquid junction in the present cases should be expected to make the experimentally obtained potentials too negative.

The previous work of Hoar and Hurlen [15-17] similarly led to a value of —v.442 V for the standard potential at 25°C. This is close to the so far accepted value [64] of —0.440 V. However, these measurements were made in more acid solutions (pH 1.5—2.4) of relatively low ferrous ion concentration (0.05—0.15 M), and the deposition reaction was accompanied by a much stronger simultaneous hydrogen evolution reaction than in the present work (in which many of the results have been obtained at very nearly 100 % deposition). Even though the sulphate solutions have a better buffer action than the chloride solutions, it may be that the potentials of iron deposition in the previous Hoar-Hurlen work have been affected by a pH-change caused by the hydrogen evolution reaction, and thereby got a too high position in the Tafel diagram (see eqn. 15b).

On this basis, and assuming the applied activity data to represent a fair approximation, the author is inclined to believe that the standard potential of the Fe/Fe^{++}.aq-electrode should be more negative than the at present accepted value of —0.440 V.

Eqn. 16b for the exchange current (as well as eqns. 12 and 15) is written according to the assumption that the observed effect of pH on the iron electrode reactions is caused by the hydroxyl ions and not directly by the hydrogen ions. This assumption is based on the facts

a) that the effect is stoichiometric,

b) that it is positive (stimulating) with regard to hydroxyl ions, but negative (inhibiting) with regard to hydrogen ions,

c) that it is easily explained by a direct interaction of hydroxyl ions in the reactions, and

d) that there seems no reason why a possible inhibiting effect of hydrogen ions should be stoichiometric.

Some evidence for the validity of this assumption is provided by the previous data of Hoar and Hurlen [15,16] on the effect of temperature on the ion electrode reactions in acid sulphate solutions. These results, when treated conventionally, give an unreasonably high value for the virtual heat of activation [2] at the reversible potential. This is most probably due to a relatively strong variation in the activity of some of the reaction participants (what is not accounted for in the conventional treatment). The change in ferrous ion activity and pH with temperature in the applied solutions is relatively small, but pOH changes by more than one and a half unit over the temperature range concerned (0—50°C). This will be more thoroughly discussed in a subsequent paper [65.]

Accepting the hydroxyl effect assumption as correct, one may rewrite eqn. 16b in the form:

$$— \log i_o \,(20°C) = 10.59 + pFe — pH + pH_2O \tag{17}$$

in which the constant is equivalent to "pK_w — 3.58". In the present case, the pH_2O-term is almost negligible. The previous work of Hoar and Hurlen [15-17] in sulphate solutions gave:

$$— \log i_o \,(25°C) = 9.7 + pFe — pH \tag{18}$$

in which equation the negligible pH_2O-term is included in the constant.

The difference between the constants in eqns. 17 and 18 is nearly what is to be expected from the temperature difference on the basis of the heats of activation and the effect of temperature on the dissociation constant of water. This strongly indicates that neither chloride ions nor sulphate ions do have any direct effect on the dissolution and the deposition reaction of an active iron electrode. As there further are distinct differences in the chemical and metallurgical conditions (impurity content, coldwork, annealing) of the electrode materials used in these cases, nor these conditions do seem to have any great effect on these reactions in the pH-range 0 to 4. The hydrogen evolution reaction, however, is strongly influenced by some of these conditions (see the above discussion of previous work).

Thermodynamically, the overall reactions of the Fe/Fe^{++}.aq-electrode are undoubtedly represented by:

$$Fe \rightleftharpoons Fe^{++}.aq + 2e^- \tag{19}$$

Kinetically, however, this equation gives a too simplified and partly wrong impression. For characterizing such reactions, the modern theory of electrode kinetics [1,2] introduces the stoichiometric number (ν), which is defined as the number of times the rate determining reaction is represented in the overall electrode reaction considered. The theory further gives the following relationships between ν and other reaction parameters:

$$\nu = b_a b_c n F / 2.303 RT (b_c - b_a) \tag{20a}$$

$$\partial \log i / \partial pQ = -q/\nu \tag{20b}$$

$$\Delta H^*_{o,a} - \Delta H^*_{o,c} = \Delta H_{o,a}/\nu \tag{20c}$$

in which pQ means the negative logarithm of the activity of a reactant Q with stoichiometric factor q in the overall reaction, and the indexes a and c refer to the anodic and the cathodic reaction, respectively. There are just as many equations of type 20b as there are activity variable components in the overall reaction (only one in the present case), and ν may be determined independently from any of these or from eqn. 20a. To be strictly valid, however, eqn. 20b usually requires that excess inert electrolyte be present. Eqn. 20c can only be used for checking, as a knowledge of ν already is required in the determination of the heats of activation. When ν is known, eqn. 20b can also be applied for determining the stoichiometric factor of a possible interacting component not appearing in the equation for the overall reaction (e.g. hydroxyl ions in the present case).

On this basis, the data presented in eqns. 11, 13, 14, and 17 above show that

$$\nu = \tfrac{1}{2} \tag{21}$$

for the Fe/Fe^{++}.aq-electrode when its overall reactions are represented by eqn. 19. The data presented in eqns. 12 and 15 further show that the hydroxyl ion effect is accounted for by regarding the hydroxyl ion as a catalytic reactant with the stoichiometric factor

$$q_{OH} = \tfrac{1}{2} \tag{22}$$

in the overall reactions. These results simply mean that the reactions occurring for each act of the rate determining step in either direction of the Fe/Fe^{++}.aq-electrode is covered by the equation:

$$2Fe + OH^-.aq \rightleftharpoons 2Fe^{++}.aq + OH^-.aq + 4e^- \tag{23}$$
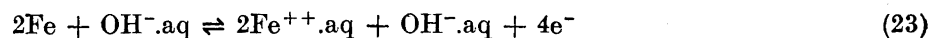
According to the present results, the above equation represents the smallest repeating reaction unit of the Fe/Fe^{++}.aq-electrode. In correspondance with

the terminology used in the crystal structure field, the term *unit reaction* or *kinetic unit reaction* may be proposed for reactions of this type. Just as a unit cell may contain more than one atom, ion, or molecule, a unit reaction may very well comprise more than one reaction step. It may even comprise more than one act of the rate determining step if defined as *the smallest reaction having integral values for all the stoichiometric factors and for the stoichiometric number.*

It is easily seen that the kinetic unit reactions arrived at in the present work (eqn. 23), is thermodynamically in accordance with the previously well established overall reactions of the Fe/Fe^{++}·aq-electrode (eqn. 19).

6.0 DISCUSSION

The hydrogen evolution reaction has been discussed in detail by many authors. As the present results on this reaction at iron cathodes moreover are essentially in agreement with previous data and with what is to be expected from theory [1,2], it will here be refrained from a further discussion of this subject, and the discussion will be confined to the Fe/Fe^{++}.aq-electrode reactions.

The results obtained in eight of the nine electrolyte solutions used in the present work, have been shown to indicate that these reactions are governed by a hydroxyl catalyzed double metal ion mechanism as that covered by eqn. 23. The results in the strange behaving solution (IV) are also in agreement with the double metal ion mechanism, but apparently show a relatively stronger hydroxyl ion interaction than found in the other solutions.

The hydroxyl ion interaction seems to occur stoichiometrically even in solutions in which the activity of this ion is as low as 10^{-14}. However, it is not the bulk activity, but the activity at the electrode surface that counts in such a catalytic interaction as in the present case. Due to the ionic distribution at electrified interfaces, to adsorption and perhaps chemisorption, and to corrosion at anodes and partial hydrogen evolution at cathodes, the latter activity may be much higher than the former. The observed stoichiometry may thus be assumed to indicate an approximately constant proportionality between these two activities, and the above mentioned deviation to be due to a breakdown of this constancy for some reason or another. Further work is needed to clarify this matter.

The Tafel slopes obtained are just what to be expected from a double metal ion mechanism without hydroxyl ion interaction, and this may indicate that the activity of the interacting hydroxyl ions does not change very much with the electrode potential over the regions in which the gradients have been determined. That corresponding Tafel lines intersect somewhat below what to be expected from the ferrous ion activity and the accepted standard potential of this electrode, however, could mean that the effective hydroxyl ion activity is somewhat higher at the anodes than at the cathodes.

According to the results of recent experiments in our laboratory [66], hydroxyl ions do also seem to interact with the Co/Co^{++}.aq-electrode reactions, but not with the reactions of the Ni/Ni^{++}.aq.-, the Cu/Cu^{++}.aq-, and the Zn/Zn^{++}.aq-electrode.

The double metal ion mechanism may be one involving two ferrous ions jointly undergoing a 4-electron process in either direction (Hoar [15]). However, it may just as well be one involving the following two steps:

$$Fe + OH^-.aq \rightleftharpoons Fe^{++}.aq + OH^-.aq + 2e^- \tag{24a}$$

$$Fe \rightleftharpoons Fe^{++}.aq + 2e^- \tag{24b}$$
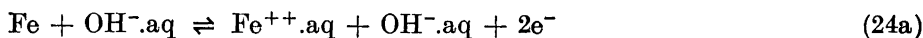
and the author is inclined to believe more in this than in the former possibility.

The above equations may give the impression that the double metal ion mechanism simply is a consequence of the hydroxyl ion interaction, but this impression obviously is an artificial one only. There must be some more basic reason why just half the iron atoms (or ions) do need the assistance of a hydroxyl ion to make the jump through the electrode interface. That the double metal ion mechanism is not a consequence of the hydroxyl ion interaction, has become even more clear by the recent findings in our laboratory [66] that the pOH-independent reactions of the Cu/Cu^{++}.aq-electrode and probably those of the Ni/Ni^{++}.aq- and the Zn/Zn^{++}.aq-electrode also are governed by such a mechanism, and that this also is the case for the Co/Co^{++}.aq-electrode reactions in which there probably is an interaction of one hydroxyl ion for each metal ion reacting in either direction. The double metal ion mechanism may thus seem to be almost a general one for metal/metalion electrodes in aqueous solutions. It is likely, therefore, that it also should have an explanation of equally general character.

As already previously suggested by the author [15-17,62], an explanation may be provided on the basis of the steric conditions at the metal/water interface. In liquid water, the volume per molecule (H_2O) is very nearly 30 $Å^3$ (see Ref.[52], p. 3). If we as a first approximation regard water as consisting of close-packed spherical molecules, we easily calculate that there should be about 9.54×10^{14} water molecules per cm^2 in a close-packed water plane. In α-iron, the approximate number of atoms per cm^2 is [67]:

1.88×10^{15} in the (111)-plane,
1.73×10^{15} in the (110)-plane,
1.22×10^{15} in the (100)-plane.

The (111)-plane is here the plane of closest packing, and we see that it contains very nearly *twice* the number of iron atoms as there are water molecules in a close-packed water plane. Just as there are more and less closely packed planes in a crystal, one may also imagine the existence of more and less closely packed planes of water molecules. It might further be that the special structure of any surface plane of an iron crystal and the interaction between this plane and the water might favour such a packing of the water molecules at the interface as to give very nearly *one* water molecule for every *two* metal atoms even in those cases where there of purely steric reasons should be space for some more water molecules.

On this basis, the anodic reaction of the Fe/Fe^{++}.aq-electrode may be imagined somewhat as follows:

Step 1:

$$Fe^{++}(M) + OH^-(S) \longrightarrow \ddagger_a \longrightarrow Fe^{++}(S) + OH^-(S)$$

Step 2:

$$Fe^{++}(M) \longrightarrow \ddagger_b \longrightarrow Fe^{++}(S)$$

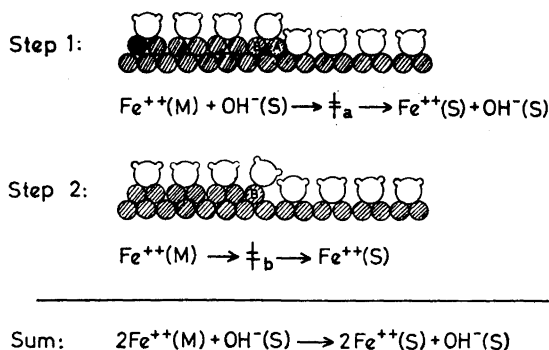Sum: $$2Fe^{++}(M) + OH^-(S) \longrightarrow 2Fe^{++}(S) + OH^-(S)$$

Fig. 11. An illustration to the possible kinetic effect of the steric conditions at an iron/ water interface.

Let us consider a "unit" of two iron atoms and one water molecule at the electrode surface. The water molecule interacts with both the iron atoms and is not quite free to "help" only one of them into the solution. The first of these two atoms to dissolve, may therefore need a relatively high energy to make the jump, unless this jump is facilitated by the interaction of a hydroxyl ion. When this atom has left the surface, the water molecule (or another water molecule) may be more free to help the remaining atom to dissolve whereby the energy needed in this case should be smaller. The rate determining step should thus be connected to the removal of the first of these two atoms from the surface. These considerations are illustrated by the sketches in Fig. 11.

Similar considerations could also be given to the cathodic reaction of the Fe/Fe^{++}.aq-electrode and to the reactions of other metal/metalion-electrodes in aqueous solutions.

The hypothesis suggested here could easily be somewhat more elaborated and refined, but it seems unprofitable to do this until more data are available. A more complete discussion will therefore be postponed until the above mentioned work on other metal/metalion-electrodes has been finished.

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