CHAPTER I

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General

The success of any scientific inquiry depends upon there-being precise and unambiguous definitions of the phenomena being studied. Evans defined corrosion as the destruction of a metal or any alloy by chemical or electrochemical reaction with its environment; mechanical destruction is referred to as erosion. In practice attack is often a mixture of erosion and corrosion, e.g., in corrosion fatigue.

Metals rarely exist in nature as pure metals. The ores are lower energy state compounds and in consequence metals inevitably tend to revert to this state. Corrosion of metals can thus never be wholly conquered but only controlled.

Although it is very difficult, if not impossible, to estimate the true cost of this control, the cost can be considered as two losses - direct and indirect in nature.

I Direct loss:

(a) Cost of metal replacement:

As a result of corrosion, metal equipment becomes useless. It is likely that attack on only 1% of the metal is sufficient in certain cases to put the equipment out of action. As a result the whole of the metal has to be replaced
and can be sold as scrap, but its value is very low as compared to its replacement. When the attack is along grain boundaries or across grains, the mass of metal actually removed may be too small to be weighed and yet the strength of the metal may be completely destroyed.

(b) **Dismantling, reassembly and maintenance charges:**

As skilled men are required for dismantling and reassembly, the cost is relatively high. The cost of maintenance can be included in direct corrosion cost. Maintenance include measures taken to combat corrosion e.g., painting, cathodic protection etc.

II **Indirect loss:**

(a) **Loss of production or efficiency:**

Loss of production is highly expensive. It is likely that when one plant has to be shut-down due to corrosion failure, other units associated with that plant have to shut-down and the loss is magnified.

(b) **Cost of contamination:**

This cost varies from industry to industry. This is particularly significant in food and pharmaceutical industries, but it is of less consequence in the heavy chemical industry.

**Corrosion costs:**

Estimates have been made of the economic cost of
corrosion. Uhlig\textsuperscript{2} made a careful survey of only the direct losses by corrosion in the United States and reported a rate in excess of $5.5$ billion annually, and that better corrosion protection could reasonably be expected to save over 900 million dollars per annum. Jelinek\textsuperscript{3} states that in the nine year interval since Uhlig's study was published, corrosion control methods have considerably improved but material and labour costs have generally risen and thus the order of magnitude of the direct costs of corrosion remains about the same. Schmitt\textsuperscript{4} states that corrosion problems cost nearly $8$ billion annually, while mining metals cost about $1$ billion annually to the United States. Gegner\textsuperscript{5} states that the cost of corrosion to the United States has been estimated by various experts to be upwards of $7.5$ billion per year of which industry's share is about $6$ billion. The direct costs due to corrosion alone are included in these estimates e.g., replacement and maintenance of corroded equipment, costs of painting, electroplating and other protective measures including application and labour costs. The indirect costs not included are such as safety hazards, product contamination, shut-down time and loss of products when equipment fails. It has been reported in a staff feature of \textit{Corrosion} (1961) that corrosion damage due to automobile exhaust systems cost American car owners over $500$ million in 1960. This loss is even more than the total
cost to the United States for the construction of the Panama Canal. Vernon\(^6\) claims that the cost of corrosion to Britain in 1953 was 600 million pounds, slightly more than the cost of the national health service that year. The cost of corrosion in India has been estimated at \(\text{Rs. } 154\) crores (\(\text{Rs. } 1540\) million)\(^8\). The annual losses due to corrosion in India have been estimated as 106 million dollars\(^9\) and the annual cost of corrosion control for India has been estimated as £ 37,500,000 per annum\(^10\).

The science of corrosion is particularly concerned with those reactions which occur at a metal surface exposed to an aggressive environment. The general ideas of the nature of matter, as well as the agnostic doctrine of thermodynamics lead us to important views of such reactions.

When a metal is immersed in an electrolyte some of the metallic atoms ionise. The energy relationships in the region of the metal surface are shown in Fig. 1.

Point 'A' refers to an atom about to ionise. Point 'B' refers to an ion about to discharge. Point 'C' refers to a state intermediate between 'A' and 'B'.\(\Delta G_1\) is the difference in free energy between atom in the metallic state, \(M\), and an atom in the intermediate state \(M^H\), \(\Delta G_1\), is the free energy which must be given to a metal atom for the following reaction to take place:-
\[ M \rightarrow M^{Z+} + Ze \quad \ldots \ldots \quad (1) \]

where 'Z' is the valency of the metal. Similarly \( \Delta G_2 \) is the free energy difference between an ion \( M^{Z+} \), and an atom in the intermediate state \( M^H \). \( \Delta G_2 \) is the free energy which must be given to an ion for the following reaction to take place:

\[ M^{Z+} + Ze \rightarrow M \quad \ldots \ldots \quad (2) \]

\( \Delta G \) represents the overall free energy change in the dissolution process.

If \( \Delta G_1 \) is > \( \Delta G_2 \) then \( \Delta G \) is +ve and the predominant process is dissolution. If \( \Delta G_1 \) is < \( \Delta G_2 \), then \( \Delta G \) is negative and the predominant process is the discharge of metal ions.

The overall free energy change is related to the electrode potential by the following expression:

\[ \Delta G = \Delta G_1 - \Delta G_2 = ZFE \quad \ldots \ldots \quad (3) \]

where \( F \) represents the number of coulombs required to dissolve one gram equivalent of the metal, and \( E \) is the electrode potential.

By Maxwell's Distribution Law, the numbers of atoms, having free energy greater than \( \Delta G_1 \) is given by:

\[ N_1 = N_A \times_{\text{Total}} e^{-\left(\frac{\Delta G_1}{RT}\right)} \quad \ldots \ldots \quad (4) \]
and the number of ions having free energy greater than $\Delta G_2$ is given by:

$$N_2 = N_1 \text{Total} \times e^{-\frac{\Delta G_2}{RT}} \quad \ldots \quad (5)$$

where $T$ is the absolute temperature and $R$ is the universal gas constant.

If all those atoms with energy greater than $\Delta G_1$ ionise and all those ions of energy greater than $\Delta G_2$ discharge then:

Ionisation Rate $= V_1 = K_1 e^{-\frac{\Delta G_1}{RT}} \quad (6)$

Discharge Rate $= V_2 = K_2 e^{-\frac{\Delta G_2}{RT}} \quad (7)$

$K_2$ is dependent on the total number of metallic ions in the solution.

When the metal is immersed in the solution, metal atoms will ionise. The greater the ionisation however, the greater the discharge rate, when the ionic concentration reaches such a level that the discharge rate becomes equal to the ionisation rate, a dynamic equilibrium is set up.

At equilibrium the metal is left with an excess of electrons and the metal is negatively charged relative to the solution. The value of this potential, the electrode potential of the metal, is a guide to the reactivity of the metal and to the way the metal will behave when immersed in
an electrolyte. The tendency for the metal to ionise is often referred to as the solution pressure and the tendency for ions to discharge as the ionic pressure.

The solution pressure is influenced by the nature of the metal, the purity and the physical state of the metal surface. The ionic pressure is dependent to a large extent on the concentration of metal ions originally in the solution, since this affects $N_1 \text{Total}$ in equation (5).

The latter influence is very large, and, in order that a proper comparison can be made, metal electrode potentials are always quoted relative to a solution which contains an original concentration of metal ions of one gram equivalent per litre.

In practice it is impossible to measure electrode potentials relative to the solution as any electrical contact with the solution means the introduction of another electrode. If however, all potentials are measured relative to a standard electrode the order of metal potentials will be the same, and the measure of this potential difference can be used as the electrode potential of the metal.

The standard used is the reversible hydrogen electrode. Hydrogen is bubbled over platinised platinum into a normal acid solution. On this electrode, provided the
platinum surface is large, the two opposing electrode reactions proceed at the same rate under thermodynamically reversible conditions, at a reproducible potential.

This electrode is too fragile and cumbersome for every-day use and various electrodes have been devised for use as substandards. The most common of these is the calomel electrode an example of which is shown in Fig. 2. This consists of a mercury electrode immersed in a saturated solution of mercurous chloride. Electrical connection is made with the metal specimen and its electrolyte by platinum wire and a solution of KCl respectively. The KCl solution virtually eliminates potentials at liquid junctions by ensuring that all the conductivity takes place by ionic transport, by potassium and chloride ions, and these have approximately equal transport numbers.

The value of the potential of the calomel electrode depends upon concentration of potassium chloride:

Potential relative to standard hydrogen electrode:

0.1 N \(0.3338 - 0.00007(t - 25)\) volts.

1.0 N \(0.280 - 0.00024(t - 25)\) volts.

Saturated \(0.2415 - 0.00076(t - 25)\) volts.

The 0.1 N potassium chloride solution electrode is very reproducible and only slightly temperature sensitive. The
saturated potassium chloride electrode is more sensitive to temperature changes but much easier to maintain.

The elements can be arranged in order of their electrode potentials. This arrangement is referred to as the electrochemical series which is shown in the Table I. Very reactive or basic metals are at the bottom of the series and are referred to as electronegative metals. Unreactive or noble metals are at the other end of the series and are referred to as electropositive.

Electronegative metals displace less electronegative metals from solution. Thus, if a strip of iron is immersed in a solution of copper sulphate, iron atoms dissolve and copper ions plate out on the surface. Similarly, if electronegative metals are placed in an acid solution hydrogen is discharged on the metal surface.

Two metals placed in a solution and joined together electrically, make up an electrolytic cell. Each metal and its neighbouring electrolyte is referred to as a half cell. Thus, the standard electrode potential is the potential difference between the standard metal electrolyte half cell and the normal hydrogen half cell.

If two metals are immersed in solutions of their salts and electrical connection made, as shown in Fig. 3,
<table>
<thead>
<tr>
<th>Equilibrium</th>
<th>Volt (normal hydrogen scale)</th>
<th>Correction for ten-fold change of activity (effective concentration), volts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au = Au^{+++} + 3e</td>
<td>+ 1.50</td>
<td>0.0197</td>
</tr>
<tr>
<td>Ag = Ag^+ + e</td>
<td>+ 0.7991</td>
<td>0.0591</td>
</tr>
<tr>
<td>Hg = (Hg_2)^{++} + 2e</td>
<td>+ 0.789</td>
<td>0.0295</td>
</tr>
<tr>
<td>Cu = Cu^{++} + 2e</td>
<td>+ 0.337</td>
<td>0.0295</td>
</tr>
<tr>
<td>Cu = Cu^+ + e (unstable)</td>
<td>+ 0.522</td>
<td>0.05911</td>
</tr>
<tr>
<td>H_2 = 2H^+ + 2e</td>
<td>0.000</td>
<td>0.0591</td>
</tr>
<tr>
<td>(arbitrary zero)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb = Pb^{++} + 2e</td>
<td>- 0.126</td>
<td>0.0295</td>
</tr>
<tr>
<td>Sn = Sn^{++} + 2e</td>
<td>- 0.136</td>
<td>0.0295</td>
</tr>
<tr>
<td>Ni = Ni^{++} + 2e</td>
<td>- 0.250</td>
<td>0.0295</td>
</tr>
<tr>
<td>Cd = Cd^{++} + 2e</td>
<td>- 0.403</td>
<td>0.0295</td>
</tr>
<tr>
<td>Fe = Fe^{++} + 2e</td>
<td>- 0.440</td>
<td>0.0295</td>
</tr>
<tr>
<td>Zn = Zn^{++} + 2e</td>
<td>- 0.763</td>
<td>0.0295</td>
</tr>
<tr>
<td>Al = Al^{+++} + 3e</td>
<td>- 1.66</td>
<td>-</td>
</tr>
<tr>
<td>Mg = Mg^{++} + 2e</td>
<td>- 2.37</td>
<td>-</td>
</tr>
</tbody>
</table>
the more base metal dissolves and the ions of the less base metal discharge. The electrode which dissolves, is referred to as the anode, and the electrode at which the metal ions discharge is referred to as the cathode. Positively charged ions are attracted to the cathode and are referred to as cations, similarly negatively charged ions are referred to as anions. It has been shown above that the potential difference between the electrode and electrolyte depends upon the concentration of its own ions in solutions.

If a metal with valency $Z$ is immersed in an electrolyte and the electrode potential is $E$, when this electrode is connected to a more positive electrode, metal atoms ionise and one gram ion of the metal dissolves upon the passage of $ZF$ coulombs of electricity. If the volume of electrolyte is sufficiently great for the ionic pressure to remain constant then, (provided the metal dissolution takes place in a thermodynamically reversible manner,) the potential also remains constant.

If the electrolyte is diluted so that the ionic pressure is reduced from $P$ to $(P - dp)$ then the same process will take place but at an electrode potential $(E - dE)$.

The electrical energy expanded in the first case is $EZF$ volt coulombs and in the second case $(E - dE)ZF$ volt coulombs.
According to the first law of thermodynamics the difference in electrical work must be equal to the work involved in transferring one gram ion from an ionic pressure of $P$ to one of $(P - dp)$.

Ionic pressures can be related to the volume of solution in the same way as gas pressure can be related to gas volumes.

The gas law relationship

$$PV = RT \quad ......... \ (8)$$

has to be modified in the case of ionic behaviour to

$$P = RTa_+ \quad ......... \ (9)$$

where $a_+$ is the activity of the ions. The activity is an idealised ionic concentration and is related to the true ionic concentration by the expression

$$a_+ = Yc \quad ......... \ (10)$$

where 'c' is the true concentration and $Y$ - the activity coefficient. Thus

$$BEF - (E - dE)ZF = VdP \quad ......... \ (11)$$

or

$$ZFdE = VdP \quad ......... \ (12)$$

$$= \frac{RTdP}{P} \quad ......... \ (13)$$

On integrating

$$ZF = RT \ln P + K \quad ......... \ (14)$$

$E = 0$ when the solution pressure is equal to the ionic pressure
\[ K = - RT \ln Ps \quad \ldots \ldots \ldots (15) \]
\[ ZEF = RT \ln P/Ps \quad \ldots \ldots \ldots (16) \]
or
\[ E = \frac{RT}{2F} \ln P - \frac{RT}{2F} \ln Ps \quad \ldots \ldots \ldots (17) \]

\( \frac{RT}{2F} \ln Ps \) is constant at constant temperature
\[ P = RTa \]
\[ \ln P = K_1 + \ln a \quad \ldots \ldots \ldots (18) \]

Hence
\[ E = \frac{RT}{2F} \ln a + \text{constant} \left( E^0 \right) \quad \ldots \ldots (19) \]
at unit ionic activity:
\[ \frac{RT}{2F} \ln a = 0 \text{ and } E \text{ is equal to } E^0. \]

\( E^0 \) is thus defined as the electrode potential of the metal in a solution of unit ionic activity. \( E^0 \) is the standard electrode potential of the metal.

If two strips of the same metal are immersed in solutions of the same salt of the metal, but at different concentrations, a potential difference is set up between the two metal-electrolyte half-cells.

The potential difference between the two half cells is given by the relation,
\[ E = E_1 - E_2 \]
\[ = \frac{RT}{2F} \ln a_1 + E^0 - \frac{RT}{2F} \ln a_2 - E^0 \]
\[ = \frac{RT}{2F} \ln \frac{a_1}{a_2} \quad \ldots \ldots \ldots (20) \]
This potential difference is referred to as the potential difference produced by a concentration cell.

For any reversible process

\[ 1A + mB + nC \rightarrow rX + sY + tZ \]

The free energy change is given by

\[-\Delta G = RT \ln K - RT \ln \frac{a_r}{a_A} \frac{a_s}{a_B} \frac{a_t}{a_C} \ldots \ldots (21)\]

where \( K \) is the equilibrium constant.

The change in free energy is equal to the electrical work done so that:

\[-\Delta G = ZFE \text{ Joules.}\]

The negative sign signifies that the free energy of the system is reduced by transfer of energy to electrical work:

\[ ZFE = RT \ln K - RT \ln \frac{a_r}{a_A} \frac{a_s}{a_B} \frac{a_t}{a_C} \ldots \ldots (22) \]

When solutions of unit ionic activities are considered:

\[ \frac{RT}{ZFE} \ln \frac{a_r}{a_A} \frac{a_s}{a_B} \frac{a_t}{a_C} = 0 \]

and
\[ E^\circ = \frac{RT}{ZF} \ln K \quad \cdots \cdots \cdots \tag{23} \]

\[ = \frac{\Delta G^\circ}{ZF} \]

Where \( \Delta G^\circ \) is the change in free energy in solutions of unit activity.

The sign and value of \( \Delta G^\circ \) has a significant effect on the tendency of the metal to corrode. In fact the absolute criteria for corrosion are \( \Delta G^1 \) and \( \Delta G^2 \) (Fig. 4), the free energy differences between the activated state and the atomic and ionic states respectively.

The variation of electrode potential with temperature can be deduced from the free energy. The free energy change in a reaction can be related to the changes in enthalpy and entropy and absolute temperature by the expression:

\[ \Delta G = \Delta H - T \Delta S \quad \cdots \cdots \cdots \tag{24} \]

Thus

\[ ZFE^\circ = \Delta H^\circ - T \Delta S^\circ \quad \cdots \cdots \cdots \tag{25} \]

or

\[ E^\circ = \frac{\Delta H^\circ}{ZF} - \frac{T \Delta S^\circ}{ZF} \quad \cdots \cdots \cdots \tag{26} \]

Both \( \Delta H^\circ \) and \( \Delta S^\circ \) can be calculated from specific heat data.

The foregoing discussion only applies to electrodes in a state of thermodynamic reversibility. This state requires
that the processes take place infinitely slowly. In corrosion practice electrode process takes place at only too swift a rate.

If a constant voltage is applied across an electrolytic cell, the current falls slowly from its initial value. The cell is said to be polarized. The current flowing is no longer related to the applied voltage by the expression:

$$I = \frac{V}{R} \quad \ldots \ldots \quad (27)$$

where $V$ is the applied voltage, $R$ is the resistance of the cell, but by the modified expression:

$$I' = \frac{V - V'}{R} \quad \ldots \ldots \quad (28)$$

$V'$ is known as the "back e.m.f."

Alternatively if a large voltage is applied across the cell and a large resistance, $R''$ placed in series with it, the current passing will remain effectively constant:

$$I'' = \frac{V''}{R'' + R} \quad \ldots \ldots \quad (29)$$

since $V'$ is small compared with $V''$.

If the potentials of each electrode are measured, they will be found to change as current is passed. The change in potential of each electrode is referred to as the over potential of the electrode. The potential changes in such a direction as to maintain the current.
In the reversible situation two reactions take place at the anode. Metal atoms ionise and metal ions discharge. As explained before the rates at which these two reactions take place are the same at equilibrium and dependent on the heights of the energy barriers between the atomic state and an activated state on one hand and the activated state and the ionic state on the other-hand.

If, as in the case of metallic dissolution, the metal atoms ionise faster than the ions discharge, the potential changes by an amount \( \mu \), the over potential. The over potential can maintain the current either by making it easier for metal atoms to ionise, or more difficult for metal ions to discharge. These two effects correspond to a decrease in the free energy of activation for the dissolution process, and an increase in the free energy of activation for the discharge process.

Under reversible conditions:

\[
V_1 = K_1 e^{\frac{\Delta G_1}{RT}} = V_2 = K_2 e^{-\frac{\Delta G_2}{RT}} \quad \cdots (30)
\]

If the fraction of the over potential making dissolution easier is then,

\[
V_1 = K_1 e^{-\frac{\Delta G_1 - \alpha nF}{RT}} V_1 e^{\frac{\alpha nF}{RT}} \quad \cdots (31)
\]

\[
-\frac{\Delta G_2 + (1 - \alpha) nF}{RT}
\]
\( V_2' = K_2 e \)
\[
\begin{align*}
&= V_2 e^{-(1 - \alpha) nF} \\
&= V_2 e^{-(1 - \alpha) nF} \\
&= V_2 e^{-(1 - \alpha) nF}RT
\end{align*}
\]
\[
(1 - \alpha) nFRT
\]
\]
\[
\begin{align*}
i_1 &= i_o e^{(\alpha nF/RT)} \\
&= i_o e^{-(1 - \alpha) nF}RT
\end{align*}
\]
\[
\begin{align*}
i_2 &= i_o e \\
&= i_o e^{-(1 + \alpha) nF}RT
\end{align*}
\]
\[
\begin{align*}
i &= i_1 - i_2 \\
&= i_o e^{(\alpha nF/RT)} - i_o e^{-(1 - \alpha) nF}RT
\end{align*}
\]

where 'i' is measured in amp/cm².

The same reasoning applies to irreversible cathodic processes. Equation (35), can be simplified for two special cases :-

**Special Case - I**

The irreversibility of the electrode process is small, overpotential is less than 0.02 volts. The expression can be expanded approximately, \( e^x = 1 + x \), so that
\[
i_a = i_o \frac{nF}{RT}
\]
\[
i_c = i_o \frac{nF}{RT}
\]
Thus the anodic and cathodic currents are linearly related to over-potential.

**Special Case - II**

If the over-potential is greater than 0.05 volts, the rate of the reaction opposed by the over-potential is negligible. Therefore, the second term in equation (5), can be ignored and

\[
 n = \frac{2.303 RT}{F} \log i_o + \frac{2.303 RT}{F} \log i_c
\]

or

\[
 n = \frac{2.303 RT}{F} \log i_o + \frac{2.303 RT}{F} \log i_a = a + b \log i,
\]

where \( a \) and \( b \) are characteristic of each electrode process.

The effect of the passage of current on the potential of an electrode can best be explained from a kinetic viewpoint. This is illustrated by the consideration of a typical cathodic reaction.

When a hydrogen ion is discharged at a cathodic electrode, the discharge process takes place by a number of distinct reactions, some possible examples of which are enumerated below :

1. The hydrogen ion, existing in fact as a hydronium ion, diffuses as to the metal surface
H$_3$O$^+$ $\rightarrow$ Cathode

(2) The hydronium ion is adsorbed at a cathodic point on the metal surface

H$_3$O$^+$ $\rightarrow$ M - H + H$_2$O

(3) As electron is transferred from the metal to the adsorbed hydrogen ion

(4) The adsorbed hydrogen atom, so formed, combines with another hydrogen atom on (or near to) the metal surface, forming a hydrogen molecule

(5) The hydrogen molecule diffuses away from the surface

The rate of any of these reactions is determined by the rate of the preceding reaction. Thus the rate of diffusion of ions to the metal surface, determines the maximum number of ions which can be adsorbed onto the surface. Similarly, the rate of transference of electrons to ions adsorbed on the metal surface is clearly dependent on the rate of adsorption of the ions.

It any reaction in the discharge process is slower than the previous reaction, then it means that the rate of the first reaction is decreased. For example, if the rate of adsorption at the electrode surface is slower than the rate of diffusion surface, then there is a build-up of ions at the surface.
The rate of diffusion is proportional to the ionic concentration gradient in the neighbourhood of the electrode.

\[
\text{Rate of diffusion} = \frac{D_L}{X} \cdot \frac{C_X - C_S}{X} \quad \text{(36)}
\]

where \( C_X \) - Ionic concentration at a distance, 
\( X \) from the metal surface
\( C_S \) - Ionic concentration at the metal surface
\( D_L \) - Diffusivity, a constant for a given ion and electrolyte, the value of which depends on the size of the ion and the temperature and viscosity of the electrolyte

Thus, if the rate of adsorption is slow, \( C_S \) will increase and the rate of diffusion decrease until the rate of diffusion is equal to the rate of adsorption.

Similar reasoning applies to the other reactions in the discharge process and it follows that the speed of the whole process is controlled by the speed of the slowest reaction. Accordingly the slowest reaction in the electrode process is referred to as the "controlling reaction." If the diffusion of ions to and from the surface is the slowest reaction, the process is said to be "diffusion controlled." If the slowest reaction is the adsorption or actual ionic discharge, then the process is said to be under "activation
control." The same reasoning applies to anodic processes. The value of 'b' in Tafel equation is dependent on the nature of controlling reaction.

Whichever reaction controls the cathodic process, the effect is to reduce the ability of the cathode to donate electrons to the cations, and hence to accept electrons from the anode. This means that the cathode becomes less cathodic and the cathode potential becomes less electropositive. Similarly, the effect on the anode is to make anode potential less electronegative.

The potential of an electrode thus varies from the reversible value if the electrode processes take place at an appreciable rate. The degree to which the potential is affected by the passage of current is dependant on the state of the electrode surface, the temperature and the electrolyte concentration. If the potential-current relationships of the metal are plotted, the resulting curve can give much information about the electrode processes.

If two dissimilar metals, e.g. iron and copper, are immersed in a solution (Fig. 6), the current passing is dependant upon the resistance of the circuit:

\[ E_C - E_A = I_R_E - I_R_M \quad \ldots \quad (37) \]

where

- \( E_C \) - Effective or polarised, cathode potential.
- \( E_A \) - Effective or polarised, anode potential.
I - Galvanic current passing.
\( R_E \) - Electrolyte resistance.
\( R_M \) - Metal connection resistance.

\( E_C \) and \( E_A \) can be thought as functions of \( E_C^0 \) and \( E_A^0 \), the equilibrium or open circuit electrode potentials of iron and copper:

\[
E_C = E_C^0 - \frac{I}{A_C} \quad \ldots \ldots \quad (38)
\]
\[
E_A = E_A^0 - \frac{I}{A_A} \quad \ldots \ldots \quad (39)
\]

where \( A_C \) is area of cathode and \( A_A \) is area of anode, and \( E_C \) and \( E_A \) are linear functions at low current densities and logarithmic functions at high current densities. The exact values of the open circuit potentials of both the iron and copper depend on the state of the metal surface, and the concentration of metal ions originally in the electrolyte, but the copper will assume a more electropositive potential than the iron. The open circuit situation is equivalent to an infinite resistance in the circuit.

If the external resistance is decreased, the current increases, the potential of the cathode becomes less electropositive and that of the anode more electropositive until at an infinitely low resistance, the current reaches a maximum, the potential of the iron being then only infinitesimally more electronegative than that of the copper.

The degree of polarisation is not necessarily the
same on both electrodes. Fig. 6 represents a galvanic cell where the cathode is easily polarisable but the anode is not. An increase in current thus affects the cathode but not the anode. This cell is said to be in a state of cathodic control.

If the anode polarises but the cathode does not, the potential-current relationships are as shown in Fig. 7. The cell is then said to be under anodic control.

If both electrodes polarise, the cell is under mixed control as shown in Fig. 8. If neither electrode polarises, the corrosion rate is controlled solely by the resistance of the circuit. The potential difference between the electrodes and hence the resistance of any galvanic cell at a current, 'I' can be obtained from the potential-current curve. The potential difference between the electrodes is represented by \( A - B \) (Fig. 9).

Metal surfaces are essentially heterogeneous in character. The existence of separate anode and cathode sites on metal surfaces was shown by Hoar\(^{12}\). The potentials, detected with a tubulus, refer to points M, N, O, P, Q and R in Fig. 10. The corroding potential of a metal is the resultant potential of a large number of short circuited galvanic couples.

If an electric current is forced through a cell,
the cathode and anode polarisation are not represented by the lines. AB and CB but by the continuations OC' and OA' and the curve C'B OBA' as shown in Fig. 11. This curve is more commonly shown in Fig. 12 or 13. Point 0 represents the zero current or resting potential.

If a strip of metal is immersed in an electrolyte and the potential changed from X to Y, the shape of the resultant curve is influenced by the nature of the electrode process in much the same way as AC and BC are affected in Fig. 8. This type of curve is referred to as a potentiostatic polarisation curve.

It will be seen that at a low current densities the over potential varies linearly with current density. At higher current densities the over potential is proportional to the logarithm of the current densities. This is in accordance with the theory outlined before.

**Corrosion in aqueous solutions:**

Owing to inhomogeneity in the surface, a metal immersed in an electrolyte has some areas acting as anodes and others as cathodes. In corrosion the anode action is the dissolution of the metal. The cathode reaction depends on the acidity of the electrolyte. A solution of high acidity has a large hydrogen ion content. The ionic pressure of hydrogen is thus high ($N_{Total}H$ in equation (6) is large), thus hydrogen can
discharge. If the solution has a low hydrogen ion content corrosion takes place by oxygen absorption.

Thus if an iron/copper couple is immersed in neutral deaerated sodium chloride solution, virtually no corrosion take place, as the predominant positive sodium ion cannot discharge at the cathode. If the solution is now aerated, an alternative cathodic reaction can take place and corrosion of the iron proceeds.

**Anode reaction:**

\[ \text{Fe} \rightarrow \text{Fe}^{++} + 2e \quad \ldots \ldots (40) \]

**Cathode reaction:**

\[ 2\text{H}_2\text{O} + \text{O}_2 + 4e \rightarrow 4\text{(OH)}^- \ldots \ldots (41) \]

If instead of aerating the solution, hydrochloric acid is added, the cathode reaction is the discharge of hydrogen:

\[ 2\text{H}^+ + 2e \rightarrow \text{H}_2 \quad \ldots \ldots (42) \]

The corrosion of a single metal can be increased by activating the electrode sites on the metal surface. Thus if a drop of water is placed on a strip of iron, the iron nearest to the outside of the drop becomes cathodic, due to the supply of oxygen, and the metal dissolves from the center of the drop. Ferrous ions, so produced, migrate from the anode surface and combine with hydroxyl ions produced at the cathode, to give ferrous hydroxide. This decomposes to give
a hydrated ferric-oxide - or rust.

**Corrosion prevention**:

Consideration of the principal mechanisms of corrosion likewise suggests the means of reducing its effects and these fall into three categories:

(i) **Applied films** acting as:
   (a) shielding films
   (b) cathodic films, and
   (c) anodic films

(ii) **Electrical treatment**
    (a) cathodic protection
    (b) anodic protection

(iii) **Addition of inhibitors**

(i) **Applied films**:
   (a) **Shielding effect**:
   Most paint or enamel films come into this category. The film acts as a barrier between the metal and its environment. Clearly any applied film acts at least partially in this way.

   (b) **Cathodic metal films**:
   The base metal which is to be protected is clad with a layer of a more noble metal. Examples of this form of treatment are chromium and tin plating.
The action is thus that of a barrier film of a noble metal. So long as the barrier effect remains good, the corrosion resistance is excellent. If, however, the barrier effect is less than 100% effective, an electrochemical couple is set-up with a tiny portion of the base metal as the anode, and the whole of the noble metal as cathode. The current density is thus very large at the anode, and the metal suffers 'severe' pitting attack. The attack is not, however, restricted to the pit. In most cases, the greatest depth of penetration is of more importance than the total weight of metal dissolved. Thus, it is of scant compensation, if a pressure vessel is taken out of service, to know that the total weight of metal dissolved has been reduced by 90%, if the vessel breaks down sooner than before.

Cathodic films are thus electrochemically unsound and should only be used with care. The coat must be uniform and non-porous and the metal should not be subjected to heat or mechanical treatment likely to break the coat.

(c) Anodic films:

Anodic films, however, do not suffer from the above disadvantages. If a zinc coated sample or iron is exposed to an corroding medium, the zinc
will tend to dissolve. If there is a break in the coat, the zinc will be anode and the small section of exposed iron, the cathode. Thus the zinc will tend to dissolve rather than the iron and the pitting attack is reduced.

Clearly there is little point in coating the metal with very active metal, for example sodium, as the protective coat would dissolve very quickly leaving the metal unprotected. A balance in choosing the cladding metal must therefore be struck between the electrochemical advantages of a reactive metal and its chemical disadvantages.

The foregoing remarks refer to metal coatings. The same applies to metal based paints.

(ii) Electrical treatment:

(a) Cathodic protection:

A metal goes into solution when acting as anode and giving up electrons. If the metal is absorbing electrons from an outside source, it acts as a cathode and does not dissolve.

The potential of the metals is not the criterion of whether it will dissolve. If a piece of zinc is attached to a piece of iron the zinc will
dissolve and the iron will be protected. The potential of both the zinc and iron will be shown by point C as shown in Fig. 14.

If iron is connected to copper rather than zinc it is now the iron that dissolves. The potential B is much more noble than C. Thus in one case iron is at a noble potential and corroding, and in the other case at a base potential, but not corroding. What matters is not the potential so much as the rate and direction of flow of electrons across the metal-electrolyte interface. If electrons can be forced from the metal to the solution, this will reduce the rate of metal dissolution by making the metal act predominantly as a cathode.

This can be done in two ways:

(1) By planning a more basic metal in contact with the metal to be protected. This causes electrons to pass from more basic metal to the less basic metal as shown in Fig. 14. This is referred to as the sacrificial anode system and the anodic coatings of (i) (c) are examples of this form of protection. Pipe lines are protected in this way by
sacrificial magnesium anodes. Again a balance must be struck between providing a sufficiently large current to achieve protection and having a metal which is too easily consumed.

(2) By including the metal in a circuit and passing electrons through. Again electrons pass through the metal to the electrolyte and the metal acts as a cathode. In this case the potential-current relationships are as shown in Fig. 11 and not in Fig. 8, but the argument still holds true.

(b) **Anodic passivation:**

Some metals have very stable, insoluble corrosion products and if these products can be formed quickly on the metal, so that the film of product is impermeable to the electrolyte, then the metal is very largely protected against further corrosion. This is known as passivity. Thus iron dipped into concentrated nitric acid is rendered passive and is immune to further attack by oxidising acids. This becomes in fact a very efficient form of cladding by a noble strata.

This passive state can be induced by electro-
chemical means. If a specimen of iron is immersed in sulphuric acid and a current passed to make the metal act as a cathode and the potential is steadily made more electronegative, the potential-current relationship is as shown in Fig. 15.

(iii) Addition of inhibitors:

The final method of combating corrosion is by the use of inhibitors. These substances when added to the electrolyte protect the metal. It is the mechanisms of these inhibitors which is dealt within this thesis and is explained in the next chapter.

Theories of inhibition:

In 1845 E. Millon\textsuperscript{14} reported that certain substances reduced the acidic corrosion of iron and in 1872 Marangoni and Stephanelli\textsuperscript{15} stated that corrosion of iron in acid solutions could be diminished by the addition of extracts of bran, glue and gelatine to the acid. In the ensuing 100 years there have been an immense number of references to substances which act in the same way.

These include sulphides, sulphonides, sulphones,\textsuperscript{16,17,18,19} sulphonic and carboxylic acids, alcohols, esters, aldehydes,\textsuperscript{20,21,22,23,24} organic bases,\textsuperscript{25,26,27} amines,\textsuperscript{25,26,27} quinolines,\textsuperscript{28} anthracenes,\textsuperscript{29} and thioureas.\textsuperscript{28,30} The range of inhibitors
covers simple molecules like formic acid\textsuperscript{30} and more complex substances such as tannin.

In view of the great range of substances which can act as corrosion inhibitors, it is not surprising that no single mechanism has yet been suggested to explain satisfactorily the mode of action of all inhibitors.

Putilova, Balezin and Barannik\textsuperscript{11} have considered corrosion inhibitors in two groups:

Type 'A' inhibitors which attack the metal surface and

Type 'B' inhibitors which act by deactivating the corrosive medium.

Examples of the latter type of inhibitor include sulphites which deactivate the solution by combining with dissolved oxygen, and hence retard the cathodic reaction. For the purpose of this survey these compounds are regarded as corrosion deactivators as opposed to corrosion inhibitors.

Type 'A' inhibitors are considered to be of three kinds:

Passivators;

Immunisers; and

Adsorption inhibitors.
Passivators, such as phosphates, act by assisting in the chemical formation of a protective layer, either of oxide or metallic salt.

Immunsers do not so much reduce the corrosion rate as delay the onset of corrosion, after which the metal corrodes as if in uninhibited solution. It seems likely, though this is not specifically stated, that the corrosive medium in this case acts with the inhibitor in preference to the metal. After the inhibitor has been poisoned or dissociated, corrosion can take place.

The third group, inhibitors, by far the largest, are used virtually exclusively in acid conditions where the cathodic reaction is the discharge of hydrogen. Uhlig\textsuperscript{31} has also distinguished between passivators and adsorption inhibitors.

It is generally agreed that the first step in the inhibition process for this group of compounds, is the adsorption of the inhibitor onto the metal surface. The quantity of inhibitor adsorbed onto the metal surface has been determined directly by chemical means.\textsuperscript{32,33,34,35,36} The nature of adsorption bond has been in dispute but that adsorption takes place, is commonly accepted.

The first theory to explain the action of adsorption
inhibitors was put forward by Chappell, Ocetheli and McCarthy. Their theory supported by Mann and Werner stated that inhibitors were substances capable of absorbing a proton and becoming positively charged. The positively charged substances were then assumed to be attracted to those points on the metal surface where positive ions are customarily discharged. Thus, the effect of inhibitors was assumed to be the polarisation of the cathodic reaction by a film of inhibitors. Andubert reported similar findings with colloids and claimed that electrolyte cations were adsorbed onto the colloids and resulting complexes were adsorbed at cathodic sites on the metal surface.

The proposition that corrosion inhibitors are truly charged particles which adsorb on cathodic areas on the metal surface, received a great deal of support in the ensuing decade. Leblanc had been quoted as saying that some alkaloids raise the hydrogen over voltage of metals in acid. Jimenco, Griffd and Moral pointed out the parallelism between the time necessary after adding inhibitor for the attainment of maximum hydrogen over-voltage, and that for the attainment of maximum inhibitor effectiveness. Several other workers using polarisation techniques, reported similar findings.
Measurements of the ohmic resistance of the inhibitor film are conflicting. Rhodes and Kuhn stated that the film had a measurable resistance but they were unable to correlate inhibitor efficiency with film resistance. Machu confirmed that the film of adsorbed inhibitor has a measurable resistance and further claimed that there is a critical film resistance above which inhibition takes place and below which corrosion is not inhibited. Machu's theory was that inhibition is due to ohmic resistance of a film of inhibitor adsorbed generally on the metal surface. The inhibitor film was considered to be porous and effective inhibition was obtained with a free pore space as high as 66%. The inhibition of corrosion, according to this theory, was brought about by the restriction of ionic diffusion by the very small pores. The hydrogen over voltage observed in adding inhibitor, was thus attributed to the concentration polarisation caused by the retarding of ionic diffusion.

Opponents of this theory, notably Fischer and Bockris, claimed that the measurements made by Rhodes and Kuhn, and Machu do not in fact represent ohmic resistance but merely an apparent resistance. The observed over potential was claimed to be an activation over potential. Bockris devised a technique by which he could measure directly the hydrogen activation over potential. The results were claimed
to be of same value as those obtained from direct reading of over voltage. He concluded that the contribution to the hydrogen over voltage due to ohmic resistance was negligible. Bockris obtained over voltages of the order of one volt and claimed that, assuming Machu's theory to be correct, over voltages of this order could only be explained, in terms of concentration polarisation, by assuming a ratio in ionic concentration, between the metal surface and the outside of the porous film of 10.20

There are however, several objections to the simple cathodic theory of inhibition.51 Mazzuchelli,52 in 1914 found that compounds of the quinine and quinoline type increase both anodic and cathodic polarisation. Isgarishew and Barkman53 showed the same effect with gelatine and gum-arabic. Hoar,54 Mears,55 and Hall56 pointed out that the polarisation measurements, on the results of which the cathodic inhibition theory was based, involved relatively high current densities and were thus not necessarily relevant to the conditions existing in the corrosion.

Cavallaro and co-workers57,58,59,60,61 found that at low current densities a number of inhibitors polarised both the anode and cathode reactions. Hackerman and Sudbury62 reported similar findings, with n-octylamine, and Kuznetsov and Iofa63 reported many cases where the anode reaction
appeared to be polarised more than the cathode reaction.

Kaesche states that the most effective adsorption inhibitors polarise both anodic and cathodic reactions. Kaesche and Hackerman studying the effect of thirteen amines on the corrosion of steel in air-free solutions found that in all cases except methyl amine, both electrode processes are polarised, the anodic process being polarised more than the cathodic reaction.

The addition of almost all inhibitors causes the resting potential of the metal to be made more noble. Hoar and Hackerman have pointed out that this effect can easily be explained on the basis of predominantly anodic polarisation, but is very difficult to explain on the basis of a theory of predominantly cathodic inhibition. This attainment while largely true is not necessarily always correct.

Elze and Fischer have explained the effect of inhibitor on the resting potential by suggesting that the cathodic reaction is depolarised. It is difficult to reconcile this view with the claim that inhibition is due to polarisation of the cathode reaction. If the electrochemical theory of corrosion is correct, it is only possible to have inhibition and cathodic depolarisation simultaneously if the anode reaction is strongly polarised.
The original theories of cathodic inhibition\textsuperscript{37} do not explain the fact that many inhibitors are specific in their action. Thus, KCN inhibits the corrosion of aluminium and zinc but has no effect on the corrosion of cadmium.\textsuperscript{63} Potassium thiocyanate, however, stimulates the corrosion of cadmium and zinc but inhibits the corrosion of aluminium and iron. This specificity of adsorption is difficult to explain on the basis of inhibition by electrostatic attraction between positively charged inhibitor particles and negatively charged areas on the metal surface. An explanation can be put forward on the basis of the modified theory of Bockris\textsuperscript{44} and Fischer.\textsuperscript{43} Neither the original nor the modified theories however are capable of explaining the ennoblement of resting potential mentioned above. Hoar\textsuperscript{66} has pointed out that the large number of hydronium ions present in acid solutions preclude any significant electrolyte migration of large, positive, inhibitor ions. He also pointed out that the potential of the cathode areas could not be cause of the preferential adsorption as, on the corroding metal surface, the anode and cathode half cells are shorted and the potentials of the anode and cathode sites are consequently very close together.

This does not exclude the possibility that positive ions should not be more likely to be adsorbed, and having been adsorbed, discharge and stay adsorbed, at the cathode.
surfaces than at anodic surfaces. By definition cathodic areas are those where electrochemical reduction takes place. Although the metal surface is almost equipotential, electrons are continually made available at the cathodic areas on the metal surface and continuously removed from the anodic areas.

Hackerman\textsuperscript{32,65,67,68,69,70,71,72,73} and Hoar\textsuperscript{66,74,75,76,77} have tended to support the hypothesis of Rhodes and Kuhn and Machu that adsorption is general over the metal surface. Rhodes and Kuhn and Machu regarded the adsorption to be physical in nature rather than the stronger chemisorption. Hackerman, however, suggests that adsorption tends to be largely chemisorption. As evidence in support of this view, he quotes the relatively high heats of adsorption and the specificity of adsorption.\textsuperscript{69} Inhibitors acting on this theory are thought to act by two simultaneous reactions.

Firstly a purely mechanical barrier to transport of the corrosive species is introduced. This is predominant at the cathode areas with many inhibitors causing an interference to the transport of hydronium ions to the cathode sites and to the discharge of hydrogen ions.

Secondly the formation of an inhibitor-metal bond reduces the free energy of the atoms at the metal surface. Addition of inhibitor would thus greatly increase the energy
barrier to 'forward' reaction in the equation:

\[ M \rightarrow \underset{\text{M}^{2+} + Z \text{e}}{\text{M}} \]

Inhibition of this type is thus anodic activation over-potential.

Both of these types of adsorption inhibition are claimed to occur simultaneously. The chemisorption and consequent anodic polarisation are assumed to be greater than the physical adsorption and consequent cathodic polarisation. Hackerman and Cook\textsuperscript{70} studying the adsorption of fatty acids onto steel powder out of benzene solution, showed that the effect of the inhibitor film, after transfer of the metal powder to an acid solution, was more closely related to strongly adsorbed material than to the total adsorption. Bordeaux and Hackerman\textsuperscript{32} showed that the firm adsorption was related to the potential shift.

A great deal of progress has been made in recent years in the study of the bonds involved in chemisorption with particular reference to the Catalysis.\textsuperscript{78,79,80,81,82,83} A detailed review of the forces involved in adsorption is beyond the scope of this thesis. Stated in its simplest form chemisorption is thought to take place by the formation of a dative link between one atom of the inhibitor molecule and the metal surface. The mechanism of the formation of this link is thought to be the donation of electrons by the 'bonding
atom' in the inhibitor molecule to 'd' shell of the atoms in the metal surface.

The chief supporting evidence for this theory of inhibition is the effect of inhibitor structure on the efficiency of inhibition.

Hackerman suggested that inhibitor molecules are characterised by the presence of easily donatable electrons. The bonding atom is often from groups 5 and 6 in the periodic table, the most common being nitrogen and sulphur. The presence of double bond in many inhibitors is also noticeable.

Sieverts and Lueg studying the inhibitive effectiveness of the molecular series consisting of pyridine, quinoline and napthoquinoline, found that the effectiveness of inhibitors increased with increase in the molecular weight of the inhibitors.

Mann found that the inhibitor efficiency of aliphatic amines increased with increased chain length. Finlay and Hackerman studying the same range of compounds found that each substitution of a methylene group increased the efficiency of inhibition by 5%.

Mann and Machu suggested that large molecules are necessary for inhibition as the large cross sectional areas
of these molecules cause a good physical barrier to the corrosive medium. The increase of efficiency of straight chain aliphatic amines on substituting a methylene group was attributed to the fact that the amine was not aligned at right angles to the metal surface. An added methylene group was thus thought effectively to increase the cross sectional area of inhibitor molecule.

Finlay and Hackerman have shown, for a series of cyclic saturated amines, that the reduction in reactivity of the metal followed the inhibitor structure more closely than it did the molecular cross-sectional area. Hayakawa and Ida showed similar effects for hydroxyazo compounds on the corrosion of aluminium.

Recently Hackerman and Hurd have shown that the marked effect of substituting methylene groups into the molecule of cyclic amines, on the inhibitive efficiency of these molecules, can be related to the change in bond angles, which this causes. This has been confirmed by X-ray measurements. It was postulated that the effect of increase in bond angle at the nitrogen atom is to increase the relative orbital character of the electrons free for forming a dative link with the metal surface. The chemisorption theory for inhibition, thus explains adequately the effect of increased ring size on the inhibitive efficiency of cyclic
amines.

The effect of substituting methylene groups into straight chain aliphatic amines on their effectiveness as corrosion inhibitors can be explained on the basis of chemisorption and the theory of induction or electron drift. The same theory explains the better inhibiting efficiency of o-toluidine compared with m-toluidine.

In recent years Frumkin and Antropov in the U.S.S.R. and De and Brasher in the U.K., have suggested that adsorption, and hence inhibition, is influenced by potential. This theory does not involve the potential of minute half-cells, but rather the charge remaining on the whole metal surface.

In order to discuss this theory, it is necessary to describe the conditions existing at the interface between a corroding metal and the electrolyte. When a metal is immersed in a solution of its salt, metal atoms tend to dissolve. Positive ions thus move into the solution and at equilibrium, there is a fixed potential difference between the metal and the solution. Helmholtz suggested that the potential difference was caused by the presence of two layers of charged particles. The positive metal ions were assumed to lie in a plane parallel to the metal surface as shown in Fig. 16. The interface between the metal and the solution was thus thought
to be analogous to a parallel plate condenser, and the capacity was assumed to be given by the equation:

\[ C = \frac{Q}{4\pi D} \]  \hspace{1cm} \text{(43)}

where 'Q' represents the change on each layer, and 'D' the distance between the layers. In practice, the capacity was found to vary according to the nature of the electrolyte and with the interfacial potential difference. The simple Helmholtz theory was thus not satisfactory.

Gouy and Chapman proposed that on the solution side of the interface, every ion in the solution attracts to itself an ion of opposite sign. The resultant diffuse layer of ions was said to be in equilibrium with the electric field of the electrode and the thermal kinetic forces of the solution. The potential-distance relationships predicted from this analysis, are shown in Fig. 17.

This model does not give a relationship between capacity and potential which agrees with experimental results.

In 1924, Stern postulated that the interface could be treated as two condensers in series. One condenser represented the Helmholtz layer, and the other condenser the diffuse layer. The total capacity then could be expressed by the equation:
\[
\frac{1}{C_S} = \frac{1}{C_H} + \frac{1}{C_D} \quad \ldots \ldots \quad (44)
\]

where

\( C_S \) - Stern capacity of the interface
\( C_H \) - The capacity contributed by the Helmholtz layer
\( C_D \) - The capacity contributed by the diffuse layer

The potential-distance relationships predicted by the Stern Model are shown in Fig. 18. Immediately attached to the electrode surface is a compact layer; this is one ionic layer and is the Helmholtz layer. The potential falls linearly across this layer. Further away from the metal surface there is a diffused layer across which the potential falls exponentially. The potential difference \( V_2 \) between the outermost face of Helmholtz layer and the bulk of the solution is sometimes referred to as the electrokinetic or zeta potential. The total potential difference between the metal and the bulk of the solution is, of course, the electrode potential of the metal-solution half cell.

Grahame has shown that the capacity of the Helmholtz layer is much less than that of the diffused layer. It will be seen from equation (44), that the capacity of the composite layer cannot be greater than the smallest of the two contributing capacities and if one capacity is much smaller than the other, then it is this capacity which largely determines the capacity of the whole system.
The Stern Model though the one in general use, is still not wholly satisfactory. Devnathan has suggested that a nearer approximation is given with a triple layer model. The potential-distance relationships for this model are shown in Fig. 19. The Helmholtz layer is assumed to consist of two layers. The inner-most layer, is according to this theory thought to consist of unsolvated, specifically adsorbed ions. The third layer, outside the Helmholtz layer, is assumed to be the diffused layer.

It is reasonable to assume that the distribution of charge and potential and the capacity of the interface should influence electrochemical reactions.

The capacity of the double layer can be measured in two ways:-

(a) Electrocapillary measurements
(b) Tracing the build-up and decay of potential on the passage of a current

(a) Electrocapillary measurements:

The electrostatic repulsion of charges of similar polarity in the Helmholtz double layer tends to oppose the attractive forces causing surface tension. A charge in the electrode potential thus causes the surface tension of the interface between the metal and the solution to change. The surface
tension is greatest when there are no charges on the Helmholtz double layer. The potential gradient in the immediate neighbourhood of the metal surface is then zero.

If the potentials of the metal surface is changed in either direction, from this potential, the surface tension is lowered. The surface tension-potential relationships for mercury are shown in Fig. 20. The potential corresponding to the maximum surface tension is referred to as the zero charge potential.

The slope of the electrocapillary curve is expressed in the equation:

$$\frac{d\gamma}{d\psi} = Q_s$$  \hspace{1cm} (45)

where

- $\gamma$ - surface tension
- $\psi$ - potential difference between the two sides of the layer
- $Q_s$ - charge density on the layer

Capillary active or strongly adsorbed, anions depress the positive branch of the capillary curve while capillary active cations depress the negative branch. In the former case, the zero charge potential is shifted in the negative direction and
in the latter case, the zero charge potential is shifted in positive direction. In practice both branches of capillary curve are usually depressed. The direction of the shift of the zero charge potential then depends on which branch of the curve is depressed the more.

These effects are analogous to those observed for polarisation curve on adding inhibitor. The most convenient metal for the study of electrocapillary phenomena is mercury and the apparatus used is the Lippmann capillary electrometer. The most important part of the apparatus is a narrow glass capillary in which is the interface between the mercury and the solution. A variable potential is applied between the mercury and a calomel electrode immersed in the solution. Changes in charge and potential distribution affect the surface tension of the interface and hence the position of the mercury meniscus in the tube. The meniscus is brought back to fixed point in the capillary tube by adjusting the height of a movable mercury reservoir. The height of mercury is then a measure of the surface tension of the interface.

The electrocapillary curves for solid metal
are more difficult to obtain, the usual laborious method being the study of the contact angles of gas bubbles on the metal surface. Frumkin has calculated the zero charge potentials of a great number of metals although not for iron.

(b) Tracing the build up and decay of potential on the passage of a current: ______________________________

Measurements of capacity are more conveniently carried out by the use of combined data of build up and decay of potential on the passage and ceasing of a current. The theory and practice of this method are described by Potter.³

Despite the difficulties involved in measuring and reproducing the zero-charge potential, this is clearly, from a theoretical point of view a useful reference potential.

Antropov⁸ suggested that electrochemical properties of a metal, including the tendency for adsorption to take place, could be related to the potential of the metal on Pi Scale where:

\[ E_{Pi} = E - E_Q = 0 \]

\( E_{Pi} \) is the electrode potential of the metal on the Pi Scale.
\[ E \] is the electrode potential of the metal relative to a reference electrode.

\[ E_0 = 0 \] is the zero charge potential of the metal to the same reference electrode.

All metals are claimed to behave in the same manner at the same \( \Pi \) potential. Hence Antropov claimed that if the electro-capillary properties of a substance are found for one metal for convenience \( \text{Hg} \), then it is possible to estimate the adsorption of the same substance on another metal, provided the potential of the other metal on the \( \Pi \) Scale is known. Antropov, Grigar'ev and Petrenko\(^{90}\) showed that the effectiveness of inhibitors of the acid corrosion of metals is directly related to the lowering of the surface tension of the mercury-solution interface at the same potential, on the \( \Pi \) Scale, as the metal corrosion potential.

Elze and Fischer\(^{43}\) showed that, in the presence of oxidising agent, the effect of a cathodic inhibitor on the cathodic reaction is greatly reduced. This, Antropov attributed to the fact that an oxidising agent shifts the potential of iron in the positive direction. This makes the adsorption of cathodic inhibitors more difficult.

Antropov\(^{89}\) and Rajagopalan\(^{91}\) have studied the combined effect of inhibitors and applied current. The general conclusions were that the application of cathodic polarisations resulting in maintenance of a negative potential, gave
increased inhibition, with cationic inhibitors and decreased inhibition with anionic inhibitors. Hoar and Holliday\textsuperscript{92} found that N-ethylquinoline and o-tolylthiourea, both cationic inhibitors, were more effective as inhibitors of the cathode reaction, the less noble the metal potential. Iofa\textsuperscript{53} showed that certain amines inhibit the corrosion of steel in hydrochloric acid more than in sulphuric acid. This theory attributed to the fact that the charge in the metal surface is slightly negative in the case of hydrochloric acid and slightly positive in sulphuric acid.

Gatos\textsuperscript{93} has shown that the effect of amines in depressing the negative branch of the electrocapillary curve of mercury increases, as does the effectiveness of inhibition with decreasing molecular weight.

Brasher\textsuperscript{89,94,95} has shown that the effectiveness of chromate as an anionic inhibitor in neutral solutions increases markedly if the potential of the metal is more noble than the zero-charge potential. Benzoate was found to inhibit the rusting of iron coupled to copper but not when coupled to zinc.

The present state of this theory can be summarised by stating that adsorption is the first step in the inhibition process. Whether adsorption takes place or not depends upon the nature of the inhibitor and upon the potential of the metal relative to the zero-charge potential, or stating this
in another way, upon the nature of the charge on the metal surface. Capillary active anions are assumed to be more easily adsorbed when the charge on the metal surface is positive. The metal potential is then more positive than the zero-charge potential. Capillary active cations are assumed to be more easily adsorbed when the charge on the metal surface is negative, this occurring when the metal potential is more negative than the zero charge potential.

Aiazian\textsuperscript{96} reported that the tendency to specific adsorption can be so strong, in the case of some inhibitors, that the forces of electrostatic repulsion are overcome, and adsorption of cations becomes possible even on positively charged surfaces.

Putilova, Balezin and Barannik claimed that the action of adsorption inhibitors is largely mechanical protection. The effects of the addition of inhibitor on such electrochemical phenomena as resting potential, polarization, and double layer capacity are, according to this theory, secondary effects brought about by the presence of a mechanical barrier on the metal surface.

None of these theories need be exclusively true and all the theories should be considered as contributions to a final, as yet unknown, theory.
Methods of studying corrosion:

Corrosion consists of reactions between a metal and its environment and thus corrosion depends both on the metal and environment to which it is exposed. It is therefore, necessary to consider and control factors associated with both phases for the establishment of satisfactory exposure conditions during a corrosion test. It is thus obvious that there is no universal standard test procedure.

The following literature provides a review of the generally accepted corrosion testing procedures and is presented to provide a basis for the methods employed in this investigation.

Jelinek and Borgmann summarize the major methods for measuring the amount and intensity of corrosion as well as certain qualitative aids in determining the amount of corrosion. Both of them point out that the use of two or more methods will remove many of the criticisms given for the individual methods. A brief description of individual methods outlining the fields of usefulness and the major advantages and limitations follows:

Visual observation may be useful to detect occurrence of attack and identify its general nature. This method is simple and valuable in conjunction with other methods. It is subject, however, to human error and is
qualitative.

Loss in weight is useful to determine the extent and rate of uniform corrosion. It is simple, quantitative and direct. The method is subject to error due to incomplete removal of corrosion products and loss of uncorroded metal. Special types of attack are not measured and multiple specimens are necessary.

Gain in weight is useful to determine the extent and rate of uniform corrosion where no loss of corrosion products occurs. The method is applicable to indoor atmosphere corrosion and high temperature corrosion studies. In this method error due to improper removal of corrosion products is eliminated. An analysis of corrosion products is, however, essential to determine the loss of metal. Moisture in corrosion products may vary and thus influence the results. Special types of attack are not measured by this method.

Electrical resistance change can be used in gaseous or poorly conducting environments or in other environments if the specimen is removed for measurement. In addition to its usefulness in evaluating environment corrosivity it can be used to follow certain property and composition changes, and the method is nondestructive and adaptable to continuous measurement. However, the method is indirect, requires calibration, does not distinguish between types of attack, is subject to surface-to-volume errors, and if small wires
are employed, the attack may be different in amount from that on a more massive specimen.

Hydrogen evolution may be followed for tests in which corrosion takes place solely with hydrogen evolution. The method is adaptable to rate measurement, but does not determine the distribution of attack.

Oxygen absorption is useful in tests where corrosion takes place mainly with the absorption of oxygen. The method is adaptable to rate measurement, but does not determine the distribution of attack, and an analysis of corrosion products is required for metals capable of existing in more than one ionic states.

Depth of pitting measurements (other than microscopic) are useful for tests made to determine the serviceability of metals as containers of fluids. This method is used in conjunction with methods of determining total attack, and it gives a correct measure of penetration of a metal by corrosion except when the corrosion is intergranular. Multiple specimens are required to determine time-penetration curves.

Microscopic methods are useful to determine the kind of attack, to measure the depth of pits, and to determine the constituents of the metal that are specially capable of initiality attack. This method is excellent to supplement other measures, but is not generally useful in
making quantitative measurements.

Physical property changes such as tensile strength, ductility, resistance and hardness of materials can be used to evaluate their deterioration. It is not possible, however, to evaluate the damage resulting from each type of attack separately by this method.

The electrochemical methods are: measurements of single electrode potential, shorted cell current measurement, potential difference between unlike metals, anode and cathode polarisation and film resistance.

Single electrode potential methods are useful to study film formation and breakdown at a metal surface. The method distinguishes between anodic and cathodic control, and measures the electro-chemical driving force. It does not measure the extent or rate of attack.

Shorted cell current measurement is useful to measure the extent of corrosion relative to a standard noble metal. An arbitrary choice of a cathode metal may distort the normal influence of such areas on the metal under study. The anode and cathode are separated by a much greater distance than usual, hence resistance of solution and unnatural formation of corrosion products are sources of error.
Anode and cathode polarisation methods are useful to study galvanic and concentration cell corrosion and to determine the total polarisation current. The method does not measure the distribution of attack.

Film resistance may be used to determine the penetrability of surface films by various anions.

The electrometric method is useful to measure the thickness of surface films. This method is only useful on adherent, thin, surface films of some metals.

Optical methods are useful to study the growth of tarnish and other surface films.

It was decided from the above information that the weight loss, visual observation, microscopic observation, electrode potential, and polarisation methods would be used for this investigation. The weight loss method facilitates a simple, direct, quantitative measure of the extent and rate of corrosion. The visual observation method is simple and of value in conjunction with other methods, is useful to detect the occurrence of attack and identify its general nature. The principal limitations of weight loss method are that multiple specimens are required and that caution need be exercised in the selection or development of a treatment to remove corrosion products.
Evans points out that in wet corrosion, the measure of attack is often the loss of weight after exposure. Fontana also states that change in weight of the specimens is most often used as a measure of corrosion. Champion also points out that the gravimetric method is normally used for determining the metal remaining after corrosion.

Champion, Borgmann and Speller present a comprehensive discussion of general corrosion testing procedures. They discuss the general procedures to be followed in total immersion corrosion tests. The American Society for Testing Materials ('ASTM') presents specific detailed test procedures for use to evaluate a number of corrosion problems. A review of factors pertaining to the metal, corrosive media, exposure conditions and assessment of effects on the metal and media important in corrosion studies follows:

Factors pertaining to the metal are selection of the specimens, size and shape of specimens, replication and number of immersion periods, preparation of specimens, and cleaning of the specimens after corrosion. Champion points out that test specimens should be representative of the material under test. He further states that rolled products are widely used because they provide the following advantages:

(a) They are most extensively used in service.
(b) A wide range of thicknesses can be obtained.
(c) Major variations in corrosion resistance over the surface of a rolled sheet are unusual.

(d) Sheets of large surface area can be obtained thus permitting the preparation of a large number of replicate specimens.

(e) Relatively simple methods of preparation of the specimens from the sheet can be employed.

The 'ASTM' in discussing test specimens and their preparation states that the shape and size of specimens will vary with the purpose of the test, the nature of the materials to be tested, and the testing apparatus to be used. The size may also be limited by the necessity of preserving a proper ratio between the area of the specimen and the volume of the testing solution when the latter must be limited. In general, an effort should be made to have the ratio of surface to mass large and that of edge area to total area small. The shape and dimensions of the specimens shall be such as to permit weighing on an accurate balance and to facilitate accurate measurement and calculation of the area of each specimen.

Champion\textsuperscript{105} and Knapp\textsuperscript{106} point out that the size and area chosen is often determined by experimental
convenience, but that it is desirable to adopt a standard size as far as possible to insure that comparable results will be obtained. According to them, it is advantageous to adopt a size and shape of specimen giving a low edge to surface area ratio and a reasonably large area. Champion states that, a thickness of 0.036 in. is convenient for many purposes. He also states that the German specification on corrosion tests in general recommends that the dimensions should not be less than 5 x 2 cm.

Fontana states that the original area is used to calculate the corrosion rate throughout the test. If the dimensions of the specimen change appreciably during the test, the error introduced is not important because the material is probably corroding at too fast a rate for its practical use.

Borgmann points out that it is not to be expected that absolute reproducibility will be achieved because there are factors beyond the control of the experimenter. However, statistical control is often achieved. The absolute error of measurement can be reduced only by increasing the number of specimens tested. The reproducibility of the results depend upon the type of attack. The reproducibility will be much greater if the attack is uniform than when it is localised.

Evans points out that in general, it is well to
perform all experiments in duplicate or triplicate. He says that in the case of localised attack, this will not be adequate for good reproducibility.

Champion recommends a minimum of three replicates. He also points out that when it is known that the corrosion rate is constant from the beginning of exposure, a single replicate set of specimens will be adequate. With non-linear corrosion time curves further replicates are necessary, and when the shape of the corrosion time curve is not known, it is suggested that at least three replicate sets should be exposed for withdrawal after increasing periods of time. The degree of replication to be adopted, however, depends on the accuracy required in the mean result and the scatter which is to be expected in the individual results.

An 'ASTM' method, which describes procedures for carrying out total immersion corrosion tests, discusses the problem of determining the number of specimens to be used from a statistical approach. They state that, observations on some typical metals immersed under controlled conditions in typical corrosive media have indicated that the coefficient of variation may reasonably be expected to be less than 7%. They refer to the work of Humes, Passano, and Hayes when presenting their statistical procedures. They state that, $E$, error of average in $\% = \frac{\frac{ZV}{N}}{N}$ where, $Z = 1.96$ for a
statistical probability, \( P \), of 0.95; \( V^* \) = Universe coefficient of variation of 7\%, and \( N \) the number of repetitions of specimens. Thus the expected errors of the average of different number of the specimens would be \( N = 8, E = \pm 4.8\% \), \( N = 4, E = \pm 6.9\% \) and \( N = 2, E = \pm 9.7\% \). It was stated that, running total immersion tests in quadruplicate would make it highly probable that the average would be within 7\% of the true average and this should be satisfactory for most corrosion research programmes.

Care must be taken to properly clean and prepare specimens for corrosion tests. The surface preparation will vary with the type of test. Surface preparation usually consists of a pre-cleaning or degreasing operation to remove surface contamination. A pickling process may be required to remove scale.

There is a strong opinion in certain groups of workers that the surface of the test specimen should be identical with the surface of the actual equipment to be used in the plant. This is however, an impossible condition, because the surface of commercial metals and alloys vary as produced and as fabricated. The degree of scaling on the equipment varies and also the condition of other surface contaminants. Moreover, the determination of the corrosion resistance of the metal or alloy itself is of prime importance.
in most cases, a clean metal surface is generally used. A standard surface condition is also desirable in order to facilitate comparison with results of others.

Champion\textsuperscript{109} states that extremely thin, invisible films of grease can interfere with the corrosion process. Evans\textsuperscript{12}, Jelinek\textsuperscript{3}, 'ASTM', Knapp\textsuperscript{106} and Meyer\textsuperscript{111} also note the importance of removal of grease and other surface contaminants.

Champion and Meyer\textsuperscript{111} discuss in considerable detail the general methods for metal precleaning and degreasing. The solvent and vapour cleaning methods are: simple solvent cleaning, emulsifiable solvent cleaning and vapour degreasing.

Evans\textsuperscript{112}, Jelinek\textsuperscript{3}, Champion\textsuperscript{113} and Speller\textsuperscript{114} point out that in tests where corrosion is assessed by weight loss, it is necessary to remove the corrosion products from the specimen after exposure. It is necessary that the specimens be thoroughly cleaned of all corrosion products without loss of any base metal. In the literature there are many satisfactory methods of cleaning specimens, but, whatever the method, its effect in removing base metal should be determined for the metal under investigation. Drastic methods are unsuited where there are indications of only a small weight loss resulting from corrosion.
Champion[113] discusses in detail the general methods for corrosion products removal from metal specimens. The various methods are: mechanical treatment such as wet scrubbing with a bristle brush, abrasive and detergent. Chemical treatments using various chemical reagents are often employed, but are generally specific for certain materials. Cathodic cleaning has been found useful with a large number of metals and alloys, but there is a possibility of deposition of metal from dissolved corrosion products or contaminants in the solution may occur.

Champion[115] observes that sulphuric acid is an appropriate solvent for the corrosion products of copper and its alloys and attacks the metal less than the other mineral acids. Concentrations of 5% and 10% are recommended.

The corrosive medium is another important factor in corrosion. Champion[116] presents a general discussion of corrosion media based on the literature. The 'ASTM'[103] points out that test solution be made up accurately, with the composition controlled to the fullest extent possible and the composition of the test solution should be checked by analysis.

A review of factors pertaining to exposure conditions is given in the following paragraphs:-

Wesley[117] states that perhaps the most common danger of mistaken interpretation of laboratory immersion test results
from exhaustion of ingredients in the original solution which control the rate or type of attack, or from accumulation of products, which are corrosion inhibitors or accelerators. This emphasises the importance of volume of solution per area of specimen and adequate replenishment of solutions. Included in the following table are some of the recommended ratios for volume of solution per square centimeter of metal surface:

<table>
<thead>
<tr>
<th>Source</th>
<th>Volume per Square cm²</th>
<th>Surface area per 500 ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot;corrosion&quot;</td>
<td>50.0 ml.</td>
<td>10.0 cm²</td>
</tr>
<tr>
<td>Wesley</td>
<td>40.0 ml.</td>
<td>12.5 cm²</td>
</tr>
<tr>
<td>Champion</td>
<td>33.3 ml.</td>
<td>15.0 cm²</td>
</tr>
<tr>
<td>Calcott, Whetzel and Whittaker</td>
<td>8.3 ml.</td>
<td>60.0 cm²</td>
</tr>
<tr>
<td>'ASTM'</td>
<td>6.7 ml.</td>
<td>75.0 cm²</td>
</tr>
</tbody>
</table>

Champion pointed out that the volume of solution recommended per square centimeter of metal surface has varied from 6 ml. to 40 ml. The important point to be noted is that the volume of the testing solution should be large enough to avoid any appreciable change in its corrosiveness through the exhaustion of corrosive constituents or the accumulation of corrosion products that might affect further corrosion.
Wesley\textsuperscript{119} and 'ASTM'\textsuperscript{103} suggest that each specimen should be tested in a separate container because it has been found that the practice of testing several specimens of the same material in a single container gives results which do not measure the true variability of the test as determined by repeated separate tests. In addition, containers and specimen supports should be used which do not affect the corrosion process.

Temperature control of the corrosive media is another important factor to be considered. Champion\textsuperscript{122} suggests that temperature control to \( \pm 0.5^\circ\text{C} \) is often regarded as adequate for many corrosion tests. Wesely\textsuperscript{119} and 'ASTM'\textsuperscript{103} point out that thermostatic control at the desired temperature, \( \pm 1^\circ\text{C} \) is usually considered satisfactory.

An important consideration in any corrosion test is its duration and the number and length of exposure period to be employed.

Speller\textsuperscript{123} remarks that in general the initial rate of corrosion is much greater than after the action has proceeded for sometime. He states that as for example the initial corrosion rate of iron in alkaline solutions is several times greater than the rate after a few hours. He mentions further that the initial rate of corrosion is dependent to a large extent upon the character of the corrosion product.
deposited on the metallic surface and that this should be
determined for a specific case. Thus it is likely that the
results of short-time tests may be misleading. It is advisable
in all cases that the length of test should be determined by
the length of time required to produce a reasonable amount
of corrosion.

Wesley\textsuperscript{119} states that a constant rate of corrosion
is encountered frequently in total immersion tests. He states
further that if the test is too short, some materials which
build-up protective corrosion product films slowly may be
ruled out as unsatisfactory, and if the test is too long, the
effects of exhaustion of ingredients or accumulation of
corrosion products may be pronounced.

According to 'ASTM' the duration of the corrosion
test will be determined by its nature and purpose. According
to them it is desirable to expose a number of specimens so
that certain of them can be removed after definite intervals
so as to provide a measure of change of corrosion rate with
time. When removal of solid corrosion products is essential,
the same specimens will not measure accurately normal changes
of corrosion with time because the effect of corrosion
products on subsequent corrosion is not evaluated. They also
suggest that higher rate of corrosion, the shorter may be the
testing period.
The next important phase is assessment of the corrosion. Champion has reviewed and discussed the assessment of corrosion effects on metal and media. He includes considerable information on quantitative and qualitative assessment by gravimetric and microscopic methods respectively. Champion points out that the analytical balance available in most laboratories provide adequate accuracy for many corrosion tests and that this general availability of suitable apparatus is no doubt largely responsible for the extensive use of gravimetric methods for the quantitative assessment of corrosion. He mentions that determinations of loss of weight can be used over a much wider range of conditions than gain in weight, although, the accuracy may be lower when cleaning of the specimen after exposure is necessary.

Fontana points out that in many cases, visual observation of the specimens on removal from the test solution provides valuable information concerning the causes or mechanism of the corrosion involved.

Champion points out that in microscopic examination, it is often useful to examine the corroded metal in two stages; first with the corrosion products still adhering to the metal, and again after removal of the corrosion products.
 METHODS OF STUDYING THE ACTION OF INHIBITORS

In order to measure the effect of inhibitors, the weight loss of a metal specimen should be measured. It is essential to know the action of the inhibitor for very short and long durations. Electrochemical method is suitable theoretically, but sometimes, the data is not concurrent with those obtained by long immersion tests. The knowledge of relation between corrosion potential and time is essential in ascertaining the effect of inhibitors. The shift of potential towards noble potential with time generally signifies adsorption of the inhibitor, or the formation of protective film. As the measurements can be made without disturbing the natural state of corrosion, this method is very important, however, in case of unknown polarisation characteristics results should be treated carefully.

The relation between the electrode potential and current is useful for evaluating the unknown corrosion system and to calculate the efficiency of the inhibitor.

In Galvanostatic method, the stationary potential is measured under a constant current between the specimen and auxiliary electrode. This method can be used as the best method for evaluating the efficiency of the inhibitor, however, the violent change which occurs in the transition from active state to passive state due to the circuit characteristic can
In galvanostatic method, the potential is measured as the sum of polarisation resistance of overvoltage and inner resistance derived from bath and apparatus. In the case of high reaction rate, it is not possible to measure exactly the change of overvoltage, which is a weak point of galvanostatic method.

In the potentiostatic method, the inner resistance in circuit is reduced and exact polarisation curves can be measured. Even by a small potential change, a strong current change is observed and the potential is deviced to keep at a certain constant value. This method is very useful in investigating the films made by inhibitors.

In pulspolariser, the potential change of metal with time under very high current density is measured oscillographically.

In the null-bridge process, polarisation values of each electrode under a constant current and film resistance of each electrode can be measured. The resistance change of each electrode can be measured independently by this method.

The efficiency of inhibitors can also be measured by A.C. impedance, however natural corrosion cannot be studied by this method as direct current is not used.

Cell current-time curve method is very simple but as both electrodes change by the corrosion conditions, and the
reaction velocity of polarisation is not constant, the results obtained by such a short time test should be carefully treated.

**EXPERIMENTAL PROCEDURES**

Rectangular specimens of area 6 cm. x 3 cm. (thickness 28 S.W.G.) with a small hole of about 2 mm. diameter just near the one end (3 cm. side end) of the specimen for suspension have been used.

A specimen of the metal was first washed with distilled water several times and dried. It was then polished using successively '0' to '0000' oakey emery papers. The final polishing was done using jeweller rouge which gave a mirror like finish. The specimen was finally degreased by immersion in A.R. Carbontetrachloride (sulfur free). The specimens were suspended by pyrex glass hooks. Each specimen was suspended to the same depth of 1.5 cm. below the surface of the liquid. The volume of the liquid for all the experiments was 230 ml. Only one specimen was suspended in each container which was a pyrex beaker of 250 ml. capacity. Triplicate experiments were performed. In long duration tests the level of the corrosive liquid was maintained by periodic addition of distilled water. Experiments were conducted at 35±0.1°C. For the satisfactory assessment of corrosion, it is necessary to remove corrosion products from
the specimen, at the same time it is essential to avoid further attack on metal during cleaning process. It was observed that for this purpose 30.0% nitric acid was satisfactory. Rajagopalan\textsuperscript{136} et al. have suggested the use of citric acid–sulfamic acid mixture in presence of thiourea and saponin for removal of corrosion products from metal surface.

**Polarisation Measurements**

For polarisation studies, the metal coupon was of a circular design, diameter 2.802 cm. with a handle 3 cm. long and 0.5 cm. wide. The handle as well as the back of the coupon were covered with perspex leaving only a circular portion of apparent surface area 6.156 cm\(^2\) exposed. The other electrode was platinum of the same dimension. For these measurements, H-type pyrex glass cell with porous partition to separate the two compartments was used. It also contained a built-in capillary to make connection to the reference saturated calomel electrode. In each compartment, the volume of the corrosive medium was 80 ml.

**Remarks**

Aluminium 57S, half hard, thickness 0.56 mm, having the following composition was used for study: Mg-2.0%, Mn-0.3%, Al-remainder and trace of Si, Cu and Ti. All the chemicals used in the investigation were of A.R. quality. Distilled
water was used throughout the work. All the volumetric apparatus like the burette, the pipette etc., were of standard quality and calibrated before use. The weights were taken on a Mettler balance, M5 type.

**SCOPE OF THE WORK**

Studies on metallic corrosion and its inhibition have been concentrated more on ferrous metals as compared to non-ferrous metals. Further, detailed studies of an academic character which are essential in order to obtain the necessary background information are lacking in literature for many systems. Apart from the practical importance of the corrosion inhibition data in the field of corrosion prevention, they are also useful in the interpretation of the mechanism of the corrosion inhibition.

Detailed investigations on the inhibition of the corrosion of aluminium in hydrochloric acid solutions was undertaken with a view to study the effect of variables on corrosion rates, inhibitor efficiencies and cathode as well as anode polarisations. The optimum conditions for satisfactory retardation of corrosion have been established. Combined cathodic protection of aluminium in 2.0N hydrochloric acid has also been investigated.
FREE ENERGY COORDINATE
ACTIVATED STATE
DISTANCE INCREASING FROM ELECTRODE

FIG. 1

FREE ENERGY COORDINATE

ACTIVATED STATE

\[ \Delta G_1 \]

\[ \Delta G_2 \]

\[ \Delta G = -ZeF \]

M ATOMS ABOUT TO IONIZE
IONIZATION M+ IONS ABOUT TO DISCHARGE
DISCHARGE

DISTANCE INCREASING FROM ELECTRODE
FIG. 1

FIG. 2.
FIG. 3
DISTANCE INCREASING FROM ELECTRODE

FIG. 4 - ELECTRON FLOW

SALT BRIDGE

Fe → Fe⁺⁺ + 2e⁻

Cu⁺⁺ + 2e⁻ → Cu

N FeSO₄

N CuSO₄

ΔG₁

ΔG₂

ΔG = -ZeF

(1-α) nF → Reversible

→ Irreversible

DISTANCE INCREASING FROM ELECTRODE

Reversible

Irreversible

FIG. 4
FIG. NO. 5 A. ARRANGEMENT OF APPARATUS FOR CATHODE POLARISATION MEASUREMENT.
CATHODIC CONTROL

ANODIC CONTROL

FIG. 6

FIG. 7

FIG. 8

FIG. 9

FIG. 10

FIG. 11

VOLTAGE ACROSS THE CELL


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