Dissolution of iron oxide under potential control

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DISSOLUTION OF IRON OXIDE

UNDER POTENTIAL CONTROL

by

PATRICK HARKINS

Supervisor: Professor N.A. Hampson

The work described in this thesis has not been submitted in full, or in part, to this or any other institution for a higher degree.
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Finally, I would like to thank my fellow students for the pleasure of their company and their friendship.
ABSTRACT
The behaviour of magnetite (Fe₃O₄), a potentially, damaging corrosion product of steel, has been investigated in acidic solution and the results are reported and discussed herein.

A review of some of the literature on the structure and electrochemistry of magnetite and on the electrochemical dissolution of crystals is presented. Emphasis is laid upon work concerned with the dissolution of magnetite, especially in acidic and/or at cathodic potentials.

A preliminary examination of the electrochemical behaviour of magnetite in terms of its current/potential characteristics and the response to potential perturbations of both stationary and non-stationary magnetite electrodes is given. The effect of an applied potential on the dissolution rate of magnetite in acidic perchlorate solution and the variation, with time, of both the dissolution and electronic currents is described, also.

It is shown that, over a wide range of potential, dissolution of magnetite occurs via a solid-state reduction of ferric to ferrous ions with subsequent transfer of ferrous ions into solution. It is shown, also, that while a relationship exists between the applied potential and the dissolution rate, it is complex and, in the main, reflects the relationship between the applied potential and the electronic current.

It has been possible to conclude that at elevated temperatures, potential regions exist within which the electronic current is controlled by a solution-state process and suggests that it is the mass-transport of protons which is the rate controlling factor.
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### List of Symbols

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<thead>
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<th>Symbol</th>
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<tr>
<td>A</td>
<td>nominal electrode area (cm²)</td>
</tr>
<tr>
<td>C</td>
<td>concentration of species, i</td>
</tr>
<tr>
<td>C_b</td>
<td>bulk concentration of species, i</td>
</tr>
<tr>
<td>D</td>
<td>diffusion co-efficient of species, i (cm² s⁻¹)</td>
</tr>
<tr>
<td>E</td>
<td>electrode potential</td>
</tr>
<tr>
<td>E_e</td>
<td>equilibrium electrode potential</td>
</tr>
<tr>
<td>E_p</td>
<td>peak potential</td>
</tr>
<tr>
<td>E₁/₂</td>
<td>potential at which current, i, equals half of peak current, i</td>
</tr>
<tr>
<td>F</td>
<td>the Faraday</td>
</tr>
<tr>
<td>G°</td>
<td>standard electrochemical free energy</td>
</tr>
<tr>
<td>G°ₚ</td>
<td>standard electrochemical free energy of activated complex</td>
</tr>
<tr>
<td>G°ₚₐc</td>
<td>standard electrochemical free energy of reactants</td>
</tr>
<tr>
<td>G°ₚₚd</td>
<td>standard electrochemical free energy of products</td>
</tr>
<tr>
<td>h</td>
<td>Planck's constant</td>
</tr>
<tr>
<td>i, I</td>
<td>current density (A cm⁻²)</td>
</tr>
<tr>
<td>iₜ</td>
<td>exchange current density</td>
</tr>
<tr>
<td>Iₜ</td>
<td>current extrapolated to infinite diffusion</td>
</tr>
<tr>
<td>J</td>
<td>flux of species, i, (mol cm⁻² s⁻¹)</td>
</tr>
<tr>
<td>K</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>k</td>
<td>potential-dependent rate constant</td>
</tr>
<tr>
<td>kₚ</td>
<td>potential-independent rate constant</td>
</tr>
<tr>
<td>N</td>
<td>number of Coulombs of electricity passed during dissolution</td>
</tr>
<tr>
<td>n</td>
<td>number of electrons transferred, overall, during reaction</td>
</tr>
<tr>
<td>r_d</td>
<td>rate of deposition of ions</td>
</tr>
<tr>
<td>r_f</td>
<td>rate of dissolution of freely dissolving crystal</td>
</tr>
<tr>
<td>r_r</td>
<td>rate of removal of ions</td>
</tr>
<tr>
<td>R</td>
<td>Gas constant</td>
</tr>
<tr>
<td>R_{ct}</td>
<td>charge transfer resistance</td>
</tr>
<tr>
<td>T</td>
<td>absolute temperature</td>
</tr>
<tr>
<td>t</td>
<td>time (seconds)</td>
</tr>
<tr>
<td>v_j</td>
<td>velocity component in j-direction</td>
</tr>
<tr>
<td>W</td>
<td>weight of iron dissolved per unit area of electrode (mg cm⁻²)</td>
</tr>
<tr>
<td>x</td>
<td>distance in direction normal to electrode surface</td>
</tr>
<tr>
<td>z_i</td>
<td>charge on species i</td>
</tr>
</tbody>
</table>
α  electron transfer co-efficient
δ  diffusion layer thickness
η  overpotential (=E-E)
μ  chemical potential
υ  potential sweep rate (mV s⁻¹) or kinematic viscosity (cm² s⁻¹)
ϕ  inner (Galvani) potential
ω  rotation rate of disc electrode (radians s⁻¹)
1. INTRODUCTION.

Magnetite, Fe₃O₄, is the major oxide formed on mild steel when it is used in steam generating equipment. This passivating oxide occurs as a double layer, in which fine, densely packed crystals are found adjacent to the steel, with larger, less compact crystals atop this layer (1). Both layers thicken simultaneously due to diffusion of iron ions outwards from the steel, and inward diffusion of oxygen-bearing ions. Whereas the thin layer of fine magnetite crystals acts as a protective coating to the steel, the more porous region is less beneficial, because zones of highly concentrated salts can form within it when boiling is taking place. Localised attack can occur within these zones and premature failure of the equipment may result. Hence it is necessary, from time to time, to remove the magnetite layer and to do so cheaply and with minimum dissolution of the steel.

Whilst processes for controlled oxide removal involving the use of mixtures of complexing and/or reducing agents (e.g. ammoniated nitric acid plus formic acid) have been developed the mechanisms of removal are not fully understood. In this thesis the report of an investigation into the dissolution of magnetite via an examination of its electrochemistry and its rate of dissolution is presented.

Electrodes were prepared from material obtained by the reduction of small blocks of haematite. The electrode behaviour was studied using standard electrochemical techniques, e.g. linear sweep voltammetry, rotating disc electrode. Following this, the influence of the electrode potential on the rate of dissolution was investigated by following the change in the concentration of dissolved iron with time by colorimetric analysis of electrolyte samples removed during periods of potential control.
A direct, though complex, relationship between the dissolution rate and the applied potential was observed. Also, the relation between the dissolution current and the electronic current was interpreted, over a wide range of potential, as mainly due to the reductive dissolution of magnetite as

$$\text{Fe}_3\text{O}_4 + 8\text{H}^+ + 2\text{e}^- \rightarrow 3\text{Fe}^{2+} + 4\text{H}_2\text{O} \quad (1.1)$$
CHAPTER 2

ELECTROCHEMICAL THEORY

When an electrode, whether it be a pure metal or, as in the case of magnetite, a metal oxide, is immersed in an electrolyte solution, the structure of the solution in the vicinity of the electrode surface will differ from the structure in the bulk of the solution as a consequence of the differing electric potentials of electrode and solution. This region is known as the electrode/electrolyte interphase and any entity which moves from the electrode into the solution, or vice versa, traverses this interphase.

The rate at which ionic species move across the interphase depends upon the potential $\phi$ of the electrode with respect to the solution. Also, since depletion or accumulation of such species may occur at the electrode surface, transport of such species from the bulk of the solution to the surface, or the reverse, is another controlling factor.

Therefore, since the dissolution of magnetite will involve the movement of iron ions and oxide ions from the solid into the solution, it will be useful to look at the structure of the interphase, and at how potential and mass transport affect the dissolution rate.

2.1. Structure of the Interphase

The present-day view of the electrode/electrolyte interphase is, the result of a rather fascinating evolutionary process which began in the last century. Over one hundred years ago Helmholtz$^3$, suggested that any excess charge on a metallic phase, which would be situated at its surface, would be balanced by an equivalent amount of charge,
of opposite sign, in the solution and that this charge, also, would reside at the surface. Thus, the interface was seen as consisting of two layers of opposite charge, with one on either side of the electrode/electrolyte boundary, rather like a parallel plate capacitor. The term double-layer originates from this picture. Gouy \(^{(4)}\) and Chapman \(^{(5)}\) improved on this model, proposing that not all the counter charge in solution is situated immediately at the surface but that it extends into the solution. This diffuse layer of charge in solution is a result of thermal processes which introduce a degree of randomness into the distribution of ions.

One of the inadequacies of this model was that the ions were treated as point charges. Stern \(^{(6)}\) allowed for the finite size of the ions and proposed that their proximity to the electrode surface was limited to a plane of closest approach passing through the centres of the ions which were treated as spherical. This model was further developed by Graham \(^{(7)}\), who postulated that specific adsorption of certain species (ions or molecules) onto the electrode surface could occur. This adsorption may be so strong that partial dehydration of the adsorbed species results.

Thus, a reasonable model of the electrode/electrolyte interphase was obtained and this is illustrated in Fig. 2.1. Immediately adjacent to the electrode surface is an inner layer of solvent molecules and specifically adsorbed molecules, through the centres of which runs the inner Helmholtz plane, IHP. The non-adsorbed hydrated ions, which are held by electrostatic forces extend from the outer Helmholtz plane, OHP, (which is equivalent to Stern's plane of closest
Fig. 2.1 Structure of an electrode electrolyte interphase. Variation of potential ($\phi$) is also shown.
approach) into the bulk of the solution. The potential varies from the electrode surface ($x = 0$) to the OHP in a linear fashion, and from the OHP into the solution exponentially\(^{(8)}\).

### 2.2. Electrode Reactions

Consider a simple electron transfer reaction in which some species, \(O^{z+}\), is reduced to species \(R^{z'+}\).

\[
O^{z+} + ne \xrightleftharpoons[k_{-1}][k_1] R^{z'+} \tag{2.2.1}
\]

where \(k_1\) and \(k_{-1}\) are the rate constants for the forward and back reactions, respectively, and \(n = (Z - Z')\). The net current, \(i\), is equal to the difference between the cathodic current, \(i_c\) (for the forward reaction) and the anodic current, \(i_a\) (for the back reaction), i.e.

\[
i = i_c - i_a \tag{2.2.2}
\]

The basic principles of chemical kinetics hold for electrode processes and so the rate of reaction is proportional to the concentration of reacting species, e.g.

\[
(\text{rate of forward reaction}) \quad r_f = k_1 (O^{z+})_s = \frac{i_c}{nF \Delta} \tag{2.2.3}
\]

where \((O^{z+})_s\) is the concentration of \(O^{z+}\) at the OHP.

The effect of the electrode potential on the rate constants, \(k_1\) and \(k_{-1}\) can be illustrated by examining how it affects the electrochemical free energies of the species involved in the reaction, and by using simple activated complex theory\(^{(8)}\), Fig. 2.2 shows a simple representation of the relationship between the standard electrochemical free energy of the reactants, \(\bar{G}^0_{\text{reactants}}\), the
Fig 2.2. Effect of applied potential on relationship between electrochemical free energies of reactants, products and activated complex.
products, $\overline{G^0}_{\text{products}}$ and the activated complex $\overline{G^0\pm}$

\[ \Delta \overline{G^0} = \overline{G^0}_{\text{products}} - \overline{G^0}_{\text{reactants}} \]  \hspace{1cm} (2.2.4)

\[ \Delta \overline{G^0_{1\pm}} = \overline{G^0_{1\pm}} - \overline{G^0}_{\text{reactants}} \]  \hspace{1cm} (2.2.5)

\[ \Delta \overline{G^0_{-1\pm}} = \overline{G^0_{-1\pm}} - \overline{G^0}_{\text{products}} \]  \hspace{1cm} (2.2.6)

These free energies may be written as a sum of chemical potentials and inner potentials. Thus,

\[ \overline{G^0}_{\text{reactants}} = \mu^0_0 Z^+ + ZF\Phi_2 + n\mu^0_0 - nF\Phi_M \]  \hspace{1cm} (2.2.7)

\[ \overline{G^0}_{\text{products}} = \mu^0 R Z^{'1} + Z'F\Phi_2 \]  \hspace{1cm} (2.2.8)

where $\Phi_2$ is the potential of the OHP, and $\Phi_M$ is the potential of the electrode surface. Assuming (9) that the potential-dependent part of $\Delta \overline{G^0}$ is some fraction $\alpha$ of the potential-dependent part of $\Delta \overline{G^0}$,

\[ (\Delta \overline{G^0_{1\pm}})_e = \alpha \left[ (\overline{G^0}_{\text{products}})_e - (\overline{G^0}_{\text{reactants}})_e \right] \]  \hspace{1cm} (2.2.9)

\[ = \alpha \left[ Z'F\Phi_2 - ZF\Phi_2 + nF\Phi_M \right] \]  \hspace{1cm} (2.2.10)

\[ = \alpha nF(\Phi_M - \Phi_2) \]  \hspace{1cm} (2.2.11)

where $\alpha$ is called the electron transfer coefficient, and the subscript e identifies the potential-dependent part of the electrochemical free energies.
From activated complex theory (10)

\[ k_1 = \frac{D_T}{h} \exp \left( -\frac{\Delta G_{1}^{\text{‡}}}{RT} \right) \]  \hspace{1cm} (2.2.12)

\[ = \frac{D_T}{h} \exp \left( -\left(\Delta G_{1}^{\text{‡}} + \alpha nF(\phi_1 - \phi_2)\right)/RT \right) \]  \hspace{1cm} (2.2.13)

where, \( k \) is the Boltzmann constant, \( h \) is Planck's constant and
\( \Delta G_{1}^{\text{‡}} \) is the chemical (i.e. potential independent) part of the free energy change for the transition from reactants to activated state.

Equation (2.2.13) may be rewritten as

\[ k_1 = k' \exp(-\alpha nF(\phi_1 - \phi_2)/RT) \]  \hspace{1cm} (2.2.14)

(where \( k'_1 = \frac{D_T}{h} \exp(-\Delta G_{1}^{\text{‡}}/RT) \))

By analogy with equation (2.2.9)

\[ (\Delta G_{-1}^{\text{‡}})_e = -(1 - \alpha) \left[ (\overline{G}^0_{\text{products}})_e - (\overline{G}^0_{\text{reactants}})_e \right] \] \hspace{1cm} (2.2.15)

\[ = -(1 - \alpha) nF(\phi_1 - \phi_2) \] \hspace{1cm} (2.2.16)

and, \( k_{-1} = k_{-1}' \exp(1 - \alpha) nF(\phi_1 - \phi_2)/RT \) \hspace{1cm} (2.2.17)

The electrode potential \( E_c \) on any scale, is related to the interfacial potential difference \( (\phi_1 - \phi_2) \) by a constant such that
\[ E = (\phi_M - \phi_2) + (\text{a constant}) \]  

Therefore, equations (2.2.14) and (2.2.17) may be written as

\[ k_1 = k_1'' \exp(-\alpha nFE/RT) \]  (2.2.19)

and, \[ k_{-1} = k_{-1}'' \exp((1 - \alpha) nFE/RT) \]  (2.2.20)

So, the cathodic and anodic currents can now be written as,

\[ i_c = nFA k_1'' \exp(-\alpha nFE/RT) \left[ O^{Z^+}_s \right] \]  (2.2.21)

and

\[ i_a = nFA k_{-1}'' \exp((1 - \alpha) nFE/RT) \left[ R^{Z^+}_s \right] \]  (2.2.22)

where \( k_1'' \) and \( k_{-1}'' \) are potential independent rate constants.

At the equilibrium potential, \( E_e \), the anodic and cathodic currents are equal, i.e. \( i_a = i_c \), and the net current is zero. Hence,

\[ nFA k_1'' \exp(-\alpha nFE_e/RT) \left[ O^{Z^+}_s \right] = nFA k_{-1}'' \exp((1 - \alpha) nFE_e/RT) \left[ R^{Z^+}_s \right] = i_o \]  (2.2.23)

where \( i_o \) is the exchange current. Therefore, at any potential, \( E \), the cathodic and anodic currents may be expressed as:

\[ i_c = i_o \left\{ \exp(-\alpha nF(E - E_e)/RT) \right\} \]  (2.2.24)

\[ = i_o \left\{ \exp(-\alpha nF\eta /RT) \right\} \]  (2.2.25)
and, \[ i_a = i_o \left\{ \exp(1 - \alpha) \frac{nF(E - E_e)}{RT} \right\} \] \hspace{1cm} (2.2.26)

\[ = i_o \left\{ \exp(1 - \alpha) \frac{nF\eta}{RT} \right\} \] \hspace{1cm} (2.2.27)

where \( \eta = (E - E_e) \) is the overpotential.

Thus, the net current, \( i \), is given by:

\[ i = i_c - i_a = i_o \left\{ \exp(-\alpha nF\eta/RT) - \exp(1 - \alpha) \frac{nF\eta}{RT} \right\} \] \hspace{1cm} (2.2.28)

This equation gives the relationship between the current, \( i \), and the overpotential for a simple redox reaction.

Equation (2.2.28) is known as the Erdey-Gruz and Volmer equation, and describes the complete \( i-E \) behaviour of the reaction. However, it is possible to simplify it.

(i) If the overpotential, \( \eta \), is small \( \left( \frac{RT}{F} \gg |\eta| \right) \) the exponential terms may be approximated as

\[ \exp(-\frac{\alpha nF\eta}{RT}) \approx 1 - \frac{\alpha nF\eta}{RT} \] \hspace{1cm} (2.2.29)

and,

\[ \exp \left( \frac{(1-\alpha)nF\eta}{RT} \right) \approx 1 + (1-\alpha) \frac{nF\eta}{RT} \] \hspace{1cm} (2.2.30)

Therefore, for small values of \( i \)

\[ i = i_o \left( \frac{nF\eta}{RT} \right) \] \hspace{1cm} (2.2.31)

According to equation (2.2.31) the current is linearly dependent on the overpotential and a plot of \( \eta \) versus \( i \) should give a straight
line, passing through the origin, with slope $R_{CT} = \left( \frac{RT}{nF} \right)$. This is known as the charge transfer resistance.

(ii) If the overpotential is high one of the exponential terms of equation (2.2.28) will be extremely small and maybe ignored. For example, if there is a large cathodic overpotential only the first term of equation (2.2.28) need be considered. Then,

$$i = i_0 \exp\left( -\frac{anF}{RT} \right)$$

Equation (2.2.32) may be rewritten as

$$\log i = \log i_0 + \frac{1}{2.303} \left( -\frac{anF}{RT} \right)$$

which may be rearranged in the form of Tafel equation,

$$\eta = a + b \log i$$

where $a = \left( \frac{RT}{2.303} \right) \log i_0$ and $b = \left( \frac{-RT}{anF} \right) 2.303$

The Tafel expression should apply whenever the current due to the back reaction (the anodic reaction in the above example) is around 1% of the current due to the forward reaction.

2.3. Mass Transport

In the previous section, the concentrations of the reacting species, $[O^{Z+}]$ and $[R^{Z'}+]$ employed in the current-potential relationship were described as the concentrations at the Outer Helmholtz Plane. At equilibrium $[O^{Z+}]_s$ and $[R^{Z'}+]_s$ are the same as
the concentration of $O^{2+}$ and $R^{Z'}^+$ in the bulk of the solution. As the potential is shifted from its equilibrium value, however, the concentration of one of the reactants will be increased, with a corresponding decrease in concentration of the other. Since, according to equations (2.2.28 and 2.2.23) the net current is a function of concentration, the current will be affected by any such change. Thus, the current observed will depend not only on the potential, but also upon the rate at which reacting species can be transported to or from the OHP. There are three modes of movement of ions in solution migration, diffusion and convection.

2.3.1. Migration is the movement of ions in solution due to an electric field. This effect can be neglected if an excess of supporting electrolyte is present.

2.3.2. Diffusion results from the movement of species due to differences of chemical potential within the solution (i.e. due to a concentration gradient).

Consider again the reaction

$$O^{2+} + ne^{-} \xrightarrow{k_1} R^{Z'+}$$

(2.3.1)

If the potential is shifted from the equilibrium value, to a more cathodic potential for example, then $\left[O^{2+}\right]_s$ will decrease and $\left[R^{Z'+}\right]_s$ will increase. The effect of this depletion of $O^{2+}$ and accumulation of $R^{Z'+}$ at the electrode surface is to cause transport of $O^{2+}$ from, and of $R^{Z'+}$ to, the electrolyte bulk. Thus a profile
of $[O^{2+}]$ and $[R^{Z' +}]$ will develop, propagating away from the electrode surface. The concentration gradient can be visualized as progressively extending into the solution bulk. Therefore, since the current is dependent on the rate of transport, which, for diffusion, is proportional to the concentration gradient, it follows that the current must be a function of time.

Fick's laws of diffusion describe the flux, $J$, of a substance in solution, and the rate of change of concentration of the substance with time. These laws may be written, for linear diffusion, as

$$J = -D \frac{\partial C}{\partial x} \quad (2.3.2)$$

and,

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (2.3.3)$$

where, $C$ is the concentration of the moving species (mole cm$^{-3}$), $D$ is the diffusion coefficient (cm$^2$ s$^{-1}$), and the flux, $J$, has units of (mole s$^{-1}$ cm$^{-2}$).

In order to use these equations to help determine the behaviour of the current under mass transport control it is first necessary to establish the boundary conditions, i.e. the conditions which exist in the solution and at the electrode surface at time, $t \geq 0$ and for distance $x > 0$. For example, for reaction (2.3.1) assume the following conditions, for the system starting from the equilibrium potential and being stepped, at $t = 0$, to a potential far into the cathodic region such that the concentration of $O^{2+}$ at the electrode surface drops almost to zero. The diffusion equations are
\[
\frac{\partial C_O}{\partial t} = D_O \left( \frac{\partial^2 C_O}{\partial x^2} \right) \quad (2.3.4)
\]

and
\[
\frac{\partial C_R}{\partial t} = D_R \left( \frac{\partial^2 C_R}{\partial x^2} \right) \quad (2.3.5)
\]

and the boundary conditions are

for \( t = 0 \), at all \( x \):
\( C_O = C_O^b \), \( C_R = C_R^b \) \quad (2.3.6)

for \( t > 0 \), at \( x = 0 \):
\( C_O + C_O^b \), \( C_R + C_R^b \) \quad (2.3.7)

where \( C_i^b \) refers to the bulk concentration of species \( i \).

For \( t > 0 \), \( x = 0 \):
\[
\begin{bmatrix} 0 \end{bmatrix}^+ = 0
\]

\[
i = nF A D_O \frac{\partial C_O}{\partial x} \quad (2.3.8)
\]

\[
= nF A \left( k_1 C_O^S - k_{-1} C_R^S \right) \quad (2.3.9)
\]

and
\[
D_O \frac{\partial C_O}{\partial x} = -D_R \frac{\partial C_R}{\partial x} \quad (2.3.10)
\]

It is possible to solve the partial differential equations, (2.3.4) and (2.3.5), using Laplace transforms. The result obtained, for this case is a current-time response of the form(8)
\[
i_t = \frac{nF A D_O^{\frac{3}{2}} C_O^b}{\pi^{\frac{3}{2}} t^{\frac{3}{2}}} \quad (2.3.11)
\]
This equation is known as the Cottrell equation\(^{11}\) according to which the result of stepping the potential of the electrode, from equilibrium, into the diffusion-controlled region is a current which is a function of \(t^{-\frac{1}{2}}\). Therefore, a plot of \(i \versus t^{-\frac{1}{2}}\) should give a straight line which passes through the origin. It should be noted that this equation predicts very large currents for very small \(t\) values and such measurements will be constrained by the limits of the measuring device. Also at very long times, i.e., large \(t\) values, deviations from the expected behaviour will be observed due to the effects of convection.

2.3.3. Convection is the flow of fluid, and may be natural or forced. Natural convection arises from density gradients. Forced convection may be caused by stirring the solution, or even by bubbling gas through it.

In the absence of migration, mass transfer of species \(i\) to the electrode surface is governed by the convection-diffusion equation

\[
\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial x^2} - \frac{\partial C_i}{\partial x} \nu \quad (2.3.12)
\]

where \(\nu\) is the velocity of a volume element in a solution moving along the \(x\)-axis and, for the specific case of a rotating disc in laminar flow, may be written\(^{8}\)

\[
\nu_x = -0.51 \omega^{\frac{3}{2}} \nu^{-\frac{1}{2}} x^2 \quad (2.3.13)
\]

where \(\omega\) = angular velocity \((\text{sec}^{-1})\) and \(\nu\) = kinematic viscosity.
In unstirred solutions, as was indicated in the previous section, stepping the potential far into the diffusion-limiting current region should result in the current decaying to zero with time, but this is not observed due to the effects of convection which are apparent for large values of t. However, in solutions which are stirred by rotating the electrode itself (the rotating disc electrode, RDE), after an initial decay the current reaches a steady value. At this value

\[ \frac{\partial C_i}{\partial t} = 0 \text{ and, hence} \]

\[ D_i \frac{\partial^2 C_i}{\partial x^2} = \frac{\partial C_i}{\partial x} V_x \]  

(2.3.14)

Therefore,

\[ \frac{\partial^2 C_i}{\partial x^2} = - \frac{0.51}{D_i} \frac{1}{\lambda} \gamma^{\frac{1}{2}} \left( \frac{\partial C_i}{\partial x} \right) \]  

(2.3.15)

This may be solved by integration to yield an expression for the concentration of species i in the bulk of the solution, \( C_i^b \), i.e. the concentration as \( x \to \infty \)

\[ C_i^b = \left( \frac{\partial C_i}{\partial x} \right)_{x=0} \left( 1.1612 \ D_i \frac{1}{\lambda} \gamma^{\frac{1}{2}} \right) \]  

(2.3.16)

Equation (2.3.16) yields a value of \( \left( \frac{\partial C_i}{\partial x} \right)_{x=0} \) which may be used with Fick's first law (2.3.2), to obtain an expression for the limiting current, \( i_L \),

15
Equation (2.3.17) is the Levich equation (12) and is applicable to a completely mass-transfer controlled process at the rotating disc electrode.

Consider, now, the effect of depletion of species \( i \) from the vicinity of the electrode surface, in an unstirred solution. Assume that the concentration of \( i \) varies linearly from the electrode surface to a distance \( \delta_i \), normal to the surface. Beyond \( \delta_i \) the concentration of \( i \) is assumed to equal the bulk concentration, \( C_i^b \). From equation (2.3.2) the current at any time, \( t \), is given by

\[
i = nFAD_i \frac{\partial C_i}{\partial x} \tag{2.3.18}
\]

which, from the above assumptions may be rewritten as

\[
i = nFAD_i \frac{C_i^b - C_i^s}{\delta_i} \tag{2.3.19}
\]

If the electrode potential is stepped into the diffusion-limited region \( C_i^s = 0 \). Therefore,

\[
i = nFA. \frac{D_i}{\delta_i} C_i^b \tag{2.3.20}
\]

For an unstirred solution, \( \delta_i \) is a function of time. With increasing time, the effect of depletion of \( i \) extends further into the solution, i.e. \( \delta_i \) increases and the current, \( i \), decays.
With the rotating disc electrode the current is a constant, and so is $\delta i$, for constant rotation speed. Comparison of equations (2.3.17) and (2.3.20) yields

$$\delta_1 = 1.61 D_1^{\frac{1}{3}} \omega^{-\frac{1}{2}} \nu^\frac{1}{3} \quad (2.3.21)$$

Consider a reaction, such as

$$0 + ne \overset{k_1}{\rightarrow} R \quad (2.3.22)$$

$$I = nFA \left( k_1 [O]_s - k_{-1} [R]_s \right) \quad (2.3.23)$$

$$= nFA \frac{D_o}{\delta_o} \left( [O]_b - [O]_s \right) = nFA \frac{D_R}{\delta_R} \left( [R]_s - [R]_b \right) \quad (2.3.24)$$

The limiting cathodic and anodic currents, $I_{c,L}$ and $I_{a,L}$ may be approximated as

$$I_{c,L} = nFA \frac{D_o}{\delta_o} [O]_b \quad \text{and} \quad I_{a,L} = nFA \frac{D_R}{\delta_R} [R]_b \quad (2.3.25)$$

Therefore,

$$I = I_{c,L} - nFA \frac{D_o}{\delta_o} [O]_s = nFA \frac{D_R}{\delta_R} [R]_s - I_{a,L} \quad (2.3.26)$$

Rearrangement of these equations allows determination of $[O]_s$ and $[R]_s$:

$$[O]_s = \left( I_{c,L} - I \right) \frac{\delta_o}{nFA \cdot D_o} \quad [R]_s = \left( I + I_{a,L} \right) \frac{\delta_R}{nFA \cdot D_R} \quad (2.3.27)$$
and, hence, \( I \), by substitution of these values into equation (2.3.23)

\[
I = k_1 \frac{\delta_0}{D_0} (I_{\theta L} - I) - k_{-1} \frac{\delta_R}{D_R} (I + I_{a L}) \quad (2.3.28)
\]

\[
I \{1 + k_1 \frac{\delta_0}{D_0} + k_{-1} \frac{\delta_R}{D_R}\} = k_1 \frac{\delta_0}{D_0} I_{\theta L} - k_{-1} \frac{\delta_R}{D_R} I_{a L} \quad (2.3.29)
\]

\[
= nFA \{k_1 [0]_b - k_{-1} [R]_b\} \quad (2.3.30)
\]

And, \( nFA \{k_1 [0]_b - k_{-1} [R]_b\} = I_\infty \quad (2.3.31) \)

where \( I_\infty \) is the current in the absence of mass transfer effects.

Thus,

\[
\frac{1}{I} = \frac{1}{I_\infty} + \frac{1}{I_\infty} \{k_1 \frac{\delta_0}{D_0} + k_{-1} \frac{\delta_R}{D_R}\} \quad (2.3.32)
\]

Substituting into this expression the value of \( \delta \) obtained from equation (2.3.21) gives

\[
\frac{1}{I} = \frac{1}{I_\infty} + \frac{1.61}{I_\infty} \left( k_1 \frac{\delta_0}{D_0} \frac{1}{\omega^2} + k_{-1} \frac{\delta_R}{D_R} \frac{2}{\omega^2}\right) \quad (2.3.33)
\]

and, for a completely mass-controlled process a plot of \( \frac{1}{I} \) versus \( \frac{1}{\omega^2} \) should yield a straight line of slope, \( S \), and intercept, \( Y \), where

\[
S = \frac{1.61 \sqrt{I_\infty^{1/6}}}{I_\infty} \left\{ k_1 D_0^{-\frac{3}{2}} + k_{-1} D_R^{-\frac{3}{2}} \right\} \quad (2.3.34)
\]

and \( Y = \frac{1}{I_\infty} \quad (2.3.35) \)
If the reverse (in this example, the anodic) reaction can be ignored, i.e. at large overpotential, equation (2.3.33) simplifies to

\[
\frac{1}{I} = \frac{1}{nFAk_1[O]_b} + \frac{1.61D_o^{-3/2}v^{1/6}}{nFA[O]_b\omega^2}
\] (2.3.36)

Therefore, plotting \(\frac{1}{I}\) versus \(\frac{1}{\omega^2}\) should give straight lines of slope, \(S\), and intercept \(Y\), where

\[
S = \frac{1.61D_o^{-3/2}v^{1/6}}{nFA[O]_b}
\] (2.3.37)

and

\[
Y = \frac{1}{nFAk_1[O]_b}
\] (2.3.38)

The slope, \(S\), according to this derivation should be independent of potential, while the intercept, \(Y\), contains the term \(k_1\) which is a function of potential, and should vary with potential. Therefore, plotting \(\frac{1}{I}\) against \(\omega^2\) for various potential, \(E\), values should produce a series of parallel straight lines.

2.4. Linear Sweep Voltammetry

Linear sweep voltammetry, which can be a very useful, investigative technique, was employed in this work in both a qualitative and a quantitative manner. Adams (13) has described some of the practical aspects of L.S.V, while Nicholson and Shain (14) have covered the theoretical side, of both single scan and cyclic methods for various systems. An in depth treatment of the theory, and derivation of the pertinent equations, of L.S.V. would be quite laborious and will not be attempted. Instead, only the final equations
and the conditions for which they apply will be stated \(^{(8)}\).

In linear sweep voltammetry, after initially holding the working electrode at some constant potential, \(E_i\) (at which no electrochemical reaction occurs), the potential is varied linearly, at some rate \(\nu\) to a final potential, \(E_f\). The rate, \(\nu\), can be as low as \(40 \text{ mV s}^{-1}\) or as high as \(10^5 \text{ mV s}^{-1}\) \(^{(8)}\). At time \(t\) after the initiation of a sweep the potential \(E_t\) of the electrode, is given by

\[
E_t = E_i + \nu t \tag{2.4.1.}
\]

Consider a simple reaction such as

\[\text{O} + \text{ne} \overset{+}{\rightarrow} \text{R} \tag{2.4.2}\]

and choose \(E_i\) so that \(\text{O}\) is not reduced. If the potential is now moved, cathodically, from \(E_i\) at very low \(\nu\) the species \(\text{O}\) is reduced and the rate of reduction is accelerated, with increasing \(t\), until mass transfer of \(\text{O}\) to the electrode surface limits the rate of reaction and the process becomes diffusion controlled. The resulting \(i-t\) curve is that observed for the steady state. As the rate \(\nu\) is increased, however, a peak on the \(i-t\) curve (see fig. 2.3) results due to a combination of high mass transfer rates in the non-steady state and progressive depletion of the concentration of \(\text{O}\) in the diffusion layer.

For a reversible reaction the peak current, \(i_p\), may be written as:

\[
i_p = 2.69 \times 10^5 \cdot n^{3/2} \cdot AD_o^{1/2} \cdot C_o^{1/2} \cdot \nu^{1/2} \quad \text{(at 25°C)} \tag{2.4.3}\]
Fig. 2.3. Diagram (a) shows potential, $E$, varying linearly with time, $t$. Diagram (b) shows current, $i$, response.

(a) [Diagram of a linear relationship between potential and time]

(b) [Diagram of a response curve with sweep rate increasing]
The peak potential is independent of sweeprate and related to the half-wave potential by the following expression

\[ E_p = E_{p/2} - \frac{0.028}{n} \text{(at 25°C)} \]  

(2.4.4)

where \( E_p \) is the potential at which \( i_p \) occurs, and \( E_{p/2} \) is the potential for which \( i = i_{p/2} \).

If a reverse sweep is carried out, i.e. electrode potential varied from \( E_i \) to \( E_f \) and back to \( E_i \) this is called cyclic voltammetry, and a peak, of opposite sign, corresponding to the reverse reaction is observed on the return. In such a case, the separation \( \Delta E_p \) of the two peaks is given by

\[ \Delta E_p = \frac{0.059}{n} \]  

(2.4.5)

for a reversible process.

For an irreversible reaction the peak characteristic is as

\[ i_p = 2.99 \times 10^5 n \left( a n_a \right)^{\frac{1}{2}} D_0^{\frac{1}{2}} C_0^{b} v^{\frac{1}{2}} \]  

(2.4.6)

where \( n \) is the number of electrons transferred up to, and including the rate determining step and the peak potential is a function of the sweep rate, \( v \). A plot of \( E_p \) versus \( v^{-\frac{1}{2}} \) goes through the limiting value \( \frac{0.059}{n} \).

When the rotating disc electrode is used in conjunction with L.S.V. reversal of the potential sweep will not cause oxidation of \( R \) since it will have been removed by stirring. Instead, at low sweep rates the original current response will be repeated.
2.5. Potential Steps.

In this technique, the potential of the working electrode is held at some value, \( E_o \), at which no reaction occurs and is then stepped, suddenly, to some new value, \( E_1 \), and the i-t response examined. The current response is determined by the magnitude of the potential step \( \Delta V (= E_1 - E_o) \). A series of potential steps may be carried out, the potential being returned to \( E_o \) and the solution stirred between each step, and information about the electrochemical behaviour of the system under study obtained.

Consider the system

\[
O + ne \rightarrow R \quad (2.5.1)
\]

The working electrode is held at potential, \( E_o \), at which no reaction occurs and the current is zero. If the potential is stepped far into the cathodic region such that the surface concentration of 0 is effectively zero, the current response will be described by the Cottrell equation (2.3.11), and increasing the magnitude of the cathodic step causes no change in the current time curve since the current is diffusion controlled. If the potential step is insufficiently large to drive the reaction into the mass transport controlled region, i.e. sufficient to reduce the concentration of 0 but not to zero, the current will be under a mixture of charge transfer and mass transfer kinetics and the current-time curve will be complex.

Fig. (2.4) shows diagrammatically, the current response to increasingly cathodic potential steps, from \( E = E_o \) into regions where
Fig. 2.4.

a) Cathodic potential steps from $E_0$. 

\[ E \]

\[ E_0 \]

\[ t \]

b) Current response to each step.

\[ i \]

\[ t \]

\[ i \]

\[ t \]

c) Resulting polarisation curve.

\[ i \]

\[ E \]
1) no electrochemical reaction occurs

2) & 3) the reaction is under mixed charge/mass transfer control
and 4) & 5) the reaction is completely mass transfer controlled.

This figure also shows how, by sampling the current at
some constant time period, \( \tau \), after initiating a potential step,
it is possible to construct a polarisation curve by plotting \( i(\tau) \)
versus \( E \).
Magnetite, \( \text{Fe}_3\text{O}_4 \), is a ubiquitous substance. It occurs throughout the world as natural deposits\(^{(15)}\) and is found in various creatures, fishes\(^{(16)}\), for example, where its presence has been used to explain their direction finding abilities. However, it is its occurrence as a corrosion product which is of interest here. Initially providing a protective coating, which reduces the rate of further corrosion, the magnetite layer can build up and eventually prove harmful. To prevent this, the magnetite layer must be periodically removed from steel structures by dissolution. To carry out this removal efficiently requires a study of the dissolution mechanism, for which a knowledge of the structure of magnetite and its electrochemical behaviour is invaluable.

Magnetite has an inverse spinel structure, see fig. 3.1, with half of the octahedral sites and one-eighth of the tetrahedral sites occupied by cations\(^{(18)}\). According to Fleet\(^{(19)}\), there is one \( \text{Fe}^{3+} \) ion per formula unit at a tetrahedral site with the remaining \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \) ions randomly distributed at octahedral positions. It is a non-stoichiometric compound which exhibits a cation deficit; the iron to oxygen ratio, \( \text{Fe} : \text{O} \), lies in the range 0.750 to 0.744\(^{(20)}\). This ratio is dependent upon both the oxygen pressure and the temperature\(^{(18)}\).

Iron forms several oxides and it is of interest to compare the structure of magnetite with the other oxides. There is the ferrous oxide, wustite (\( \text{FeO} \)), which has a sodium chloride-type
Fig. 3.1. The spinel lattice
crystal structure and is another cation-deficient compound; better written as $F_{0.83-0.925} \cdot 0.83-0.9$. There are two ferric oxides; the $\alpha$ and $\gamma$ forms of haematite, $Fe_2O_3$. The $\alpha$-form has a trigonal structure with the ferric ions occupying octahedral sites, while the $\gamma$-form has a structure very similar to magnetite, being a cation-deficient inverse spinel with an iron to oxygen ratio in the range $0.67$ to $0.72^{(20)}$. This similarity in atomic structure accounts for the reputed ease of interconversion of magnetite and $\gamma$-haematite$^{(21)}$.

The above descriptions of the oxides of iron are rather simplified, and the compounds may contain hydrogen. In 1938, Verwey$^{(22)}$ proposed that the presence of water was necessary for the stabilisation of $\gamma$-$Fe_2O_3$, while, in 1965, Bloom and Goldenberg$^{(23)}$ suggested that the $\gamma$-$Fe_2O_3$ produced atop magnetite was formed by substitution of the ferrous ions of $Fe_3O_4$ by protons. In that same year, the presence of hydrogen in the passive layer of stainless steel was reported by Okamoto and Shibata$^{(24)}$. Radiotracer studies, by Kudo et al$^{(25)}$, of the oxide layer, formed on iron in sodium borate buffer solution, confirmed the presence of hydrogen. In agreement with Verwey$^{(22)}$, the hydrogen was postulated as existing in the form of water molecules, and the water content was calculated as $Fe_2O_3 \cdot 1.99 H_2O$. Other workers, Yolken et al$^{(26)}$, for instance, have supported the view of hydrogen as a constituent of the spinel oxide lattice. A more recent examination of the passive layer on iron, using ESCA and SIMS$^{(27)}$, found no traces of $H_2O$, but hydrogen was identified as existing as $-OH$ in the outer parts of the film.

Continuing this comparison of the iron oxides, their electrical resistivities are listed in Table 1.
Iron has a very low resistivity, typical of electrical conductors and at the opposite extreme, haematite, with a resistivity of the order of $10^{12}$ $\Omega$ m, is a non-conductor or insulator. Although its resistivity is not as great as that of haematite, wustite is another non-conducting material. Of the three oxides, magnetite has the lowest resistivity, $1 \times 10^{-4}$ $\Omega$ m, and is, conversely, the most conductive. This relatively, very high conductivity has been attributed to exchange of electrons between neighbouring Fe$^{2+}$ and Fe$^{3+}$ ions, by Kofstad$^{(18)}$. However, Fleet$^{(19)}$ has suggested that a proper explanation of the high conductivity of magnetite requires the use of the semi-conductor band model. Magnetite has been classified as a p-type semi-conductor$^{(31)}$. According to Stimming and Schultz$^{(32)}$ the $\gamma$-Fe$_2$O$_3$ of the passive layer on iron may behave like an n-type or a p-type semi-conductor (or even an insulator) depending upon the potential. This concurs with the view, taken by Vetter$^{(33)}$ that changes in the potential of the passive layer cause changes in the composition of the oxide and, hence, in its semi-conducting properties.

### TABLE 1

<table>
<thead>
<tr>
<th>Material</th>
<th>Resistivity/ $\cdot \Omega$ m</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron, Fe</td>
<td>$1 \times 10^{-7}$</td>
<td>(28)</td>
</tr>
<tr>
<td>Wustite, FeO</td>
<td>$6 \times 10^{3}$</td>
<td>(29)</td>
</tr>
<tr>
<td>Magnetite, Fe$_3$O$_4$</td>
<td>$1 \times 10^{-4}$</td>
<td>(18)</td>
</tr>
<tr>
<td>Haematite, Fe$_2$O$_3$</td>
<td>$10^{12}$</td>
<td>(30)</td>
</tr>
</tbody>
</table>
Since the much more resistive wustite and haematite have both been described as defect structures, it is obvious that the presence of ferrous and ferric ions above is not sufficient to produce high conductivity and that it is probably the relative numbers of Fe\(^{3+}\) and Fe\(^{2+}\) ions and their arrangement within the crystal which is significant. Itai et al\(^{(34)}\) showed the importance of the Fe\(^{3+}/Fe^{2+}\) ratios on the resistivity of magnetite samples obtained from molten mill scale. The resistivity decreased to a minimum as the Fe\(^{3+}/Fe^{2+}\) ratio was increased from 1 to 2 (corresponding to stoichiometric magnetite) and any further increase in the ratio caused an abrupt, approximately one-hundred-fold, increase in resistivity.

3.2. Electrochemistry.

Fig. 3.2. shows a Pourbaix\(^{(35)}\) diagram illustrating the conditions (pH and potential), as predicted from thermodynamic data, under which iron is stable. Under very alkaline conditions anodic polarisation may result in corrosion due to the formation of species such as HFeO\(_2^-\). Also, there is a wide range of pH (pH < 8) over which, as the potential of the iron is increased in the positive direction (E > -500 mV), corrosion occurs with iron dissolving as Fe\(^{2+}\), or, at high positive potential values, as Fe\(^{3+}\). Between these two regions there is a range of pH (8 < pH < 12), within which corrosion of iron, at positive potentials, is inhibited due to the formation of a protective oxide layer. Initially, as the potential is made more positive (E > - 700 mV), magnetite, Fe\(_3\)O\(_4\), is formed and this may be oxidised, as the potential is further increased, to give haematite.
Fig. 3.2. Potential–pH equilibrium diagram for the iron-water system.
(Fe₂O₃). At extremely high positive potential values species such as FeO₄²⁻ may be formed, although this is not definite. Using more recent thermodynamic data, Silverman (36) constructed a potential-pH diagram, similar to that of Pourbaix, but with a solid Fe(OH)₂ region interposed between the iron and the magnetite layer, and cited reports of the formation of Fe(OH)₂ on iron, albeit in very alkaline (pH > 14) solution, to support the possibility of such a region existing.

These potential-pH diagrams, although useful, are merely indicative of the thermodynamically possible behaviour of magnetite and cannot predict, unequivocally, how a magnetite electrode will perform. Also, magnetite electrodes have been manufactured in a variety of ways – from a paste prepared by mixing powdered magnetite with graphite and a few drops of Nujol (37) and from single crystals of natural magnetite (38) are just two examples – and it is, therefore, perhaps not too surprising that reports of their electrochemical behaviour are sometimes in disagreement.

Using electrodes prepared from magnetite ore Sukhotin et al (39) obtained a static potential of between +650 and +700 mV in a 1N sulphuric acid solution while in 1975 Hickling and Ives (37) studied magnetite graphite paste electrodes, again in 1N H₂SO₄ solution, and reported the static potential to be ill-defined, lying within the range +600 to +700 mV and drifting with time. They noted, however, that much more stable values were obtained by adding solid FeSO₄·7H₂O to the paste and measuring the potential in FeSO₄ saturated electrolyte solutions whereupon a static potential of +576 mV for magnetite was obtained. They also report an approximately linear dependence of the static potential on the pH, with a
slope of about $-50\text{mV per pH unit}$. Hickling\(^{(40)}\) measured the static potential of magnetite electrodes, prepared from fused $\text{Fe}_3\text{O}_4$ powder, in $1\text{N }\text{H}_2\text{SO}_4$ solution and found they gave a well-defined value of $+580\text{mV}$. However, Allen et al\(^{(41)}\) measured the rest potential of compact magnetite electrodes, prepared by cold pressing an admixture of powdered magnetite and graphite, in solutions of $1\text{M}$ sodium perchlorate solution and found the value to be around $+60\text{mV}$ over the pH range $2 < \text{pH} < 13$. This apparent insensitivity of the rest potential to the hydrogen ion concentration was not explained by the authors.

These few examples of variations in measurement of the rest potential of magnetite and its pH-dependence serve to illustrate the difficulties inherent in a study of the material. Slight changes in a magnetite electrode, due to its source or method of manufacture, may result in deviations from expected behaviour.

Sukhotin and Kartashova\(^{(42)}\) investigated the anodic behaviour of magnetite electrodes, prepared from natural magnetite, in $7\text{N }\text{HClO}_4$ and reported a) a stationary potential of close to $+600\text{mV}$ b) a dissolution rate independent of potential for $+600 < E < +1350\text{mV}$, c) increasing dissolution for $E > +1350\text{mV}$, after which point the iron passes into solution as $\text{Fe}^{3+}$,

$$\text{i.e. } \text{Fe}_3\text{O}_4 + 8\text{H}^+ \rightarrow 3\text{Fe}^{3+} + 4\text{H}_2\text{O} + \text{e} \quad (3.1)$$

and d) oxygen evolution occurring at $E > +1800 \text{ mV}$. The presence of $\text{Fe}^{3+}$ in such highly acidic solutions, at these anodic
potentials, is consistent with the behaviour predicted by the Pourbaix(35) diagram. Novakovskii and Likhachev(38) studied the anodic dissolution of magnetite and found the dissolving iron species to be Fe$^{3+}$, and remarked on the similarity in the anodic reactions of magnetite and passive iron. Similar conclusions were reached by Allen et al(43) who considered the surface of magnetite to have a character akin to γ-Fe$_2$O$_3$ of potentials greater than +400mV. Sukhotin and Khentov(44) examined the anodic behaviour of iron oxides in acidic solutions and took the view that there is always a film of γ-haematite atop the magnetite and that partial dissolution of the magnetite can occur across this film.

In less acidic solutions (1N H$_2$SO$_4$), Sukhotin et al(39) found no evidence for reaction (3.1) occurring for $+600 < E < +1300$mV, but reported the existence of a cathodic reaction beginning at $E^\infty + 50$mV and exhibiting a maximum value at +260mV. This reaction was considered due to the electrochemical reduction of magnetite to produce ferrous ions in solution as,

$$\text{Fe}_3\text{O}_4 + 8\text{H}^+ + 2\text{e}^- \rightarrow 3\text{Fe}^{2+} + 4\text{H}_2\text{O}$$

(3.2)

Reaction (3.2) was in agreement with the results of colorimetric analysis of the electrolyte solutions which contained approximately 1.5g-ions of Fe$^{2+}$ per Faraday of electricity. Small amounts of ferric ions in the solution were explained as resulting from oxidation of ferrous ions by dissolved oxygen.

This cathodic peak for acidic dissolution of magnetite was observed by Allen et al(43), who quote it as occurring at +250mV.
and also by Haruyama and Masamura (45) who examined dissolution in acidic perchlorate solutions, and described the peak as having a maximum at +140mV, with a pH-dependent positive branch and a negative branch uninfluenced by pH.

This cathodic peak represents a region of enhanced dissolution and is worthy of further mention. Haruyama and Masamura (45) studied the acidic dissolution of magnetite using both potential sweep and impedance measurements. A slow potential sweep, \(1mVs^{-1}\), in pH2 perchlorate solution revealed three cathodic peaks. The peak at +140mV was described as unaffected by changes in sweep rate or rate of stirring. This behaviour was interpreted as consistent with a reaction controlled by a transfer process at the interface. The current in the region of the second peak, at -660mV, was found to be diffusion controlled, but colorimetric analysis of the electrolyte solutions showed the current over the region of both peaks, from +240 to -660mV, to occur with 100% current efficiency according to reaction (3.2). To account for the change in dissolution mechanism between the two peaks, it was suggested that, in the region of the second peak, the magnetite was covered by ferrous hydroxide produced by proton adsorption. The third peak, at -960mV, was attributed to reduction of magnetite to metallic iron as

\[
\text{Fe}_3\text{O}_4 + 8\text{H}^+ + 8\text{e}^- \rightarrow 3\text{Fe} + 4\text{H}_2\text{O}
\]  

(3.3)

Allen et al (33) reported that iron nucleation occurred by stepping the potential to \(E < -800mV\), and that after a layer of metallic iron is produced the predominant reaction is hydrogen evolution.
However, Sukhotin et al(39) observed the evolution of hydrogen of much higher potential, viz -400mV.

In a potentiodynamic investigation of magnetite over the pH range 3-9, Allen et al(41) found the current to be controlled, in general, by a solid-state diffusion process and postulated the $H^+$ ion as the diffusing species. In a later paper, Allen et al(43) suggested that diffusion of $H^+$ into the magnetite crystal was necessary for maintenance of electroneutrality following changes in the $Fe^{3+}/Fe^{2+}$ ratio. Gorichev et al(47) studied the dissolution of powders of magnetite and haematite and determined a reaction order, with respect to hydrogen ions of almost 0.5. Dissolution was believed controlled by adsorption of protons and their subsequent diffusion into the solid. The role of protons in the reduction of oxides was discussed by Lukovtsev(48) in 1968. The movement of protons was described as occurring via two stages. The first stage required adsorption of the proton onto the surface and reduction of a metal ion at the surface.

$$e^- + M_s^{z+} + O_s^{2-} + H_{aq}^+ \rightarrow M_s^{(z-1)+} + OH_{(s)}^- \quad (3.4)$$

In the next stage the proton migrated deeper into the crystal via neighbouring oxygen ions of the lattice and concurrent electron transfer between metal ions

$$M_s^{(Z-1)+} + OH_{S}^- + M_o^{Z+} + O_o^{2-} \rightarrow M_s^{Z+} + O_{S}^{2-} + M_o^{(Z-1)+} + OH_{o}^- \quad (3.5)$$

where the subscript o refers to ions within the interior of the crystal. A minimum possible value for the diffusion coefficient of $H^+$ in magnetite has been estimated as $8 \times 10^{-10}$ cm$^2$ s$^{-1}$(41).

32
A general feature of agreement on the dissolution of magnetite is that, except where dissolution occurs at highly anodic and/or in highly acidic solutions, the dissolving iron species is in the II rather than the III oxidation state, i.e. reduction occurs in the solid state rather than in solution. This has also been observed for the reductive dissolution of a magnetite film in alkaline solution. Similar behaviour has been reported for the dissolution of other iron oxides. The mechanism for dissolution of wustite, FeO, in hydrochloric acid solution was interpreted as involving the ferrous ions at the surface forming complexes, such as FeOH⁺ads, (FeOH⁺.H₂O)ads and (FeOHCl)ads, which react with protons and simultaneously pass into solution.

The dissolution of lepidocrocite, γ-FeOOH, in alkaline solution, was found to occur as FeIII(Solid) + e⁻ → FeII(Soln)

although this reaction was blocked by reduction of the FeIII to metallic iron. In a very interesting study of the reduction of iron oxides, Lecuire examined the dissolution by, amongst other methods, adding O-phenanthroline to the electrolyte solution and following the dissolution spectrophotometrically. Reduction of α-Fe₂O₃, γ-Fe₂O₃, Fe₃O₄ and Fe₁₋ₓO was shown to occur with total destruction of the crystal, e.g. reaction (2) rather than via a reaction such as Fe₃O₄ + 2H⁺ + 2e⁻ → 3FeO + H₂O

Lecuire suggested that, by measuring the current causing reduction and the amount of material passing into solution, the degree of non-stoichiometry of the crystal could be established.
Dissolution of Metal Oxides

In 1956, the effect of electrode potential on the dissolution of polar crystals was considered by Engell\textsuperscript{(53)}. Engell began by suggesting that a crystal, $A^+B^-$, would dissolve as

\begin{align}
1A^+ & \rightarrow 2A^+ \quad (3.8a) \\
1B^- & \rightarrow 2B^- \quad (3.8b)
\end{align}

where the subscripts 1 and 2 refer to the crystal and the solution phases, respectively. Then, using the following equations, (in which $k = \text{rate constant}, c = \text{concentration}, \alpha = \text{transfer coefficient and } z = \text{valency})$

\begin{align}
I_A^+ &= k_A^+ C_A \exp \left( \alpha_A Z_A FE \right) \frac{\alpha_A Z_A FE}{RT} - (1 - \alpha_A Z_A FE) \frac{\alpha_A Z_A FE}{RT} \quad (3.9a) \\
I_B^- &= k_B^- C_B \exp \left( \alpha_B Z_B FE \right) \frac{\alpha_B Z_B FE}{RT} - (1 - \alpha_B Z_B FE) \frac{\alpha_B Z_B FE}{RT} \quad (3.9b)
\end{align}

to relate the partial current densities, $I_A^+$ and $I_B^-$ for (3.8a) and (3.8b) to the electrode potential, $E$, Engell made four main assumptions to establish a relationship between the dissolution current, $I$, and the electrode potential. These assumptions were

(i) that both partial processes occurred far from equilibrium (i.e. the second terms in equations (3.9a) and (3.9b) could be neglected).

(ii) that the concentration of an ion, $i$, in the crystal was given by
where $\mu = \text{chemical potential}$ and $\mu_1^{\circ} = \text{standard chemical potential}$

(iii) that a steady-state process occurred such that,

$$I_A^+ = I_B^-$$

(3.11)

and (iv) that there was no large deviation from stoichiometry, and that

$$\mu_A + \mu_B = \mu_{AB} = \text{a constant}$$

(3.12)

where $\mu_{AB}$ was supposed independent of the electrode potential.

From equations (3.9a) and (3.9b) and making the above four assumptions, Engell derived the expression

$$\frac{d \ln I}{d E} = (\alpha_A |Z_A| - \alpha_B |Z_B|) \frac{F}{2RT}$$

(3.13)

According to this expression

(i) if $\alpha_A |Z_A| > \alpha_B |Z_B|$ an increased dissolution rate accompanies an increase in $E$,

(ii) if $\alpha_A |Z_A| < \alpha_B |Z_B|$ an increased dissolution rate accompanies a decrease in $E$,

and (iii) if $\alpha_A |Z_A| = \alpha_B |Z_B|$ the dissolution rate is independent of $E$.

In the case of one of the partial processes occurring close to equilibrium; process (3.8a), for example, Engell derived an expression of the form,
Engell studied the effect of potential on the dissolution rate of wustite, magnetite and, also, of cuprous oxide (to which had been added 2 mol % Li$_2$O and Nb$_2$O$_5$, for increased conductivity).

For wustite, a linear relationship between lnI and $E$ was, indeed, observed and equation (3.13) could be applied, i.e. dissolution occurred for both processes far from equilibrium. A similar result was obtained for the dissolution of magnetite with the value of $(d\ln I/dE)$ dependent on the nature of the material used in the electrodes. Also, the potential/current curves showed an inflection, i.e. the $(d\ln I/dE)$ value gave two different results depending on the potential region. It was suggested that this might be due to changes in the solution mechanism on moving from one potential region to another for example, ferric ions going into solution before reduction in the higher potential range and ferrous ions being the dissolving species in the more cathodic region - but no conclusive explanation was possible.

Vermilyea's treatment of ionic dissolution, although in qualitative agreement with Engell differed in several ways. Taking the rate of removal of ions, $r_r$, from a crystal as given by,

$$r_r = n k_r \exp \left\{ \frac{\alpha ZFE}{RT} \right\}$$

(3.15)

where $n$ = number of ions/cm$^3$, and $k_r$ = rate constant, and the deposition rate of ions from solution onto the crystal as
given by, \( r_d \), where

\[
\begin{align*}
\cdot \quad r_d &= C k_d \exp\left\{ - \frac{(1-\alpha) ZeF}{RT} \right\} \quad (3.16)
\end{align*}
\]

where \( C \) = ion concentration in solution

and \( k_d \) = rate constant

and assuming that

\[
\begin{align*}
\bar{n}_A + \bar{n}_B &= 2n^0 
\end{align*}
\]

where \( 2n^0 \) is the surface concentration of ions at the isoelectric point, Vermilyea derived an expression relating the rate of dissolution, \( r \), to the overpotential, \( \eta \):

\[
\begin{align*}
\text{viz} \quad r &= \frac{2r_f}{\exp\left\{ - \frac{\alpha_A Z_A F \eta}{RT} \right\} + \exp\left\{ - \frac{\alpha_B Z_B F \eta}{RT} \right\}} \quad (3.18)
\end{align*}
\]

where \( r_f \) = the rate of dissolution for the freely dissolving crystal,

and \( \eta \) = the overpotential

\[
\eta = (E - E_f), \text{ with } E_f \text{ the potential of the freely dissolving crystal,}
\]

For very small values of \( \eta \) this expression can be approximated to

\[
\begin{align*}
r &= \frac{2r_f}{2 - \frac{F \eta}{RT (\alpha_A Z_A + \alpha_B Z_B)}} \quad (3.19)
\end{align*}
\]

From equation (3.19) according to the relative values of \( \alpha_A Z_A \) and \( \alpha_B Z_B \) the dissolution rate, \( r \), can increase, decrease or remain unchanged for a positive increase in overpotential. This is similar to the result obtained earlier in equation (3.13), but
in Engell's treatment there was no restriction on the degree of change of dissolution rate with change in potential, while Vermilyea's results indicate a maximum increase in dissolution rate of a factor of two. Also, while Engell assumed equation (3.12) that the sum of the chemical potentials of the ions was a constant, Vermilyea disputed this, considering the change in surface concentration accompanying application of potential to be so large as to render this assumption invalid. Vermilyea considered the surface of the oxide crystals to have such a large capacitance, that very little of any applied potential would appear across the crystal/solution interface and, therefore, that Engell's results were unlikely to be due to double layer potential changes. As a possible interpretation of Engell's results, Vermilyea suggested that the observed changes in dissolution rate were due to cation valence changes. Vermilyea, also, gave a physical interpretation of dissolution, which was in accordance with the inflection in the potential/current curves for magnetite obtained by Engell. The explanation was that, when the crystal was freely dissolving, \( n_A = n_B \), but application of a large overpotential would change the surface composition greatly, until only the ion of charge opposite to the sign of \( \eta \) was left on the surface. Then, any further increase in \( \eta \) could not really change the surface composition, but would inhibit the rate of removal of the remaining ion. Thus, after initially increasing the rate of dissolution, a potential is reached after which further changes decrease the rate of dissolution.

Vermilyea also considered the dependence of the dissolution rate on the hydrogen ion concentration and predicted the order of the dissolution rate, with respect to proton concentration, for
various oxide ion dissolution mechanisms e.g. initial protonation to yield hydroxide ions followed by further reaction with $H^+$ and removal as water molecules, or protonation and removal as $OH^-$ ions.

Yeager et al\(^{(55)}\), in a study of the dissolution kinetics of lithiated NiO in aqueous acid solutions obtained results which were in agreement with the predicted results from Vermilyea's equation (equation (3.19)). However, the dissolution rate of ZnO in alkali was shown, by Landsberg and Furtig\(^{(56)}\) to be independent of potential over the range, $-300 < E < +900$ mV. This contradicts the response predicted by Vermilyea, and Engell's expression only holds if $(\alpha_A Z_A - \alpha_B Z_B)$ equals zero over this entire potential range.

A study of the dissolution of metal sulphides, by Scott and Nicol\(^{(57)}\) showed the dissolution rate/potential curve to exhibit a maximum in some cases though not at the expected values, possibly because of the highly covalent character of the sulphides.

Diggle\(^{(31)}\) reviewed thoroughly the theoretical and experimental data on metal-oxide dissolution and covered the various parameters which could influence the dissolution rate.

Diez\(^{(58)}\) examined the dissolution rate of metal oxides when redox couples were present in solution and, not surprisingly in view of the relationship between dissolution rate and potential, found it to vary with the value of the redox couple. A dependence of the dissolution rate on the anions present, was also established; wustite, for example, dissolving faster with increasing $Cl^-$ concentration. In the presence of EDTA, after a preliminary induction period, a marked increase in dissolution rate was observed; the
increase depended on the EDTA concentration.

Diez also looked at the theoretical aspect of dissolution and suggested that it is inadequate to illustrate the dissolution of
A⁺B⁻ as A⁺ c + A⁺(aq) and B⁻ c + B⁻(aq) when dealing with oxides. Diez considered the change in environment of the metal ion, from six oxide ion ligands in the crystal to six water molecules, perhaps, in solution as important and noted that the oxygen ions do not go into solution as such but must first react with hydrogen ions. Thus a better description is

\[ M^{2+} \text{(crystal)} \rightleftharpoons M(H_2O)_6^{2+} \] (3.20)

and \[ O^{2-} \text{(crystal)} + H^+ \rightleftharpoons OH^- (aq) \] (3.21)

or \[ O^{2-} \text{(crystal)} + 2H^+ \rightleftharpoons H_2O(l) \] (3.21a)

Diez expanded this further by allowing that another factor controlling the rate of dissolution could be the rate of removal of ions from kink sites on the crystal surface.

Yet another possible influence on the rate of dissolution is the rate of diffusion in the solution. This might involve the transport of acid molecules or hydrogen ions to the surface, which was an early explanation (58) or the movement of the dissolution species, OH⁻(aq) M²⁺(aq), or whatever, away from the electrode surface.
4.1. Apparatus and Materials

All solutions used were prepared with triply-distilled water, and 1 M sodium perchlorate (NaClO₄); appropriate amounts of perchloric acid (HClO₄) or sodium hydroxide (NaOH) being added to achieve the desired pH. All chemicals used were of Analar grade. The glassware employed in the experiments was thoroughly cleaned, firstly by soaking overnight in a 50/50 mixture of concentrated nitric and concentrated sulphuric acid, and secondly by repeated washings (at least six) with triply-distilled water.

The experiments were carried out under a nitrogen atmosphere. The nitrogen was purified before use by passing it over heated (300-400°C) copper turnings - to remove any traces of oxygen. Also, the nitrogen was passed through a sample of the working electrolyte solution to pre-saturate the gas before introducing it into the cell. The nitrogen gas was bubbled through the working electrolyte solution before each experiment and passed over the solution during the experiment.

The electrolytic cell was a simple three compartment construction (Fig. 4.1).

Experiments were carried out with 150.0mL electrolyte;1.0M sodium perchlorate solution divided between compartments A and B. Compartment C contained 1.0M sodium chloride solution.

The temperature of the system was controlled by partially immersing the cell in a water-bath, the temperature of which could be controlled to within less than one centigrade degree, by a thermostat (Grant Instruments).
Fig. 4.1. The electrolytic cell.

A = Secondary electrode compartment
B = Working " "
C = Reference " "

Glass frit
Luggin probe
Stopper
The secondary electrode, SE, consisted of a piece of platinum mesh, about 2 cm$^2$ affixed to a length of platinum wire. This electrode was positioned in compartment B.

The reference electrode, RE, employed was a silver/silver chloride electrode (Ag/AgCl/$\text{I M Cl}^-$ (aq)) immersed in 1.0M sodium chloride solution, (under these conditions the Ag/AgCl/$\text{I M Cl}^-$ (aq) electrode has a potential of $+222 \text{ mV}$ at 25°C, wrt SHE). This electrode was chosen for its suitability at high temperatures, (Fig. (4.2)) shows a graph of the variation in potential of the electrode with temperature$^{(59)}$. The RE was placed in limb C.

The sodium chloride solution was separated from the working electrolyte solution by a ground glass stopper fitted into a Luggin probe which was positioned just below the electrode surface. Two such reference electrodes were prepared together, following the thermal method given by Ives and Janz$^{(61)}$. Only one electrode of the pair was used in the experiments, and this was continually compared with the other electrode as a check on the condition of the RE. Any deterioration of the RE would result in a substantial potential difference between the pair. Initially, the pair of electrodes differed by $< 0.1 \text{ mV}$ and when this value was exceeded the electrodes were discarded and a fresh pair prepared. Fortunately, the electrodes were physically robust and the average life-time of a pair of electrodes was several months.

Various attempts were made to prepare a working electrode, WE, of magnetite. One such attempt involved compressing powdered magnetite (pressure $\approx 25$ tons) to form cylindrical blocks (approx.
Fig. 4.2. Variation of $E^\circ/V$ for Ag/AgCl/Cl$^-$ with temperature, $T/\degree C$. 
1 cm in diameter and several mm thick. These blocks were quite solid and non-porous but the extremely high resistance (≈ 10⁴ Ω) through the discs rendered them unsuitable. Two methods of preparation both involving reduction of haematite to magnetite, were employed and the material obtained used in the experiments described later. In the first method (method A) haematite rods (approximately 10 mm x 3 mm x 3 mm) were submerged in 100 ml 1 M sodium hydroxide and heated in an autoclave at 300°C, and under a pressure of 500 lb/in² of hydrogen gas, for 48 hours. The resulting material had a resistance ≈ 10 Ω through the length of the blocks and was magnetic. This method was also used on some larger slabs of haematite (about 1 cm² face and 2 mm thick). However, after the treatment described above, the slabs had a resistance of several hundred kΩ and were only weakly magnetic. Examination of these slabs under the microscope showed that only small sections of them had been reduced. These small sections, which could be broken off from the rest of the slab, were similar in appearance to the rods after their reduction, having a shiny, black porous surface and being magnetic and of low resistance. The rest of the slab retained its original dull grey appearance and non-magnetic, high resistance characteristics. These slabs were reduced by heating them in vacuo at 400°C (21) for several hours. Following this treatment the slabs were weakly magnetic and their resistance has fallen to ≈ 80 Ω. X-ray analysis of these slabs showed them to consist of only 10% magnetite, but it was considered worthwhile to examine the effects of potential on their dissolution rate. This method will be referred to as method B. The materials thus obtained were formed into electrodes by embedding them in a Teflon
sleeve (the larger slabs were held in place with non-conducting epoxy resin). Electrical contact to the rear of the material was made via a steel spring under compression. Before each experiment the exposed face of the electrode was ground flat using successively finer grades of silicon carbide paper and, finally, smoothed on ground glass. Thus, a fresh, flat surface was obtained each time. The electrode face was positioned about 1 mm above the tip of the Luggin probe.

The basic electrical arrangement was as shown in Fig (4.3). The potential was controlled using an IC20-0.5 A type potentiostat, and the current through the cell was determined by measuring the potential difference across a counting resistor, CR, fitted to the potentiostat, and through which a current, equal to that through the cell, was passing. This voltmeter, 1, was a Hewlett-Packard 3490A multimeter. Controlled variations in the potential could be made using the Function Generator (Newcastle University), for example, for Linear Sweep Voltammetry, and the resulting changes in current with time observed using an XY Recorder (Bryans 26000 A4) to replace voltmeter V1. The working electrode, WE, was connected to a motor which allowed this electrode to be rotated at speeds up to 1400 r.p.m. The rotation speed control was calibrated, periodically, using a stroboscope.

In the dissolution experiments the solutions were analysed colorimetrically using a Pye Unicam SP8-100 ultra-violet spectrophotometer at a wavelength of 505 nm. The cuvettes had a 1 cm path length.
Fig. 4.3. Basic electrical arrangement.
4.2. Electrochemical Procedures

4.2.1. Polarization Curves

The general behaviour of magnetite in acid solution was initially established by the construction of a polarization curve. This was done by assembling the cell, partially immersing it in the water-bath and flushing the system vigorously with nitrogen gas, for 30 minutes, to deoxygenate it, and to allow the electrolyte solution to come to thermal equilibrium with its surroundings. The potential of the W.E. was monitored, with respect to the R.E., and after one hour the W.E. potential had reached a relatively stable value. This value was taken as the "rest potential". The W.E. was potentiostatted at this value for 1 minute and the current through the cell measured (from the voltage drop across the counting resistor, C.R., on the potentiostat). The potential of the W.E. was increased by 50mV, and potentiostatted there, for 10 minutes, before the current was again measured. The W.E. was potentiostatted at the "rest potential" for 1 minute and the W.E. potential was decreased by 50mV; held there for 10 minutes, the current measured and the potential, again, returned to the "rest potential" for 1 minute. This procedure was repeated for potential changes of \( \pm 100 \), \( \pm 150 \), \( \pm 200 \)mV, etc, with respect to the "rest potential" until the onset of hydrogen evolution, at very cathodic potentials, or of oxygen evolution, at very anodic potentials, was achieved. The current values were plotted against the corresponding overpotential values (0, \( \pm 50 \), \( \pm 100 \), \( \pm 150 \) mV,...) to obtain a polarization curve.
4.2.2. **Linear Sweep Voltammetry**

Linear sweep voltammetry was used, both qualitatively and quantitatively, to obtain information concerning the electrical behaviour of magnetite. The electrical arrangement was as shown in fig. 4.3, with the XY recorder connected across the C.R. of the potentiostat. The potential of the W.E. was, initially, held constant by the potentiostat. Then, a linearly varying potential was applied, via the function generator, and the current response to this potential perturbation collected on chart paper on the XY recorder.

The cell was assembled, partially immersed in the waterbath and flushed with nitrogen gas (as described in the previous section). The W.E. was potentiostatted at a potential $E_s$ at which no electrochemical reaction occurred (as predicted from the polarization curves). The W.E. was held at this potential for between 30-60 minutes, (i.e. until the current was reasonably constant) in order to obtain qualitative information about the number, or magnitude, of electrochemical reactions occurring under the particular conditions, a wide sweep was made to cover the whole of the potential spectrum between oxygen evolution.

\[
2H_2O(l) \rightarrow O_2(g) + 4H^+_{(aq)} + 4e
\]  \hspace{1cm} (4.2.1)

and hydrogen evolution

\[
2H^+_{(aq)} + 2e^- \rightarrow H_2(g)
\]  \hspace{1cm} (4.2.2)

In effect, two sweeps were made; from the starting potential, $E_s$ to some, more cathodic, potential $E_c$, in the vicinity of the hydrogen evolution reaction and back to $E_s$, followed by an anodic sweep to the
oxygen evolution region, $E_a$, and back again to $E_s$. These sweeps were made at relatively slow sweep rates ($9.4 \text{ mVs}^{-1}$ usually).

Linear sweep voltammetry was also used in conjunction with the rotating disc technique. The procedure for L.S.V/R.D.E. combination was, initially, as previously described, i.e. cell assembly, deoxygenation and heating to water-bath temperature. The W.E. was potentiostatted at +700 mV, for 5 minutes. Next, the electrode was set rotating at some chosen speed, the nitrogen flow stopped and the potential swept from +700 mV to -50 mV, and back to +700 mV of 9.4 mVs$^{-1}$. This potential sweep cycle was carried out twelve times at a variety of rotation speeds ranging from 50 to 500 r.p.m., with about 1 minute between each sweep. During the 1 minute pause between sweeps, the nitrogen gas was used to flush the system, the W.E. potential was held at +700 mV and the electrode set at the next rotation speed.

When checking the dependence of the current, $i$, on the rotation speed at a particular potential value, the reciprocal of the current, ($1/i$) was plotted against $\left( \frac{1}{2 \times \pi \times \text{rotation speed}} \right)^{\frac{1}{2}}$ (where the rotation speed was measured in revolutions per second) and straight lines fitted to the points using least squares analysis. The goodness of the fit, that is, the likelihood that there was a linear relationship between $(\frac{1}{i})$ and $\left( \frac{1}{2 \pi \times \text{rot. speed}} \right)^{\frac{1}{2}}$ was estimated using Pearson's Correlation Coefficient. The criterion of a linear relationship between the two being a P.C.C. $> \pm 0.95$. 


4.2.3. **Potential Pulse Technique**

The electrical arrangement was, basically, as shown in fig. 4.3. The electrolytic cell was assembled, flushed with nitrogen gas and warmed to the desired temperature in the water bath, as usual. The W.E. was potentiostatted at some value \( E \), until the current was relatively constant. The nitrogen gas flow was arrested and potential of the W.E. pulsed to a more negative value \( (E - \Delta E) \) for 1 second. The current response to the potential change \( E + (E - \Delta E) \) was too rapid to be collected directly on the XY-recorder; accordingly, the current time response was measured using a Gould Storage Oscilloscope (capable of recording responses as fast as \( 1 \mu s \ cm^{-1} \)). The curve obtained on the oscilloscope could be magnified and transferred onto chart paper via the X-Y recorder.

On completion of a pulse, the nitrogen gas flow was re-started and the system left for 15 minutes, with the W.E. at potential \( E \), to permit the system to return to its original state. This was repeated for some new value of \( \Delta E \). Thus, for a variety of \( E \) values, a collection of current time curves was obtained.

4.3. **Dissolution Experiments**

4.3.1. **Procedure**

After the usual cell assembly and deoxygenation and heating of the electrolyte solution, the W.E. was potentiostatted initially, for 5 minutes, at a potential at which no electrochemical reaction occurred, as predicted by the appropriate polarization curve. A sample of the electrolyte solution was taken, and the W.E. potential stepped to the desired value. The working electrode
potential was kept at this value for several hours and, during this period of potential control, the current, i, through the cell was continually monitored and electrolyte samples removed for later analysis of their iron content.

The time at which the potential was stepped was taken as \( t = 0 \) and the time (in seconds) of removal of solution samples measured from this base line. The weight of iron (mg) in the first sample taken (i.e. at \( t = 0 \)) was subtracted from the weights of iron in later samples. This gave the weight of iron, \( W_t \), which had dissolved in a known period of time, \( t \). Then, \( W_t/(\text{mg}) \) was plotted against \( t/(\text{sec}) \), which illustrated the behaviour of the dissolution rate during the course of the experiment. Also, the current through the cell, \( i \), was plotted against time, \( t \).

The effects of varying parameters, such as potential, rotation speed of the W.E. and pH on the rate of dissolution and on the current were examined.

4.3.2. Sampling

A known quantity (150.0 ml) of electrolyte was placed in the electrolytic cell, initially. Samples (1.00 ml) of the electrolytic solution were removed, by pipette, at convenient time intervals throughout the course of a dissolution experiment. Access to the solution, to obtain a sample, was gained by removing the gas bubbler for as short a time as possible. The brisk flow of nitrogen through the cell prevented the ingress of oxygen. The samples were stored in 10.00 ml volumetric flasks. During dissolution the current through the cell was continually noted and, by calculating the approximate number of Coulomb of electricity passed, \( N \), a rough estimate of the
amount of iron in each sample was obtained and the sampled diluted accordingly. As soon as possible after the completion of each experiment the solutions were analysed as a batch.

4.3.3. Analysis

Initially, it was intended that the sample solutions should be analysed using Atomic Absorption Spectroscopy. This method was chosen because of its generally high sensitivity (down to 0.1 ppm, \(^{(62)}\)). Analysis of the sample solutions on a Pye Unicam SP90A-AA spec. using the flame method - in which solution is aspirated into a flame (air/acetylene) which atomized the constituents of the solution rendering them available to absorb light at characteristic wavelengths, e.g 2483 \(\AA\) for Fe - foundered due to constant breakdown of the flame structure. The absence of a constant flame structure resulted in a change in the path length of the transmitted light and adsorption decreased with time as the path length shrunk. The breakdown of the flame was due to salting out of the sodium chloride, which caused blockage of the slit on the burner. Removal of the ferrous ion from the NaClO\(_4\) background by complexing it with APDC (ammonium pyrrolidine dithiocarbamate), extracting this complex with methyl isobutyl ketone and then injecting the iron-bearing organic solvent phase into the flame proved no more successful.

Next, a flameless method, in which micro-litre samples are placed on a graphite rod and atomization achieved by heating the graphite rod by passing a current through it was employed, using a Pye Unicam SP9 AA spectrophotometer. With this method a consistently high background reading was obtained which masked the absorption of the iron in the solutions, and so this method was abandoned.
According to Walton and Reyes\textsuperscript{(60)} for concentrations of iron around 1-10 ppm spectrophotometric determinations with 1,10-phenanthroline may give better accuracy than Atomic Absorption methods and may be preferrable to them. Therefore, this technique was finally adopted. The procedure employed was as follows:

to the solution to be analysed was added
1.00 ml 0.1% hydroxylamine hydrochloride (\text{HO.NH}_2\text{Cl}) solution
1.0 ml 0.01% 1,10-phenanthroline solution
1.0 ml 0.7% sodium acetate (\text{CH}_3\text{COONa}) solution,
3 drops dilute ammonium hydroxide solution,
and triple-distilled water to bring the total volume to 10.00 ml.

The solutions were left standing for one hour for the colour to develop. The absorbance of the solutions at 505 nm was then measured using a Pye Unicam SP8-100 UV spectrophotometer. From absorption values obtained for standard solutions, prepared alongside the sample solutions, it was then possible to determine the iron concentration in the samples. A computer program was written to fit a straight line to the data obtained for the standard solutions, using the least squares method, and to output the appropriate iron concentration value following input of the measured absorbance. Fig. (4.4) shows a typical calibration curve for a series of standard solutions and, also, gives the values obtained from the least-squares method, and the limit-of-detection.

In this reaction, the ferric iron gives a green, not very stable complex. The hydroxylamine hydrochloride reduces any ferric...
Fig. 4.4. Calibration curve: Absorbance vs. [Fe$^{3+}$]/ppm.
ions present (though none was expected) to ferrous ions. Three molecules of 1,10-phenanthroline complex with each ferrous ion to produce a bright red solution. The dilute ammonia solution was added to raise the pH — a pH value between 3 and 8 being required.
CHAPTER 5

ELECTROCHEMICAL BEHAVIOUR OF MAGNETITE

5.1. Polarization Curves

Using electrodes which had been prepared by method A, polarization curves for magnetite, in various solutions, at 42°C, were obtained. Figures 5.1, 5.2 and 5.3, show the curves obtained for magnetite in solutions of pH 1.3, 5.9 and 12.5 respectively.

In the almost neutral solution, pH 5.9, there appeared (see fig. 5.2) to be no electrochemical reactions occurring between \( E = +1200 \text{ mV} \) and \( E = -1000 \text{ mV} \). The current was almost linear between these limits and ranged from \( +20 \mu \text{A} \) to \(-20 \mu \text{A}\). The current increased abruptly at the cathodic limit, but increased in a more gentle fashion at the anodic limit.

A similar response was observed in the alkaline solution, pH 12.5, (see fig. 5.3). Within the cathodic and anodic potential extremes, the current was almost zero (± 5 \( \mu \text{A} \)), but again, increased abruptly at around \(-1000 \text{ mV} \). In this solution, however, a very sharp increase in current was recorded at the positive extreme \( (E = +800 \text{ mV}) \).

A strikingly different curve was obtained in highly acidic solution (see fig. 5.1). A sharp increase in anodic current was observed for \( E > +1600 \text{ mV} \), and, as the potential was moved into the cathodic region, \( E > -100 \text{ mV} \) the current increased relatively sharply. However, the feature unique to the acidic solution curve was the cathodic peak, with a maximum current value at about \(+210 \text{ mV} \).
Fig. 51. Polarisation curve (i/μA versus E/mV) for Fe₂O₄ in 1.0 M NaClO₄ at 42°C: pH 1.3
Fig. 5.2. Polarisation curve for Fe₄ as in Fig. 5.1.

pH 5.9

\[ i/\mu A \]

\[ E/(mV) \]
Fig. 5.3. Polarisation curve for FeO₃⁺ as in Fig. 5.1. : pH 12.5
The anodic current observed at high positive potentials, in each case, was considered likely to be due to oxygen evolution. The large cathodic currents at \( E = -1000 \text{ mV} \), were thought, initially, to be due to hydrogen evolution but this was later dismissed since the reaction appeared to occur at the same potential at pH 5.9 and pH 12.5 and this was not compatible with a pH-dependent reaction such as hydrogen evolution. In strongly acid solution, pH 1.3, a cathodic reaction was observed at \( E < -100 \text{ mV} \), and this increased with increasing cathodic potential but the current was very large and prevented a greater foray into the more negative potential region.

Polarization curves, with 1% EDTA added to the solution, were constructed for solutions at pH 5.8 and 12.5, and are shown in figs 5.4 and 5.5. As fig 5.4 shows, with EDTA present in pH 5.8 solution, there was a much narrower region \((-200 < E < +400 \text{ mV})\) within which virtually no reaction occurred. Outside these limits the current increased relatively slowly. In pH 12.5 solution, with EDTA present, the curve produced (see fig. 5.5) was similar to that obtained in the absence of EDTA, except that, again, the limits were narrower \((-500 < E < +900 \text{ mV})\), and the current within this region greater than in the absence of EDTA. No comparable polarization curve of magnetite in highly acidic solution with EDTA present was obtained.

It was not possible, from the polarization curves, to ascribe unequivocally a particular reaction to a particular potential region.
Fig. 5.4. Polarisation curve for FeO in 1.0 M NaClO₄ solution with 1% EDTA added. T = 42°C; pH 5.8.
Fig. 5.5. Polarisation curve for $\text{Fe}_3\text{O}_4$ as in Fig. 5.4. : pH 12.5.
The currents, in all these curves, were examined using a rotating disc electrode, but only in the region of the cathodic peak (in the highly acidic solution) was any relationship between current and rotation speed detected.

5.2. Linear Sweep Voltammetry

The linear sweep voltammetry technique was chosen to investigate, further, the behaviour of magnetite in the vicinity of the cathodic peak observed in acid solution (see fig. 5.1). This method was employed because of its simplicity and because it was less time consuming than the lengthy procedure involved in obtaining polarization curves.

The electrical arrangement used was as shown in fig. 4.3. The Function Generator applied a linearly varying potential to the W.E. and the current response was recorded as the Y-co-ordinate on the XY-recorder, while the potential was recorded as the X-co-ordinate.

Initially, several wide range cyclic sweeps were made on a stationary magnetite electrode (prepared using method A) at 42°C, in acidic solutions of 9.4 mV/s. Figures 5.6, 5.7 and 5.8 show the results obtained in solutions of pH 0.8, 1.3 and 3.1 respectively. At pH 0.8 a very large cathodic peak ((-1)10^3 μA), which went off scale, was observed. Since a number of sweeps were to be made in each experiment this would have resulted in excessive corrosion of the electrode surface and so less acidic solutions were required. In the least acidic solution, pH 3.1 (see fig. 5.8), no cathodic peak was detected and so, solutions of this pH were undesirable.
Linear Sweep, 9.4 mV/s
pH 0.8

Fig. 5.6.
Linear Sweep, 9.4 mV/s
pH 1.3

Fig. 5.7.
Linear Sweep, 9.4 mV/s
pH 3.1

Fig. 5.8.
also. At pH 1.3, the cathodic peak was observed, with a maximum value $i_a = 200 \mu A$. Therefore, it was decided that solutions of pH 1.3 should be used in the rotation speed dependency investigations.

Therefore, a series of linear sweep experiments were carried out on a rotating disc electrode at $9.4 \text{ mV s}^{-1}$, in pH 1.3 solution, following the procedure described in section 4.2.2. The sweeps were carried out at temperatures ranging from $25^\circ \text{C}$ to $65^\circ \text{C}$. Of the twelve sweeps carried out at each temperature the first three were considered to merely cleanse the electrode surface and were not employed in the subsequent calculations. Also, only the negative going sweep paths were used. Figure 5.9 shows a typical result from this experiment; this result was obtained for 50, 150, 300 and 500 r.p.m. in pH 1.3 solution with a sweep rate of $9.4 \text{ mV/s}$, at $55^\circ \text{C}$.

At each temperature the sweeps were examined and, at various potential values, $E$, throughout the range employed, the currents at the different rotation speeds determined. Then, plots of $(\frac{1}{i})$ versus $(\frac{1}{\omega^2})$ (where $\omega$, the angular frequency = $(2 \times \pi \times \text{rotation speed (in revs per sec)})$, were made for each $E$ value, at each temperature, and straight lines fitted using least squares analysis.

At $25^\circ \text{C}$, the maximum value of the Pearson's Correlation Coefficient was 0.5, for the current, $i$, and angular frequency, $\omega$, values obtained at $E = +220 \text{mV}$. The values of the P.C.C. decreased in a regular manner on moving to either side of this point. So "reasonable" straight lines could not be fitted at any
LSV/RDE.
T = 55°C

Fig. 5.9.
potential, to the points obtained at 25°C.

At 35°C, the maximum value of the P.C.C. was 0.95 for 

\[ E = 191\text{mV}. \]

Again, the P.C.C. values decreased in a regular manner on moving in either direction from this potential. However, the P.C.C. values at this temperature were greater than those determined at 25°C, although, as before, "reasonable" straight lines could not be fitted to these points (except for those at 

\[ E = +191\text{mV}. \]

At higher temperatures, 42, 55 and 65°C, straight lines could be fitted to the plots of \( \frac{1}{i} \) versus \( \frac{1}{(2\pi(\text{rotation speed}))^{1/2}} \) over a range of potentials (see Table 5.1). Examples of some of the resulting slopes are shown in Figs. 5.10, 5.11, and 5.12.

for \( T = 42, 55 \) and 65°C, respectively. The goodness of fit of the lines obtained tended to a maximum near the tip of the cathodic peak. It was assumed that the reaction occurring in the region of the cathodic peak could be treated as a simple reduction reaction and that the reverse, anodic reaction could be ignored. Therefore, using the equation

\[
\frac{1}{i} = \frac{1}{nFAk_{\text{e}}C} + \frac{1}{0.62 nFACD^{3/2} v^{-1/6} \omega^{1/2}} \tag{5.2.1}
\]

(see section 2.3.3) the values of the slopes, \( S \), and intercepts, \( Y \), were obtained where

\[
S = \left\{ \frac{1}{0.62nFAD^{3/2} v^{-1/6} C} \right\} \tag{5.2.2}
\]

and

\[
Y = \left\{ \frac{1}{nFk_{\text{e}}C} \right\} \tag{5.2.3}
\]

57
Table 5.1.

<table>
<thead>
<tr>
<th>T/℃</th>
<th>Potential range/(mV)</th>
</tr>
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<tbody>
<tr>
<td>42</td>
<td>100 ≤ E ≤ 220</td>
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<tr>
<td>55</td>
<td>76 ≤ E ≤ 301</td>
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<tr>
<td>65</td>
<td>92 ≤ E ≤ 242</td>
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</table>
Fig. 5.10. Plots of $1/i/(A \cdot \text{cm}^2)$ vs. $1/\omega^k/(s^k)$ obtained from L.S.V. at 42°C, at various potentials, $E$/mV.
Fig. 5.11. Plots of $1/i$ vs $1/\omega^2$ as in Fig. 5.10, but at 55°C.
Fig. 5.12. Plots of $1/i$ vs. $1/\omega^k$ as in Fig. 5.10, but at 65°C.

$10^3 \times 1/i$ / (A cm$^2$)

$1/\omega^k/(s^k)$
As stated earlier, according to equations (5.2.2) and (5.2.3) the slopes, $S$, should be constant while the intercepts should vary with potential. Inspection of the slopes in figures 5.10, 5.11 and 5.12, show that straight lines were obtained and that it is possible to use this model to describe the dissolution process under these conditions, (although nearer the limits of the rotation-speed dependent regions given in Table 5.1, the correlation coefficients were lower and the constancy of slope of the lines not so apparent).

From equations (5.2.2) and (5.2.3) it was possible to estimate the size of the rate constant $k_f$ for the reduction reaction. From rearrangement of (5.2.2) and (5.2.3)

$$k_f = \frac{0.620D^{\frac{3}{2}} \nu^{-1/6}}{Y} S \quad (5.2.4)$$

and by taking $D = 5 \times 10^{-6}$ cm$^2$s$^{-1}$ and $\nu = 0.01$ cm$^2$s$^{-1}$, as approximate values for diffusion in aqueous solution

$$k_f \approx 3.90 \times 10^{-4} \frac{S}{Y} \quad (5.2.5)$$

Table 5.2. lists values of $k_f$ obtained from plots of $\left(\frac{1}{t}\right)$ versus $\left(\frac{1}{w_0^2}\right)$ which had high correlation coefficients. It appeared from these figures that $k_f$ did not behave monotonically with temperature, as expected, but passed through a maximum in the temperature range $42 < T < 65^\circ$C, which was unlikely.

From equation (5.2.2) using the values of $D$ and $\nu$ given above, and by assuming $n = 1$, and taking the area, $A$, as the nominal area $= 0.04$ cm$^2$, it was possible to obtain an approximate
Table 5.2.

<table>
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<tr>
<th>$E/(mV)$</th>
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<th>$E/(mV)$</th>
<th>$10^{-6} k_f/(cm^2)$</th>
<th>$E/(mV)$</th>
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<td>8.3</td>
<td>160</td>
<td>24.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
value of $C$, the bulk concentration of the diffusing species,

$$C = \frac{10^3 \nu^{1/6}}{0.62 \text{nFA} D^3 S} \text{ mole} \, 1^{-1} \quad (5.2.6)$$

The values of $C$, at each temperature, were:

- $T = 42^\circ C$: $C = 0.27 \text{ mole} \, 1^{-1}$
- $T = 55^\circ C$: $C = 0.20 \text{ mole} \, 1^{-1}$
- $T = 65^\circ C$: $C = 0.30 \text{ mole} \, 1^{-1}$

Because of the many approximations made in arriving at these $C$ values, these results are only very rough estimates.

However, the magnitude of the $C$ values do provide a guide to the identity of the diffusing species. Such large values suggest that the species exerting diffusion control on the reaction is not an iron species, but is likely to be the proton concentration, $H^+$, in solution. That the values of $C$ obtained are greater than calculated from the pH may be due to the approximations made in $D$, $\nu$, $A$, or $n$.

It was expected that the rate constant would be related to the potential by an expression of the form,

$$k_f = k_f^0 \exp \left( -\frac{\alpha n F E}{RT} \right) \quad (5.2.7)$$

where $k_f^0$ is potential independent. Therefore, a plot of $E$ versus $\log k_f$ should give a straight line of slope $\left( -\frac{RT}{\alpha n F} \right)$. This was carried out for the values given in Table 5.2. and the results shown in figures 5.13, 5.14 and 5.15 for $T = 42$, 55 and $65^\circ C$ respectively. The theoretical value of the slope $\left( -\frac{RT}{\alpha n F} \right)$ and the experimental values are given in Table 5.3. As can be seen from figures 5.13 5.14 and 5.15, the resulting plots deviated from the predicted...
Fig 5.13. Plot of $\ln k_f$ vs. $E$/mV for results of LSV/RDE expts. at 42°C.
Fig. 5.14. Plot of $\ln k_f$ v E/mV for results of LSV/RDE expts, at 55°C.
Fig. 5.15. Plot of $\ln k_f$ vs. $E$/mV for results of LSV/RDE expts. at 65°C.
Table 5.3.

<table>
<thead>
<tr>
<th>T/°C</th>
<th>-(RT/αnF)/(mV dec⁻¹) Theor</th>
<th>Expt</th>
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<tr>
<td>42</td>
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</tr>
<tr>
<td>65</td>
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<td>289</td>
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</table>
behaviour. At $T = 42^\circ C$ and $T = 65^\circ C$ the points lay on a straight line initially, but appeared to curve away from it at potentials very near to the cathodic peak, and at $T = 55^\circ C$ the resulting plot could best be fitted by two straight lines, or a gentle curve. It is possible that, while equations (5.2.1) and (5.2.7) hold at potentials below the maximum on the cathodic peak, there is a change in the cathodic reaction and in the parameters $\alpha$ and $n$ at potentials close to the cathodic peak and that it is this change which causes the decrease in the cathodic current. Alternatively, the differences between the theoretical and calculated results, especially the magnitude of the $\frac{RT}{\alpha n F}$ values, may be explained in terms of the semi-conductor properties of magnetite. Thus, not all of the applied potential falls across the Helmholtz plane, and instead some fraction of it falls across the space charge layer of the electrode and the remainder across the Helmholtz plane. Also, the fraction of the applied potential, which falls across each, is itself potential dependent and this would explain both the non-linearity of the $E$ versus $\log k_f$ lines, and of their apparently anomalously high slopes.

The effect of the hydrogen iron concentration on peak height was measured by carrying out a series of linear sweeps, between $+700$ and $0 \text{mV}$ at $30 \text{mV s}^{-1}$ in $1.0 \text{M NaClO}_4$ solution at various pH values. The height of the cathodic peak, $i_p$, was measured and $(\log i_p)$ plotted against pH. A straight line graph of slope $0.93 \omega_{03}$ obtained (see fig. 5.16). This suggested that the peak height was directly proportional to the hydrogen ion concentration, and that the reaction causing the reduction peak was first order with respect to $H^+$. 60
Fig. 5.16. Plot of $\log(i_p)$ v pH from LSV expts.
Assuming that the equation,

\[ i_p = 2.99 \times 10^5 \cdot n(\alpha_n)\frac{1}{2}D_{H^+}^{\frac{1}{2}}C_{H^+}^{\frac{1}{2}} \text{ (at 25°C)} \]

holds, then it should be possible to estimate \( D_{H^+} \) from the value of the slope of the \( i_p \) vs \( C_{H^+} \) plot. Therefore, \( i_p \) was plotted against \( C_{H^+} \) for \( v = 30 \text{ mV s}^{-1} \) fig. 5.17.

5.3. Potential Pulse Experiments

Employing the method described in section 4.2.3, a magnetite electrode, prepared using method A, was subjected to cathodic potential pulses and the current response examined.

The electrolytic cell was assembled with 1.0M NaClO\(_4\) solution, and adjusted to pH 1.3 by the addition of concentrated perchloric acid. The cell was partially immersed in a water-bath at 25°C and deoxygenated in the normal manner. When the system had attained thermal equilibrium the potential of the working electrode was set at +720mV and held there until the current through the cell was constant. The working electrode potential was stepped cathodically. Cathodic steps of magnitudes 100, 200, 300, 400 and 500mV were applied to the system each of duration 1sec, with a 15 minute pause between each step in order to allow the system to return to equilibrium.

Fig. 5.18 shows the current response obtained for these pulses, plotted as \( i/(\mu A) \) versus \( 10^3 \times t/(\sec) \). The i-t curves for \( \Delta V = -100 \) and -200mV were virtually identical and lie one atop the other. Within 30 or 40ms the current, for these pulses, had dropped to about 20 \( \mu A \). It was considered that, at these potentials, no reaction occurred and that the initial, high, currents were due to double-layer charging. As the magnitude of the pulses was increased, reduction occurred and the current increased with
Fig. 5.17. Variation of peak height, $i_p$, with $[H^+]/(\text{mole}^l)$.
Fig. S.18. Current response of magnetite electrode to cathodic pulses, $\Delta E$/mV.

The graph illustrates the current response ($i/\mu A$) of a magnetite electrode to cathodic pulses of varying $\Delta E$ values (300, 400, 500 mV) as a function of time ($10^3 t$/s).
increasing potential.

Figure 5.19 shows plots of current, \( i/(\mu A) \) versus \( t^{-\frac{1}{2}}/(sec)^{-\frac{1}{2}} \), for these potential pulses. At the lower values of \( \Delta V \) the plots appeared non-linear. But, at \( \Delta V = -500\text{mV} \), the plot gave a straight line over much of the \( t^{-\frac{1}{2}} \) region. This suggested, contrary to the results obtained using linear sweeps, that there was a degree of diffusion control at \( T = 25^\circ\text{C} \) although the \( i \) versus \( t^{-\frac{1}{2}} \) plot did not pass through the origin. The deviation of the plot from a straight line for very small values of \( t^{-\frac{1}{2}} \), which correspond to large values of \( t \), may be due to convective effects. The slope of the \( i \sqrt{t^{-\frac{1}{2}}} \) line was measured as \( \sim 120 \times 10^{-6}\text{As}^{-\frac{1}{2}} \).

If the Cottrell equation is assumed to hold at this potential, i.e.

\[
i = \frac{nFAD^\frac{1}{2}C}{\pi^\frac{1}{2}t^\frac{1}{2}}
\]

then

\[
\frac{\partial i}{\partial t^{-\frac{1}{2}}} = \frac{nFAD^\frac{1}{2}C}{\pi^\frac{1}{2}}
\]

And, taking the values of \( n, A, \) and \( D \) from section 5.2. i.e.

\( n = 1, A = 0.04\text{cm}^2 \) and \( D = 5 \times 10^{-6}\text{cm}^2\text{s}^{-1} \), and assuming a value of \( 0.2 \times 10^{-3}\text{mole cm}^{-3} \) for \( C \), the \( \text{H}^+ \) concentration, \( \frac{\partial i}{\partial t^{-\frac{1}{2}}} \)

should equal \( \sim 970 \times 10^{-6}\text{As}^{-\frac{1}{2}} \). Noting, again, the various approximations made in arriving at this figure it seems of the right order of magnitude as the value obtained \( (120 \times 10^{-6}\text{As}^{-\frac{1}{2}}) \)
Fig. 5.19. Plots of $i/(\mu A) \times t^k/(s^k)$ for pulses of Fig. 5.18.
CHAPTER 6
DISSOLUTION OF IRON OXIDE UNDER POTENTIAL CONTROL

6.1. The electrodes employed in these experiments were manufactured using "magnetite" which had been prepared by both of the methods (A and B) outlined previously. Although the electrodes responded to a linear potential sweep in a manner characteristic of magnetite, X-ray analysis later showed the haematite to magnetite reduction process to have been in complete in both instances. Method A produced material which consisted of 70% magnetite, while method B resulted in the conversion of only about 10% of the haematite to magnetite. Therefore, iron oxide is, perhaps, a better description of the electrode material.

Following the procedure described earlier, (section 4.3), that is, by potentiostatting the magnetite electrode in an acidified solution of 1.0M sodium perchlorate, and monitoring both the current through the cell and the amount of oxide dissolving (by colorimetric analysis of samples of the electrolyte solution to determine their ferrous ion content) during the course of the experiment, the effect of the applied potential on dissolution was examined. The weight of iron dissolved (in time, t/(sec)) and the current, i, through the cell were plotted against time. The electrodes employed were all of slightly different dimensions and so, to allow comparison between electrodes to be made, all the values of the weight of iron dissolved, W, and current, i, were scaled up, from their nominal areas, to 1cm\(^2\). Thus, graphs of W/(mg cm\(^{-2}\)) versus t/(sec), and i/(mA cm\(^{-2}\)) versus t/(sec) were obtained.
6.2. Dissolution of Magnetite (Iron Oxide type A)

The effect of the applied potential on the rate of dissolution of rotating magnetite electrodes, prepared by method A, was investigated in 1.0M sodium perchlorate solution at pH 1.5, T = 72°C and a rotation speed of 1400 r.p.m. Figures 6.1(a) and (b) show the observed behaviour of such electrodes in the form of plots of weight of iron dissolved, W/(mg cm\(^{-2}\)), versus \(10^{-3} x t/(sec)\), and of the electronic current, i/(mA cm\(^{-2}\)), versus \(10^{-3} x t/(sec)\). These graphs cover the potential range \(E = +285mV\) to +135mV, and are typical of the results obtained in this potential region, which spans the cathodic peak observed using linear sweep voltammetry.

The first point to note is that, contrary to expectations based upon the results of other workers, the dissolution rate was not constant during the course of each experiment, which lasted about three hours, generally. Instead, the dissolution rate decreased as \(t\) increased. The result was that plots of \(W v t\) gave shallow curves. This behaviour was repeated, also, at potentials outside the region covered in figures 6.1(a) and (b). The current response to a potential step into this region was an, initially, rapid decrease in current density followed by a more gentle, eventually asymptotic, decay.

At potentials more positive than \(E = +385mV\) the dissolution rate was too slow to be followed by the methods used here or to be of much practical interest. As the potential was moved cathodic
Fig. 6.1(a) Plot of $W/(\text{mg cm}^2)$ weight of iron dissolved, $v \times 10^3 \text{ t/(s)}$, time elapsed, for various $E/\text{mV}$.

$T = 72^\circ C, \text{pH}.15$
Fig. 6.1 (b) Plots of $i/(\text{mA cm}^2)$ vs $10^3 t/\text{s}$ at various $E$. 

![Graph showing the relationship between current density ($i$) and time ($t$) for different values of potential ($E$). The graph indicates that the current density decreases exponentially with increasing time, with each curve corresponding to a different potential value (185, 135, 234, and 285).]
of $E = +385\text{mV}$, the dissolution rate increased and maximum values ($\approx 4 \times 10^{-6}\text{ g cm}^{-2}\text{s}^{-1}$) were obtained at around $E = +160\text{mV}$ (the $W$ vs $t$ and $i$ vs $t$ curves for $E = +185\text{mV}$, and $+135\text{mV}$, overlapped almost perfectly). On moving slightly more cathodic than $E = +135\text{mV}$, the dissolution rate began to decrease. The current behaviour across this potential region, mirrored that of the dissolution rate, i.e. increasing as $E$ was driven more cathodic than $+385\text{mV}$ and exhibiting maximum values for $E = +185$, $+135\text{mV}$. Thus, the observed behaviour might be predicted from examination of a linear sweep scan of the region.

Figure 6.2. shows the effect on dissolution, of driving the electrode potential progressively more negative. As the potential was made more cathodic than $E = +135\text{mV}$ the dissolution rate decreased, and continued to do so for potentials down to $-315\text{mV}$. Also, the $W$ vs $t$ curves were very shallow and, in some cases, could better be described as linear. An increase in dissolution rate was observed at potentials around $E = -440\text{mV}$, but it decreased again at $-510\text{mV}$, whereafter it began to increase with increasingly negative potential. The large increase in the dissolution rate, at $E = -715\text{mV}$, ($\approx 6 \times 10^{-6}\text{ g cm}^{-2}\text{s}^{-1}$), coincided with the sudden, sharp jump in current observed when using linear sweep voltammetry.

As can be seen, from figure 6.3, at more negative potentials the response of the current density to a potential step was different from that in the cathodic peak region. At these potentials, after an initial increase in current density, which lasted in some
Fig. 6.2. Plots of \( \frac{W}{(\text{mg cm}^2)} \) vs. \( 10^3 t/\text{s} \) for dissolution of Fe\(_2\)O\(_4\) at potential, \( E/\text{mV} \).
Fig 6.3. Current time curves from dissolution at potential, E (mV).

\[ i/(\text{mA cm}^2) \]

\[ 10^3 t/(\text{S}) \]
instances for almost one hour, the current density decayed. Again, the relative magnitudes of the dissolution currents were mirrored in the electronic current densities.

The electrode potential was stepped to \(-810\text{mV}\), and the results shown in figures 6.4(a) and (b). Examination of fig. 6.4(a) shows that, after an initial increase to around 5 mg cm\(^{-2}\), the value of \(W\) remained relatively constant throughout the course of the experiment. The current density, \(i\), had the same appearance as the other cathodic \(i\ v\ t\) curves, but the magnitude of the current density was much larger than that obtained at those potentials.

Thus, except at potentials more negative than \(\approx -800\text{mV}\), there appeared to be an intimate relationship between the electronic and dissolution currents. Therefore, following the example of Lecuire (52), the number of Coulombs of electricity passed in the course of the dissolution experiments, \(N_e\), was estimated and compared with the total number of moles of ferrous ion, \(N_{Fe}\), going into solution. The value of \(N_e\) was determined by measuring the area under the \(i\) versus \(t\) curves. Then, the ratio, \(R\), where

\[
R = \frac{N_e}{N_{Fe}} \quad (6.2.1)
\]

was estimated over a variety of potentials. Around the cathodic peak region, \((E = +180\text{mV})\) values of \(R\) around 0.7 were obtained. Such values are consistent with dissolution occurring according to

\[
\text{Fe}_3\text{O}_4 + 8\text{H}^+ + 2e^- \rightarrow 3\text{Fe}^{2+} + 4\text{H}_2\text{O} \quad (6.2.2)
\]
Fig. 6.4. a) Plot of $W$ (mg cm$^2$) of Fe$_{2+}^{2+}$ vs. $10^3 t$ at -810 mV. b) Corresponding $i-t$ curve.
which, for stoichiometric magnetite, would have an R value of 0.67.

At more negative potentials the value of R increased gradually, attaining a maximum value of 1.2, at $E = -715\text{mV}$, before decreasing. At $E = -810\text{mV}$ where, as stated above, the magnitude of the current density had appeared anomalously high compared to size of the dissolution current, the calculated R value was 19. The R value of 0.67, for reaction (6.2.2) quoted above assumes 100% current efficiency and, if this is not so, different R values are to be expected. This very high R value, of 19, suggests that some other very facile, cathodic reaction is occurring simultaneously with the dissolution of magnetite at this very negative potential; possibly hydrogen evolution. At less negative potentials, the deviations R, from 0.67, may be due to the existence of concurrent reactions, or they may indicate changes in the dissolution reaction on moving cathodic of the reduction peak.

It was found that, at potentials around the cathodic peak the behaviour of the dissolution curve could be described by an Avrami-type expression of the form,

$$W' = W_\infty (1 - e^{-\beta t})$$

(6.2.3)

where $W'$ is the theoretical weight of iron dissolved in time t, $W_\infty$ is the weight of iron dissolved for $t = \infty$ and $\beta$ is a constant.

Using a standard library programme computer match curves were fitted to the W and t points, by an iterative method, and values of $W_\infty$ and $\beta$ were obtained. Figures 6.5(a), 6.6(a) and 6.7(a) show plots of experimental values, W, and theoretical values, W', against time, for potential values, $E = +235$, +185 and +135mV.

67
Fig. 6.5. Theoretical, ■, and exp t, ▲, plots of a) W and b) i for E = +235 mV

10^3 t for E = +235 mV

W/(mg cm^2)

I/(mA cm^2)

10^3 t/(s)
Fig. 6.6(a) As Fig. 6.5(a) for $E=185$ mV.
Fig. 6.7(a). As Fig. 6.5(a) for $E = 135 \text{mV}$.
Within the region of the cathodic peak, as is apparent from these plots, the correlation between experimental, $W$, and theoretical, $W'$, weight values was very good. A further check on the suitability of this model was made by taking the first differential of $W'$ with respect to $t$ (and multiplying the result by the appropriate factor) to give the dissolution current, $i_{\text{diss}}$. Thus, 

\[ i_{\text{diss}} = \frac{dW'}{dt} \]  \hspace{1cm} (6.2.4)  

\[ = \beta W' e^{-\beta t} \]  \hspace{1cm} (6.2.5)  

Then, $i_{\text{diss}}$ was plotted against $t$. Such plots, and the corresponding $i$ versus $t$ plots, for $E = +235$, $+185$ and $+135$ mV are shown in figs. 6.5(b), 6.6(b) and 6.7(b). It is obvious that the correlation between the theoretical $i_{\text{diss}}$ and experimental, $i$, values is much less good than in the case of the $W$ v $t$ and $W'$ v $t$ curves.

The dependence of the dissolution rate on pH, in this region, was investigated also. Figs. 6.8(a) and (b) show plots of $W$ versus $t$, and $i$ versus $t$, at $E = +285$ mV for $pH = 1.1, 1.5$ and $2.0$. Since the result of the L.S.V. examination of this region had shown that the peak height increased with increasing $H^+$, and dissolution experiments had shown dissolution to be linked to the current density, it was anticipated that the degree of dissolution would be greatest in the most acidic solution. Therefore, the lack of such a pattern in these curves, both for $W$ v $t$ and $i$ v $t$, was disregarded and the result for pH 2.0 considered spurious.
Fig. 6.6(b) As Fig. 6.5(b) for $E = 185$ mV.
Fig. 6.7(b). As Fig. 6.5(b), for $E = 135 \text{ mV}$. 

Graph showing the current density ($/ \text{mA cm}^2$) as a function of time ($10^3 t / \text{s} = 10^5$).
Fig. 6.8(a). Effect of \([H^+]\) on dissolution:
Plots of \(W \times 10^3t\) at \(E=285\text{mV}\), and various pH.
Fig. 6.8(b). Effect of $[H^+]$ on dissolution: current time curves (conds. as in Fig. 6.8(a).)

Current density $i$ in $(\text{mA cm}^{-2})$ vs. time $t$ in $\times 10^3$ s for different pH values:
- pH 2
- pH 1.5
- pH 1.1

The graph shows a decrease in current density with time for each pH level, indicating a decrease in dissolution rate.
Figures 6.9 and 6.10, which are plots of W versus t for E = +235 and +135mV, show that dissolution did, indeed, increase with increasing hydrogen ion concentration. That corresponding changes in the electronic current resulted from changing the pH is illustrated by the i v t plots in figures 6.11 and 6.12.

The values of R obtained for dissolution in acidic solution at potentials within this region were around 0.70, which is in close agreement with dissolution occurring according to reaction (6.2.2).

Next, the effect of the temperature on dissolution in acid solution was investigated. The dissolution experiments were carried out at pH 1.5, with an electrode rotating of 1400 r.p.m. and at temperatures up to 72°C. As can be seen from figures 6.13 (a) and (b), which show the resulting W versus time and current density, i, versus time plots, respectively, for dissolution of E = +185mV, for temperatures ranging from 40°C to 72°C, the behaviour of the electrode was independent of temperature, i.e. both the dissolution rate and the current density decreased with time and R values of 0.68 were obtained. As expected, increasing the temperature promoted dissolution.

The effect of the rotation speed of the electrode on the dissolution reaction was examined by submitting the magnetite electrode to potential steps, and measuring the current density at various rotation speeds (between 50 r.p.m. and 1400 r.p.m.) at each potential. The general current-density/rotation speed behaviour is shown in figure 6.14, which shows plots of
Fig. 6.9 Effect of [H\(^+\)] on dissolution:
Plots of \( W v 10^3 t \) at \( E = 235 \text{ mV} \)
Fig. 610. Effect of [H+] on dissolution:
Plots of W vs $10^3 t$ at $E = 135$ mV.
Fig. 6.11. Current-time curves:
see Fig. 6.9.
Fig. 6.12. Current-time curves:

see Fig. 6.10.
Fig. 6.13a. Effect of temperature, $T/°C$, on dissolution.

$W/(mg cm^2)\quad (E = 185mV)$

$10^3 t/10$

40

30

20

10

0
Fig. 6.13b. Effect of temperature, T/°C, on dissolution.
(E = 185 mV)
Fig. 6.14. Dependence of current on rotation speed: Plots of $1/i\,\text{A/cm}^2$ vs $1/\omega^2\,\text{s}^4$ at potential $E/\text{mV}$.
$\frac{1}{i^1/(mA cm^{-2})^{-1}}$ versus $\frac{1}{\omega^1/(rad s^{-1})^{-1}}$ for several different potentials.

The values of $\frac{1}{i}$ varied with potential as expected, on the basis of the L.S.V. curves obtained previously, i.e. $\frac{1}{i}$ tended to decrease as the potential was shifted cathodic of $E = +385mV$, going through a minimum around +185mV, before increasing and then decreasing, yet again, at even more negative potentials. There appeared to be a definite dependence of the current density on the rotation speed and, between $E = +335mV$ and $E = -205mV$, plots of the reciprocal of the current density, $\frac{1}{i}$, against the reciprocal of the square root of the angular rotation speed, $\frac{1}{\omega}$, were found to be linear. At more positive, $E = +385mV$ for instance, a plot of $\frac{1}{i}$ versus $\frac{1}{\omega^2}$ yielded a curve suggesting that the dissolution process was under only partial mass transport control. The other plots, of $\frac{1}{i}$ versus $\frac{1}{\omega^2}$ for various potentials, gave straight lines of roughly similar slope, but different intercept, which was the type of behaviour observed during the linear sweep voltammetry experiments. That the $\frac{1}{i}$ v $\frac{1}{\omega^2}$ slope, for $E = -205mV$, appears quite different from the other slopes, and its intercept almost overlaps that for dissolution at $E = +235mV$ maybe due to a change in the dissolution process at more negative potentials.

Since it was established earlier that, except at very negative potentials, $E < -800mV$, the current density, $i$, appeared to result, with 100% current efficiency, from dissolution occurring as

$$Fe_3O_4 + 8H^+ + 2e \rightarrow 3Fe^{2+} + 4H_2O$$
it is reasonable to assume that, if the current is dependent on the rotation speed, and according to the results described above it is, dissolution, also, is a function of rotation speed.

In order to discern whether or not the rotation speed dependence was a result of the accumulation of iron species at the electrode surface, i.e. whether the dissolution reaction was controlled by mass transport of dissolved ferrous complexes away from the electrode surface, the magnetite electrode was examined in solutions to which had been added ferrous ammonium sulphate. This was done by carrying out a check on the rotation speed dependence of the current during a normal dissolution experiment, adding sufficient ferrous ammonium sulphate solution to increase Fe$^{2+}$ to about 100 p.p.m. and, finally, re-checking the rotation speed dependence of the current. Figure 6.15 shows the typical result of such an experiment, (carried out at $E = +185$ mV).

Lines 1 and 2 were produced by plotting $(\frac{1}{I})$ v $(\frac{1}{\omega})$ before and after addition of the ferrous solution, respectively. As can be seen the two lines lie very close together and it appears as though the addition of Fe$^{2+}$ to the solution has had no significant effect on the rate of reaction. The slightly higher values of $(\frac{1}{I})$ may be due to the decay in current density with time which has been repeatedly observed during potential step experiments. This indifference of the $(\frac{1}{I})$ v $(\frac{1}{\omega})$ plot with respect to the ferrous ion concentration suggests that mass transport of dissolved iron species is not the rate controlling factor.
Fig. 6.15. Effect of $[\text{Fe}^{2+}]$ on dissolution.

- ▲: In 10 M NaClO$_4$ solution: pH 1.5
- ■: On addition of Fe$^{2+}$
Similarly dissolution experiments were carried out in which, after checking the rotation speed dependence of the current density, the pH of the solutions were adjusted by the addition of small quantities of concentrated perchloric acid and the rotation speed dependence checked again. Then, plots of \( \frac{1}{I} \) and \( -\frac{1}{\omega^2} \) before and after acid addition, were constructed. It was found that addition of acid caused the current density to increase, and \( \frac{1}{I} \) to decrease, as expected from earlier results, which showed \( I \) increasing with increasing \( H^+ \). However, another consequence of acid addition was to decrease the slope of the \( \frac{1}{I} \) versus \( \frac{1}{\omega^2} \) lines. This decrease in the dependence of the current density on the rotation speed of the electrode indicated that it was mass transport of \( H^+ \) to the electrode surface which was the rate controlling factor in the dissolution process.

Examples of the pH dependence of \( \frac{1}{I} \) versus \( \frac{1}{\omega^2} \) slopes are shown in figures 6.16 and 6.17. The lines in fig 6.16 were obtained in, initially pH 1.5 solution, at \( E = -15mV \), and addition of acid to the solution caused the slope to be more than halved; the slope decreased from \( 768(mA^{-1} cm^2 rad^{1/2}s^{-1}) \) to \( 331(mA^{-1} cm^2 rad^{1/2}s^{-1}) \). Figure 6.17 for \( E = +35mV \), illustrates that, for large values of \( t \), i.e. on the flatter parts of the \( i \ vs \ t \) curves, the current density is rotation speed dependent still and that the controlling factor is the movement of \( H^+ \) to the electrode surface.

Examination of the electrode surface on completion of dissolution showed that corrosion occurred preferentially at the electrode perimeter (see photographs (6,a,6,b)). This selective
Fig. 6.16. Effect of pH on rotation speed dependence.

1) 1.0 M NaClO₄ soln: pH = 1.5
2) On increasing [H⁺]
Fig. 6.17. Effect of pH on rotation speed dependence.

\[ \frac{1}{i} \left( \text{A cm}^{-2} \right) \]

\[ \frac{1}{\omega^{1/3}/(s^{1/3})} \]

- pH 0.4
- 0.4 < pH < 1.5
- pH 1.5
Photographs 6 (a) and (b) showing localised corrosion on a magnetite electrode.
dissolution was observed on a stationary electrode also, indicating that it was a result of the electrode material rather than due to the geometry or the rotation speed of the electrode. X-ray analysis of the electrode surface revealed that the haematite to magnetite conversion was restricted to the outer edges of the electrode blocks. Thus, the electrode blocks had a haematite core surrounded by magnetite.

6.3. Dissolution of Iron Oxide – type B

The relationship between the applied potential and the dissolution rate of electrodes prepared by method B was examined, using similar techniques as those employed in section 6.2, and under similar conditions i.e. pH 1.5 1.OM sodium perchlorate solution, at 72°C with electrode rotation speed of 1400 r.p.m.

Again, no simple relation between the electrode potential and dissolution was found, but dissolution appeared to increase or decrease in the same way as the current varied with potential when a potential sweep was applied. Figures 6.18 (a) and (b) show the variation in W, with time, t, for different potential values. As with dissolution of the more magnetite-like electrodes the dissolution rate decreased with time, and plots of W versus t were shallow curves. For potentials anodic of E = +285mV, dissolution was negligible and, at E = +285mV, was very slow (∼1 x 10⁻⁶ g cm⁻² s⁻¹). As the electrode was shifted to more negative potentials dissolution increased and maximum rates (∼6 x 10⁻⁶ g cm⁻² s⁻¹) were observed around E = -65mV. After a slight decrease in dissolution rates at more negative potentials, the dissolution rate fluctuated, rising and falling as the potential was changed, but the overall trend
Fig. 6.18(a). Dissolution of oxide-B at pH 1.5 and potential E/(mV).
Fig. 6.18(b). Dissolution of oxide B at pH 15 and potential E/(mV).
was increased dissolution with increasingly negative electrode potential. Figures 6.19 and 6.20 show the corresponding plots of current density, $i$, against time, $t$. It is apparent that the current response of the electrode depended on the magnitude of the potential step. At anodic potentials, such as $E = +285$, the $i$ versus $t$ curve was very shallow, while at more negative potentials, $E = +85$, $+35\text{mV}$ for example, the current increased slightly before decreasing. At even more negative potentials, $E < -15\text{mV}$, a steep, decaying $i$ versus $t$ curve was observed.

The $R$ values for the dissolution of this type-B oxide were in the region $0.9 - 1.0$ which reflects the more haematite-like nature of this material, and suggests that dissolution may have occurred as,

$$\text{Fe}_2\text{O}_3 + 6\text{H}^+ + 2e^{-} \rightarrow 2\text{Fe}^{2+} + 3\text{H}_2\text{O} \quad (6.3.1)$$

The variation in $R$ was due, probably, to variations in the composition of the electrode. For example, the curves shown in fig. 6.18(a) all had high $R$ values of approximately $1.0$ (except for a curve obtained at $E = +35$, where $R = 0.5$; a result considered spurious), while the curves shown in fig. 6.18(b) mainly, had $R < 0.9$. The curves shown in figs 6.18(a) and (b) were obtained using different electrodes and the lower $R$ values of the latter were due, possibly, to the electrode having a slightly higher magnetite content. Again, as the electrode potential was shifted to more cathodic values, $R$ increased indicating either a change in the dissolution mechanism or the onset of other electrochemical reactions.
Fig. 6.19. Current-time curves for dissolution of oxide-B.
(see Fig. 6.18(a).)
Fig. 6.20. Current time curves for dissolution of oxide-B.
(see Fig. 6.18(b).)
The dissolution of the type-B oxide was, essentially the same as for the more magnetite-like type-A oxide. For example, dissolution increased with increasing temperature, and with increasing $[\text{H}^+]$, also. As with magnetite, it was possible to describe the dissolution behaviour, i.e. the variation in $W$ with time, $t$, by the Avrami-type expression,

$$W' = W_a (1 - e^{-\beta t})$$  \hspace{1cm} (6.32)

Although again, while this expression gave a good fit to the $W$ versus $t$ curve, a plot of the first differential, $\left(\frac{dW}{dt}\right) = i_{\text{diss}}'$ against time, $t$, did not fit nearly as well.

Another similarity between the behaviour of the two oxides was that the type-B oxide also exhibited a current density rotation speed dependence. Figs. 6.21 (a) and (b), were obtained by carrying out a normal dissolution experiment, at $E = -115\text{mV}$ and 1200 r.p.m., for approximately one hour, then decreasing the rotation speed to 300 r.p.m. An obvious decrease in current density with lowered rotation speed is displayed in fig. 6.21(b) but no change in dissolution rate, which in this example appeared almost constant, was detected. In the foregoing experiments it was found that the current density and rotation speed were linked by an expression of the form:

$$\frac{1}{i} = C + \frac{m}{\omega^2}$$  \hspace{1cm} (6.33)

which is merely another way of writing equation (2.3.36). Thus, the current density is not directly related to $\omega^4$, and the effect on $i$ of changing $\omega$ is influenced by the magnitude of $C$. Therefore,
Fig. 6.21(a). Dissolution of oxide-B: effect of rotation speed. 
\( E = 115\text{mV} \)
Fig. 6.21(b). Effect of rotation speed on current during dissolution of oxide-B.
although in this example the rotation speed was decreased such that \((\omega_2^{1/2}/\omega_1^{1/2}) = 0.5\), the current density was not halved. In fact, the current density only decreased by about 6%, and this may be why no change in dissolution rate was observed.

A similar experiment was carried out, under the same conditions, and this time the rotation speed was reduced, from 1550 r.p.m. after approximately one hour, to 100 r.p.m. for about 30 minutes and finally, increased to 1050 r.p.m. The results are shown in figures 6.22 and 6.23, which show the \(W\) versus \(t\), and \(i\) versus \(t\) plots, respectively. Again, there is an obvious correlation between the rotation speed and the current density; both rising and falling together. As in previous experiments, the current was not constant and, therefore, the extrapolated current density at \(t = 3500s\) was determined for rotation speeds of 1550 and 100 r.p.m. The ratio of the higher to the lower current density was 1.5. Examination of the \(W\) versus \(t\) plots showed not only that, once again, the dissolution rate appeared constant for constant rotation speed, but that the dissolution rate had decreased when the rotation speed was lowered to 100 r.p.m. The slopes \((dW/dt)\) for 1550 and 100 r.p.m. were measured as \(4.9 \times 10^{-6} g s^{-1} cm^{-2}\) and \(3.7 \times 10^{-6} g s^{-1} cm^{-2}\) respectively. The ratio of these two dissolution rates is 1.3, which is in reasonable agreement with the ratio of current densities.

Figures 6.24(a) and (b) show the variation in \(W\), and \(i\), with \(t\) for another type-B oxide, at \(E = -35mV\). The difference in magnitude of the current and dissolved iron values compared to earlier results is attributed to the change in the electrode
Fig. 6.22. Effect of rotation speed on dissolution of oxide-B.

\( (E = -115 \text{mV}) \)
Fig. 6.23. Effect of rotation speed on dissolution of oxide-B. 
(E = -115 mV)

\[ i/(mA \text{cm}^2) \]

1550 r.p.m. 100 r.p.m. 1050 r.p.m.
Fig. 6.24 a) Dissolution of a type-B oxide at $E = -35\text{mV}$ and b) corresponding $i-t$ curve.
material. The response of the oxide to a potential step was similar to that from other oxides, i.e. a non-linear $W$ versus $t$ plot, and a decaying current. During the course of the experiment, the rotation speed dependence of the current was checked at various time intervals. The current density was found to depend on the rotation speed throughout the time scale of the experiment. Plots of $\frac{1}{i}$ versus $\frac{1}{\omega^4}$ were made and the changing values of the slope and intercept of the $\frac{1}{i} v \frac{1}{\omega^4}$ plot with time are shown in figure 6.25, and the values of the slope and intercept are tabulated in Table 6.1. The value of the slope appeared to decrease with time, while the intercept value increased.

Figure 6.26 also shows the $\frac{1}{i}$ versus $\frac{1}{\omega^4}$ relationship for type B oxides, and the dependence of the current density on the pH of the solution. Another interesting feature of this figure is that the linearity of the plots decreases with decreasing $H^+$. Hence, while a plot of $\frac{1}{i}$ versus $\frac{1}{\omega^4}$ at pH 1.25 was a reasonably straight line at pH 2.0 a definite curve was obtained. Also, the slope of the lines decreases with increasing $H^+$ in the same way as was observed for the dissolution of magnetite. These last two points, the curvature and slope of the points are obviously inter-related.

To determine whether the curvature of the $W$ versus $t$ plots, and the decay of the current density with time, was a result of changes in the solution composition, e.g. perhaps a build up of iron species in solution, or a diminution of $H^+$ resulting in increased pH, causing inhibition of dissolution, a normal dissolution experiment was carried out and the solution replaced during the
Fig. 6.25. Rotation speed dependence of current at various times, $t$, during dissolution of oxide-B. (see Fig. 6.24(b).)

$1/(I/A \cdot cm^2)$

$t$ increasing

$1/(\omega^{1/2}/(s^{1/2})$
<table>
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<tr>
<th>Slope / (Å/cm² s⁻¹)</th>
<th>Intercept / (Å² cm⁻¹)</th>
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<td>892</td>
<td>520</td>
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<tr>
<td>808</td>
<td>590</td>
</tr>
<tr>
<td>782</td>
<td>646 increasing time</td>
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<td>706</td>
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<tr>
<td>688</td>
<td>794</td>
</tr>
<tr>
<td>670</td>
<td>834</td>
</tr>
</tbody>
</table>
Fig. 6.26. Effect of pH on rotation speed dependence of current.

$\frac{1}{i}$ (A cm$^{-2}$)

pH 2.0

pH 1.5

pH 1.25

$\frac{1}{i}$ (A cm$^{-2}$)

$\frac{1}{\omega^2}$ (s$^{-1}$)

$\frac{1}{\omega^2}$ (s$^{-1}$)
experiment. This was done by dissolving the electrode for ~3hrs in pH 1.5 solution, at $E = -35\text{mV}$. Then, the potentiostat was switched off, and the electrolyte solution siphoned off and fresh pH 1.5 1.0M sodium perchlorate solution, which had been pre-heated to 72°C, quickly pumped into the electrolytic cell. The potentiostat was switched back on and the experiment continued. The results were plotted as $W$, and $i$ versus $t$, and are shown in figures 6.27(a) and (b). At the point where the solution was changed there is a very slight jump in the current density slope and this is understandable at the beginning of a potential step but not considered significant.

Overall, changing the electrolyte during the course of the dissolution experiment appeared to have no effect, which was interpreted as evidence that the non-constant nature of the dissolution rate was due to a solid-state or surface-state feature of the electrode rather than due to solution state properties.

This last experiment was not entirely satisfactory due to the need to switch off the potentiostat in the middle of the experiment and also because of the exposure of the electrode surface to the air, albeit for a short time, after removing the initial solution. Therefore, additional experiments were made in order to see whether or not it was the build up of ferrous complexes in solution which was retarding dissolution. This was attempted by carrying out dissolution in the presence, from the very beginning, of almost 200 ppm of $\text{Fe}^{2+}$ introduced into the electrolyte solution by dissolving ferrous ammonium sulphate into the 1.0M sodium perchlorate solution. Dissolution of the iron oxide into such an
Fig. 6.27a. Effect of renewing solution during dissolution of oxide-B and b) corresponding i-t curve.
Iron bearing solution appeared to proceed as in the absence of added Fe\(^{2+}\). Therefore, either there was insufficient Fe\(^{2+}\) added, although attempts with higher concentrations resulted in precipitation of ferrous hydroxide, or Fe\(^{2+}\) in solution did not control the dissolution rate.

**6.4. Dissolution of B-type oxides in the presence of EDTA**

Due to a shortage of both time and material, it was not possible to examine properly the effect of added EDTA on the dissolution of the haematite-like oxide (type B). Therefore, dissolution at only a few potentials was examined. The dissolution experiments were carried out as before but with 0.25\% Na\(_4\)EDTA dissolved in the electrolyte solution. The controlled potential dissolution experiments which were carried out showed similarities with dissolution in EDTA-free medium. As figure 6.28 shows, plots of \(W\) versus \(t\) were shallow curves for several potentials. At \(E = +315 \text{ and } +190\text{mV}\), dissolution was very slow (\(\sim 0.4 \times 10^{-6} \text{ g cm}^{-2} \text{s}^{-1}\)) occurring at rates comparable with dissolution in EDTA-free solution for similar potentials. Dissolution of more cathodic potentials, negative of the cathodic peak, were much higher (e.g. \(\sim 4 \times 10^{-6} \text{ g cm}^{-2} \text{s}^{-1}\) at \(E = -215\text{mV}\)).

The behaviour of the current in response to a potential step (figure 6.29) was not quite as regular as in the case of dissolution in the absence of EDTA. At the more anodic potentials the current appeared almost constant throughout the experiment. At \(E = -15\text{mV}\), the current increased steeply before showing a more gentle decline. A different response was observed at \(E = -215\text{mV}\) where the current density showed a very sharp increase in the early
Fig. 6.28. Dissolution of oxide-B in EDTA-containing soln.
Fig. 6.29. Current-time curves for dissolution when EDTA present.
stages of dissolution, before decaying in the usual manner. When dissolution was carried out at \( E = -360 \text{mV} \), the current density increased rapidly for the first 1000s, then settled down to a more gradual increase.

For dissolution occurring at anodic potentials (\( E = +315, +190 \text{mV} \)) the associated R values were low (0.1 and 0.3 respectively), which suggested that dissolution by a chemical process was occurring at a greater rate than was electrochemical dissolution. Chemical dissolution could be described, in a simplified manner as,

\[
\text{Fe}_2\text{O}_3 + 6\text{H}^+ + 2\text{Fe}^{3+} + 3\text{H}_2\text{O} \quad (6.4.1)
\]

or

\[
\text{Fe}_2\text{O}_3 + 6\text{H}^+ + 2\text{Y}^{4-} + 2\text{Fe}^{3+} + 3\text{H}_2\text{O} \quad (6.4.2)
\]

where \( \text{Y}^{4-} \) represents the EDTA complex.

As the potential was shifted cathodically, the value of R increased to 1.0 indicating that it was electrochemical reduction which had become the factor controlling the dissolution rate.

The current density during dissolution was found, as in the case of EDTA-free dissolution, to be dependent on the rotation speed of the electrode. Also, this current density/rotation speed dependence was influenced by \( \text{H}^+ \). These points are illustrated in figure 6.30, which is a plot of \( \frac{1}{i} \) versus \( \frac{1}{\omega^2} \), for a haematite-like electrode at \( E = -360 \text{mV} \). A linear relationship between \( \frac{1}{i} \) and \( \frac{1}{\omega^2} \) is depicted (slope 1). Also, when acid was added to the solution the current density increased and the dependence of the current
Fig. 6.30. Effect of $[H^+]$ on rotation speed dependence
density on the rotation speed decreased dramatically. Similar experiments, involving the addition of Fe⁺ containing solutions, appeared to indicate that the dissolution rate was unaffected by the levels of Fe²⁺ present during dissolution.

Thus, although the presence of EDTA (0.25%) in the electrolyte appeared to enhance the dissolution rate at anodic potentials, this was outweighed by the effect of the applied potential at more cathodic values. When subjected to a cathodic potential dissolution occurred at the rate at which reduction of Fe³⁺ to Fe²⁺ occurred, and the rate controlling factor was mass transport of H⁺ to the electrode surface.
CHAPTER 7
FINAL DISCUSSIONS AND CONCLUSIONS

7.1. Discussion

Magnetite is a non-stoichiometric compound and in order to obtain reproducible, comparable results for different electrodes it is essential to be able to produce electrode material of constant composition. The absence of such a standard material is the reason for the difficulties encountered in trying to compare results from one experiment with the results of another. An obvious difference was the slight variations in current/potential characteristic between electrodes prepared by the two, very different methods A and B. However, even among electrodes prepared by the same method it was found that the rest potential varied from experiment to experiment. Such variations in rest potential are common as is evident by comparing the results of other workers (see section 3.2).

From both polarization curves and linear sweep scans it appeared that at potentials more anodic than $E = +1200\text{mV}$ an oxidation reaction, possibly oxygen evolution occurred,

$$4OH^- + 2H_2O + 4e^- + O_2$$

(7.11)

In the opposite extreme, hydrogen evolution occurred at potentials around $E = -1200\text{mV}$, while another reaction which appeared at $E = -1000\text{mV}$ was observed over a wide range of pH. This very facile reaction, which appeared as a sudden, cathodic jump on the potential sweep scan was unidentified, but may be due to reduction of magnetite to metallic iron,

$$Fe_3O_4 + 8H^+ + 8e^- \rightarrow 3Fe + 4H_2O$$

(7.12)
Another reaction occurring at $E \approx 0.0\text{v}$ which was of interest because of the accompanying enhanced dissolution, was detected only in acid solution ($\text{pH} < 3.0$) was, also, not specified completely but was considered to be associated with reduction of ferric ion to ferrous ion in the solid followed by dissolution of the crystal lattice, which may be described as,

$$
\text{Fe}^{3+}_{(c)} + \text{e} \rightarrow \text{Fe}^{2+}_{(c)} \quad (7.13)
$$

$$
\text{Fe}^{2+}_{(c)} \rightarrow \text{Fe}^{2+}_{(s)} \quad (7.14)
$$

$$
\text{Fe}^{2+}_{(s)} \rightarrow \text{Fe}^{2+}_{(b)} \quad (7.15)
$$

$$
\text{O}^{2-}_{(c)} + 2\text{H}^{+} \rightarrow \text{H}_{2}\text{O} \quad (7.16)
$$

Overall reaction

$$
\text{Fe}_3\text{O}_4 + 8\text{H}^{+} + 2\text{e} \rightarrow 3\text{Fe}^{2+} + 4\text{H}_2\text{O} \quad (7.17)
$$

where the subscripts $c$, $s$ and $b$ refer to the crystal, the electrode surface and the solution bulk, respectively.

This cathodic reaction has been reported by other workers, Haruyama and Masamura$^{(45)}$, for example, but its observed behaviour was different from what was expected. Contrary to other observations$^{(41,45)}$, the magnitude of the current density for this reaction was found to be both rotation speed and potential sweep rate dependent. These findings suggested that the reaction was under solution-state control, rather than solid-state control$^{(43)}$. Most other work on magnetite had been carried out at room temperature and linear sweep...
voltammetry showed that the rotation speed dependence of the current was only apparent at higher temperatures ($T > 40^\circ C$), which explains the disagreement in findings. At elevated temperatures it is possible that the dissolution process changes, but it may just be that increasing the temperature accelerates reaction 7.17 to such an extent that the process becomes mass-transport controlled.

Examination of the cathodic peak obtained at the higher temperatures showed that, with increasing temperature, there was an increasingly wide potential region within which $(\frac{1}{i})$ was linearly dependent on $(-\frac{1}{\omega^2})$. Assuming that the cathodic reaction could be treated as a simple, irreversible one-electron process, the equation

$$\frac{1}{i} = \frac{1}{A F k_f C} + \frac{1}{0.62 F A C D^{\frac{4}{3}} \nu^{-1/6} \omega^{\frac{1}{2}}}$$

(7.18)

(see equation 5.2.1) was used to obtain a value for $C$, which might give some indication of the identity of the diffusing species. Using rough values for $A, D$ and $\nu$ a value of $C \approx 0.25$ mole l$^{-1}$ was obtained, suggesting that transport of $H^+$ in solution was the dissolution controlling step. Values of $k_f$ at various potentials, were found by similar means, but attempts to show a linear relationship between $\log k_f$ and $E$ foundered, possibly due to the semi-conducting nature of the magnetite.

The potential step experiments provided very little information and only confirmed that diffusion in solution played a role in the dissolution process and supported the belief that $H^+$ was the diffusing species.
From the dissolution experiments it was found that the type-A oxides were dissolving as

$$\text{Fe}_3\text{O}_4 + 8\text{H}^+ + 2e \rightarrow 3\text{Fe}^{2+} + 4\text{H}_2\text{O} \quad (7.19)$$

while type-B oxides dissolved as

$$\text{Fe}_2\text{O}_3 + 6\text{H}^+ + 2e \rightarrow 2\text{Fe}^{2+} + 3\text{H}_2\text{O} \quad (7.1.10)$$

Equation (7.19) is in agreement with the findings of Haruyama and Masamura(45) who reported dissolution occurring by this process, in acid solutions, with 100% current efficiency over a wide range of potential. However it was not possible to explain the changes in magnitude of dissolution with changing electrode potential. Certainly, it was not possible to ascribe a simple log (dissolution current)/electrode potential linear relationship to the process, as postulated by Engell(53), and Vermilyea(54). Since the current appeared to be directly attributable to the dissolution process, it was obvious that the dissolution rate would vary, in a complex manner, over a wide range of potential.

The non-linearity of the $W$ versus time plots, i.e. a varying dissolution rate is very difficult to explain. One early explanation based upon the applicability of the Avrami-type expression,

$$W' = W_0 (1 - e^{-\beta t}) \quad (7.1.11)$$

was that, since the electrodes were known to consist of incompletely reduced haematite, perhaps the magnetite dissolved preferentially leaving behind islands of insoluble oxide. Then, as dissolution
proceeded these islands might grow causing a decrease in the area of magnetite remaining and, hence, a decrease in both dissolution rate and current.

A later explanation arose from the observation that there was localized corrosion of the electrode surface. The perimeter of magnetite dissolved preferentially so that a continually receding electrode was presented to the solution. This would mean that the boundary conditions applying to the electrode were continually changing throughout the dissolution experiment and this was considered a possible cause for the decay in dissolution rate. However, it was found that dissolution of B-type oxides, for which there did not appear to be any evidence of localized corrosion also exhibited a decaying dissolution rate. Therefore, although the receding electrode surface model would affect the dissolution rate it is not considered the main cause of the decay.

It is possible that the dissolution rate is controlled by changes in solution composition. As the oxide, Fe$_3$O$_4$ or Fe$_2$O$_3$ dissolves there is addition of Fe$^{2+}$ to the solution and removal of H$^+$ from the solution. Thus, during the dissolution period there will be an increase in pH, which, as was found influences the dissolution rate. It is possible to consider the dissolution of magnetite, for example,

$$\ce{Fe_3O_4 + 8H^+ + 2e^- \rightarrow \frac{k_f}{k_b} \ce{3Fe^{2+} + 4H_2O}}$$

(7.1.12)
as having a dissolution rate, $R_d$, given by
\[ R_d = \frac{d[Fe^{2+}]}{dt} = k_f[H^+] - k_b[Fe^{2+}] \] (7.1.13)

Therefore, as \( H^+ \) decreases, and \( Fe^{2+} \) increases with time, the rate will decrease.

Another solid state feature which would influence dissolution is the particle size. The electrodes used, in both cases, were poly crystalline materials and it is possible that, as dissolution progressed, the surface area of the oxide grains on the electrode surface decreased and so dissolution decreased.

Changes in \( R \), with increasingly negative potential \( R \) increased, were explained as due either to the occurrence of simultaneous cathodic reactions or as a result of a change in the dissolution process. Some support for the first of these models was given by Sukhotin(39) who reported hydrogen evolution occurring at potentials as low as \( E = -620 \text{mV} \). However, it was not possible to define the reactions occurring at these potentials.

As has been stated previously, the apparently anomalous rotation speed dependence of the cathodic current observed in this study may be explained by the higher temperatures at which the dissolution experiments were carried out. The deviations of the \( \frac{1}{I} \) versus \( \frac{1}{\omega^2} \) plots, at high rotation speeds which lead to a slight curvature of the plots may be due to surface roughness. At low rotation speeds the diffusion layer thickness is large and the effective area of the electrode is its projected, or nominal area. However, as the rotation speed is increased, the diffusion layer thickness decreases and the effective electrode area is the true area which is larger than the nominal value. Therefore, the current
increases and, consequently, the reciprocal current decreases which explains the downward curve of the $\left(\frac{1}{I}\right)$ versus $\left(-\frac{1}{\omega^2}\right)$ plot.

Since it was not possible to explain the reason for the current decay with time, the changing position of the $\left(\frac{1}{I}\right)$ versus $\left(-\frac{1}{\omega^2}\right)$ plots during dissolution cannot be explained either. If the changes in current, $I$, were due to changes in the electrode surface area, as modeled above, and if equation (7.1.8) is valid the ratio slope, $S$, to intercept, $Y$, would be a constant. However, examination of the figures in Table 6.1 show this to be untrue and to indicate that, although the cathodic reaction can be approximated as a simple, irreversible electron transfer process under complete mass transfer control, there are other factors involved.

Dissolution of haematite, or at least haematite which was adulterated with magnetite and so was conducting, occurred in a similar manner to dissolution of the magnetite blocks. At first glance, the dissolution rate of both oxides seems comparable. However, the magnetite blocks underwent localized corrosion. Therefore, only a fraction of the nominal surface was magnetite and, hence, the dissolution and electronic currents were much greater than they seem.
7.2. Conclusions

(i) A necessary, prerequisite of a quantitative study of the dissolution of magnetite is a supply of electrode material of constant composition.

(ii) Dissolution of magnetite is especially sensitive to pH. Therefore, tight control of the pH of the electrolyte, possibly using a pH-stat arrangement, is highly recommended.

(iii) Dissolution increases with increasing temperature. Hence, on the basis of empirical methods, the removal of magnetite is carried out at elevated temperature.

(iv) With increasing temperature the dissolution process becomes mass transport controlled, and the transfer of $\text{H}^+$ to the electrode surface appears to be the controlling step. Thus, agitation of the solution during cleaning is required to promote dissolution and not just to remove particulate matter from the cleaning surfaces.

(v) Insufficient information is available to say much of the effect of EDTA on dissolution. The figures available suggest, however, that when the electrode is driven negative the dissolution reaction is controlled by the rate at which $\text{Fe}^{3+}$ is reduced to $\text{Fe}^{2+}$, rather than by how fast the EDTA complexes with surface metal ions.

(vi) Obviously, further study of the magnetite is required to determine the reactions occurring throughout the potential region, and to discover the reason for the changes in dissolution mechanism, which controls reductive dissolution of magnetite. Also, a more systematic study, using a wide range of complexing agents to examine dissolution of magnetite is needed.
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