COMPUTER-AIDED ANALYSIS OF GALVANIC CORROSION UNDER SIMULTANEOUS CHARGE AND MASS TRANSFER CONTROL

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Submitted to the College of Engineering of
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Requirements for the Degree of Master of Science
in Chemical Engineering

by

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April 2005

CERTIFICATION

We certify that the preparation of this thesis titled "**Computer-Aided Analysis of Galvanic Corrosion under Simultaneous Charge and Mass Transfer Control**" was made by **Baker Muthanna Abood Al-Zaidy** under our supervision at Al-Nahrain University, College of Engineering, in partial fulfillment of the requirement for the degree of Master of Science in Chemical engineering.

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Abstract

The importance of corrosion is techno — economic ,i.e. reducing material losses resulting from corrosion of piping, tanks, metal components of machines, ships, bridges, marine structures, etc. in addition to improved safety of operating equipment, which through corrosion may fail with catastrophic consequences, and also conservation of metal resources and associated losses of energy ,water reserves ,and human effort.

Because of practical importance of protecting industrial equipments from galvanic corrosion, the need arises to analyse the effects of variables, such as temperature, acidity, velocity, pressure and area fraction of metals on galvanic corrosion in de-aerated acid media when the system is under activation control and in seawater under mass transfer control of Fe – Zn couple. For these reasons computer program is developed which can be used for a general number or type of coupled metals with a range for pH of 1, 2, 3, 4, and 7, temperature of 25, 40, and 60 ^{0}C, pressure of 0.5, 0.75, 1, 3. and 5 atm, Re of 5000 - 50000 and area fraction of 0.1-0.9 of Fe. The program can also be used for free corrosion of metals.

The results show that the free corrosion rate of Fe and Zn increased with increasing temperature and decreasing pH under activation control. At diffusion control free corrosion rate of Fe and Zn increased with increasing Re and pressure while temperature leads to decrease the corrosion rate of both metals via decreasing O_2 concentration as dictated by limiting current density.

For galvanic coupling of Fe – Zn, the results showed that for activation control, decreasing pH and increases temperature lead to increase the corrosion rate of Zinc. Increasing area fraction of more noble metal (Fe) increases the galvanic corrosion rate of more active metal (Zn). No effect of Re on the galvanic corrosion under activation control is noticed.

For diffusion controlled galvanic corrosion, the result showed that increasing Re and pressure lead to increase the galvanic corrosion rate of Zinc while the temperature increase leads to decrease the galvanic corrosion of Zinc. Slight effect of area fraction on the corrosion rate of Zinc is noticed.

When the system is under mixed control (charge and mass transfer) the results revealed that increasing pH leads to decrease the corrosion rate for free corrosion and galvanic corrosion. For free corrosion increasing temperature leads to slight decrease of corrosion rate of zinc while increasing Re and pressure lead to considerable increase of corrosion rate of zinc. For mixed control galvanic corrosion increasing temperature increases the corrosion rate of more active metal for $pH < 4$, and decreases the corrosion rate of zinc at $pH = 7$. No appreciable effect of both Re and pressure is noticed on the galvanic corrosion rate of zinc under mixed control for $pH < 4$ while for $pH=7$ the galvanic corrosion rate of zinc increases with Re and pressure. Increasing area fraction of iron increases the corrosion rate of zinc for $pH < 4$ while it affects the corrosion rate slightly at $pH=7$.

Generally, results showed that corrosion potential is shifted to more noble (positive) with increasing Re and pressure, while it is shifted to more active (negative) with increasing temperature and pH, except in mixed control it exhibits both trends with pH increase.

List of Content

CHAPTEER ONE

CHAPTER TWO
CORROSION

CHAPTER THREE
GALVANIC CORROSION

CHAPTER FOUR

THEORATICAL ASPECTS

CHAPTER FIVE

RESULTS

CHAPTER SIX

DISCUSSION

CHAPTER SEVEN
CONCLUTIONS AND RECOMMENDATIONS FOR FUTURE WORK

APPENDICES

Nomenclature

A	Surface area of specimen	m^2
A_a,A_c	Anodic and cathodic area	M^2
$a_{\mathbf{red}}$	Activities (concentration) of reduced species	Mol/liter
$a_{\mathbf{oxid}}$	Activities (concentration) of oxidized species	Mol/liter
C_b	Bulk concentration	mole/m^3
C_s	Surface concentration	mole/m^3
D	Diffusion coefficient of reacting ion	m^2/s
d	Pipe diameter	m
E, E_i	Electrode potential	V
$E_{\mathbf{eq}}$	Equilibrium potential	V
E_g	Galvanic potential	V
E_{act}	Activation energy	J/mol
E^o	Standard electrode potential	V
F	Faradays constant (96487)	Coulomb/g.eq
f	Friction factor	
f_a,f_c	Anodic and cathodic area fraction	
gmd	Gram per square meter per day	
I_a^{system}	Total anodic current	µA
I_c^{system}	Total cathodic current	µA
i	Current density	µA/cm^2
$i_{\mathbf{a}}$, i_c	anodic and cathodic current density respectively	µA/cm^2
$i_{\mathbf{app}}$	Applied current density	µA/cm^2
$I_{\mathbf{Corr}}$	Total corrosion current	µA
I_L	Maximum rate of a possible reaction for a given system (limiting current density)	µA/cm^2
i_0	Exchange current density at concentration C_s	µA/cm^2
i	Anodic and cathodic current density	µA/cm^2
J	Flux of substance	Mol/m^2.sec
J_d	J-Factor for mass transfer	
k	Mass Transfer Coefficient	m/s
L	Distance between the pressure taps	m
mpy	Meter penetration per year	
n	Number of electrons transfer	
Nu	Nusselt number.	

Pr	Prandtl number	
P	Partial Pressure	atm
P_T	total pressure	KPa
q	Electric charge	Coulomb
R	Gas constant	8.314 J/mol.K
R_{sol}	The electrical resistance of solution	Ω cm
R_f	Resistance produced by film or coatings	Ω cm
Re	Reynolds number	
Sc	Schmidt number.	
T	Temperature	^oC or K
u	Velocity	m/s
u_{ave}	Average velocity	m/s
z	Number of electron	

Greek symbols

β_a, β_c	Anodic and cathodic Tafel slope	V/dec
α	Symmetry factor	
μ	Viscosity	Kg/m.sec
ν	Kinematic viscosity	m^2/s
ρ	Density	Kg/m^3
η	Overpotential	mV
η_a,η_c	Anodic and cathodic overpotential respectively	mV
η^c	Concentration polarization potential	mV
η^t	Total polarization	mV
η^A	Activation Polarization	mV
η^R	Resistance overpotential Polarization	mV
δ_m	Thickness of the diffusion layer	μm

CHAPTER ONE

INTRODUCTION

Corrosion is the deterioration of materials by chemical interaction with their environment. The term corrosion is sometimes also applied to the degradation of plastics, concrete and wood, but generally refers to metals.

The consequences of corrosion are many and varied and the effect of these on the safe, reliable and efficient operation of equipment or structures are often more serious than the simple loss of a mass of metal. Failures of various kinds and the need for expensive replacements may occur even though the amount of metal destroyed is quite small. Some of the major harmful effects of corrosion are [1] : reduction of metal thickness ,hazards or injuries to people arising from structural failure ,loss of time ,reduced value of goods ,contamination of fluids in vessels and pipes ,perforation of vessels and pipes .loss of technically important surface properties of a metallic component. mechanical damage to valves, pumps, etc,

Galvanic corrosion, often misnamed "electrolysis," is one common form of corrosion in marine environments. It occurs when two (or more) dissimilar metals are brought into electrical contact under corrosive environment. When a galvanic couple forms, one of the metals in the couple becomes the anode and corrodes faster than it would all by itself, while the other becomes the cathode and corrodes slower than it would alone. Either (or both) metal in the couple may or may not corrode by itself (themselves) in seawater. When contact with a dissimilar metal is made, however, the self-corrosion rates will change: corrosion of the anode will accelerate; corrosion of the cathode will decelerate or even stop. We can use the seawater Galvanic Series, which is a list of metals and alloys ranked in order of their tendency to corrode in marine environments. If any two metals from the list table 3-1 are coupled together, the one closer to the anodic (or active) end of the series, the upper end in this case, will be the anode and thus will corrode faster, while the one toward the cathodic (or noble) end will corrode slower.

The two major factors affecting the severity of galvanic corrosion are

1. The voltage difference between the two metals on the galvanic series

2. The size of the exposed area of cathodic metal relative to that of the anodic metal. Corrosion of the anodic metal is more rapid and more damaging as the voltage difference increases and as the cathode area increases relative to the anode area.

Corrosion as an action with its different types causes a disastrous economical losses for many countries beyond their ability to immune themselves with the right vaccine against this cancer called "corrosion". This is clear from the annual cost of corrosion and corrosion protection in the United States on the order of $ 300 billion [2], far more than the annual budgets of some small countries. Yet corrosion engineering and science are no longer an empirical art; dissecting a large corrosion problem into its basic mechanisms allows the use of quite sophisticated electrochemical techniques to accomplish satisfactory results. On that positive side, there is real satisfaction and economic gain in designing a component that can resist punishing service conditions under which other parts fail. In some cases, no one can completely prevent corrosion, but can try to avoid obsolescence of the component due to corrosion.

This work aims to perform theoretical study to investigate the influence of area fraction, temperature, pH, Reynolds number and pressure on the corrosion rate for single metal and galvanic corrosion rate for binary galvanic system under activation control (acidic medium) and mass transfer (diffusion) control (neutral medium).It is aimed also to investigate the effect of these parameters on the galvanic corrosion rate when the system is under activation complicated with mass transfer effects.

CHAPTER TWO

CORROSION

2.1 Definitions of Corrosion

The term corrosion [3] invariably refers to deterioration from chemical causes, but a similar concept is not necessarily applicable to metals. Many authorities' consider that the term metallic corrosion embraces all interactions of a metal or alloy (solid or liquid) with its environment, irrespective of whether this is deliberate and beneficial or adventitious and deleterious. Thus this definition of corrosion, which for convenience will be referred to as the transformation definition, will include, for example, the deliberate anodic dissolution of zinc in cathodic protection and electroplating as well as the spontaneous gradual wastage of zinc rooting sheet resulting from atmospheric exposure. On the other hand, corrosion has been defined as the undesirable deterioration of a metal or alloy, i.e. an interaction of the metal with its environment that adversely affects those properties of the metal that are to be preserved. This definition which will be referred to as the deterioration definition is also applicable to non-metallic materials such as glass, etc. and embodies the concept that corrosion is always deleterious.

2.2 Factors Influence Corrosion

2.2.1 Solution pH [2]:

The relationship between pH and corrosion rates tends to follow one of three general patterns***:***

1. Acid-soluble metals such as iron have a relationship as shown in Fig. 2.1. In the middle pH range (≈ 4 to 10), the corrosion rate is controlled by the rate of transport of oxidizer (usually dissolved O_2) to the metal surface. At very high temperature such as those encountered in boilers, the corrosion rate increases with increasing basicity as shown by the dashed line.

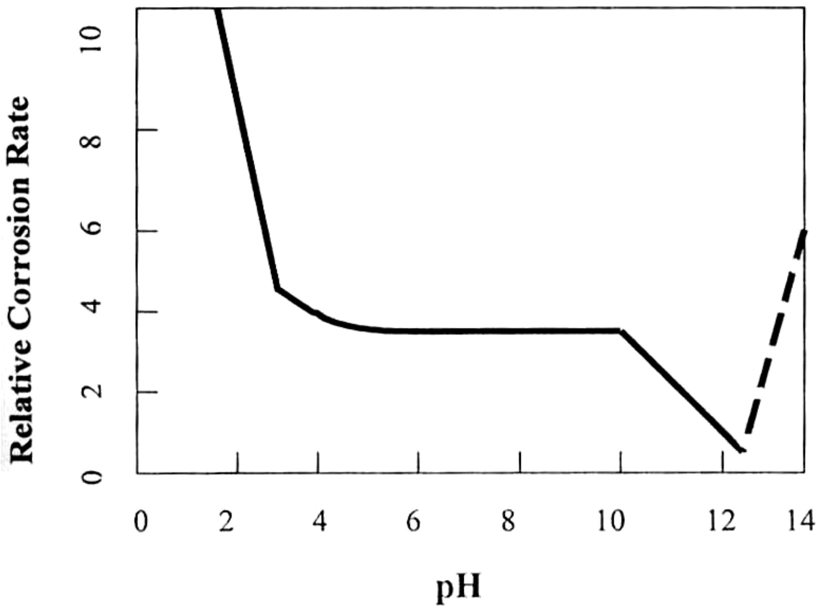


Figure 2.1: Effect of pH on Corrosion Rate of Iron [2]

2. Amphoteric metals such as aluminum and zinc have a relationship as shown in Fig.2.2. These metals dissolve rapidly in either acidic or basic solutions.

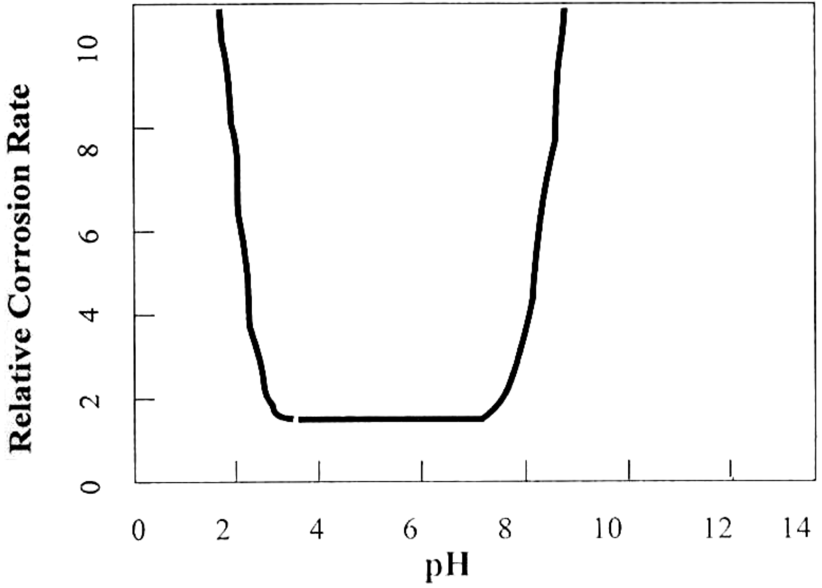


Figure 2.2: Effect of pH on the Corrosion Rate of Amphoteric Metals (Aluminum and Zinc) [2]

3. Noble metals such as gold and platinum are not appreciably affected by pH as shown in Fig.2.3.

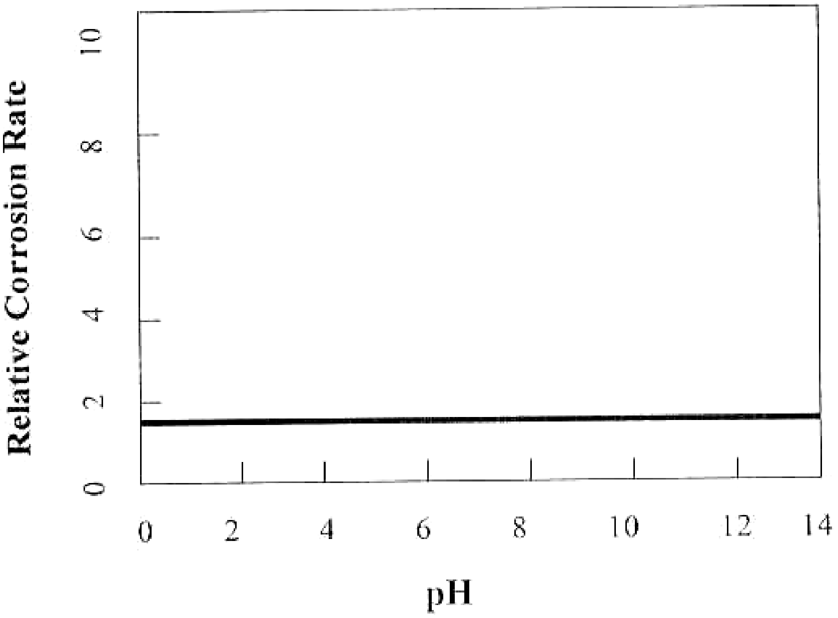


Figure 2.3: Effect of pH on the Corrosion Rate of Noble Metals [2]

2.2.2 Oxidizing agents

In some corrosion processes [2], such as the dissolution of zinc in hydrochloric acid, hydrogen may evolve as a gas. In others such as the relatively slow dissolution of copper in sodium chloride, the removal of hydrogen, which must occur so that corrosion may proceed, is effected by a reaction between hydrogen ion and some oxidizing chemical such as oxygen to form water. Because of the high rates of corrosion that usually accompany hydrogen evolution, metals are rarely used in solution from which they evolve hydrogen at an appreciable rate. Most of the corrosion observed in practice occurs under conditions in which the oxidation of hydrogen to form water is a necessary part of the corrosion process. For this reason, oxidizing agents are often powerful accelerators of corrosion and in many cases the oxidizing power of a solution is most important property in so far as corrosion is concerned.

$$4H^{+} + O^{2} + 4e^{-} \longrightarrow 2H_2O$$

Oxidizing agents that accelerate the corrosion of some materials may also retard corrosion of other through the formation on their surface of oxides or layers of adsorbed oxygen which make them more resistant to chemical attack. This property of chromium is responsible for the principal corrosion-resisting characteristics of the stainless steels. It follows then, oxidizing substances, such as dissolved air, may accelerate the corrosion of one class of materials and retard the corrosion of another class. In the latter case, the behavior of the material usually represents a balance between the power of oxidizing compounds to preserve a protective film and their tendency to accelerate corrosion when the agencies responsible for protective-film breakdown are able to destroy the films.

2.2.3 Temperature

As a general rule [4], increasing temperature increases corrosion rates. This is due to a combination of factors- first, the common effect of temperature on the reaction kinetics themselves and the higher diffusion rate of many corrosive by-products at increased temperatures. This latter action delivers these by-products to the surface more efficiently. Occasionally, the corrosion rates in a system will decrease with increasing temperature. This can occur because of certain solubility considerations. Many gases have lower solubility in open systems at higher temperatures. As temperatures increase, the resulting decrease in solubility of the gas causes corrosion rates to go down.

2.2.4 Fluid velocity

Velocity primarily affects corrosion rate through its influence on diffusion phenomena. It has no effect on activation controlled processes. The manner in which velocity affects the limiting diffusion current is a marked function of the physical geometry of the system. In addition the diffusion process is affected differently by velocity when the flow conditions are laminar as compared to a situation where turbulence exists. For most conditions the limiting diffusion current can be expressed by the equation:

$$i_L = k\, u^n \qquad \ldots(2\text{-}1)$$

where k is a constant, u is the velocity of the environment relative to the surface and n is a constant for a particular system. Values of n vary from 0.2 to 1[5]. Fig.2.4 shows the effect of velocity on the limiting current density.

The effect of velocity on corrosion rate, like the effect of oxidizer addition, complex and depends on the characteristics of the metal and the environment to which it is exposed. Fig.2.5 shows the typical observations when agitation or solution velocity is increased [7].

For corrosion processes which are controlled by activation polarization, agitation and velocity have no effect on the corrosion rate as illustrated in curve B. If corrosion process is under cathodic control, then agitation or velocity increases the corrosion rate as shown in curve A, section 1. This effect generally occurs when an oxidizer present in very small amounts as in the case of dissolved oxygen in acids or water. If the process is under diffusion control and the metal is readily passivated, then the behavior corresponding to curve A, section 1 and 2, will be observed, curve C show that the passive metals at high velocity the passive film is remove [7].

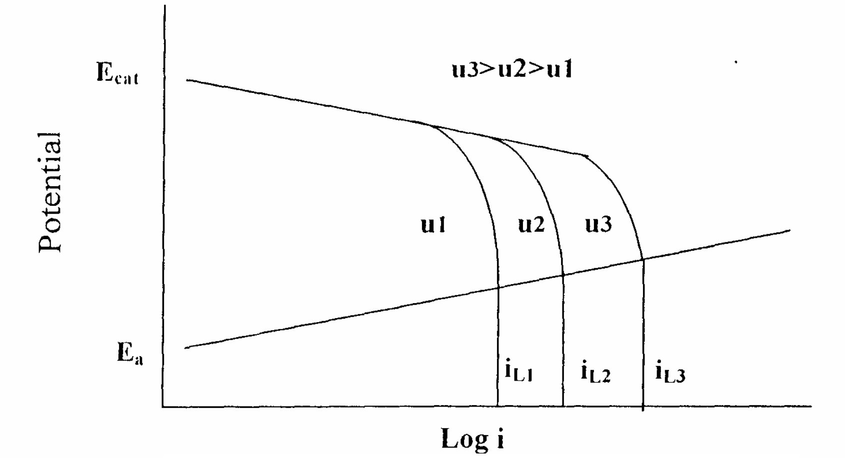


Figure 2.4: Effect of velocity on I_L.[6]

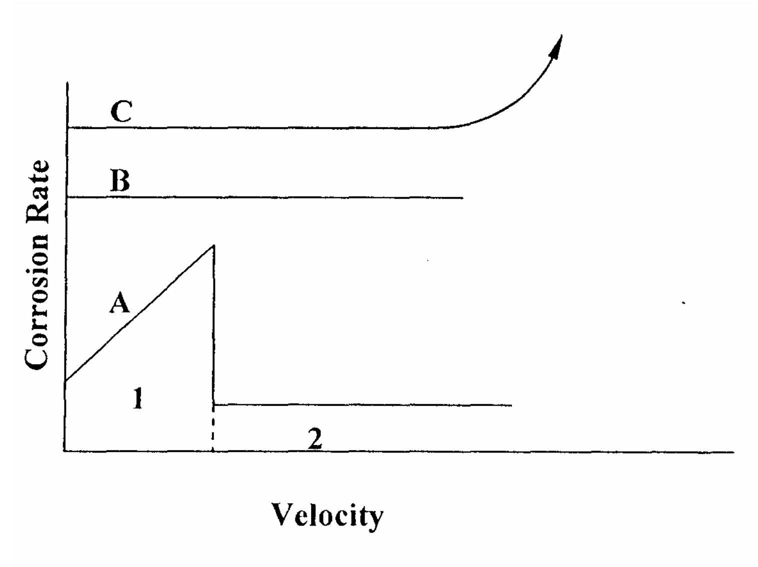


Figure 2.5: Effect of Velocity on the Corrosion Rate. [7]

2.2.5 Suspended Solids

An increase in suspended solids levels will accelerate corrosion rates. These solids include any inorganic or organic contaminants present in the fluid. Examples of these contaminants include clay, sand, silt or biomass [4].

2.3 Forms of Corrosion

Almost all corrosion problems and failures encountered in service can be associated with one or more of the eight basic forms of corrosion: general corrosion, galvanic corrosion, concentration-cell (crevice) corrosion, pitting corrosion, intergranular corrosion, stress corrosion cracking, dealloying, and erosion corrosion [8].

2.4 Polarization

When the metal is not in equilibrium with a solution of its ions, the electrode potential differs from the equilibrium potential by an amount known as the polarization. Other terms having equivalent meaning are overvoltage and overpotential. The symbol commonly used is η. Polarization [9] is an extremely important parameter because it allows useful statements to be made about the rates of corrosion process. In practical situations, polarization sometimes defined as the potential change away from some other arbitrary potential and in mixed potential experiments, this is the free corrosion potential [10,11,12].The change in the electrode potential from equilibrium potential depends on the magnitude of the external current and its direction. The direction of potential change always opposes the shift from equilibrium and hence opposes the flow of current or is of galvanic origin. for example, the anode always becomes more cathodic in potential and the cathode becomes more anodic, the difference of potential becoming smaller.

2.4.1 Activation Polarization η_A

The most important example is that of hydrogen ion reduction at a cathode [7]:

$$2H^+ \longrightarrow H_2 + 2e^- \qquad \ldots(2.1)$$

The corresponding polarization term being called hydrogen overvoltage.

$$2H^+ \longrightarrow 2H_{ads} + 2e^- \qquad \ldots(2.2)$$

where (H_{ads}) represents hydrogen atoms adsorbed on the metal surface. This relatively rapid reaction is followed by a combination of adsorbed hydrogen atoms to form hydrogen molecules and bubbles of gaseous hydrogen [13].

$$2H_{ads} \longrightarrow H_2 \qquad \ldots(2.3)$$

This reaction is relatively slow, and its rate determines the value of hydrogen overvoltage on platinum. The controlling slow step of H^+ discharge is not always the same but varies with metal current density and environment.

Pronounced activation polarization also occurs with discharge of OH^- at an anode accompanied by oxygen evolution:

$$4OH^- \longrightarrow O_2 + 2H_2O + 4e^- \qquad \ldots(2.4)$$

This is known as oxygen overvoltage. The activation polarization η_A of any kind increases with anodic and cathodic current density accord according to Tafel equation [7]:

$$\eta_A = \frac{2.303RT}{\alpha F}\log\left(\frac{i_a}{i_o}\right) \quad \text{For anodic reaction} \qquad \ldots(2.5)$$

$$\eta_c = \frac{2.303RT}{\alpha F}\log\left(\frac{i_c}{i_o}\right) \quad \text{For cathodic reaction} \qquad \ldots(2.6)$$

These equations may be simplified to:

$$\eta_A = \beta_A \log\left(\frac{i_a}{i_o}\right) \qquad \ldots(2.7)$$

$$\eta_C = -\beta_C \log\left(\frac{i_c}{i_o}\right) \qquad \ldots(2.8)$$

where β_A , β_c & i_o are constants of a given metal and environment and are dependent on temperature. The exchange current density i_o represents the current density equivalent to the equal forward and reverse reactions at the electrode at equilibrium. The larger the value of i_o and the smaller the value of β_A & β_c, the smaller is the corresponding overvoltage.

Activation polarization refers to electrochemical reactions which are controlled by a slow step in the reaction sequence. The species must first be adsorbed or attached to the surface before the reaction can proceed according to step1. Following this, electron transfer (step2) must occur, resulting in a reduction of the species. As shown in step3, two hydrogen atoms then combine to form a bubble of hydrogen gas (step4) as shown in Fig.2.6. The speed of reduction of the hydrogen ions will be controlled by the slowest of these steps [7].

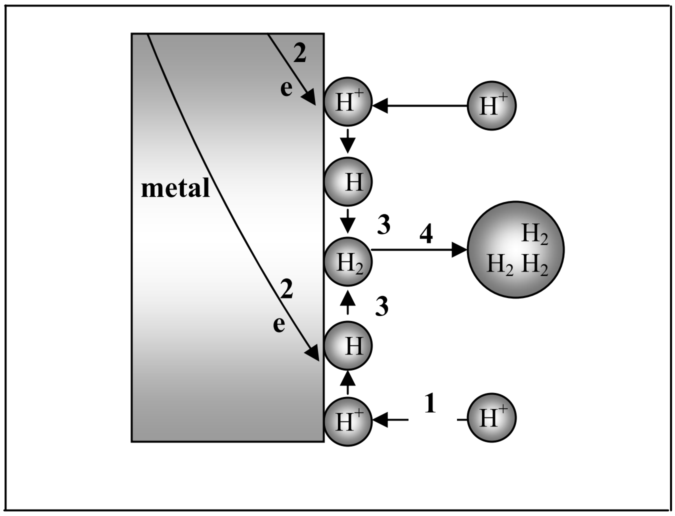


Figure 2.6: Hydrogen-Reduction Reaction Under Activation Control (Simplified)[7]

2.4.2 Concentration Polarization η_C

Concentration polarization refers to electrochemical reactions which are controlled by the diffusion in the electrolyte. It is the slowing down of a reaction due to an insufficiency of the desired species or an excess of the unwanted species at the electrode. This type of polarization occurs at the cathode when reaction rate or the cathode current is so large that the substance being reduced cannot reach the cathode at a sufficiently rapid rate. Since the rate of reaction is determined by the slowest step, the diffusion rate will be the rate determining step. At very high reduction rates, the region adjacent to the electrode surface will become depleted of ions. If the reduction rate is increased further, a limiting rate will be reached which is determined by the diffusion rate of ions to the electrode surface. This limiting rate is the limiting diffusion current density i_L. It represents the maximum rate of reduction possible for a given system; the expressing of this parameter is [7, 14]:

$$i_l = \frac{DzFC_B}{\delta} \qquad \ldots(2.9)$$

where i_L is the limiting diffusion current density, D is the diffusion coefficient of the reacting ions, C_B is the concentration of the reacting ions in the bulk solution, and δ is the thickness of the diffusion layer.

By combining the laws governing diffusion with Nernest equation [7]:

$$\boldsymbol{E = E_o + 2.3\frac{RT}{nF}\log\frac{a_{oxid}}{a_{red}}} \quad \ldots(2.10)$$

the following expression can be developed [7,14]:

$$E_i - E_{eq} = \eta_c = \frac{2.303RT}{nF}\log\left(1-\frac{i}{i_l}\right) \quad \ldots(2.11)$$

This equation is shown in Fig.2.7. For the case of hydrogen evolution any change in the system which increases the diffusion rate will decrease the effects of concentration polarization and hence increases reaction rate. Thus, increasing the velocity or agitation of the corrosive medium will increase rate only if the cathodic process is controlled by concentration polarization [7] Fig.2.8.

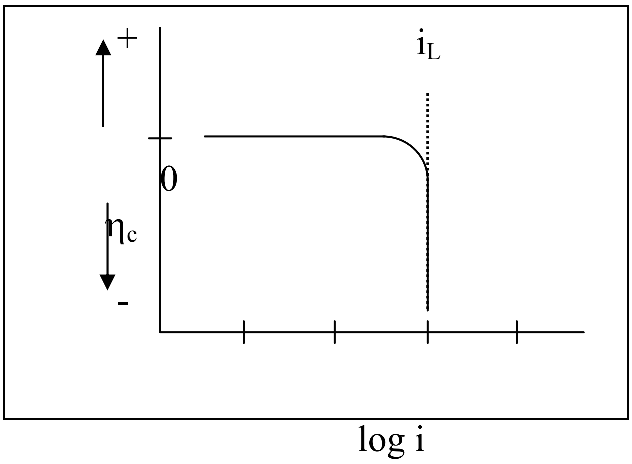


Figure 2.7:Concentration Polarization Curve (Reduction Process)[7].

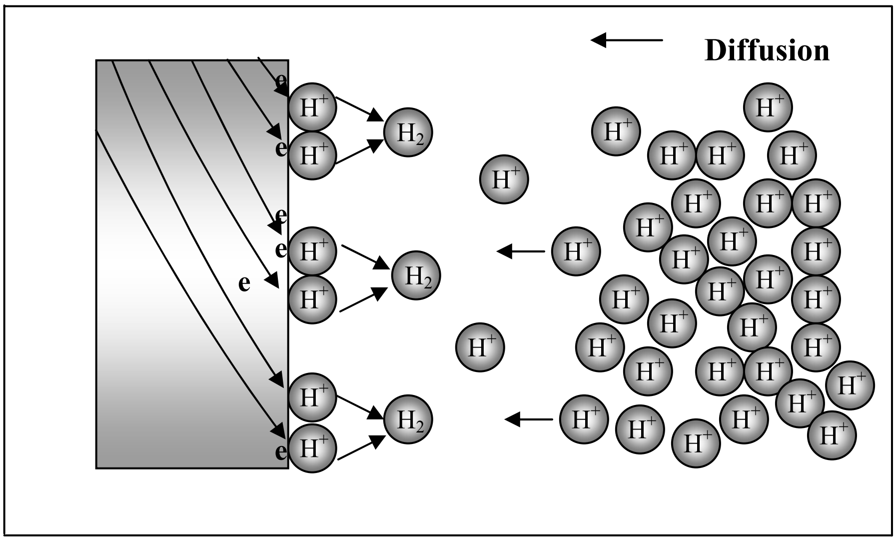


Figure 2.8: Concentration Polarization During Hydrogen Reduction [7].

2.4.3 Combined Polarization

Both activation and concentration polarization usually occur at an electrode. At low reaction rates activation polarization usually controls, while at higher reaction rates concentration polarization becomes controlling. The total polarization of an electrode is the sum of the contribution of activation polarization and concentration polarization [7, 9]:

$$\eta_t = \eta_A + \eta_C \qquad \ldots(2.12)$$

During reduction process such as hydrogen evolution or oxygen reduction, concentration polarization is important as the reduction rate approaches the limiting diffusion current density. The overall reaction for activation process is given by [7, 9]:

$$\eta_{red} = -\beta_c \log\frac{i}{i_o} + \frac{2.303RT}{nF}\log\left(1-\frac{i}{i_l}\right) \qquad \ldots(2.13)$$

This case is shown in Fig.2.9.

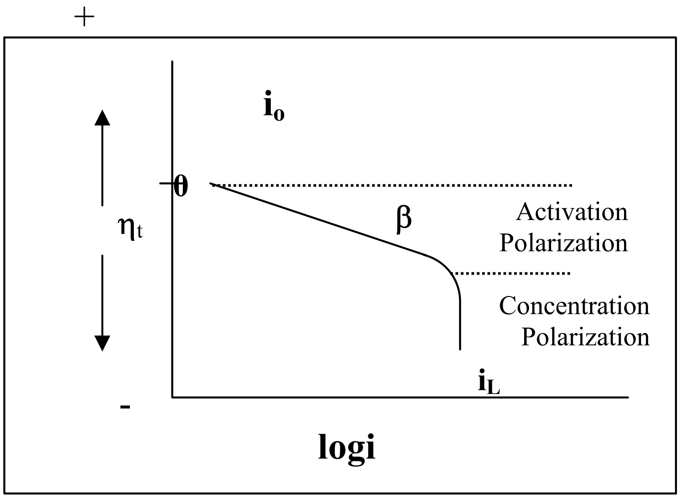


Figure 2.9: Combined Polarization Curve [7].

2.2.4 Resistance Polarization

In corrosion the resistance of the metallic path for charge transfer is negligible. Resistance overpotential η_R is determined by factors associated with the solution or with the metal surface. Resistance polarization η_R is only important at higher current densities or in higher resistance solution. It may be defined as [7, 9, 14]:

$$\eta_R = I(R_{solution} + R_f) \quad \ldots(2.14)$$

where $R_{slutionn}$ is the electrical resistance of solution, which is dependent on the electrical resistivity (Ω cm) of the solution and the geometry of the corroding system, and R_f is the resistance produced by films or coatings formed on the surface of the sites, which block contact between the metal and the solution, and increase the resistance overpotential.

The total polarization at a metal electrode then becomes as the algebraic sum of the three types described above [7, 9, 14].

$$\eta = \eta_A + \eta_C + \eta_R \quad \ldots(2.15)$$

CHAPTER THREE

GALVANIC CORROSION

3.1 Introduction

When two different metals are in a corrosive environment, they corrode at different rates, according to their specific corrosion resistances to that environment, however, if the two metals are in contact, the more corrosion prone (metal 1) corrodes faster and the less corrosion prone (metal 2 the more noble one) corrodes slower than originally, i.e. when no contact existed. The accelerated damage to the less resistant metal is called galvanic corrosion, and is heavily dependent on the relative surface areas of the metals. In galvanic corrosion, the added anodic currents (on metals 1 and 2) equal the added cathodic currents (on metals 1 and 2) [28], so that

$$I_{a.1}+I_{a.2}=|I_{c.1}|+|I_{c.2}| \qquad \ldots(3.1)$$

or .in terms of current densities and areas

$$i_{a.1}A_1+i_{a.2}A_2=|i_{c.1}A_1|+|i_{c.2}A_2| \qquad \ldots(3.2)$$

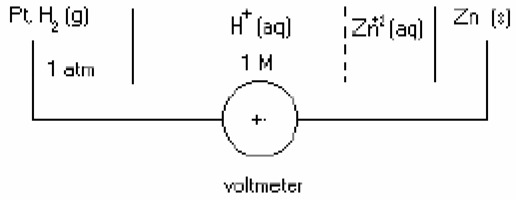
If $I_{a.1} >> I_{a.2}$

This equation is reduced to

$$i_{a.1}A_1=|i_{c.1}A_1|+|i_{c.2}A_2| \qquad \ldots(3.3)$$

3.2 Galvanic Corrosion Theory

Metals, when immersed in a polar solvent (e.g. water in which the molecules have a non-uniform distribution of electrical charge) have a tendency to dissolve in the form of ions. This “tendency to dissolve” is quantified by the standard electrode potential, E_0, which is measured using the standard hydrogen electrode as the reference or datum level. The word “standard” implies that the measurement was made with the pure metal immersed in a 1 M aqueous solution of its ions relative to the hydrogen electrode using pure hydrogen gas at 1 atm pressure bubbled over platinum metal immersed in a 1 M solution of H+ ions. The electrochemical cell which is implied by the above is written for Zn as [29]:



Some typical values are, at a temperature of 25 °C:

Zn^{+2} (aq) $\longrightarrow$ $2e^-$ (Zn) + Zn(s), E^o= -0.76V …(3.4)

Fe^{2+} (aq) $\longrightarrow$ $2e^-$ (Zn) +Fe(s), E^o= -0.440V …(3.5)

Cu^{2+} (aq) $\longrightarrow$ $2e^-$ (Zn) +Cu(s), E^o= 0.340V …(3.6)

Note that the metal (e.g. Zn in the cell written above) is connected to the positive terminal of the voltmeter. In this case the voltmeter will indicate a negative reading. If two different metals, (e.g. Zn and Cu), are immersed in water (natural water contains dissolved salts and oxygen) a potential difference will develop. This can be measured with a voltmeter. Generally this will not be the same as the difference of the standard potentials of the respective metals as the solution is non-standard. However the polarity is generally in agreement with that predicted from the standard electrode potentials. Zinc will be found to be negative relative to the Cu. The reaction:

Zn(s) $\longrightarrow$ Zn^{+2} (aq) + $2e^-$ (Zn) …(3.7)

is generating a greater concentration of electrons on the Zn than the reaction:

Cu(s) $\longrightarrow$ Cu^{2+} (aq) +$2e^-$ (Cu) …(3.8)

is on the copper.

Connection of the Cu and Zn by a wire will permit electrons from Zn to flow to the Cu. Hence eq. (3.7) will proceed to the right and Zn metal will form Zn^{+2} ions in the aqueous solution. This process is called corrosion. In general, any process that causes the metal to form ions in solution or an ionic compound of the metal is termed corrosion. It should be noted that when the metal corrodes gives up electrons.

The electrons arriving at the copper will cause eq. (3.8) to be driven to the left provided Cu^{2+} ions are present in the solution. If Cu^{2+} ions are not present, the electrons will be consumed by reaction with H^+ ions:

$$2H^+ + 2e^- \longrightarrow 2H \longrightarrow H_2\,(g) \qquad \ldots(3.9)$$

or by reaction with dissolved oxygen:

$$\tfrac{1}{2}\,O_2\,(aq) + H_2O + 2e^-\,(Cu) \longrightarrow OH^-\,(aq) \qquad \ldots(3.10)$$

The overall reaction is given by the sum of eq. (3.7) and (3.9) or (3.7) and (3.10)

$$Zn(s) + 1/2\;O_2 + H_2O \longrightarrow Zn^{+2}\,(aq) + 2OH^-\,(aq) \qquad \ldots(3.11)$$

As the zinc corrodes, a flow of electrons (a current) proceeds from the Zn (defined as an anodic current) to the Cu (defined as a cathodic current). Eq. (3.7), the anodic reaction, proceeds at the zinc surface. Eq. (3.9) and/or (3.10), the cathodic reactions, proceed at the copper surface. Notice that both these cathodic reactions consume a dissolved component (H^+ or O_2 eq.). The reaction cannot continue at a rate which exceeds the rate at which this component can reach the cathode surface. Galvanic corrosion [30] results from two different metals being in contact in the environment. Examples would be brass plumbing fitting on a cast iron pipe. In this case several reactions are possible, but in general the corrosion rate of the most anodic or active metal is increased and the corrosion rate of the more cathodic metal is decreased. This is shown in figures 3.1, 3.2 and 3.3. The first figure shows the corrosion rate for a single metal in solution.

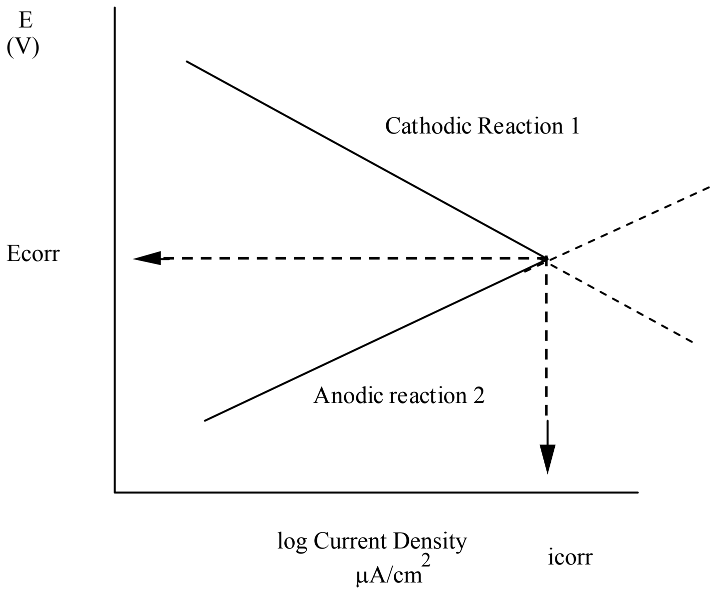


Figure 3.1: Corrosion Rate Determination for a Two Electrode Process System[30]

Figs. 3.2 & 3.3 shows the rate determination when a third electrode process is added at a potential between the first two electrode reactions. The rule is that must be applied is that the total oxidation rate must equal the total reduction rate. In figures 3.2 and 3.3 the dashed lines represent the total rates.

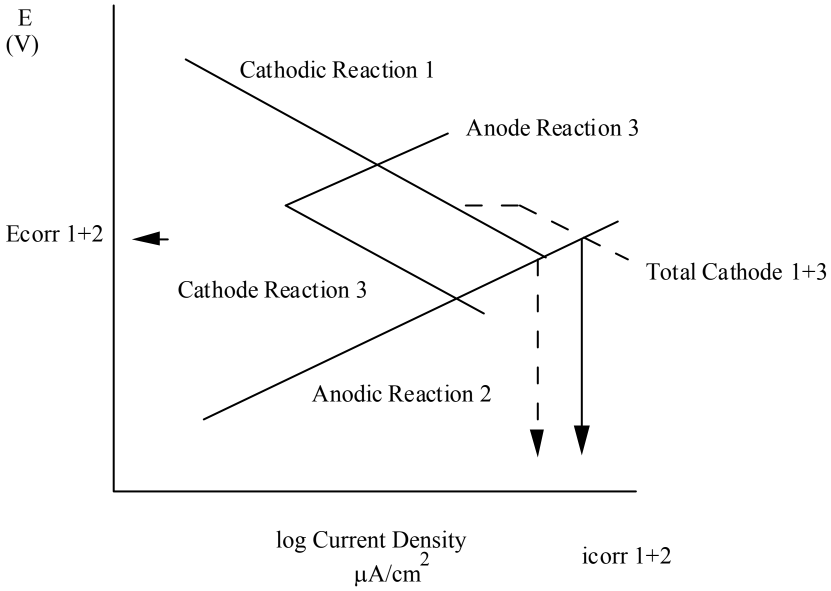


***Figure 3.2: Corrosion Rate Determination for a Three Electrode System*.**[30]

The corrosion rate for electrode 2 has increased from i_{corr} to i_{corr} 1+2 as it is the only anodic reaction. Two cases are shown; figure 3.2, when the corrosion potential for three electrodes is above the two electrode potential and figure 3.3, when the three electrode corrosion potential is below the two electrodes potential. In figure 3.2 the resulting corrosion potential is more negative than the third electrode reverse potential. As such it can only contribute to the cathodic reaction rate. The third electrode is therefore protected from corrosion. The second electrode dissolution rate increased significantly by the introduction of the third electrode processes.

In figure 3.3, the resulting corrosion potential from the three electrodes is more negative than the double electrode potential. In this case both the second and third electrodes are corroding, but the third electrode is at a lower rate than if the second electrode was not present.

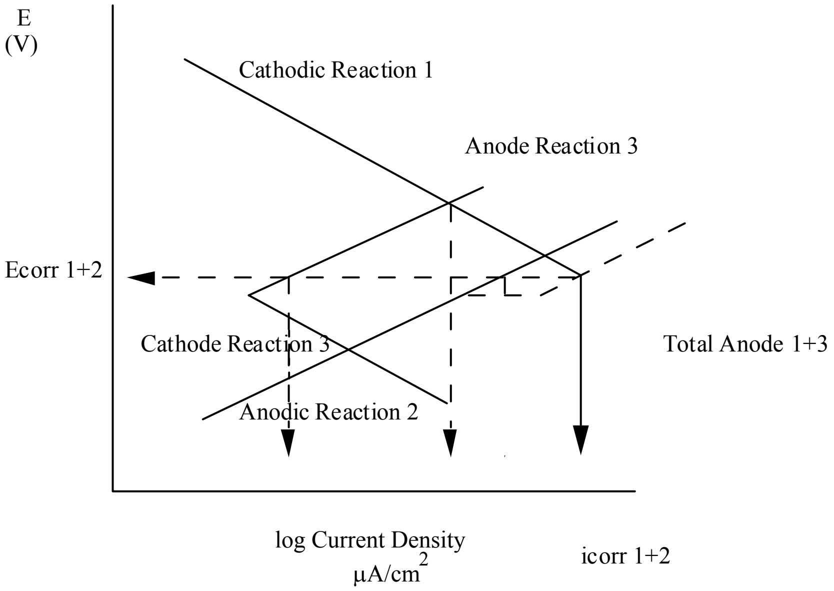


Figure 3.3: The introduction of a Less Noble Metal Will Decrease the Corrosion Rate of the More Noble Metal.[30]

Both these figures show that introducing a more anodic metal will decrease the corrosion rate in a more noble metal. This is the process behind galvanic corrosion. It can also be used for protection by galvanizing.

3.3 Oxidation-Reduction Potentials

Table 3.1 is listing some useful oxidation-reduction potentials. These values represent the thermodynamic tendency for the indicated reaction to occur on a relative basis. All potential values are compared to an arbitrary value of 0.00 volts which is assigned to the hydrogen oxidation reaction. The more negative a value, the more likely the reaction will proceed in the direction shown in the Table. Thus we see that zinc oxidation. [31]

$$Zn \rightarrow Zn^{+2} + 2e^{-},\quad E = -0.763 \text{ volts} \qquad \ldots(3.12)$$

is more likely to occur than iron oxidation

$$Fe \rightarrow Fe^{+2} + 2e^{-},\quad E = -0.44 \text{ volts} \qquad \ldots(3.13)$$

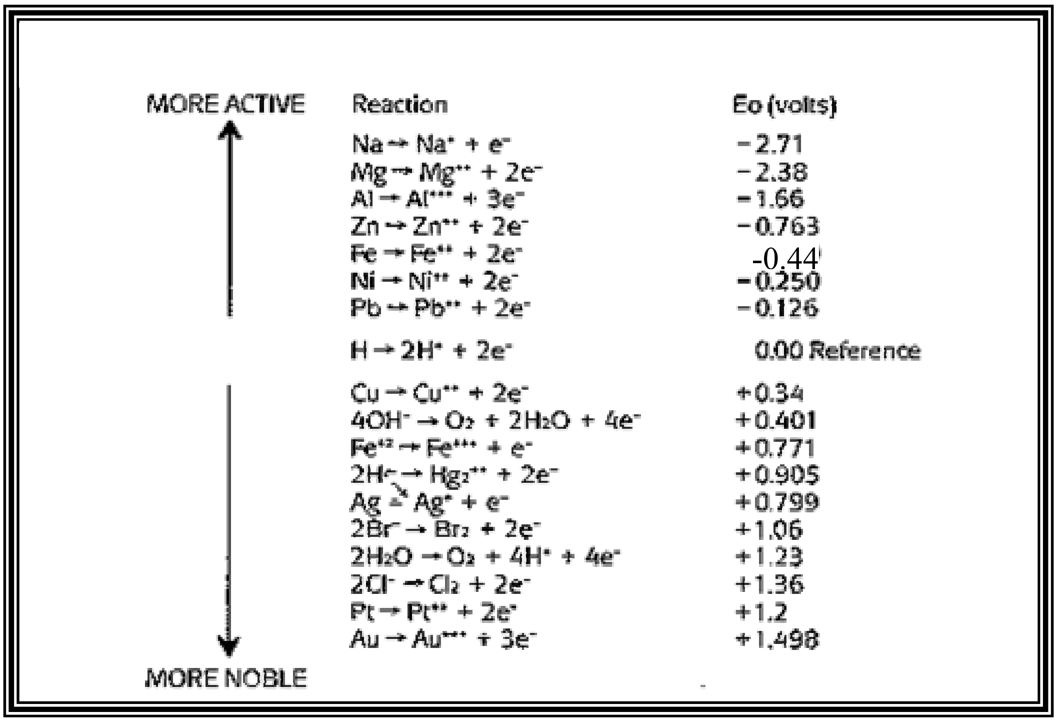
which, in turn, is more likely than hydrogen oxidation

$$H2 \rightarrow 2H^{+} + 2e^{-},\ E = 0.00 \text{ volts} \qquad \ldots(3.14)$$

Some other generalizations drawn from the standard oxidation reduction potential table are:

1. Oxygen is a stronger oxidizing agent than hydrogen ion.
2. Iron is more reactive than lead, copper or silver.
3. Gold is very uncreative.

Table 3.1: Standard Oxidation – Reduction Potential at 25 °C [31]

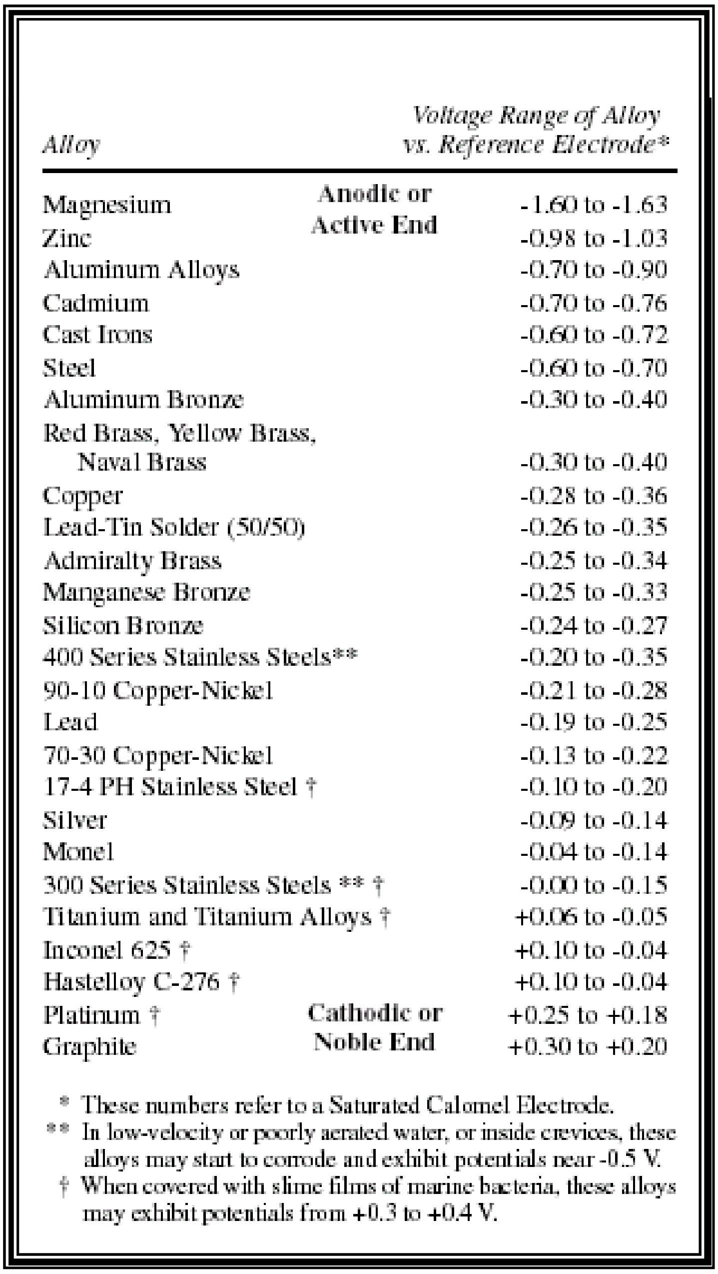


MORE ACTIVE	Reaction	Eo (volts)
	$Na \rightarrow Na^+ + e^-$	−2.71
	$Mg \rightarrow Mg^{++} + 2e^-$	−2.38
	$Al \rightarrow Al^{+++} + 3e^-$	−1.66
	$Zn \rightarrow Zn^{++} + 2e^-$	−0.763
	$Fe \rightarrow Fe^{++} + 2e^-$	-0.44
	$Ni \rightarrow Ni^{++} + 2e^-$	−0.250
	$Pb \rightarrow Pb^{++} + 2e^-$	−0.126
	$H \rightarrow 2H^+ + 2e^-$	0.00 Reference
	$Cu \rightarrow Cu^{++} + 2e^-$	+0.34
	$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$	+0.401
	$Fe^{+2} \rightarrow Fe^{+++} + e^-$	+0.771
	$2H^- \rightarrow Hg_2^{++} + 2e^-$	+0.905
	$Ag \rightleftharpoons Ag^+ + e^-$	+0.799
	$2Br^- \rightarrow Br_2 + 2e^-$	+1.06
	$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$	+1.23
	$2Cl^- \rightarrow Cl_2 + 2e^-$	+1.36
	$Pt \rightarrow Pt^{++} + 2e^-$	+1.2
	$Au \rightarrow Au^{+++} + 3e^-$	+1.498
MORE NOBLE		

3.4 Galvanic Series

Table 3.2 is a simple version of the galvanic series of alloys in seawater. Because electrode (oxidation/reduction) potentials only apply to pure elements and true compounds, another system was developed compares-ion. If a pair of alloys listed in the series are coupled, the alloy higher in the list will be corroded more rapidly than if it were uncoupled, and the alloy lower in the series will be protected, or corrode more slowly than if it were uncoupled. The table shows why alloys of aluminum and magnesium are galvanically coupled to steel to protect the steel. Coupling steel to copper, brass or stainless steel accelerates the corrosion of steel.[32]

Table 3.2: Galvanic Series in Flowing Seawater [32]



Alloy		*Voltage Range of Alloy vs. Reference Electrode**
Magnesium	**Anodic or Active End**	-1.60 to -1.63
Zinc		-0.98 to -1.03
Aluminum Alloys		-0.70 to -0.90
Cadmium		-0.70 to -0.76
Cast Irons		-0.60 to -0.72
Steel		-0.60 to -0.70
Aluminum Bronze		-0.30 to -0.40
Red Brass, Yellow Brass, Naval Brass		-0.30 to -0.40
Copper		-0.28 to -0.36
Lead-Tin Solder (50/50)		-0.26 to -0.35
Admiralty Brass		-0.25 to -0.34
Manganese Bronze		-0.25 to -0.33
Silicon Bronze		-0.24 to -0.27
400 Series Stainless Steels**		-0.20 to -0.35
90-10 Copper-Nickel		-0.21 to -0.28
Lead		-0.19 to -0.25
70-30 Copper-Nickel		-0.13 to -0.22
17-4 PH Stainless Steel †		-0.10 to -0.20
Silver		-0.09 to -0.14
Monel		-0.04 to -0.14
300 Series Stainless Steels ** †		-0.00 to -0.15
Titanium and Titanium Alloys †		+0.06 to -0.05
Inconel 625 †		+0.10 to -0.04
Hastelloy C-276 †		+0.10 to -0.04
Platinum †	**Cathodic or Noble End**	+0.25 to +0.18
Graphite		+0.30 to +0.20

* These numbers refer to a Saturated Calomel Electrode.

** In low-velocity or poorly aerated water, or inside crevices, these alloys may start to corrode and exhibit potentials near -0.5 V.

† When covered with slime films of marine bacteria, these alloys may exhibit potentials from +0.3 to +0.4 V.

3.5 Factors Affecting Galvanic Corrosion [33]

1. *Electrode Potentials:*

The standard electrode potential of a metal in a solution of its ions gives a rough guide to the position of that metal in a galvanic series. In practice however usually concerned with alloys rather than pure metals, and in environments that do not contain the metal ions. To check the best method of obtaining a "galvanic series" of potentials is to actually measure these potentials in the environment under considerations.

2. *Reaction Kinetics:*

Electrode potential data will indicate whether or not galvanic corrosion can occur. The reaction kinetic data indicate how quickly corrosion can take place. The metal dissolution kinetics give information on the rate of the anodic reaction in the corrosion cell; the oxygen reduction or hydrogen evolution overpotential on the metals or alloys involved, or both, give information on the rate of cathodic reactions and whether they will occur on one or both materials.

3. *Area Ratio:*

One of the most important parameters in galvanic corrosion is the "area ratio" a high cathode to anode ratio usually resulting in rapid corrosion or high anode to cathode ratio giving low or no corrosion. Distribution of the area is obviously important as is surface shape and condition. The number of galvanic cells in a given system is also important,

4. *Mass Transport:*

Depending on the particular system being considered, one, two, or all of the three forms of mass transport, migration, diffusion, and convective can play an important role in galvanic corrosion.

5. *Bulk Solution Environment:*

Included in this group of factors are the solution temperature, volume, height above the couple, and the flow rate across the surface. All these can affect whether or not galvanic corrosion will occur to any great extent.

6. Bulk Solution Properties:

This group of factors is one of the most important; the oxygen level، and pH. The corrosivity of the solution determines whether corrosion can occur, and the conductivity determines the geometric extent to which it can occur.

7. Alloy Composition:

The composition of an alloy affects galvanic corrosion by directly affecting the alloys corrosion resistance. In addition the constituents affect the corrosion potential and the kinetics of the cathodic processes involved; minor constituents can play an important role in this respect.

8. Protective Film Characteristics:

The characteristics of the protective film, which exists on most metals and alloys, are important in determining whether or not galvanic corrosion will occur and what form it will take, for example, general or localized, in a particular environment. In particular the potential dependence, pH dependence, and resistance to various solution constituents are important.

3.6 Literature Review on Galvanic Corrosion

Copson [34] studied the galvanic action between steel coupled to nickel in tap water, with 3 to 1 area ratio of Ni/ Fe and found that the galvanic corrosion of steel was appreciable. The addition of 300 ppm of sodium chromate to the water effectively made the steel more noble and inhibited corrosion.

Wranglen et al.[35] studied the difference between the galvanic corrosion rates of high and low carbon steel in acid solutions and concluded that the engineers should not depend only on the galvanic series in the selection of their materials of construction,

Tsujino et al.[36] studied the galvanic corrosion of steel coupled to noble metals (Pt, Cu, 304 stainless steel), in sodium chloride solution and found that the local currents on the steel depend on the area ratio of the steel to the cathodic metal and these currents are not related to the concentration of sodium chloride in neutral solutions.

Bardal et al.[37] predicted galvanic corrosion rates by means of numerical calculation and experimental models based on boundary element method.

Fangteng et al.[38] presented a theoretical approach for galvanic corrosion allowing for cathode dissolution, and found that the cathode of the couple is also corroded at the galvanic corrosion potential where the corrosion is controlled by the rate of oxygen diffusion to the electrode surfaces and the cathode dissolution in a galvanic system leads to a decrease in the galvanic current and it has been shown that the current density through the anode is independent of the area ratio of the electrodes, providing that the ratio of cathode to anode area is large and the free corrosion potential of the alloys are similar.

Pryor [39] investigated the galvanic corrosion of Al/steel couple in chloride containing solution and found that aluminum completely protects steel cathodically within the pH range 0-14, and the galvanic current and the corrosion rate of aluminum are at a minimum in the nearly neutral pH range.

Morris and Smyrl [40] found the Galvanic currents and potentials have been calculated on heterogeneous electrode surfaces comprised of random configurations of coplanar anodes and cathodes, for the purpose of investigating system behavior on different electrode geometries. The electrochemical transport equations were solved in the absence of mass-transfer effects with a three-dimensional application of the finite element method. The galvanic currents and potentials so calculated were investigated for similarities linking behavior on different electrode geometries. It has been found that for a wide range of system parameters galvanic currents scale with the active perimeter separating anodic and cathodic regions on the electrode surface. Moreover, this effect enables the accurate prediction of galvanic current for an arbitrarily complex electrode surface geometry.

Lee , Kang and Shin [41] In the present study, the corrosion behavior of an as-cast magnesium alloy was studied focusing on the galvanic corrosion between a precipitate and Mg-rich matrix. Through immersion and electrochemical tests, the variation of the corrosion behavior with the alloy composition and alloy system was discussed in detail. The corrosion rate of an as-cast alloy increased abruptly to 9 wt.% Al in both alloys, but in the composition range of >12 wt.% Al, the corrosion rate reveals a different tendency than the alloy system. The beta -phase that is a typical precipitate in an Mg-xAl alloy is a more potent cathodic phase than is the ternary precipitate in a Mg-xAl-1Zn alloy. In the case of the Mg-zAl alloy, the formation of a galvanic cell between the precipitate and matrix promotes the preferred dissolution of the matrix, but the precipitate in the Mg-xAl-1Zn alloy has a minor effect on the corrosion behavior of the Mg-rich matrix. However, the corrosion rate of as-cast Mg-xAl and Mg-xAl-1Zn alloys which contain precipitate, depends mainly upon the corrosion behavior of the Mg-rich matrix, which is influenced by the Al content. It depends additionally upon the variation of the Anode-Cathode Area Ratio (ACAR) and the chunk breakage of precipitate during corrosion.

Chang, Beatty, Kane and Beck [42] stated that from an environmental perspective, tungsten is a more desirable material than depleted uranium (DU) for penetrate applications. However, the ballistic performance attained by current W alloys is inferior to DU. Recently, advanced tungsten-metal composites have been developed to improve their ballistic penetration, but the corrosion properties are unknown, and need to be determined. In this work, the galvanic corrosion behavior of tungsten coupled with several selected metals/alloys was investigated. Electrochemical potentiodynamic polarizations and galvanic couplings were employed. The testing was conducted in a 1 wt.% sodium sulfate solution. The selected metals/alloys were: pure tungsten, pure titanium, titanium 6Al-4V, hafnium, invar, pure iron and CDA 260 brass. The galvanic corrosion of these couples are examined and discussed based on the results from electrochemical tests and visual observations.

Jones and Paul [43] stated that many semi conducting minerals have sufficient conductivity to permit electrochemical reactions on their surfaces. Consequently, galvanic interactions will occur when such minerals are coupled to metals or other conducting minerals. Accelerated galvanic corrosion of metals coupled to noble minerals is quite likely, because most minerals exhibit potentials in solution which are noble to the corrosion potentials of metal alloys. Anodic and cathodic polarization diagrams can be used to predict the galvanic corrosion rates to be expected from any given galvanic couple in a particular corrosive electrolyte. Polarization diagrams in sulfuric acid for numerous minerals and alloys are presented, and some examples are extracted from the diagrams to demonstrate how the curves can be utilized to estimate the likelihood of galvanic corrosion and the reaction rates to be expected in metal-metal,

CHAPTER FOUR

THEORETICAL ASPECTS

4.1 Introduction

The increasing availability of electrochemical data for a number of material/environment systems of industrial interest enable chemical and materials engineers to predict corrosion potentials and corrosion rates using equations derived from electrochemical principles. In this chapter we obtain corrosion rates and corrosion potentials from equations [28]:

4.2 Activation Control

4.2.1 Equilibrium Potential

To determine the potential of a system, in which the reduced and oxidized species are not at unit activity, the familiar Nernest equation can be employed [7]:

$$E = E_0 - \frac{RT}{nF} \ln \frac{a_{red}}{a_{oxid}} \qquad \ldots(4.1)$$

or written as:

$$E = E_0 - \frac{2.303RT}{nF} \log \frac{a_{red}}{a_{oxid}} \qquad \ldots(4.2)$$

where E is the equilibrium half cell potential, E_0 the standard equilibrium half-cell potential, R is the gas constant (8.314 J/K .mol), T is absolute temperature (K), n is the number of electrons transferred, F in the faraday constant(96487 coulomb/equiv.), $\mathbf{a_{red}}$ and $\mathbf{a_{oxid}}$ are activities or (concentrations) of oxidized and reduced species.

Hydrogen ion activity is commonly expressed, for convenience, in terms of pH. This is defined as [9]:

$$pH = -\log (H^+) \qquad \ldots(4.3)$$

Hence, for the half-cell reaction $2H^+ + 2e \longrightarrow H_2$

$$E_{H2} = -.0592PH \qquad \ldots(4.4)$$

4.2.2 Tafel Equation

Tafel slopes (Tafel constants) are determined from the following equations [7]:

$$\beta_a = \frac{RT}{nF\ \alpha} \text{ (for anode reaction)} \qquad \ldots(4.5)$$

$$\beta_c = -\frac{RT}{(1-\alpha)nF} \text{ (for cathode reaction)} \qquad \ldots(4.6)$$

or using natural logarithm:

$$b_a = 2.303\frac{RT}{\alpha nF} \qquad \ldots(4.7)$$

$$b_c = -2.303\frac{RT}{(1-\alpha)nF} \qquad \ldots(4.8)$$

where α is the symmetry coefficient which describes the shape of the rate controlling energy barrier.

The relationship between reaction rate and overvoltage for activation polarization is :

$$\eta^A = \pm\beta\log\frac{i}{i_0} \qquad \ldots(4.9)$$

where η_a is overvoltage, β as before, and i is the rate of oxidation or reduction in terms of current density. This equation is called Tafel equation.

The reaction rate is given by the reaction current or current density, so the high field approximation gives [28]:

$$i_a = i_{0,a} e^{(E-E_{e,a}/\beta_a)} \qquad \ldots(4.10)$$

and:

$$|i_c| = -i_{0,c} e^{(E-E_{e,c}/\beta_c)} \qquad \ldots(4.11)$$

4.2.3 Exchange current density

The effect of temperature is to change the value of the exchange current density i_0 as follows [28]:

$$i_{0.T} = i_{0,298} \exp\left[\frac{E_{act}}{R}\left(\frac{1}{298}-\frac{1}{T}\right)\right] \qquad \ldots(4.12)$$

4.2.4. Corrosion Current

Anodic reaction rate is [28]:

$$I_a = i_{0,a} A_a \exp\left[\frac{\alpha_a n_a F}{RT}(E_a - E_{e,a})\right] \qquad \ldots(4.13)$$

$$i_a = i_{0,a} f_a \exp\left[\frac{\alpha_a n_a F}{RT}(E_a - E_{e,a})\right] \qquad \ldots(4.14)$$

and the cathodic one:

$$I_c = i_{0,c} A_c \exp\left[-\frac{\alpha_c n_c F}{RT}(E_c - E_{e,a})\right] \qquad \ldots(4.15)$$

$$i_c = i_{0,c} f_c \exp\left[-\frac{\alpha_c n_c F}{RT}(E_c - E_{e,a})\right] \qquad \ldots(4.16)$$

4.3 Diffusion Control

In this case, the reaction current is given by Fick's law [28]:

$$|\, I \,| = z_c \text{ F D A} \left(\frac{\partial c}{\partial x} \right) \qquad \ldots(4.17)$$

or its equivalent

$$|\, I \,| = z_c \text{ F D A} \frac{(C_b - C_s)}{\delta} \qquad \ldots(4.18)$$

The limiting current, i.e. the maximum current under diffusion control is obtained when C_s=0, so

$$|\, I_L \,| = z_c \text{ F D A } \frac{C_b}{\delta} \qquad \ldots(4.19)$$

or

$$|\, I_L \,| = z_c \text{ F K A } C_b \qquad \ldots(4.20)$$

where the mass transfer coefficient is defined as

$$K = \frac{D}{\delta} \qquad \ldots(4.21)$$

The corrosion current is then

$$I_{corr} = I_L = z_c \text{ F A K } C_b \qquad \ldots(4.22)$$

z_c is used in equations (4.17) – (4.22) because in corrosion processes the cathodic reaction is the one likely to be controlled by diffusion. C_b solubility of oxygen in water. The bulk concentration of oxygen changes with pressure, for barometric pressures other than 101.325 KPa (sea level), bulk concentration of oxygen can be computed from the following equation [47]:

$$C_b = C_{101.325} (P_T - p) / (101.325 - p) \qquad \ldots(4.23)$$

C_b = bulk concentration of oxygen

$C_{101.325}$= saturation value at 101.325 (Table 4.1)

P_T= total pressure (KPa)

p= vapor pressure of water.

Table 4.1 Solubility of Oxygen in See Water at 101.325 KPa[48]

Temperature ^{0}C	Solubility of oxygen mg/l
25	7.8
40	6.0
60	3.1

The mass transfer coefficient (K) in Eq. (4.21) varies with flow or relative speed between metal and environment, the geometry of the system and the physical properties of the liquid. To calculate the variation of K in dynamic environment, dimensionless group are used such as [28]:

$$Sh = \frac{Kd}{D} \quad \text{(Sherwood number)} \qquad \ldots(4.24)$$

$$Re = \frac{du\rho}{\mu} \quad \text{(Reynolds number)} \qquad \ldots(4.25)$$

$$Sc = \frac{\mu}{D\rho} \quad \text{(Schmidt number)} \qquad \ldots(4.26)$$

are often applied . For instance, for the particular case of flow inside a pipe, the Poulson and Robinson [27] relationship applies in the case of turbulent regime.

$$Sh=0.026\, Re^{0.82}\, Sc^{0.35} \qquad \ldots(4.27)$$

from Eq.(4.24) to (4.27) the expression for K is then

$$K=(\frac{D}{d})0.026\ Re^{0.82}\ Sc^{0.35} \qquad \ldots(4.28)$$

The effect of temperature and pressure on diffusion coefficient is shown in the following equation [21]:

$$D_{P,T} = D_0\ \frac{P_0}{P}\left(\frac{T}{T_0}\right)^n \qquad \ldots(4.29)$$

where the exponent n varies from 1.75 to 2.0 ,T_0 reference temperature in K, D_0 diffusion coefficient at reference temperature and pressure, P_0 reference pressure.

4.4 Galvanic Corrosion

For activation control [28] at (E_g):

$$I_{corr.}^{system} = I_{a}^{system} = \left|I_{c}^{system}\right| \qquad \ldots(4.30)$$

and

$$\sum I_a = \sum I_c \qquad \ldots(4.31)$$

for one metal

$$I_a = |I_c| \qquad \ldots(4.32)$$

$$i_a = i_{0,a}\ \exp[\frac{\alpha_a n_a F}{RT}(E_a - E_{e,a})] \qquad \ldots(4.33)$$

$$i_c = i_{0,c}\ \exp[\frac{\alpha_c n_c F}{RT}(E_c - E_{e,a})] \qquad \ldots(4.34)$$

$$i_a = i_{0,a}\, f \exp[\frac{\alpha_a n_a F}{RT}(E_{corr} - E_{e,a})] \qquad \ldots(4.35)$$

$$i_c = i_{0,c}\, f \exp[-\frac{\alpha_c n_c F}{RT}(E_{corr} - E_{e,c})] \qquad \ldots(4.36)$$

for two metals

$$I_{a.1}+I_{a.2}=|I_{c.1}|+|I_{c.2}| \qquad \ldots(4.37)$$

or .in terms of current densities and areas

$$i_{a.1}A_1+i_{a.2}A_2=|i_{c.1}A_1|+|i_{c.2}A_2| \qquad \ldots(4.38)$$

or

$$i_{a.1}f_1+i_{a.2}f_2=|i_{c.1}f_1|+|i_{c.2}f_2| \qquad \ldots(4.39)$$

if $I_{a.1} >> I_{a.2}$, eq. 4.33 reduce to

$$i_{a.1}A_1=|i_{c.1}A_1|+|i_{c.2}A_2| \qquad \ldots(4.40)$$

$E_{e.c1}= E_{e.c2}= E_{e.c}$ and $\alpha_{c1}=\alpha_{c2}=\alpha_c$

$$i_{a.1}=i_{0,a1}\exp[\frac{\alpha_{a1}F}{RT}(E_g-E_{e,a.1})] \qquad \ldots(4.41)$$

$$i_{c.1}=i_{0,c1}\exp[\frac{\alpha_{c}F}{RT}(E_g-E_{e,c})] \qquad \ldots(4.42)$$

$$i_{c.2}=i_{0,c2}\exp[-\frac{\alpha_{c}F}{RT}(E_g-E_{e,c})] \qquad \ldots(4.43)$$

for diffusion control [28]

$$\sum I_a=\sum I_L \qquad \ldots(4.44)$$

for one metal

$$I_a=|I_c| \qquad \ldots(4.45)$$

$$I_c=I_L$$

$$I_L=I_{corr}=z_c F A K C_b \qquad \ldots(4.46)$$

for two metals

$$\sum I_a=\sum I_L \qquad \ldots(4.47)$$

$$i_{a.1}f_1+i_{a.2}f_2=i_L f_1+i_L f_2 \qquad \ldots(4.48)$$

where f_1 and f_2 are the anodic and cathodic electrode area fractions.

$$f_1+f_2=1 \qquad \ldots(4.49)$$

Equation (4.49) became

$$i_{a.1}\, f_1 + i_{a.2}\, f_2 = I_L \qquad \text{...(4.50)}$$

For binary galvanic system under activation control (acidic medium) and mass transfer (diffusion) control (neutral medium),

for one metal:

$$\sum Ia = \sum Ic + I_L \qquad \text{...(4.51)}$$

$$i_a = i_{0,a}\, f_a \exp[\frac{\alpha_a n_a F}{RT}(E_g - E_{e,a.})] \qquad \text{...(4.52)}$$

$$i_c = i_{0,c}\, f_c \exp[-\frac{\alpha_c n_c F}{RT}(E_g - E_{e,c})] \qquad \text{...(4.53)}$$

$$I_L = z_c\, F\, A\, K\, C_b \qquad \text{...(4.54)}$$

when two metals at (E_g):

$$I_{a.1} + I_{a.2} = I_{c.1} + I_{c.2} + I_L \qquad \text{...(4.55)}$$

$$i_{a.1}\, f_1 + i_{a.2}\, f_2 = i_{c.1}\, f_1 + i_{c.2}\, f_2 + i_L\, f_1 + i_L\, f_2 \qquad \text{...(4.56)}$$

4.5 Numerical Method

Simplifications leading to analytic solutions of the above equations are so complex, so numerical solutions must be attempted. As an example, a numerical method implemented on a microcomputer. The sweeping method is as follows:

a. Estimate equilibrium potentials for metals and for hydrogen from equation (4.1) at T of 25, 40 and 60 ^{0}C. For different pH values use equation (4.3) to calculate hydrogen ion concentrations.
b. Tafel slopes for anodic and cathodic reactions are established from equations (4.7) and (4.8) at α =0.5 and T of 25, 40 and 60 ^{0}C.
c. The exchange current density is calculated from equation (4.12) for three values of temperatures (25, 40 and 60 ^{0}C).

d. Bulk concentration of oxygen in water is calculated from Eq. (4.23) at different pressures 0.5, 1, and 5 atm, and temperatures 25, 40 and 60 ^{0}C, by using, Table (4.1).

e. The value of oxygen diffusivity is estimated from Eq. (4.29) at different temperatures 25, 40 and 60 ^{0}C and pressures 0.5, 1, and 5 atm.

f. The mass transfer coefficient K is calculated by using Eq. (4.28)

g. The limiting current is estimated of from Eq. (4.22) at different temperatures 25, 40 and 60 ^{0}C, and pressures 0.5, 1, and 5 atm.

h. It is necessary to realize that the galvanic corrosion potentials (E_g) of the reactions involved are chosen between the more negative (or less positive) equilibrium potential of the metals and the equilibrium potential of hydrogen evolution.

i. The values of E_{eq}, β, i_0, E_g ($=E_a=E_c$) are substituted in Eqs.(4.13) and (4.15) to determine anodic and cathodic currents.

For activation control:

j. The summations of the anodic and cathodic currents are compared to determine the absolute value of their difference.

k. A new value of E_g is assumed as in (h) and the program is executed again, showing the difference between the summation of the anodic and cathodic currents to decrease

l. Step (k) is repeated until a minimum difference current is found. The minimum will be detected when the sweeping procedure goes beyond the true galvanic potential value as the difference starts increasing. The precision will be greater the smaller the potential step while the processing time will increase accordingly.

For mass transfer control:

m. The difference between the summation of the anodic currents and limiting currents, Eq. (4.44), are calculated and compared to determine the absolute value of their difference.

n. A new value of E_g is assumed as in (h) and the program is executed again, showing the difference between the summation of the anodic and limiting currents to decrease

o. Step (k) is repeated until a minimum difference is found. The minimum will be detected when the sweeping procedure goes beyond the true galvanic potential value as the difference starts increasing. The precision will be greater the smaller the potential step while the processing time will increase accordingly.

For cathode reaction under activation control complicit with mass transfer :

p. The difference between the summation of the anodic and cathodic currents and limiting currents Eq. (4.51), are calculated and compared to determine the absolute value of their difference.

q. A new value of E_g is assumed as in (h) and the program is executed again, showing the difference between the summation of the anodic and cathodic currents and limiting currents to decrease

r. Step (k) is repeated until a minimum difference is found. The minimum will be detected when the sweeping procedure goes beyond the true galvanic potential value as the difference starts increasing. The precision will be greater the smaller the potential step while the processing time will increase accordingly.

A program written in Quick Basic for free corrosion rate single metal and binary galvanic system under activation control (acidic medium) and mass transfer (diffusion) control (neutral medium).and also to calculate galvanic corrosion rate when the system is under both activation and mass transfer control.

CHAPTER FIVE

RESULTS

5.1 Activation Control

5.1.1 Free corrosion:

I. Effect of pH

Tables 5.1 to 5.4 show the effect of pH on the corrosion current and corrosion potential of iron and zinc at different values of temperature, the corrosion current of iron and zinc were calculated by using Eq.(4.32).

i) Iron:

Table 5.1: Corrosion of iron versus pH under the following conditions: $[Fe^{++}] = 10^{-6}$ M, Alpha of H_2=0.5, Alpha of Fe=0.5, T=25°C, P=1atm in de-aerated acid solutions.

pH	E_{corr}(V)* vs. SHE	i_{Fe} ($\mu A/cm^2$)
1	-0.39187572	65.1534
2	-0.41158445	30.2411
3	-0.43129353	14.0363

Table 5.2: Corrosion of iron versus pH under the following conditions: $[Fe^{++}] = 10^{-6}$ M, Alpha of H_2 =0.5, Alpha of Fe=0.5, T=60°C, P=1atm in de-aerated acid solutions.

pH	E_{corr}(V) vs. SHE	i_{Fe} ($\mu A/cm^2$)
1	-0.40344939	96.8138
2	-0.4254728	44.93666
3	-0.44749646	20.8573

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[*] To obtain summation equal zero, the computer program is sensitive for at least 7 decimals for corrosion potential.

ii) Zinc:

Table 5.3: Corrosion of zinc versus pH under the following conditions: $[Zn^{++}] = 10^{-6}$ M, Alpha of H_2 =0.5, Alpha of Zn =0.5, T=25°C, P=1atm in de-aerated acid solutions.

pH	E_{corr}(V) vs. SHE	i_{Zn} (μA/cm^2)
1	-0.8918877	176.389
2	-0.9115962	81.872
3	-0.9313049	38.001

Table 5.4: Corrosion of zinc versus pH under the following conditions: $[Zn^{++}] = 10^{-6}$ M, Alpha of H_2 =0.5, Alpha of Zn =0.5, T= 60°C, P=1atm in de-aerated acid solutions.

pH	E_{corr}(V) vs. SHE	i_{Zn} (μA/cm^2)
1	-0.9371317	7598.20
2	-0.9591548	3526.77
3	-0.981178	1636.98

II. Effect of Temperature

Tables 5.5 and 5.6 show the effect of temperature on the corrosion current and corrosion potential of iron and zinc, which calculated by using Eq. (4.32) and Eq. (4.1) respectively.

i) Iron:

Table 5.5: Corrosion of iron versus temperature under the following conditions: $[Fe^{++}] = 10^{-6}$ M, Alpha of H_2 =0.5, Alpha of Fe =0.5, pH=1, P=1atm in de-aerated acid solutions.

Temp.(^{0}C)	E_{corr}(V) vs. SHE	I_{fe} (μA/cm^2)
25	-0.3918757	65.1534
40	-0.3968359	78.0480
60	-0.4034494	96.8138

ii) Zinc:

Table 5.6: Corrosion of zinc versus temperature under the following conditions: [Zn^{++}] = 10^{-6} M, Alpha of H_2 =0.5, Alpha of Zn =0.5, pH=1, P=1atm in de-aerated acid solutions.

Temp.(^{0}C)	E_{corr}(V) vs. SHE	i_{Zn} (μA/cm^2)
25	-0.8918877	176.389
40	-0.9112779	980.876
60	-0.9371317	7598.20

5.1.2 Galvanic coupling:

I. Effect of pH

The effect of pH on galvanic corrosion rate and corrosion potential is shown in Tables 5.7 and 5.8 at different values of temperature and area fraction, corrosion currents were evaluated by using Eq. (4.37).

Table 5.7: Galvanic corrosion of Fe/Zn couple versus pH under the following conditions: [Fe^{++}] = [Zn^{++}] =10^{-6} M, $f_{Fe=}$0.1, f_{Zn}=0.9, alpha of H_2=0.5, alpha of Zn= Fe=0.5, T=25°C, P=1atm in de-aerated acid solutions

pH	Eg (V)	I_{Fe} (μA)	I_{Zn}(μA)	$I_{H2/Fe}$ (μA)	$I_{H2/Zn}$ (μA)
1	-0.7798546	0	12461.16	12443.25	17.91
2	-0.799563	0	5783.955	5775.649	8.316
3	-0.8192715	0	2684.671	2680.820	3.8603

Table 5.8: Galvanic corrosion of Fe/Zn couple versus pH under the following conditions: [Fe^{++}]=[Zn^{++}]=10^{-6} M, $f_{Fe=}$0.1,f_{Zn}=0.9,alpha of H_2=0.5,alpha of Zn= Fe=0.5,T=60°C,P=1atm in de-aerated acid solutions

pH	Eg (V)	I_{Fe} (μA)	I_{Zn}(μA)	$I_{H2/Fe}$ (μA)	$I_{H2/Zn}$ (μA)
1	-0.8835287	0	44285.873	41598.697	2687.18
2	-0.9055519	0	20555.677	19308.406	255.828
3	-0.927575	0	9541.0970	8962.1701	25.582

II. Effect of Temperature

The effect of temperature on galvanic corrosion rate and corrosion potential is shown in Tables 5.9 and 5.10 at different values of pH and area fraction, corrosion currents were evaluated by using Eq. (4.37).

Table 5.9: Galvanic corrosion of Fe/Zn couple versus temperature under the following conditions: $[Fe^{++}]=[Zn^{++}]=10^{-6}$ M, $f_{Fe}=0.5, f_{Zn}=0.5$, alpha of $H_2=0.5$, alpha of Zn=Fe=0.5, pH=2 ,P=1atm in de-aerated acid solutions

Temp (^{0}C)	Eg (V)	I_{Fe} (μA)	I_{Zn}(μA)	$I_{H2/Fe}$ (μA)	$I_{H2/Zn}$ (μA)
25	-0.7619716	0	13891.339	13889.126	2.222
40	-0.8059912	0	24321.172	24299.159	22.023
60	-0.8645816	0	47617.653	47278.321	339.341

Table 5.10: Galvanic corrosion of Fe/Zn couple versus temperature under the following conditions: $[Fe^{++}]=[Zn^{++}]=10^{-6}$ M, $f_{Fe}=0.9, f_{Zn}=0.1$, alpha of $H_2=0.5$, alpha of Zn= Fe=0.5, pH=3 ,P=1atm in de-aerated acid solutions

Temp. (^{0}C)	Eg (V)	I_{Fe} (μA)	I_{Zn}(μA)	$I_{H2/Fe}$ (μA)	$I_{H2/Zn}$ (μA)
25	-0.7440693	0	5579.057	5578.96	9.92E-02
40	-0.7871997	0	9763.587	9762.61	0.98314
60	-0.8446954	0	19045.23	19030.0	15.1765

III. Effect of Area Fraction

The effect of Area Fraction on galvanic corrosion rate and corrosion potential is shown in Tables 5.11 and 5.12 at different values of pH and temperature, corrosion currents were evaluated by using Eq. (4.37).

Table 5.11: Galvanic corrosion of Fe/Zn couple versus area fraction under the following conditions: $[Fe^{++}]=10^{-6}$ M:,$[Zn^{++}]=10^{-6}$ M, pH= 1 , alpha of Fe=Zn=0.5, alpha of $H_2=0.5$, T=25°C, P=1atm in de-aerated acid solution

Area f_{Fe}	Eg (V)	I_{Fe} (μA)	I_{Zn}(μA)	$I_{H2/Fe}$ (μA)	$I_{H2/Zn}$ (μA)
0.1	-0.7798546	0	12461.16	12443.25	17.918
0.2	-0.7659863	0	19009.16	18997.01	12.158
0.3	-0.7567641	0	23820.42	23811.5	8.88963
0.4	-0.7492028	0	27408.65	27402.09	6.5764
0.5	-0.7422632	0	29927.99	29923.21	4.78771
0.6	-0.7353232	0	31372.29	31368.95	3.3460
0.7	-0.7277603	0	31587.85	31585.69	2.1658
0.8	-0.718534	0	30163.10	30161.91	1.2064
0.9	-0.7046524	0	25895.71	25895.26	0.4603

Table 5.12: Galvanic corrosion of Fe/Zn couple versus area fraction under the following conditions: $[Fe^{++}]=10^{-6}$ M:,$[Zn^{++}]=10^{-6}$ M, pH= 3 , alpha of Fe=Zn=0.5, alpha of H_2=0.5,T=60˚C, P=1atm in de-aerated acid solution

Area f_{Fe}	Eg (V)	I_{Fe} (μA)	I_{Zn}(μA)	$I_{H2/Fe}$ (μA)	$I_{H2/Zn}$ (μA)
0.1	-0.927575	0	9541.0970	8962.170	578.936
0.2	-0.9127187	0	14233.308	13836.08	397.236
0.3	-0.9026319	0	17700.39	17408.84	291.556
0.4	-0.8942929	0	20288.571	20072.47	216.10
0.5	-0.8866048	0	22102.153	21944.65	157.508
0.6	-0.8788941	0	23132.90	23022.7	110.164
0.7	-0.8704748	0	23266.026	23194.68	71.3488
0.8	-0.8601887	0	22198.12	22158.37	39.7606
0.9	-0.8446954	0	19045.23	19030.06	15.1765

5.2 Mass Transfer Control

5.2.1 Free Corrosion

I. Effect of Renolds Number

Tables 5.13 to 5.16 show the effect of Renolds number on Limiting current on iron and zinc at different values of temperature and pressure at constant pH, which are calculated from Eq. (4.46)

i) Iron :

Table 5.13: Corrosion of iron versus Renolds Number under the following conditions: T=25˚C, P=1 atm, pH= 7 in sea water.

Re	Limiting current (μA/cm^2)	Corrosion current (gmd)	Corrosion current (mpy)
5000	101.34	25.41	46.61
10000	178.91	44.85	82.29
15000	249.48	62.55	114.75
20000	315.86	79.19	145.28
25000	379.28	95.097	174.46
30000	440.44	110.43	202.5
35000	499.79	125.31	229.89
40000	557.62	139.81	256.49

45000	614.16	153.98	282.50
50000	669.58	167.88	307.99

Table 5.14: Corrosion of iron versus Renolds Number under the following conditions: T=60˚C, P=5 atm, pH= 7 in sea water.

Re	Limiting current ($\mu A/cm^2$)	Corrosion current (gmd)	Corrosion current (mpy)
5000	76.73	19.23	35.29
10000	135.46	33.96	62.30
15000	188.89	47.36	86.88
20000	239.145	59.96	110.0
25000	287.163	71.99	132.08
30000	333.47	83.610	153.38
35000	378.40	94.87	174.05
40000	422.18	105.85	194.19
45000	464.99	116.58	213.8
50000	506.95	127.10	233.18

ii) Zinc :

Table 5.15: Corrosion of zinc versus Renolds Number under the following conditions: T=25˚C, P=1 atm, pH= 7 in sea water.

Re	Limiting current ($\mu A/cm^2$)	Corrosion current (gmd)	Corrosion current (mpy)
5000	101.34	29.4942	59.3273
10000	178.91	52.0693	104.737
15000	249.48	72.6066	146.047
20000	315.86	91.9234	184.903
25000	379.28	110.38	222.029
30000	440.44	128.18	257.833
35000	499.79	145.451	292.573
40000	557.62	162.282	326.429
45000	614.16	178.737	359.528
50000	669.58	194.866	391.971

Table 5.16: Corrosion of zinc versus Renolds Number under the following conditions: T=60˚C, P=5 atm, pH= 7 in sea water.

Re	Limiting current ($\mu A/cm^2$)	Corrosion current (gmd)	Corrosion current (mpy)
5000	76.73	22.33	44.91
10000	135.46	39.42	79.29
15000	188.89	54.97	110.57
20000	239.14	69.59	139.99
25000	287.16	83.57	168.10
30000	333.47	97.04	195.21
35000	378.40	110.12	221.51
40000	422.18	122.86	247.14
45000	464.99	135.32	272.20
50000	506.95	147.53	296.77

II. Effect of Temperature

Tables 5.17 to 5.20 show the effect of temperature on Limiting current on iron and zinc at different values of Renolds number and pressure at constant pH, limiting current was calculated from Eq.(4.46)

i) Iron :

Table 5.17: Corrosion of iron versus temperature under the following conditions: Re=5000, P=1 atm, pH= 7 in sea water.

Temp. (^0C)	Limiting current ($\mu A/cm^2$)	Corrosion current (gmd)	Corrosion current (mpy)
25	101.34	25.41	46.61
40	73.74	18.48	33.91
60	36.52	9.158	16.80

Table 5.18: Corrosion of iron versus temperature under the following conditions: Re=30000, P=5 atm, pH= 7 in sea water.

Temp. (^0C)	Limiting current ($\mu A/cm^2$)	Corrosion current (gmd)	Corrosion current (mpy)
25	793.60	198.98	365.04
40	598.30	150.01	275.20
60	333.47	83.61	153.38

ii) Zinc :

Table 5.19: Corrosion of zinc versus temperature under the following conditions: Re=5000, P=1 atm, pH= 7 in sea water.

Temp. (^{0}C)	Limiting current (μA/cm^2)	Corrosion current (gmd)	Corrosion current (mpy)
25	101.34	29.49	59.32
40	73.74	21.46	43.16
60	36.52	10.62	21.38

Table 5.20: Corrosion of zinc versus temperature under the following conditions: Re=30000, P=5 atm, pH= 7 in sea water.

Temp. (^{0}C)	Limiting current (μA/cm^2)	Corrosion current (gmd)	Corrosion current (mpy)
25	793.60	230.95	464.57
40	598.30	174.12	350.24
60	333.47	97.047	195.21

III. Effect of pressure

Tables 5.21 to 5.24 show the effect of pressure on the Limiting current on iron and zinc at different values of Renolds number and pressure at constant pH, limiting current was calculated from Eq.(4.46)

i) Iron :

Table 5.21: Corrosion of iron versus pressure under the following conditions: Re=10000, T=40 ^{0}C, pH= 7 in sea water.

Pressure (atm)	Limiting current (μA/cm^2)	Corrosion current (gmd)	Corrosion current (mpy)
0.5	94.11	23.59	43.28
0.75	114.62	28.74	52.72
1	130.18	32.64	59.88
3	201.24	50.45	92.56
5	243.04	60.93	111.79

Table 5.22: Corrosion of iron versus pressure under the following conditions: Re=50000°C, T=60 ^{0}C, pH= 7 in sea water.

Pressure (atm)	Limiting current ($\mu A/cm^2$)	Limiting current (gmd)	Limiting current (mpy)
0.5	142.94	35.84	65.75
0.75	200.38	50.24	92.17
1	241.32	60.50	111.00
3	412.38	103.39	189.68
5	506.95	127.10	233.18

ii) Zinc :

Table 5.23: Corrosion of zinc versus pressure under the following conditions: Re=10000, T=25 ^{0}C, pH= 7 in sea water.

Pressure (atm)	Limiting current ($\mu A/cm^2$)	Corrosion current (gmd)	Corrosion current (mpy)
0.5	94.11	27.38	55.09
0.75	114.62	33.36	67.10
1	130.18	37.88	76.20
3	201.24	58.56	117.80
5	243.04	70.73	142.2

Table 5.24: Corrosion of zinc versus pressure under the following conditions: Re=50000, T=60 ^{0}C, pH= 7 in sea water.

Pressure (atm)	Limiting current ($\mu A/cm^2$)	Corrosion current (gmd)	Corrosion current (mpy)
0.5	142.94	41.60	83.68
0.75	200.38	58.31	117.30
1	241.32	70.23	141.26
3	412.38	120.01	241.40
5	506.95	147.53	296.77

5.2.2 Galvanic coupling:

I. Effect of Renolds Number

The effect of Renolds number on galvanic corrosion rate and corrosion potential is shown in Tables 5.25 and 5.26 at different values of pressure, area fraction and temperature at constant pH, limiting current was calculated from Eq.(4.46)

Table 5.25: Galvanic corrosion of Fe/Zn couple versus Renolds number under the following conditions: $[Fe^{++}] = [Zn^{++}] = 10^{-6}$ M, $f_{Fe=}0.1$, $f_{Zn}=0.9$, pH= 7, alpha of Fe=Zn=0.5, T=25˚C, P=1 atm in sea water.

Re	Eg (V)	I_{Fe} (μA)	I_{Zn}(μA)	$i_{Limiting}$ (μA/cm^2)
5000	-0.638703	0	101.3368	101.3464
10000	-0.6241072	0	178.9081	178.9176
15000	-0.6155694	1.07E-07	249.47781	249.487
20000	-0.6095118	1.36E-07	315.85319	315.8622
25000	-0.6048132	1.63E-07	379.27458	379.2834
30000	-0.6009742	1.89E-07	440.43701	440.4458
35000	-0.5977284	2.15E-07	499.78263	499.7915
40000	-0.5949167	2.40E-07	557.6163	557.6251
45000	-0.5924367	2.64E-07	614.15861	614.1682
50000	-0.5902182	2.88E-07	669.57964	669.5893

Table 5.26: Galvanic corrosion of Fe/Zn couple versus Renolds number under the following conditions: $[Fe^{++}] = [Zn^{++}] = 10^{-6}$ M, $f_{Fe=}0.9$, $f_{Zn}=0.1$, pH= 7, alpha of Fe=Zn=0.5, T=60˚C, P=5 atm in sea water.

Re	Eg (V)	I_{Fe} (μA)	I_{Zn}(μA)	$i_{Limiting}$ (μA/cm^2)
5000	-0.707122	0	76.721606	76.73149
10000	-0.6908115	0	135.45229	135.4622
15000	-0.6812708	0	188.88182	188.8918
20000	-0.6745016	0	239.13625	239.1458
25000	-0.6692511	0	287.15387	287.1634
30000	-0.6649612	0	333.46142	333.4707
35000	-0.6613341	0	378.39313	378.4025
40000	-0.6581922	0	422.18016	422.1895
45000	-0.6554208	0	464.99058	464.9995
50000	-0.6529418	0	506.9505	506.9599

II. Effect of Temperature

The effect of temperature on galvanic corrosion rate and corrosion potential is shown in Tables 5.27 and 5.28 at different values of pressure, area fraction and Renolds number at constant pH, limiting current was calculated from Eq.(4.50).

Table 5.27: Galvanic corrosion of Fe/Zn couple versus Temperature under the following conditions: $[Fe^{++}] = [Zn^{++}] = 10^{-6}$ M, f_{Fe}=0.1, f_{Zn}=0.9, pH= 7, alpha of Fe=Zn=0.5, Re=5000, P=1 atm in sea water.

Temp.(^{0}C)	Eg (V)	I_{Fe} (μA)	I_{Zn}(μA)	$i_{Limiting}$ (μA/cm^2)
25	-0.638703	0	101.3368	101.3464
40	-0.7002004	0	73.731692	73.74163
60	-0.7914715	0	36.515892	36.52586

Table 5.28: Galvanic corrosion of Fe/Zn couple versus Temperature under the following conditions: $[Fe^{++}] = [Zn^{++}] = 10^{-6}$ M, f_{Fe}=0.9, f_{Zn}=0.1, pH= 7, alpha of Fe=Zn=0.5, Re=30000, P=3 atm in sea water.

Temp.(^{0}C)	Eg (V)	I_{Fe} (μA)	I_{Zn}(μA)	$i_{Limiting}$ (μA/cm^2)
25	-0.5341339	2.30E-05	660.88642	660.8963
40	-0.5895636	5.54E-06	495.4073	495.4167
60	-0.6708861	0	271.24903	271.2584

III. Effect of Pressure

The effect of pressure on galvanic corrosion rate and corrosion potential is shown in Tables 5.29 and 5.30 at different values of temperature, area fraction and Renolds number at constant pH, limiting current was calculated from Eq.(4.50).

Table 5.29: Galvanic corrosion of Fe/Zn couple versus pressure under the following conditions: $[Fe^{++}] = [Zn^{++}] = 10^{-6}$ M, f_{Fe}=0.1, f_{Zn}=0.9, pH= 7, alpha of Fe=Zn=0.5, Re=5000, T=25 ^{0}C in sea water.

Pressure (atm)	Eg (V)	I_{Fe} (μA)	I_{Zn}(μA)	$i_{Limiting}$ (μA/cm^2)
0.5	-0.645776	0	76.937763	76.94764
0.75	-0.6415667	0	90.642815	90.65271
1	-0.638703	0	101.3368	101.3464
3	-0.6282819	0	152.06259	152.072
5	-0.6235828	0	182.59938	182.6092

Table 5.30: Galvanic corrosion of Fe/Zn couple versus pressure under the following conditions: $[Fe^{++}] = [Zn^{++}] = 10^{-6}$ M, $f_{Fe=}0.9$, f_{Zn}=0.1, pH= 7, alpha of Fe=Zn=0.5, Re=50000°C, T=60 ^{0}C in sea water.

Pressure (atm)	Eg (V)	I_{Fe} (μA)	I_{Zn}(μA)	$i_{Limiting}$ (μA/cm^2)
0.5	-0.6892677	0	142.93956	142.9494
0.75	-0.6795754	0	200.37836	200.3877
1	-0.6742414	0	241.31465	241.324
3	-0.6588667	0	412.3719	412.3815
5	-0.6529418	0	506.9505	506.9599

IV. Effect of Area Fraction

The effect of area fraction on galvanic corrosion rate and corrosion potential is shown in Tables 5.31 and 5.32 at different values of temperature, pressure and Renolds number at constant pH. Limiting current was calculated from Eq.(4.46).

Table 5.31: Galvanic corrosion of Fe/Zn couple versus area fraction under the following conditions: $[Fe^{++}] = [Zn^{++}] = 10^{-6}$ M, P =1 atm, pH= 7, alpha of Fe=Zn=0.5, Limiting current = 101.34 μA/cm^2 , Re=5000, T=25 ^{0}C in sea water.

Area f_{Fe}	Eg (V)	I_{Fe} (μA)	I_{Zn}(μA)
0.1	-0.638703	0	101.3368
0.2	-0.6356786	0	101.33677
0.3	-0.6322498	0	101.33681
0.4	-0.6282916	0	101.33662
0.5	-0.62361	0	101.33657
0.6	-0.6178802	0	101.33645
0.7	-0.6104931	9.15E-07	101.33669
0.8	-0.6000817	1.57E-06	101.33652
0.9	-0.5822832	3.53E-06	101.33659

Table 5.32: Galvanic corrosion of Fe/Zn couple versus area fraction under the following conditions: $[Fe^{++}] = [Zn^{++}] = 10^{-6}$ M, P =0.5 atm, pH= 7, alpha of Fe=Zn=0.5, Limiting current = 80.97 μA/cm^2, Re=25000, T=60 ^{0}C in sea water.

Area f_{Fe}	Eg (V)	I_{Fe} (μA)	I_{Zn}(μA)
0.1	-0.7686245	0	80.962573

0.2	-0.7652449	0	80.962509
0.3	-0.7614134	0	80.962509
0.4	-0.7569902	0	80.962672
0.5	-0.7517587	0	80.962765
0.6	-0.7453559	0	80.96277
0.7	-0.7371013	0	80.96265
0.8	-0.725467	0	80.962748
0.9	-0.7055781	0	80.962723

5.3 Activation and Mass Transfer Control

5.3.1 Free Corrosion

I. Effect of pH

Tables 5.33 to 5.36 show the effect of pH on the corrosion current and corrosion potential of iron and zinc at different values of temperature , pressure and Renolds number, limiting current was calculated from Eq.(4.46),corrosion current of metals were calculated from Eq.(4.51)

i) Iron

Table 5.33: Corrosion of iron versus pH under the following conditions: [Fe^{++}] = 10^{-6} M, alpha of Fe=0.5, Re=10000, P=0.5 atm, T=25 ^{0}C, Limiting current = 135.84 μA/cm^2

pH	E_{corr} (V)	I_{Fe} (μA/cm^2)	$I_{H2/Fe}$ (μA/cm^2)
1	-0.366428	175.52905	39.69524
2	-0.37056	149.4383	13.60448
4	-0.372744	137.25337	1.419552
7	-0.136519	135.83852	0

Table 5.34: Corrosion of iron versus pH under the following conditions: [Fe^{++}] = 10^{-6} M, alpha of Fe=0.5, Re=50000, P=5 atm, T=60 ^{0}C, Limiting current = 506.95 μA/cm^2

pH	E_{corr} (V)	I_{Fe} (μA/cm^2)	$I_{H2/Fe}$ (μA/cm^2)
1	-0.353727	547.65581	40.70588
2	-0.355206	520.15812	13.20819
4	-0.355868	508.28609	1.336155
7	-.091194398	506.95557	0

ii) Zinc

Table 5.35: Corrosion of zinc versus pH under the following conditions: $[Zn^{++}] = 10^{-6}$ M, alpha of Zn=0.5, Re=10000, P=1 atm, T=25 ^{0}C, Limiting current = 178.917599 µA/cm^2

pH	E_{corr} (V)	I_{Zn} (µA/cm^2)	$I_{H2/Zn}$ (µA/cm^2)
1	-0.877274988	311.617	132.7093
2	-0.885300571	227.972	49.06488
4	-0.890752349	184.364	5.455999
7	-0.626812604	178.908	6.32E-04

Table 5.36: Corrosion of zinc versus pH under the following conditions: $[Zn^{++}] = 10^{-6}$ M , alpha of Zn=0.5, Re=30000, P=5 atm, T=40 ^{0}C, Limiting current = 598.303168 µA/cm^2

pH	E_{corr} (V)	I_{Zn} (µA/cm^2)	$I_{H2/Zn}$ (µA/cm^2)
1	-0.901395606	1414.97	816.6745
2	-0.913041671	918.784	320.4908
4	-0.92292928	636.79	38.49676
7	-0.646575508	598.298	4.53E-03

II. Effect of Temperature

Tables 5.37 to 5.40 show the effect of temperature on the corrosion current and corrosion potential of iron and zinc at different values of pH, pressure and Renolds number, limiting current was calculated from Eq.(4.46),corrosion current of metals were calculated from Eq.(4.51)

i) Iron

Table 5.37: Corrosion of iron versus temperature under the following conditions: $[Fe^{++}] = 10^{-6}$ M, alpha of Fe=0.5, Re=10000, P=0.5 atm, pH=1

Temp.(^{0}C)	E_{corr} (V)	I_{Fe} (µA/cm^2)	$I_{H2/Fe}$ (µA/cm^2)	$i_{Limiting}$ (µA/cm^2)
25	-0.366428	175.52905	39.69524	135.844
40	-0.379155	150.33776	56.23603	94.1117
60	-0.396394	123.80144	85.61466	38.1968

Table 5.38: Corrosion of iron versus temperature under the following conditions: $[Fe^{++}] = 10^{-6}$ M, alpha of Fe=0.5, Re=50000, P=5 atm, pH=7

Temp.(^{0}C)	E_{corr} (V)	I_{Fe} (μA/cm^2)	$I_{H2/Fe}$ (μA/cm^2)	$i_{Limiting}$ (μA/cm^2)
25	-0.080438405	1206.482	0	1206.49
40	-0.082210906	909.56766	0	909.572
60	-0.0916752	506.95557	0	506.96

ii) Zinc

Table 5.39: Corrosion of zinc versus temperature under the following conditions: $[Zn^{++}] = 10^{-6}$ M, alpha of Zn=0.5, Re=10000, P=0.5 atm, pH=1

Temp.(^{0}C)	E_{corr} (V)	I_{Zn} (μA/cm^2)	$I_{H2/Zn}$ (μA/cm^2)	$i_{Limiting}$ (μA/cm^2)
25	-0.880328939	276.674	140.8405	135.844
40	-0.909580508	1044.59	950.4921	94.1117
60	-0.937035598	7623.69	7585.499	38.1968

Table 5.40: Corrosion of zinc versus temperature under the following conditions: $[Zn^{++}] = 10^{-6}$ M, alpha of Zn=0.5, Re=50000, P=5 atm, pH=7

Temp.(^{0}C)	E_{corr} (V)	I_{Zn} (μA/cm^2)	$I_{H2/Zn}$ (μA/cm^2)	$i_{Limiting}$ (μA/cm^2)
25	-0.577804325	1206.48	2.43E-04	1206.49
40	-0.635278217	909.566	3.68E-03	909.572
60	-0.719005376	507.056	0.106135	506.96

III. Effect of Renolds Number

Tables 5.41 to 5.44 show the effect of Renolds number on the corrosion current and corrosion potential of iron and zinc at different values of pH, pressure and temperature, limiting current was calculated from Eq.(4.46),corrosion current of metals were calculated from Eq.(4.51)

i) Iron

Table 5.41: Corrosion of iron versus Renolds number under the following conditions: $[Fe^{++}] = 10^{-6}$ M, alpha of Fe=0.5, T=25 °C, P=1atm, pH=1

Re	E_{corr} (V)	I_{Fe} (μA/cm^2)	$I_{H2/Fe}$ (μA/cm^2)	$i_{Limiting}$ (μA/cm^2)
10000	-0.361244077	214.79186	35.88426	178.918
30000	-0.341420833	464.82889	24.39306	440.446
50000	-0.331292201	689.60609	20.02684	669.589

Table 5.42: Corrosion of iron versus Renolds number under the following conditions: $[Fe^{++}] = 10^{-6}$ M, alpha of Fe=0.5, T=60 °C, P=5 atm, pH=7

Re	E_{corr} (V)	I_{Fe} ($\mu A/cm^2$)	$I_{H2/Fe}$ ($\mu A/cm^2$)	$i_{Limiting}$ ($\mu A/cm^2$)
10000	-.1295451074	135.45	0	135.46
30000	-.1036949008	333.46666	0	333.471
50000	-0.0916752	506.95557	0	506.96

ii) Zinc

Table 5.43: Corrosion of zinc versus Renolds number under the following conditions: $[Zn^{++}] = 10^{-6}$ M, alpha of Zn=0.5, T=25 °C, P=1 atm, pH=1

Re	E_{corr} (V)	I_{Zn} ($\mu A/cm^2$)	$I_{H2/Zn}$ ($\mu A/cm^2$)	$i_{Limiting}$ ($\mu A/cm^2$)
10000	-0.877274988	311.617	132.7093	178.918
30000	-0.863103236	541.142	100.7062	440.446
50000	-0.85455683	754.847	85.26731	669.589

Table 5.44: Corrosion of zinc versus Renolds number under the following conditions: $[Zn^{++}] = 10^{-6}$ M, alpha of Zn=0.5, T=60 °C, P=5 atm, pH=7

Re	E_{corr} (V)	I_{Zn} ($\mu A/cm^2$)	$I_{H2/Zn}$ ($\mu A/cm^2$)	$i_{Limiting}$ ($\mu A/cm^2$)
10000	-0.756837604	135.657	0.205194	135.462
30000	-0.73101952	333.592	0.130851	333.471
50000	-0.719005376	507.056	0.106135	506.96

IV. Effect of Pressure

Tables 5.45 to 5.48 show the effect of pressure on the corrosion current and corrosion potential of iron and zinc at different values of pH, Renolds number and temperature, limiting current was calculated from Eq.(4.46), corrosion current of metals were calculated from Eq.(4.51)

i) Iron

Table 5.45: Corrosion of iron versus pressure under the following conditions: $[Fe^{++}] = 10^{-6}$ M, alpha of Fe=0.5, T=25 °C, Re=10000, pH=1

Pressure (atm)	E_{corr} (V)	I_{Fe} ($\mu A/cm^2$)	$I_{H2/Fe}$ ($\mu A/cm^2$)	$i_{Limiting}$ ($\mu A/cm^2$)
0.5	-0.366427519	175.52905	39.69524	135.844
1	-0.361244077	214.79186	35.88426	178.918
5	-0.348672677	350.46199	28.09263	322.379

Table 5.46: Corrosion of iron versus pressure under the following conditions: $[Fe^{++}] = 10^{-6}$ M, alpha of Fe=0.5, T=40 °C, Re=30000, pH=7

Pressure (atm)	E_{corr} (V)	I_{Fe} ($\mu A/cm^2$)	$I_{H2/Fe}$ ($\mu A/cm^2$)	$i_{Limiting}$ ($\mu A/cm^2$)
0.5	-0.119096704	231.67222	0	231.677
1	-0.110345699	320.47098	0	320.477
5	-0.093508303	598.29634	0	598.303

ii) Zinc

Table 5.47: Corrosion of zinc versus pressure under the following conditions: $[Zn^{++}] = 10^{-6}$ M, alpha of Zn=0.5, T=25 °C, Re=10000, pH=4

Pressure (atm)	E_{corr} (V)	I_{Zn} ($\mu A/cm^2$)	$I_{H2/Zn}$ ($\mu A/cm^2$)	$i_{Limiting}$ ($\mu A/cm^2$)
0.5	-0.897447419	142.05	6.215728	135.844
1	-0.890752349	184.364	5.455999	178.918
5	-0.876079386	326.469	4.100064	322.379

Table 5.48: Corrosion of zinc versus pressure under the following conditions: $[Zn^{++}] = 10^{-6}$ M, alpha of Zn=0.5, T=40 °C, Re=50000, pH=7

Pressure (atm)	E_{corr} (V)	I_{Zn} ($\mu A/cm^2$)	$I_{H2/Zn}$ ($\mu A/cm^2$)	$i_{Limiting}$ ($\mu A/cm^2$)
0.5	-0.660866475	352.204	5.91E-03	352.208
1	-0.652115517	487.201	5.02E-03	487.206
5	-0.635278217	909.566	3.68E-03	909.572

5.3.2 Galvanic coupling:

I. Effect of pH

The effect of pH on galvanic corrosion rate and corrosion potential is shown in Tables 5.49 and 5.50 at different values of temperature, pressure, area fraction and Renolds number, limiting current was calculated from Eq.(4.46), corrosion current of metals were calculated from Eq.(4.55)

Table 5.49: Galvanic corrosion of Fe/Zn couple versus pH under the following conditions: $[Fe^{++}]=[Zn^{++}]=10^{-6}$ M, $f_{Fe=}0.9$,$f_{Zn}=0.1$,alpha of H_2=0.5alpha of Zn= Fe=0.5,Re=10000,T=25˚C,P=0.5 atm , Limiting current =135.84 μA/cm^2

pH	Eg (V)	I_{Fe} (μA^2)	I_{Zn}(μA)	$I_{H2/Fe}$ (μA)	$I_{H2/Zn}$ (μA)
1	-0.7045627	0	25986.4	25850.1	4.60E-02
2	-0.72416775	0	12110.5	11974.4	2.13E-02
4	-0.7628876	0	2680.91	2545.03	4.52E-03
7	-0.57134607	5.40E-06	155.149	19.3152	2.15E-05

Table 5.50: Galvanic corrosion of Fe/Zn couple versus pH under the following conditions: $[Fe^{++}]=[Zn^{++}]=10^{-6}$ M, $f_{Fe=}0.1$, $f_{Zn}=0.9$, alpha of H_2=0.5, alpha of Zn = Fe=0.5, Re=30000,T=60˚C, P=1 atm , Limiting current= 158.73 μA/cm^2

pH	Eg (V)	I_{Fe} (μA)	I_{Zn}(μA)	$I_{H2/Fe}$ (μA)	$I_{H2/Zn}$ (μA)
1	-0.88346017	0	44391.8	41549	2683.98
2	-0.90540434	0	20661.6	19258.8	1244.08
4	-0.94891668	0	4535.03	4110.76	265.546
7	-0.74339314	0	195.063	36.1879	0.1461

II. Effect of Temperature

The effect of temperature on galvanic corrosion rate and corrosion potential is shown in Tables 5.51 and 5.52 at different values of pH, pressure, area fraction and Renolds number, limiting current was calculated from Eq.(4.46), corrosion current of metals were calculated from Eq.(4.55)

Table 5.51: Galvanic corrosion of Fe/Zn couple versus temperature under the following conditions: $[Fe^{++}]=[Zn^{++}]=10^{-6}$ M, $f_{Fe=}0.9$, $f_{Zn}=0.1$, alpha of H_2=0.5, alpha of Zn = Fe=0.5, Re=10000,pH=1, P=1 atm

T (^{0}C)	Eg (V)	I_{Fe} (μA)	I_{Zn} (μA)	$I_{H2/Fe}$ (μA)	$I_{H2/Zn}$ (μA)	$i_{Limiting}$ (μA/cm^2)
25	-0.70453428	0	26015.1	25835.8	0.4593	178.918
40	-0.74574711	0	45405.4	45270.7	4.55899	130.184
60	-0.80063512	0	88443.2	88308.3	70.4262	64.483

Table 5.52: Galvanic corrosion of Fe/Zn couple versus temperature under the following conditions: $[Fe^{++}]=[Zn^{++}]=10^{-6}$ M, $f_{Fe}=0.1$, $f_{Zn}=0.9$, alpha of $H_2=0.5$, alpha of Zn = Fe=0.5, Re=50000,pH=7, P=5 atm

T (^{0}C)	Eg (V)	I_{Fe} (µA)	I_{Zn} (µA)	$I_{H2/Fe}$ (µA)	$I_{H2/Zn}$ (µA)	$i_{Limiting}$ (µA/cm^2)
25	-0.57504985	5.1984E-07	1208.783	2.3066	2.08E-04	1206.487
40	-0.63225532	0	915.700	6.13496	3.13E-03	909.57238
60	-0.71476583	0	529.013	21.9745	8.8719E-02	506.95

III. *Effect of Renolds Number*

The effect of Renolds number on galvanic corrosion rate and corrosion potential is shown in Tables 5.53 and 5.54 at different values of pH, pressure, area fraction and temperature, limiting current was calculated from Eq.(4.46), corrosion current of metals were calculated from Eq.(4.55)

Table 5.53: Galvanic corrosion of Fe/Zn couple versus Renolds number under the following conditions: $[Fe^{++}]=[Zn^{++}]=10^{-6}$ M, $f_{Fe}=0.9$, $f_{Zn}=0.1$, alpha of $H_2=0.5$, alpha of Zn = Fe=0.5, T=25˚C ,pH=1, P=1 atm

Re	Eg (V)	I_{Fe} (µA)	I_{Zn} (µA)	$I_{H2/Fe}$ (µA)	$I_{H2/Zn}$ (µA)	$i_{Limiting}$ (µA/cm^2)
10^4	-0.70453428	0	26015.1	25835.8	0.4593	178.91
$3*10^4$	-0.70436209	0	26190.2	25749.3	0.45777	440.44
$5*10^4$	-0.70421169	0	26344	25674	0.45643	669.58

Table 5.54: Galvanic corrosion of Fe/Zn couple versus Renolds number under the following conditions: $[Fe^{++}]=[Zn^{++}]=10^{-6}$ M, $f_{Fe}=0.9$, $f_{Zn}=0.1$, alpha of $H_2=0.5$, alpha of Zn = Fe=0.5, T= 40˚C ,pH=7, P=1 atm

Re	Eg (V)	I_{Fe} (µA)	I_{Zn} (µA)	$I_{H2/Fe}$ (µA)	$I_{H2/Zn}$ (µA)	$i_{Limiting}$ (µA/cm^2)
10^4	-0.61800583	1.93E-06	172.5704	42.39623	2.67E-03	130.18
$3*10^4$	-0.59891688	3.91E-06	350.2273	29.76017	1.87E-03	320.47
$5*10^4$	-0.58868490	5.72E-06	511.8142	24.61808	1.55E-03	487.20

IV. Effect of Pressure

The effect of pressure on galvanic corrosion rate and corrosion potential is shown in Table 5.55 and 5.56 at different values of pH, area fraction Renolds number and temperature, limiting current was calculated from Eq.(4.46), corrosion current of metals were calculated from Eq.(4.55)

Table 5.55: Galvanic corrosion of Fe/Zn couple versus pressure under the following conditions: [Fe^{++}]=[Zn^{++}]=10^{-6} M, f_{Fe}=0.9, f_{Zn}=0.1, alpha of H_2=0.5, alpha of Zn = Fe=0.5, T= 25˚C ,pH=1, Re=10000

Pres. (atm)	Eg (V)	I_{Fe} (µA)	I_{Zn} (µA)	$I_{H2/Fe}$ (µA)	$I_{H2/Zn}$ (µA)	$i_{Limiting}$ (µA/cm^2)
0.5	-0.70456297	0	25986.08	25850.21	4.60E-01	135.84
1	-0.704534553	0	26014.86	25835.91	4.59E-01	178.91
5	-0.704440022	0	26110.81	25788.39	4.58E-01	322.37

Table 5.56: Galvanic corrosion of Fe/Zn couple versus pressure under the following conditions: [Fe^{++}]=[Zn^{++}]=10^{-6} M, f_{Fe}=0.1, f_{Zn}=0.9, alpha of H_2=0.5, alpha of Zn = Fe=0.5, T= 60˚C ,pH=7, Re=50000

Pres. (atm)	Eg (V)	I_{Fe} (µA)	I_{Zn} (µA)	$I_{H2/Fe}$ (µA)	$I_{H2/Zn}$ (µA)	$i_{Limiting}$ (µA/cm^2)
0.5	-0.745589272	0	180.6908	37.59963	0.1518035	142.94
1	-0.733844839	0	272.0788	30.64109	0.12370932	241.32
5	-0.714765831	0	529.0131	21.97447	8.87E-02	506.95

V. Effect of Area Fraction

The effect of area fraction on galvanic corrosion rate and corrosion potential is shown in Tables 5.57 and 5.58 at different values of pH, pressure, Renolds number and temperature, limiting current was calculated from Eq.(4.46), corrosion current of metals were calculated from Eq.(4.55)

Table 5.57: Galvanic corrosion of Fe/Zn couple versus area fraction under the following conditions: [Fe^{++}]=[Zn^{++}]=10^{-6} M, P=1 atm, alpha of H2=0.5, alpha of Zn = Fe=0.5, T= 25˚C ,pH=1, Re=10000, Limiting current=178.91µA/cm^2

Area f_{Fe} (Fe)	Eg (V)	I_{Fe} (µA)	I_{Zn} (µA)	$I_{H2/Fe}$ (µA)	$I_{H2/Zn}$ (µA)
0.1	-0.77960937	0	12580.724	12384	17.8329

0.2	-0.76582545	0	19128.63	18937.6	12.1201
0.3	-0.75663564	0	23939.848	23752.1	8.86744
0.4	-0.74909119	0	27528.064	27342.6	6.56222
0.5	-0.74216098	0	30047.385	29863.7	4.77819
0.6	-0.73522563	0	31491.683	31309.4	3.33967
0.7	-0.72766343	0	31707.248	31526.2	2.16179
0.8	-0.71843252	0	30282.505	30102.4	1.2041
0.9	-0.70453428	0	26015.135	25835.8	0.4593

Table 5.58: Galvanic corrosion of Fe/Zn couple versus area fraction under the following conditions: $[Fe^{++}]=[Zn^{++}]=10^{-6}$ M, P=5 atm, alpha of H_2=0.5, alpha of Zn = Fe=0.5, T= 25˚C ,pH=7, Re=30000, Limiting current=793.60 μA/cm^2

Area f_{Fe} (Fe)	Eg (V)	I_{Fe} (μA)	I_{Zn} (μA)	$I_{H2/Fe}$ (μA)	$I_{H2/Zn}$ (μA)
0.1	-0.58576306	3.43E-07	796.44113	2.84168	2.56E-04
0.2	-0.58265791	7.73E-07	798.94931	5.34991	2.14E-04
0.3	-0.57916023	1.33E-06	801.09588	7.49651	1.75E-04
0.4	-0.57514603	2.07E-06	802.84315	9.24382	1.39E-04
0.5	-0.57042301	3.11E-06	804.13881	10.5395	1.05E-04
0.6	-0.56466869	4.67E-06	804.90606	11.3068	7.54E-05
0.7	-0.55727795	7.27E-06	805.02239	11.4232	4.90E-05
0.8	-0.54689071	1.25E-05	804.26362	10.6644	2.67E-05
0.9	-0.52916159	2.79E-05	802.09413	8.49496	9.44E-06

CHAPTER SIX

DISCUSSON

6.1 Introduction

Chapter five introduced the theoretical of analysis results. The variables involved are pH, temperature, area fraction, pressure, Renolds number and their interactions. The influence of these variables on the analysis results needs to be interpreted.

In discussing the results, the following manner is followed: section 6.2 deals with activation control and the effect of pH, temperature and area fraction on galvanic and corrosion currents and potentials ,section 6.3 deals with mass transfer control and the effect of temperature, pressure, Renolds number and area fraction on galvanic and corrosion currents and potentials, and section 6.4 deals with both activation and mass transfer control and the effect of pH, temperature, pressure, Renolds number and area fraction on galvanic and corrosion currents and potentials for mixed control corrosion.

6.2 Activation Control

6.2.1 Free Corrosion

I. ***Effect of pH***:

The equilibrium potential of the metal electrodes (Fe, Zn) is more active than the hydrogen electrode (see galvanic series, Table 3.1), therefore metal will behave as an anode (oxidation) and the hydrogen behaves as cathode (reduction).It was mentioned that pH as a factor plays an important role in H^+ concentration affecting the corrosion rate of metals. This is clear in results from

Tables 5.1 to 5.4, which are plotted in Fig. 6.1 and Fig. 6.2, in which the current density is decreasing and corrosion potential shifts to more negative values by increasing pH. The behavior is attributed to the fact that increasing pH at the interface between metal and solution leads to decrease the rate of reaction for metal dissolution

$$M \longrightarrow M^{++} + 2e \qquad \ldots(6.1)$$

$$2H^{++} + 2e \longrightarrow H2 \qquad \ldots(6.2)$$

therefore the higher the pH is the lower the corrosion rate of metal.

It is to be noticed from Figs 6.1 and 6.2, that as pH increases corrosion potential (E_{corr}) decreases (becomes more negative).This behavior can be understood by noting Fig. 6.3, increasing pH (decreases a_{H+}) decreases $E_{eq.,C}$ and $i_{0,H}$ [3]. From figure 6.4 within the acid region (pH < 4), the ferrous oxide film is dissolved, the surface pH falls, and iron is more or less in direct contact with the aqueous environment. The increasing rate of reaction is then the hydrogen evolution rate. Within the range of about pH 4-10, the corrosion rate is independent of pH, and depends only on how rapidly oxygen diffuses to the metal surface [9].

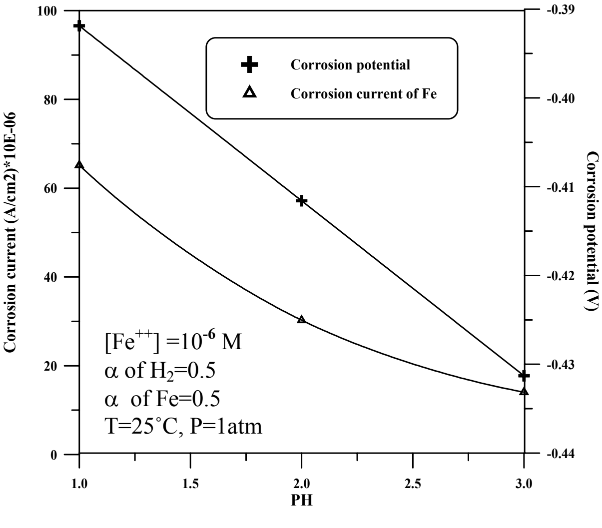

Figure 6.1: Variation of Corrosion Current & Potential with pH in de-aerated Acid Solutions.

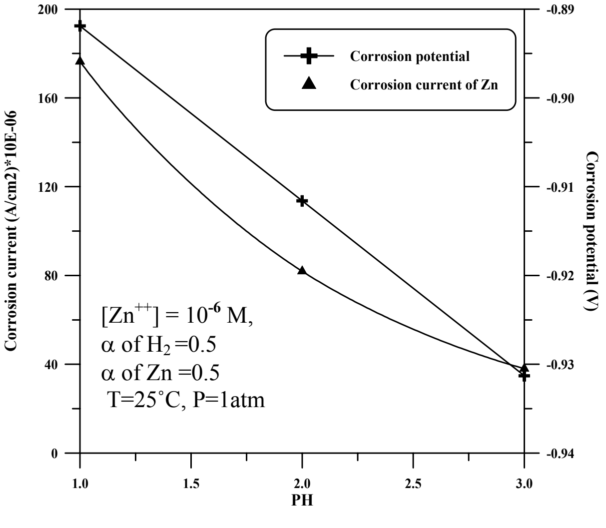

Figure 6.2: Variation of Corrosion Current & Potential with pH in de-aerated Acid Solutions.

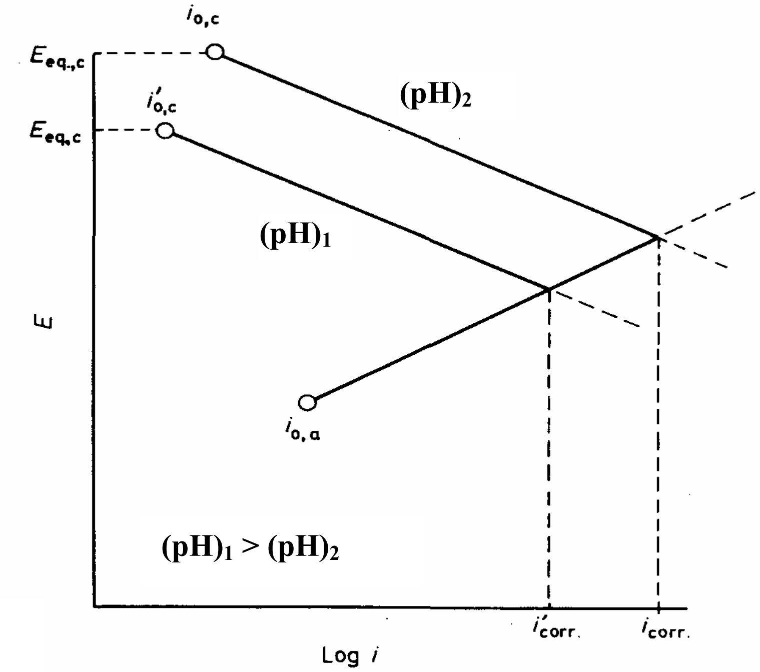

Figure 6.3: Effect of Increasing pH on Corrosion Rate and Corrosion Potential [3].

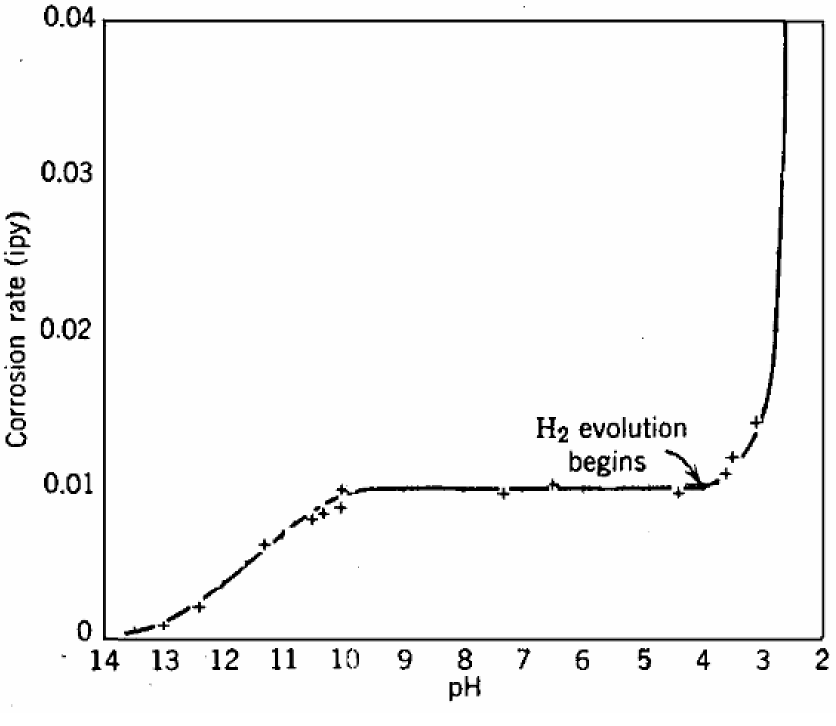

Figure 6.4: Effect of PH on Corrosion of Iron in Aerated Soft Water [9]

II. Effect of Temperature

Temperature changes have the greatest effect when the rate determining step is the activation-controlled process. In general, in activation processes the corrosion rate may be increased by 10-l00 times, depending on the magnitude of the activation energy. Hydrogen evolution process in de-aerated solutions when this process is under activation control the main effect of increasing the temperature is to increase the exchange current. Typical examples of the magnitude of this change have been given by Conway et al. [45] who found that for nickel the exchange current increased from approximately 10^{-2} A/m^2 to 1.0 A/m^2 when the temperature changed from 10 to 75 ^{0}C and the activation energy was about 59 kJ/mol. Thus the rate of corrosion would be increased by at least 100 times if the anode process was unaffected by the temperature increase, the diffusion coefficient for hydrogen ions would increase perhaps only twice over the same temperature range leading to increase corrosion rate [3]. The results in chapter five in Tables 5.5 and 5.6 are plotted in Fig. 6.5 and Fig. 6.6, in which the current density increases and corrosion potential shifts to more negative direction with increasing temperature as illustrated in Fig.6.7.

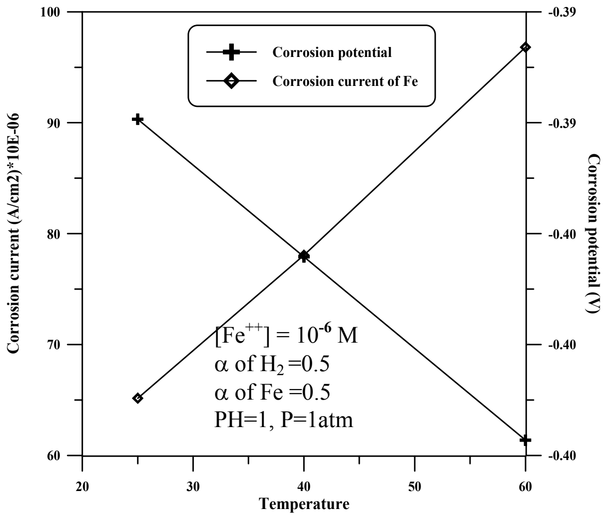

Figure 6.5: Variation of Corrosion Current& Potential of Fe with Temperature in de-aerated Acid Solutions.

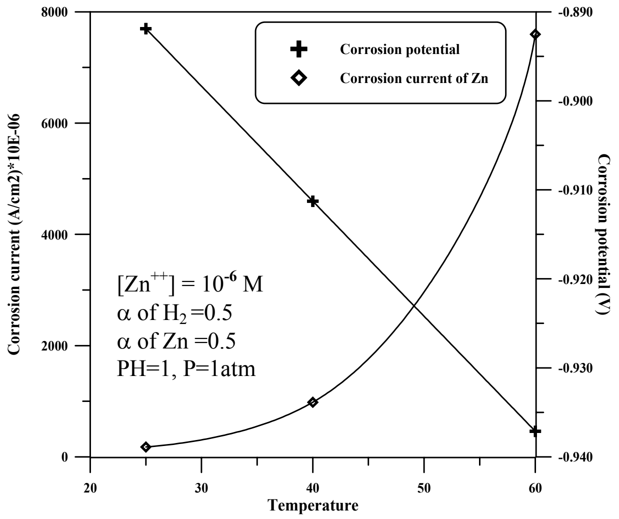

Figure 6.6: Variation of Corrosion Current & Potential of Zn with Temperature in de-aerated Acid Solutions.

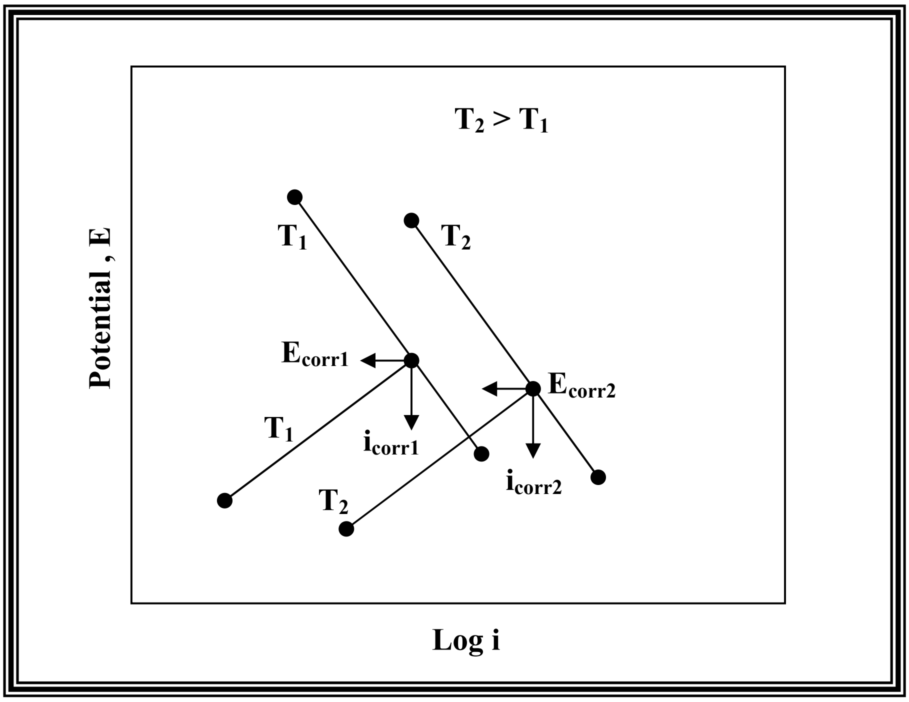

Figure 6.7: Effect of Temperature on Corrosion Rate & Potential of Fe & Zn in de-aerated Acid Solution

6.2.2 Galvanic Coupling:

I. Effect of pH:

When coupled metals are exposed to de-aerated acid solutions for which corrosion is accompanied by hydrogen evolution, corrosion rate will decrease when pH increases [9]. According to Tables 5.7 and 5.8 (shown graphically in Figs. 6.8.and 6.9.) it can be seen that the galvanic corrosion current of Zn and hydrogen evolution currents on Fe and Zn decrease with increasing pH. Decreasing pH leads to increase the rate of dissolution of Zn because it is more active metal than Fe. Increasing pH decreases the rate of the cathodic reaction and consequently decreases corrosion rate of zinc, but hydrogen evolution current on Zn is low, because i_0 of hydrogen evolution on zinc is exceedingly small. Decreasing pH leads to increase rate of reaction for zinc dissolution which leads to increase hydrogen evolution current on Fe by increasing electron transfer from Zn to Fe and then to H+ in the solution.

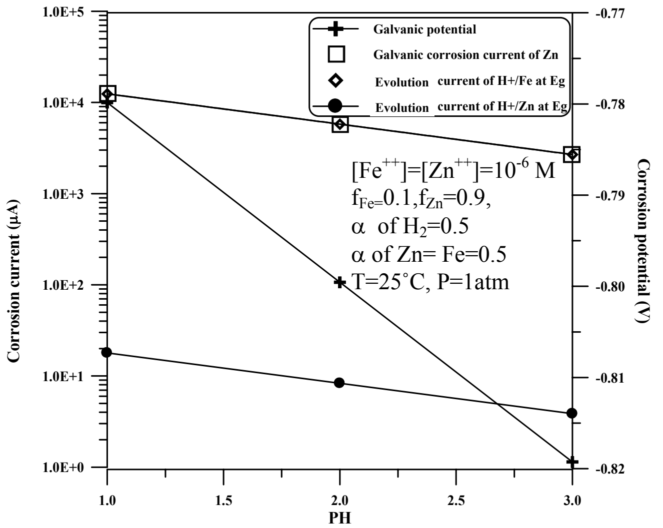

Figure 6.8: Galvanic Corrosion of Fe/Zn Couple Versus PH in De-Aerated Acid Solutions.

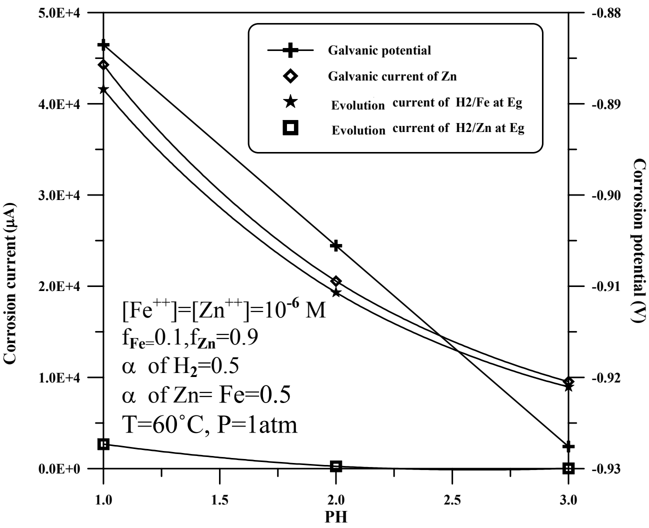

Figure 6.9: Galvanic Corrosion of Fe/Zn Couple Versus PH in De-Aerated Acid Solutions.

II. Effect of Temperature

The results in Tables 5.9 and 5.10 are plotted in Fig. 6.10 and Fig. 6.11, in which the corrosion current of Zn increasing and corrosion potential shifts to more negative values with increasing temperature. It can be seen that the galvanic corrosion current of Zn and hydrogen evolution currents on Fe increase with increasing temperature. Thus temperature increases rate of cathodic reaction and consequently increases corrosion rate of zinc, but hydrogen evolution current on Zn is negligible, because i_0 of hydrogen evolution on zinc is exceedingly small. Furthermore, Fe is cathodically protected as $Eg < E_{eq,Fe}$.

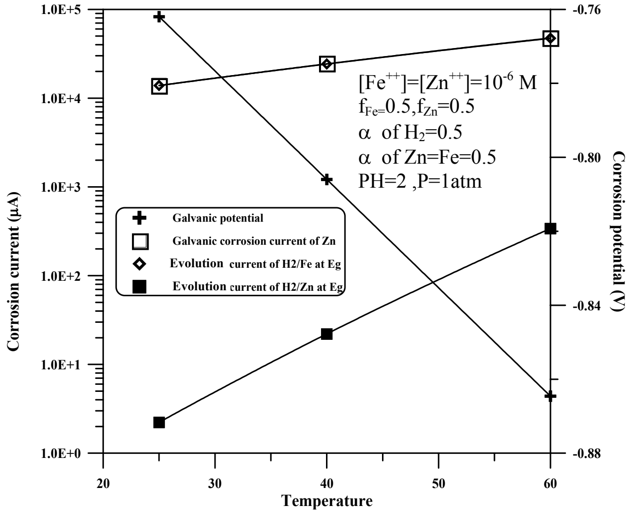

Figure 6.10: Effect of Temperature on Galvanic Corrosion of Fe/Zn Couple in De-aerated Acid Solutions.

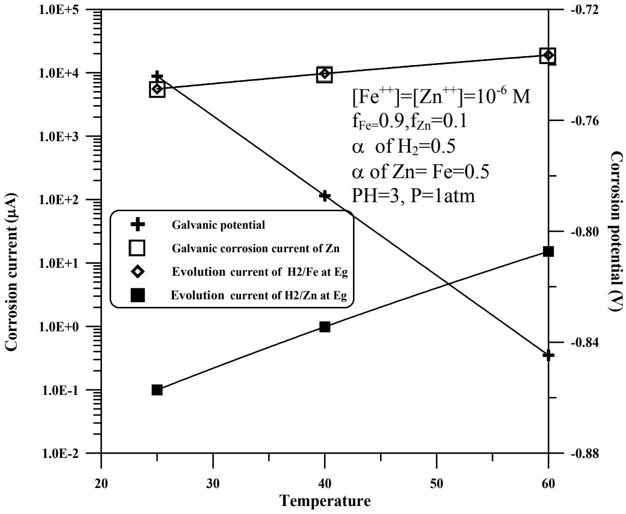

Figure 6.11: Effect of Temperature on Galvanic Corrosion of Fe/Zn Couple in De-aerated Acid Solutions.

III. Effect of Area fraction

Area fraction plays an important role in galvanic corrosion as it was found from results obtained in chapter five and other studies [44]. It plays a comprehensive role as shown in the Tables 5.11 and 5.12 and in Figs.6.12 and 6.13 which show that increasing area fraction of Fe increases galvanic corrosion of Zn up to $f_{Fe} \cong 0.7$. Increasing area fraction of more positive electrode (Fe) increase corrosion rate of more negative electrode while the more positive electrode will be protected .This fact is true for the whole range of area fraction. Also Figs. reveal that the highest galvanic corrosion current occurs at area fraction of Fe about of 0.7, while from the same figs. it is obvious that hydrogen evolution current on Zn for both coupling systems is almost negligible. This phenomena can be ascribed to the same fact mentioned above that of H_2 evolution on Zn is exceedingly low becouse atomic hydrogen adsorption on Zn is greatly lower then on metals , e.g, Fe. The figures show that galvanic corrosion potential shifts to less negative direction with increasing area fraction of Fe, because Fe is less active than Zn and due to increased rate of H_2 evolution on Fe which is compensated by increased rate of Zn corrosion rate.

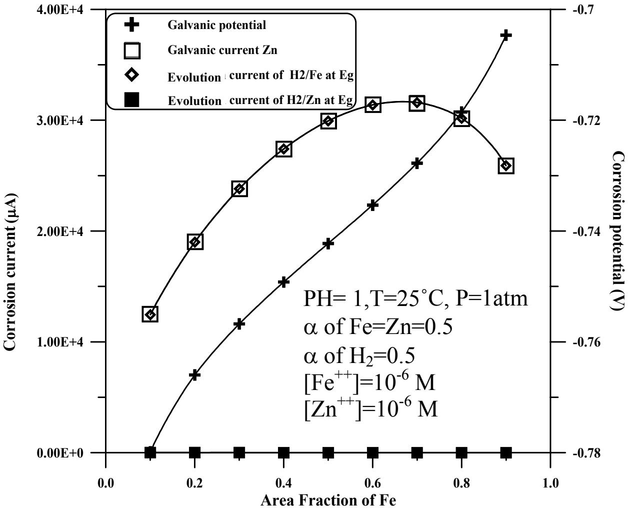

Figure 6.12: Effect of cathode Area Fraction on Galvanic Corrosion of Fe/Zn Couple

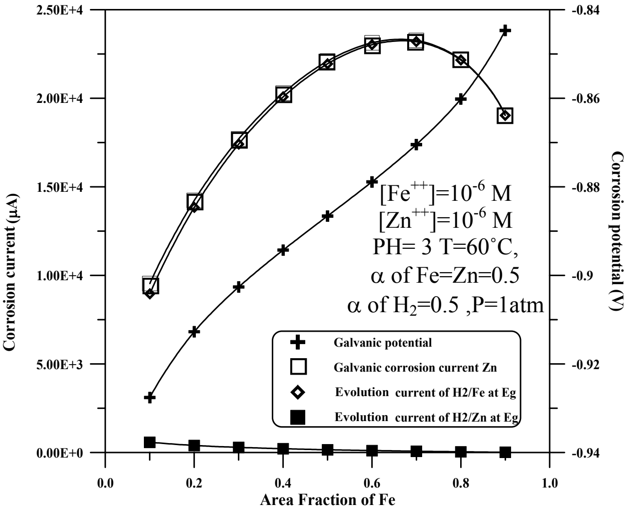

Figure 6.13: Effect of cathode Area Fraction on Galvanic Corrosion of Fe/Zn Couple

6.3 Diffusion Control

6.3.1 Free Corrosion

I. Effect of Renolds Number

Fig. 6.14 and Fig.6.15 show the variation of corrosion rate (or limiting current) with Re. It is evident that at a particular temperature, the corrosion rate increases with Re. Since the corrosion of iron and zinc in aerated water is a mass transfer controlled, therefore increasing Re (or velocity) will increase the amount of oxygen arriving to the surface and hence leads to higher corrosion rate. Increasing Re leads to decrease the thickness of diffusion layer that represents the main resistance to oxygen transport [3].

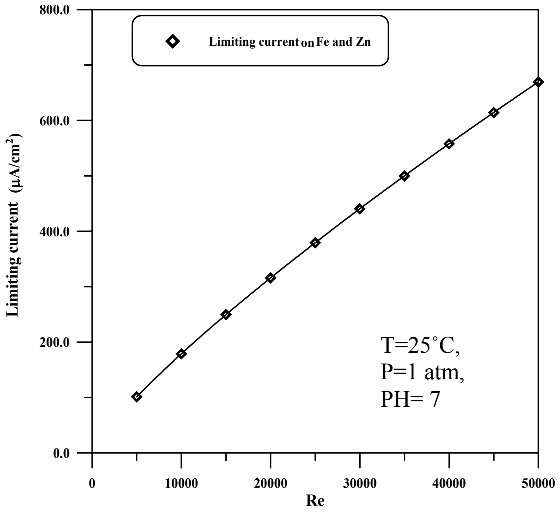

Figure 6.14: Corrosion of Iron & Zinc versus Renolds Number

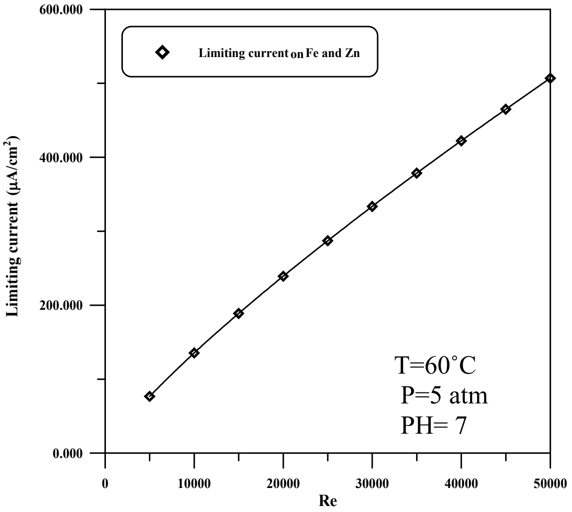

Figure 6.15: Corrosion of Iron & Zinc versus Renolds Number

II. Effect of Temperature

This can occur because of certain solubility considerations. Many gases (such as O_2) have lower solubility in open systems at higher temperatures. As temperature increases, the resulting decrease in solubility of the gas causes corrosion rates to go down [4] as shown in fig. 6.16. The results in Tables 5.17 and 5.20 are plotted in Fig. 6.17 and Fig. 6.18, in which the limiting current decreases with temperature. The corrosion current of Fe and Zn is the same because the mass transfer relation gives the same mass transfer coefficient since it depends on Re and Sc, and not on the metals, thus i_L (limiting current density)of O_2 will be equal regardless the metal kind, but when i_L is converted to gmd or mpy the corrosion rate will be different between metals because of different densities and molecular weights.

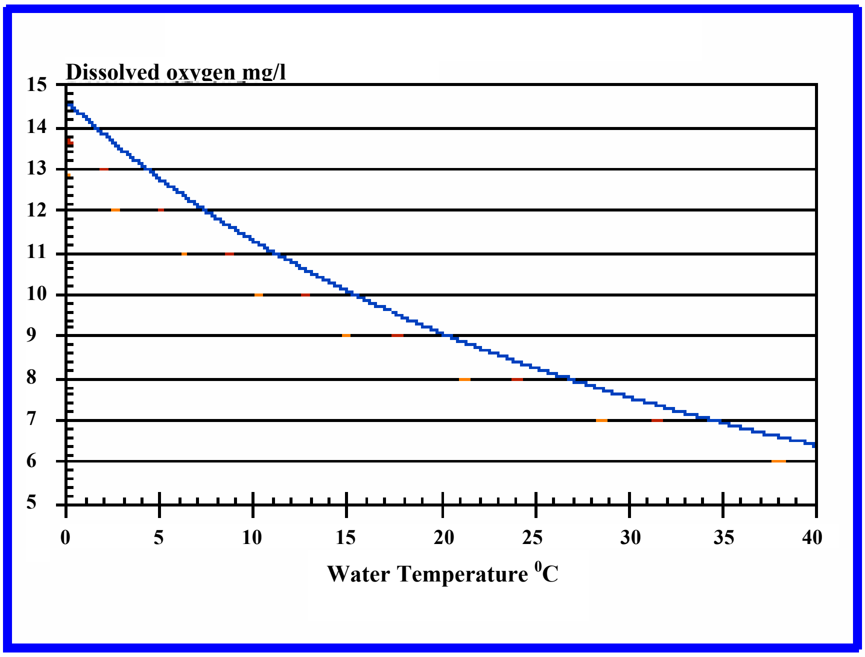

Figure 6.16: Oxygen Solubility Versus Temperature [46]

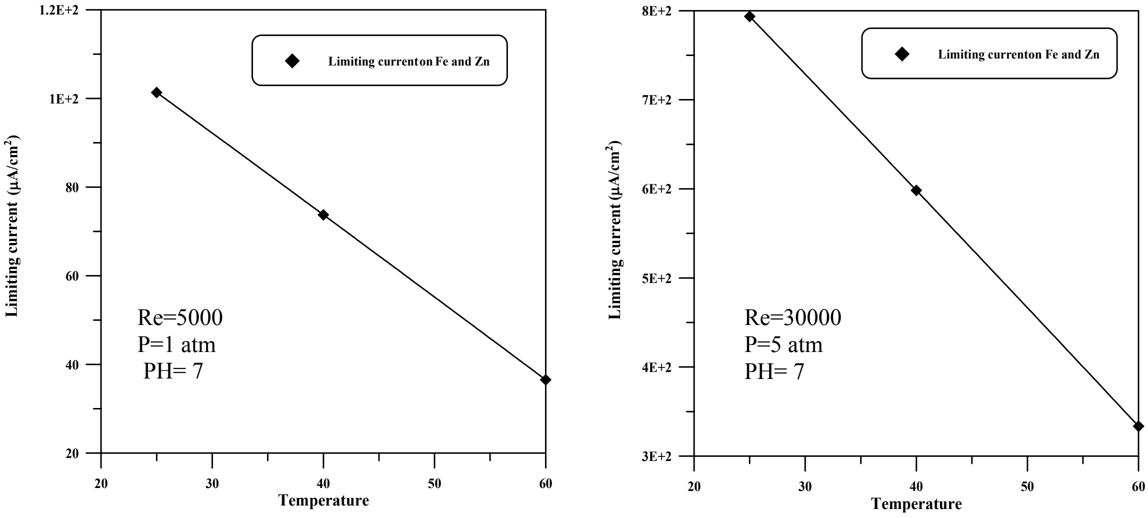

Figure 6.17: Corrosion Rate of Iron & Zinc Versus Temperature

Figure 6.18: Corrosion Rate of Iron & Zinc Versus Temperature

III. Effect of Pressure

As a general rule, the solubility of oxygen in water depends upon the partial pressure of oxygen in the atmosphere in contact with the water and on the temperature and salinity of the water. The solubility of oxygen increases with an increase in the partial pressure of oxygen and decreases with increasing temperature and salinity of the water. The corrosion rates in a system will increase with increasing pressure. This can occur because of certain solubility considerations [4]. As pressure increases, the resulting increase in solubility of the gas causes corrosion rates to go up. The results presented in Tables 5.21 and 5.24 are plotted in Fig. 6.19 and Fig. 6.20, in which the limiting current density increases at all temperatures and Renolds number for iron and zinc.

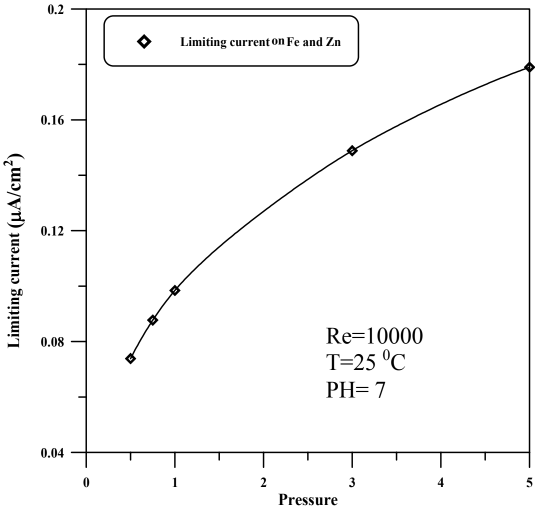

Figure 6.19: Corrosion Rate of Iron & Zinc Versus Pressure

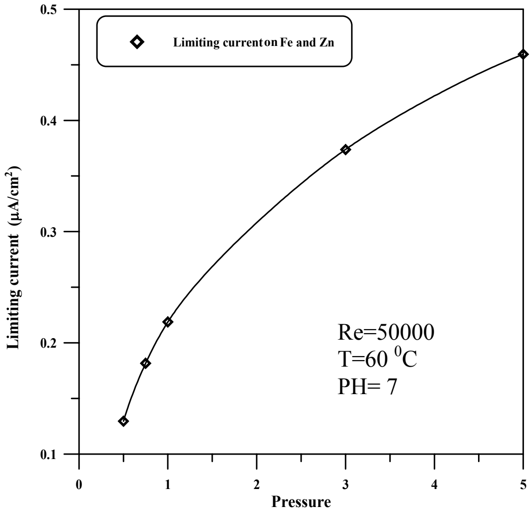

Figure 6.20: Corrosion Rate of Iron & Zinc Versus Pressure

6.3.2 Galvanic Coupling

I. Effect of Renolds Number

The results presented in Tables 5.25 and 5.26 are plotted in Fig. 6.21 and Fig. 6.22, in which the corrosion current increases and corrosion potential shifts to less negative with increased Re. It can be seen that the galvanic corrosion current of Zn coupled with Fe and limiting current density increase with increasing Renolds number. This variable increases the rate of the cathodic reaction of oxygen reduction and consequently increases the corrosion rate of zinc, but corrosion current of Fe is almost negligible, because i_0 of Fe is exceedingly small. Also Figures refer that the limiting current density is nearly equal to the Zn corrosion current indicating that the Fe is cathodically protected by Zn, i.e., negligible or no corrosion of Fe due to O_2

The increase in corrosion rate or limiting current is attributed to the increased supply of oxidized species (such as O_2) via increasing eddy diffusion. As a consequence of increasing limiting current density the corrosion potential is shifted to more positive as shown in Figures below.

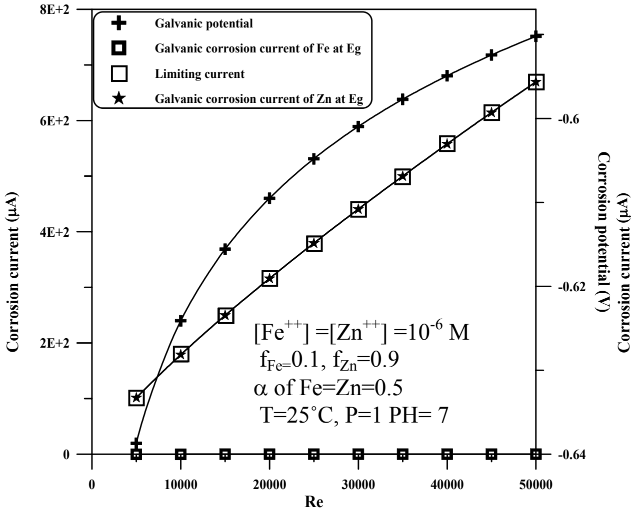

Figure 6.21: Effect of Re on the Galvanic Corrosion of Fe/Zn Couple

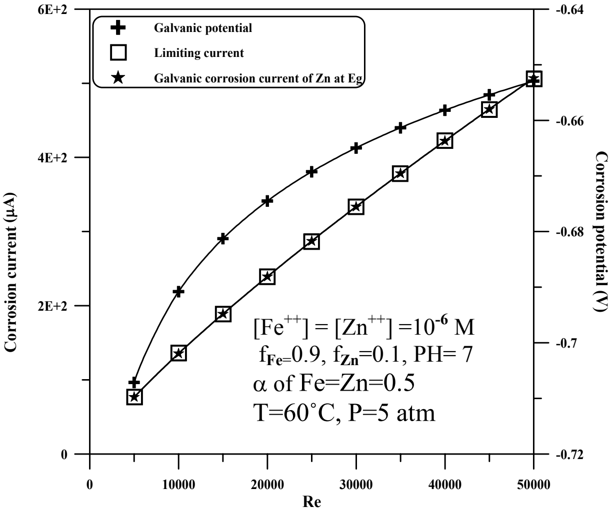

Figure 6.22: Effect of Re on the Galvanic Corrosion of Fe/Zn Couple

II. Effect of Temperature

The corrosion rates in a system may decrease or increase depending on the nature of system temperature. This can occur because of certain solubility considerations. As temperature increases, the resulting decrease in solubility of the gas causes corrosion rates to go down. This behavior is encountered in mass transfer control systems. Tables 5.27 and 5.28 are plotted in Fig. 6.23 and Fig. 6.24, in which the limiting current density and corrosion of Zn is decreasing with increase of temperature, also corrosion rate of Fe decreases. Corrosion Potential shifts to more negative values. This is ascribed to the decrease in the oxidizer concentration [4].

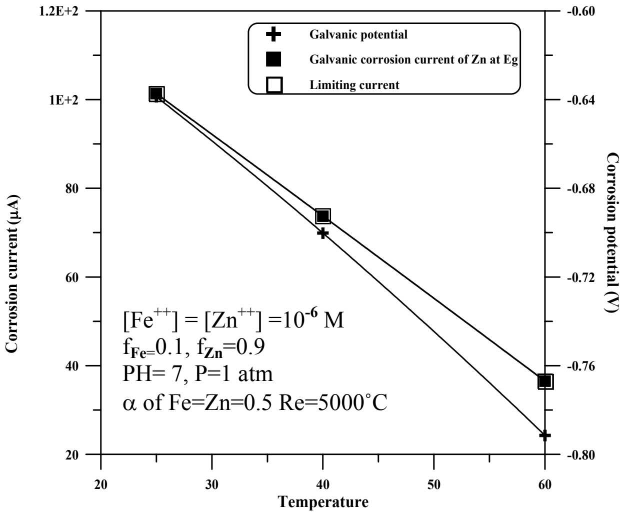

Figure 6.23: Effect of Temperature on the Galvanic Corrosion of Fe/Zn Couple

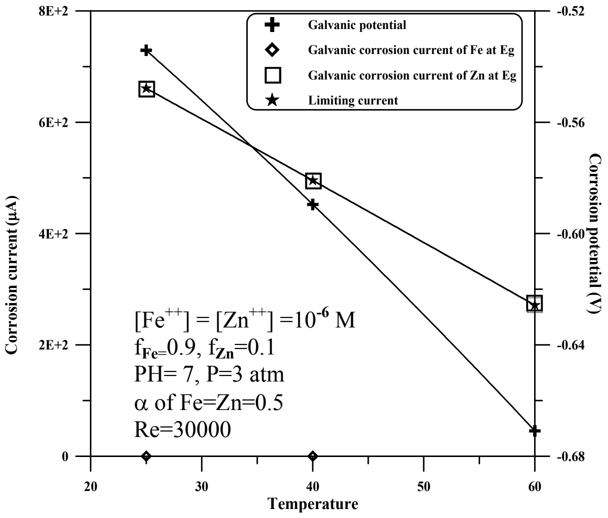

Figure 6.24: Effect of Temperature on the Galvanic Corrosion of Fe/Zn Couple

III. Effect of Pressure

Tables 5.29 and 5.30 are plotted in Fig. 6.25 and Fig. 6.26, in which the limiting current (or corrosion rate) of Zn is increasing with increasing pressure while corrosion rate of Fe is negligible (i.e. galvanically protected), because of the increase in O_2 concentration at all pressures the corrosion potential becomes less negative.

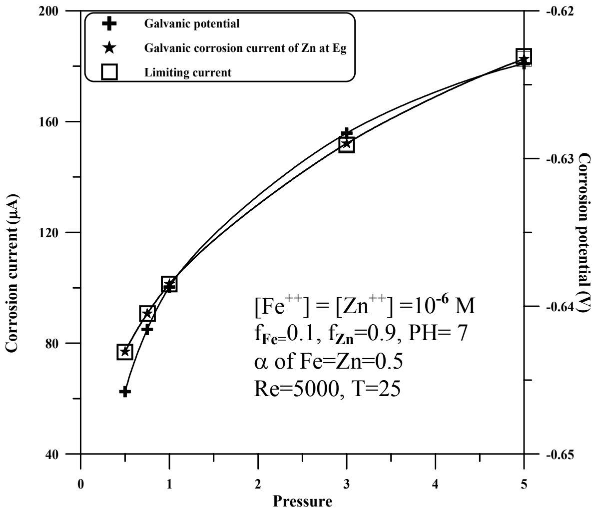

Figure 6.25:Variation of Galvanic Corrosion Current with P for Fe/Zn Couple

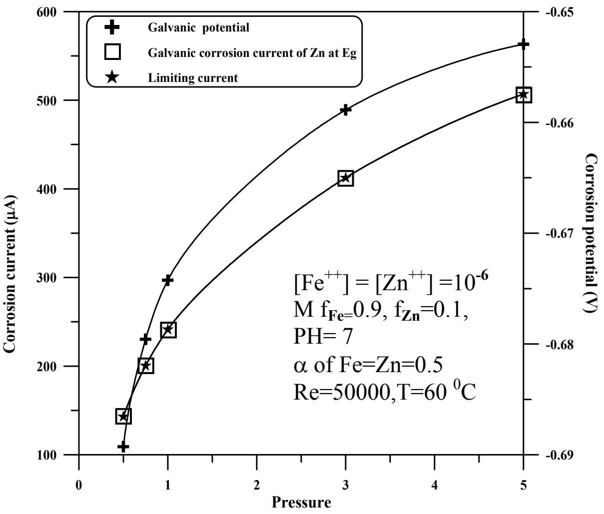

Figure 6.26:Variation of Galvanic Corrosion Current with P for Fe/Zn Couple

IV. Effect of Area Fraction

The effect of area fraction in diffusion control is very small or negligible because it does not affect O_2 solubility or diffusivity and therefore the limiting current is not changing or constant (for given Re, T & P) and corrosion rate of Fe is negligible, so the corrosion rate of Zn equals to the limiting current. As shown in the Tables 5.31 and 5.32 and Figs.6.27 and 6.28, with increasing area fraction of Fe the corrosion potential is shafted to less negative direction, since the iron potential is less negative (more noble than zinc).

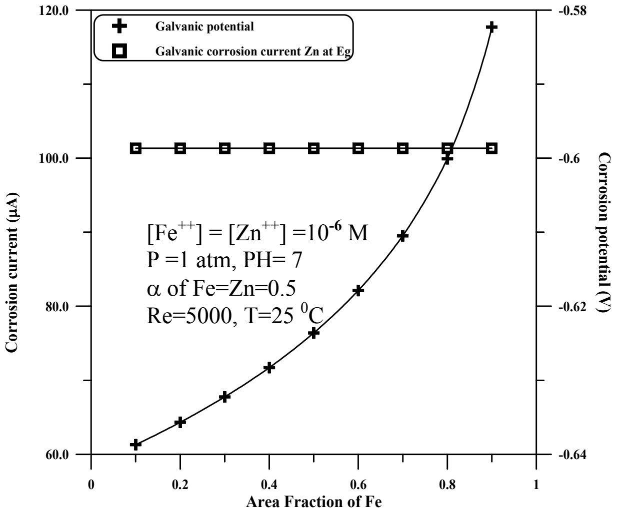

Figure 6.27: Effect of Area Fraction on the Galvanic Corrosion of Fe/Zn Couple

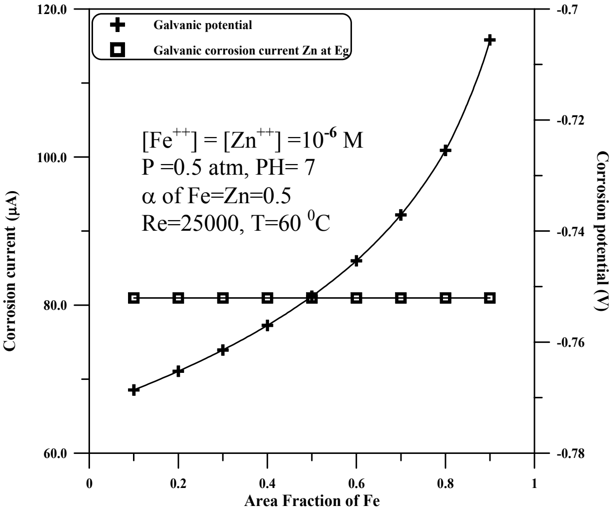

Figure 6.28: Effect of Area Fraction on the Galvanic Corrosion of Fe/Zn Couple

6.4 Activation and Mass Transfer Control (Mixed Control)

6.4.1 Free Corrosion

I. Effect of pH:

This is clear in results from chapter five in Tables 5.33 and 5.36 which are plotted in Fig. 6.29 and Fig. 6.30. The corrosion rate of Fe or Zn and hydrogen evolution currents on Fe and Zn are decreasing and corrosion potential shifts to less negative when pH increases from (1 to 7) for all values of temperature while the limiting current is assumed constant with change in pH. It can be seen that the corrosion rate of Fe or Zn is decreasing with pH until pH=7 when hydrogen concentration is low, so the corrosion current of Fe or Zn is dictated by limiting current, i.e. activation process is replaced by a diffusion process effected by limiting current (see Fig 6.4).

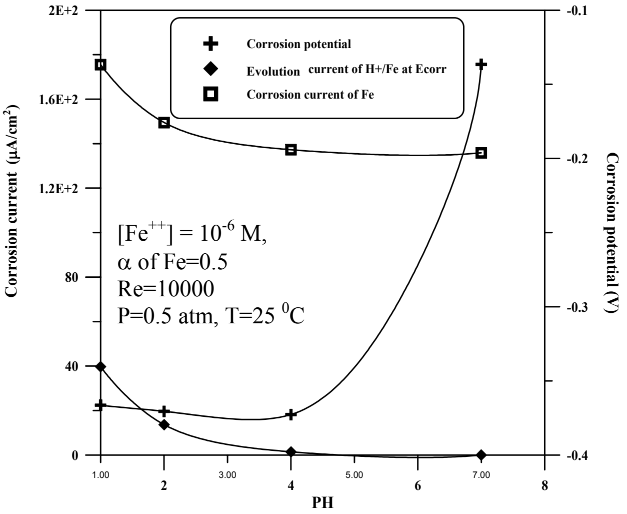

Figure 6.29: Corrosion of Iron Versus pH

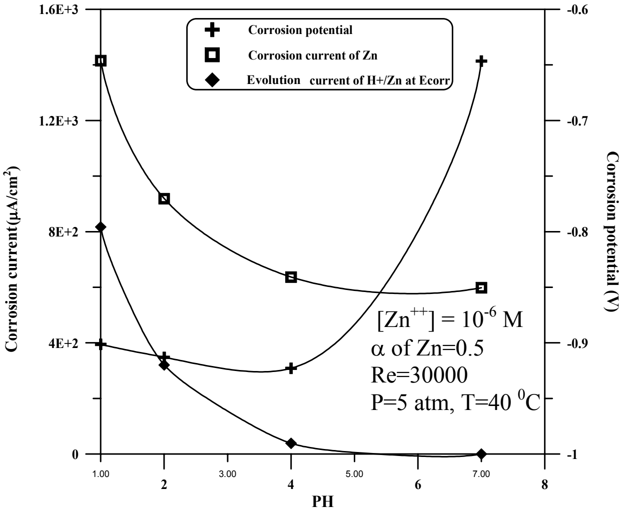

Figure 6.30: Corrosion of Zinc Versus pH

II. Effect of Temperature

It is clear in Tables 5.37 and 5.40 or Fig. 6.31 and Fig. 6.32, in which the corrosion rate of Fe or Zn decreases and hydrogen evolution currents on Fe or on Zn is increasing and corrosion potential shifts to more negative when temperature increasing from (25 to 60) for all values of Renolds number as the limiting current decreases with increase in temperature. In fig. 6.32, limiting current on Zn equals corrosion current of Zn because pH is neutral and H^+ concentration is low. When pH is equal 1 it can be shown that corrosion current of Fe is equal the limiting current with hydrogen evolution on it (Fig.6.31).

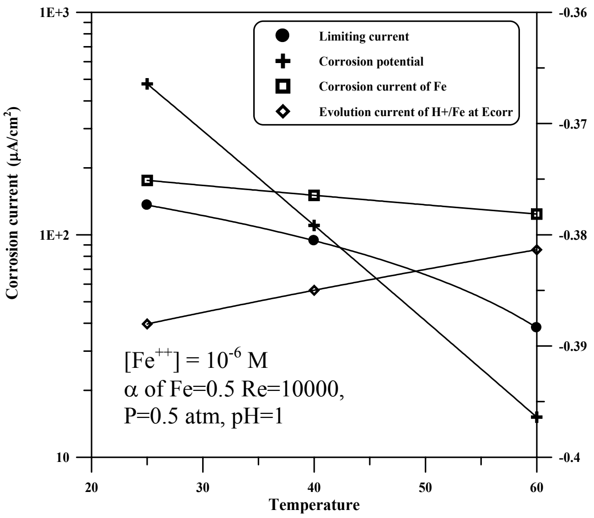

Figure 6.31: Corrosion of Iron Versus Temperature

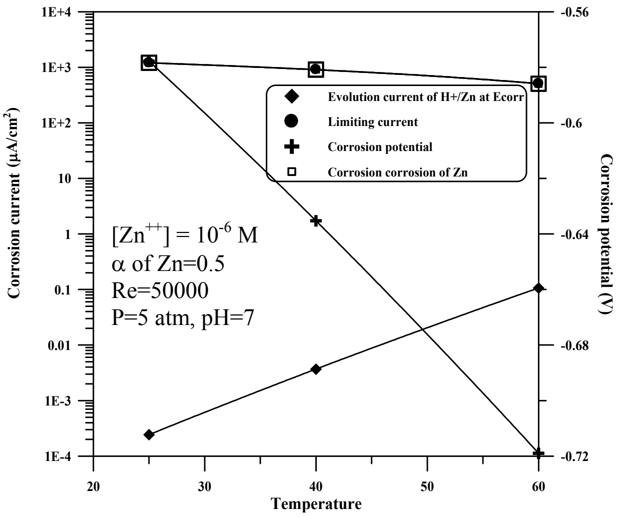

Figure 6.32: Corrosion of Zinc Versus Temperature

III. Effect of Renold Number

The results in chapter five (Tables 5.41 and 5.44) are plotted in Fig. 6.33 and Fig. 6.34. In Fig. 6.33, the corrosion current is increasing with increasing Re and corrosion potential is shifted to less negative values, so corrosion rate of Fe equals the sum of hydrogen evolution current on Fe and limiting current because Re is not affecting activation controlled H_2 evolution but affecting mass transfer controlled oxygen reduction. In Fig. 6.34, corrosion current increases and corrosion potential shifts to less negative values, while corrosion current of Zn is equal the limiting current.

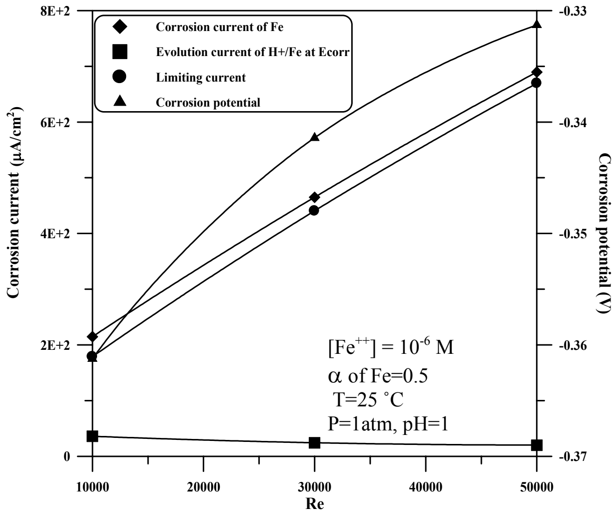

Figure 6.33: Corrosion of Iron Versus Renolds Number

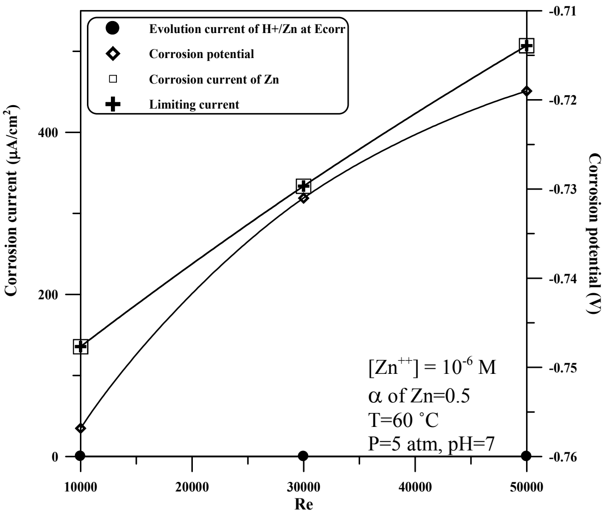

Figure 6.34: Corrosion of Zinc Versus Renolds Number

IV. Effect of Pressure

The results in Tables 5.45 and 5.48 are plotted in Fig. 6.35 and Fig. 6.36. In Fig. 6.35, corrosion current increases with increasing pressure and corrosion potential is shifted to less negative values, so pressure is affecting corrosion rate of Fe and thus equals hydrogen evolution currents on Fe plus limiting current in acidic media. In Fig. 6.36, the corrosion current increases and corrosion potential shifts to less negative values and the corrosion current of Zn is equal the limiting current because pressure increases oxygen solubility while H^+ concentration is very low.

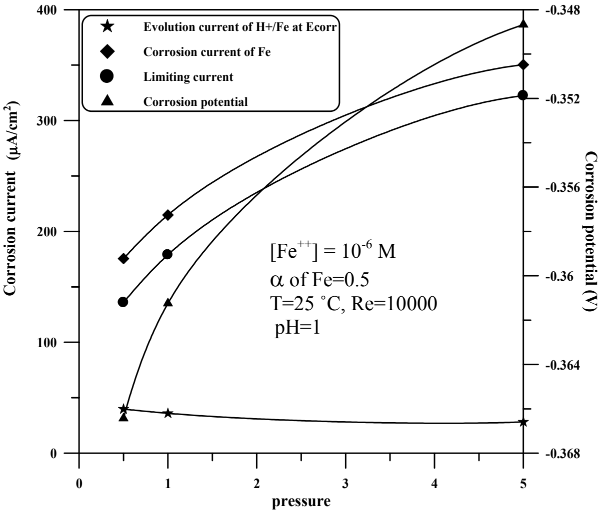

Figure 6.35: Corrosion of Iron Versus Pressure

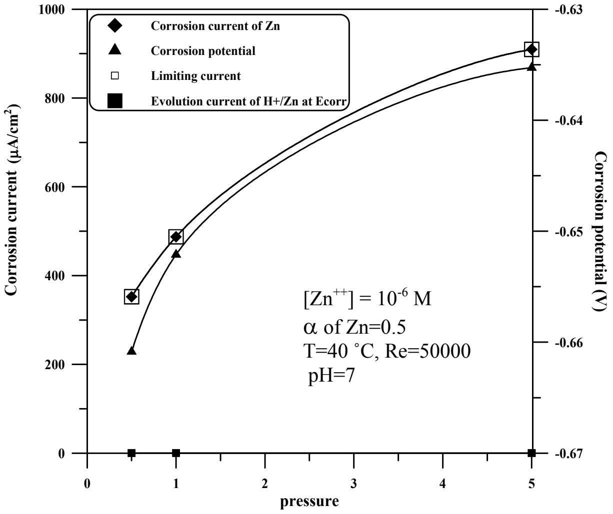

Figure 6.36: Corrosion of Zinc Versus Pressure

6.4.2 Galvanic Coupling

I. Effect of pH

When coupled metals exposed to environment, corrosion rate will decrease when pH increases. According to Tables 5.49 and 5.50 shown graphically in Figs. 6.37, and 6.38, it can be seen that the galvanic corrosion current of Zn and hydrogen evolution current on Fe decrease with increasing pH, as decreasing pH leads to increase the rate of dissolution of Zn because it is more active metal than Fe. This variable decreases rate of cathodic H^+ reaction and consequently decreases corrosion rate of zinc, but hydrogen evolution current on Zn is negligible because i_0 of hydrogen evolution on zinc is exceedingly small. Decreasing pH leads to increase rate of reaction for zinc dissolution which leads to increase hydrogen evolution current on Fe. See figure 6.4 within the acid region (pH < 4), the ferrous oxide film is dissolved, the surface pH falls, and iron is more or less in direct contact with the aqueous environment. The increasing rate of reaction is then the hydrogen evolution rate. Within the range of about pH 4-10, the corrosion rate is independent of pH, and depends only on how rapidly oxygen diffuses to the metal surface. While when pH =7 galvanic corrosion current of Zn equals hydrogen evolution current on Fe and limiting current

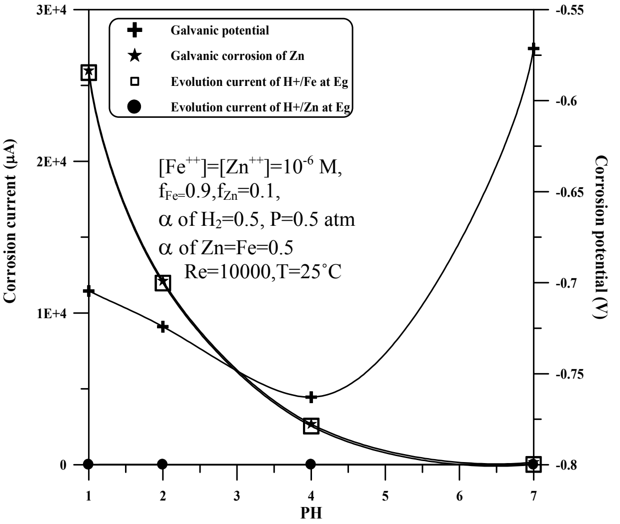

Figure 6.37: Effect of pH on the Galvanic Corrosion of Fe/Zn Couple

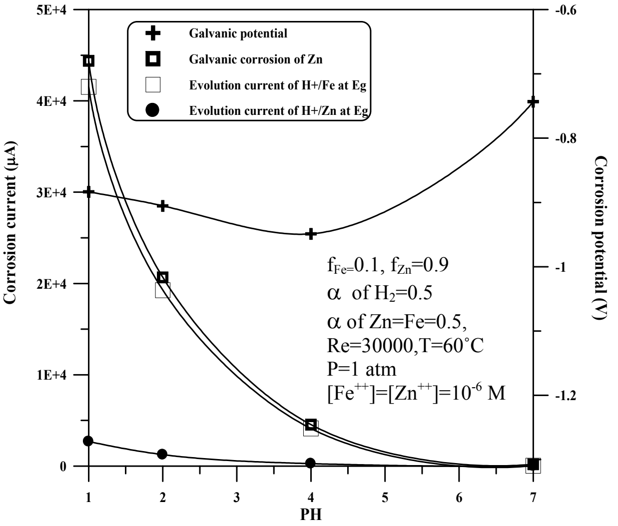

Figure 6.38: Effect of pH on the Galvanic Corrosion of Fe/Zn Couple

II. *Effect of Temperature*

Two cases are found, the first case, from results in chapter five in Table 5.51 shown in Figure 6.39, the corrosion rates in this system will increase with increasing temperature, as activation controlled processes may be increased by 10-100 times, depending on the magnitude of the activation energy [9]. Hydrogen evolution process in de-aerated solutions, when this process is under activation control, the main effect of increasing the temperature is to increase the exchange current, so in figures 6.39, the galvanic corrosion rate of Zn is equals the hydrogen evolution on Fe, limiting current and hydrogen evolution on Zn, so the system will show increases with increasing temperature because H^+ concentration is high (i.e. activation process). The second case, from Table 5.52, shown in Figure 6.40, the corrosion rate of Zn & Fe are equal limiting current plus hydrogen evolution on Fe & Zn, so the galvanic corrosion rate of Zn and limiting current will decrease with increasing temperature; this behavior is attributed to the fact that at increasing temperature the solubility of O_2 (cathodic species) decreases leading to decrease the corrosion rates because the resulting decrease in solubility of the gas causes corrosion rates to go down (diffusion - controlled).

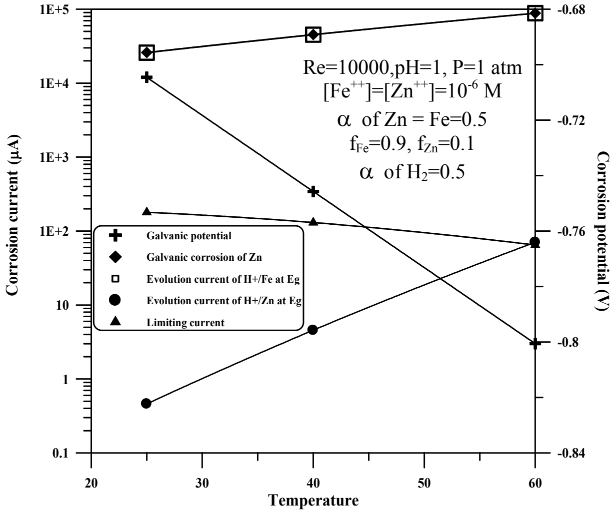

Figure 6.39: Galvanic Corrosion of Fe/Zn Couple Versus Temperature

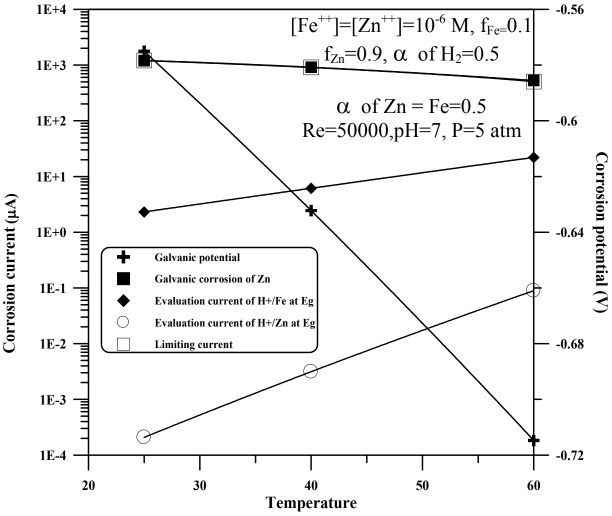

Figure 6.40: Galvanic Corrosion of Fe/Zn Couple Versus Temperature

III. Effect of Renolds Number

The results in Tables 5.53 and 5.54 are plotted in Fig. 6.41 and Fig. 6.42. In Fig. 6.41, the corrosion current is constant and corrosion potential shifts to less negative values, so corrosion rate of Zn equals hydrogen evolution currents on Fe because pH is low, as Re dose not affect H$^+$ ions reaction ,but affects the oxygen reduction and hence the limiting current density. In Fig 6.42, the corrosion current increasing and corrosion potential shifts to less negative values, so corrosion current of Zn is equal the limiting current. See figure 6.43 , the corrosion rate of steel by seawater increases as the velocity increases [49].

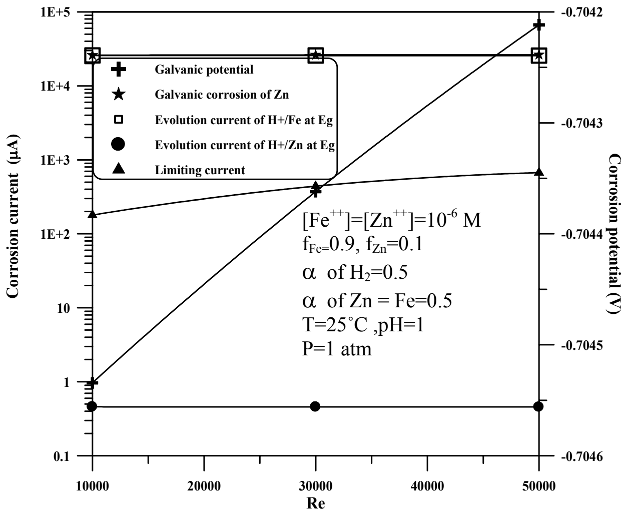

Figure 6.41: Galvanic Corrosion of Fe/Zn Couple Versus Renolds Number

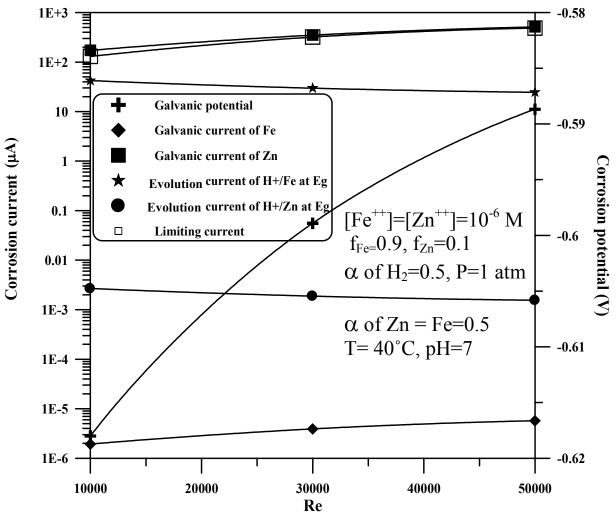

Figure 6.42: Galvanic Corrosion of Fe/Zn Couple Versus Renolds Number

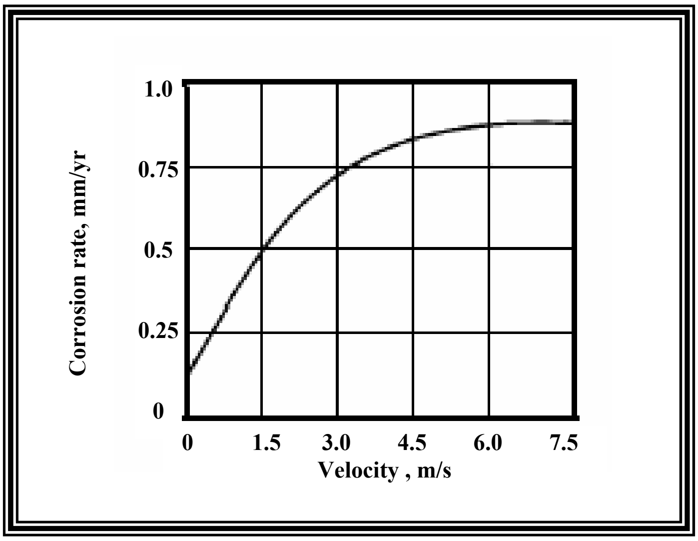

Figure6.43: Effect of velocity of Seawater at Atmospheric Pressure and Temperature on Corrosion Rate of Steel [49].

IV. Effect of Pressure

Observing Fig.6.44indicates that increasing the partial pressure of O_2 leads to shift the galvanic corrosion potential to less negative values via increasing O_2 concentration .No effect of pressure on galvanic corrosion of Zn or on the H_2 evolution on the Fe, since these processes are activation controlled. Also the Figure includes that as pressure increases the limiting current density increases, this is due to the increased O_2 concentration. Fig.6.45 indicates that increasing the partial pressure of O_2 leads to shift the galvanic corrosion potential to less negative values via increasing O_2 concentration. The effect of pressure on galvanic corrosion of Zn and limiting current is due to increased O_2 concentration, since galvanic corrosion of Zn equals limiting current plus H_2 evolution on the Fe & Zn.

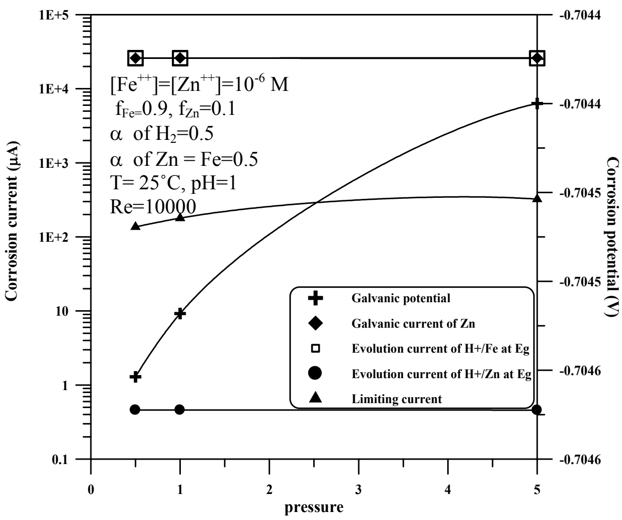

Figure 6.44: Galvanic Corrosion of Fe/Zn Couple Versus Pressure

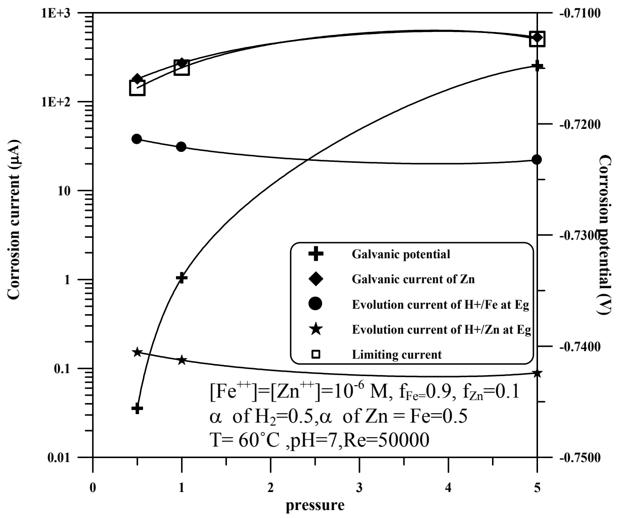

Figure 6.45: Galvanic Corrosion of Fe/Zn Couple Versus Pressure

V. Effect of Area Fraction

Area fraction plays an important role in galvanic corrosion as it was found from results obtained in chapter five. It plays a comprehensive role as shown in the Table 5.57 and in Fig. 6.46, which shows that increasing area fraction of Fe increases galvanic corrosion of Zn. Increasing area fraction leads to increase the exposed area to corrosive solution, i.e. the more negative electrode will corrode and the more positive electrode is protected. Table 5.58 presented in Fig.6.47 shows that the effect of area fraction on diffusion control is negligible because the limiting current depends mainly on the cathodic species (such as O_2) concentration, so the corrosion rate of Zn equals limiting current, increasing area fraction shifts the corrosion potential to less negative value and slightly increases the corrosion rate of Zn.

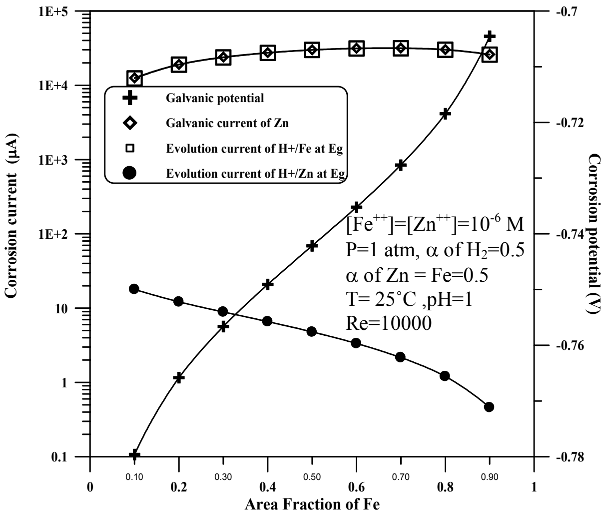

Figure 6.46: Galvanic Corrosion of Fe/Zn Couple Versus Area Fraction

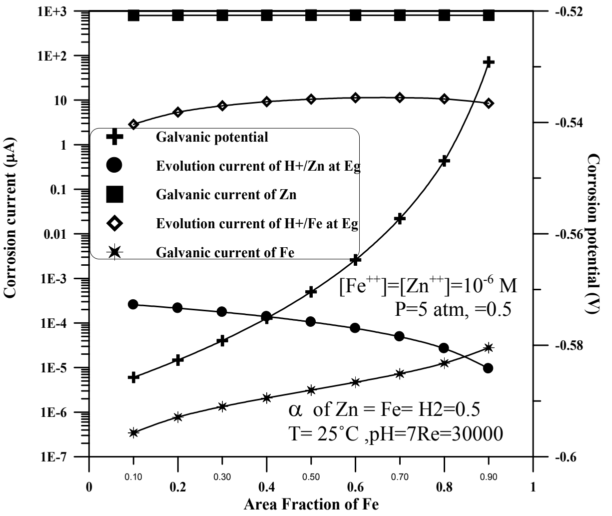

Figure 6.47: Galvanic Corrosion of Fe/Zn Couple Versus Area Fraction

CHAPTER SEVEN

CONCLUTIONS AND RECOMENDATIONS FOR FUTURE WORK

7.1 Conclusions

1. For activation control increasing temperature and decreasing pH lead to increase the corrosion rate of zinc in both free and galvanic corrosion. Increasing area fraction for noble metal leads to increasing the corrosion rate of more active metal until 0.67 then decreases. No effect of Re on the galvanic corrosion is noticed
2. For mass transfer (Diffusion) controlled corrosion process, increasing Re and pressure lead to increase the corrosion rate of free corrosion while it increases the corrosion rate of more active metal. Increasing temperature leads to decrease both free and galvanic corrosion while slight effect of area fraction on the corrosion rate of zinc is noticed.
3. For mixed control corrosion process increasing pH leads to decrease the corrosion rate of zinc for free and galvanic corrosion while temperature leads to slight decreases of corrosion rate of zinc in free corrosion, increasing Re and pressure lead to increase corrosion rate of free corrosion of zinc corrosion. for galvanic corrosion increasing temperature increases corrosion rate of more active metal for $pH < 4$, and decreasing corrosion rate of zinc at $pH=7$

4. For the system that is under both activation and mass transfer control , no appreciable effect both Re and pressure on the galvanic corrosion rate of zinc for pH < 4 while at pH = 7 galvanic corrosion rate of zinc increases with Re and pressure. Increasing area fraction of iron increases the corrosion at pH < 4 while it affects the corrosion rate slightly at pH = 7.
5. Corrosion potential is shifted to more noble value with increasing Re and pressure, while it is shifted to more active direction with increasing temperature and pH, expect in mixed control it exhibits both trends with pH increase.

7.2 Recommendations for Future Work

The following suggestions are to be considered in greater detail for future work:

1. Carrying out experimental work to investigate the influence Re, temperature, pH, pressure and area fraction on galvanic corrosion of couple metals (e.g., Fe-Zn) and compare results present theoretical work.
2. Perform analysis for more than two metals and study the influence of all variables on corrosion rate and corrosion potential.
3. Study the effect oxygen of concentration on galvanic corrosion experimentally by supplying O_2 to the system.
4. Study the effect of the distance between the two metals and time on the galvanic corrosion.
5. Study the effect of presence of salts and solution conductivity on galvanic corrosion.

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Appendix A

```
REM **********************************************
REM ************* Activation Control **************
REM **********************************************
DECLARE SUB MULT ()
OPEN "d:\ma&ac.txt" FOR OUTPUT AS #7
OPEN "d:\mass1.txt" FOR OUTPUT AS #8
OPEN "d:\activ.txt" FOR OUTPUT AS #1
OPEN "d:\massfe.txt" FOR OUTPUT AS #2
OPEN "d:\masszn.txt" FOR OUTPUT AS #3
OPEN "d:\masscapl.txt" FOR OUTPUT AS #6
CLS
INPUT "no. of metal="; p
DIM h(p): DIM u(3): DIM x$(2): DIM v(10)
R = 8.314: f = 96487
FOR t = 298 TO 328 STEP 15
IF t = 328 THEN t = t + 5
FOR h = 1 TO p
IF t = 313 OR t = 333 THEN
IF h = 1 THEN x$ = q1$
IF h = 2 THEN x$ = q2$
ELSE
INPUT "METAL="; x$
IF h = 1 THEN q1$ = x$
IF h = 2 THEN q2$ = x$
END IF
i = .000001: PRINT x$
IF x$ = "FE" OR x$ = "fe" OR x$ = "Fe" THEN 50
IF x$ = "ZN" OR x$ = "Zn" OR x$ = "zn" THEN 60
50 E = -.44: z = 2: i0 = .01 * EXP(2825 * (1 / 298 - 1 / t)): ih2 = .1 * EXP(2825 * (1 /
298 - 1 / t)): GOTO 70
60 E = -.76: z = 2: i0 = 30 * EXP(13609.009# * (1 / 298 - 1 / t)): ih2 = .000016 *
EXP(13609.009# * (1 / 298 - 1 / t)): GOTO 70
70 eeq#(h) = E - ((R * t / (z * f)) * LOG(1 / i))
E(h) = E: z(h) = z: i0(h) = i0: ih2(h) = ih2
NEXT
FOR ph = 1 TO 3
IF ph = 1 THEN c = .1
IF ph = 2 THEN c = .01
IF ph = 3 THEN c = .001
eh2# = -(t * R / f) * LOG(1 / c)
FOR h = 1 TO p
PRINT #1, "Eeq for metal", , , "Temperature", , "I for H+", , "I0", , "pH", , "E for H+"
PRINT #1, "______________", , , "____________", , "_________", , "__", , "__", , 
"_________"
```

```
PRINT #1, eeq#(h), , t, , ih2(h), , i0(h), , ph, , eh2#
PRINT "Eeq for metal", , , "Temperature", , "I for H+", , "I0", , "pH", , "E for H+"
PRINT "______________", , , "_____________", , "_________", , "__", , "__", , "_________"
PRINT eeq#(h), , t, , ih2(h), , i0(h), , ph, , eh2#
NEXT h
PRINT #1, "Ecorr", , "area F", "Ife(mA/cm2)", , "Izn (mA/cm2)", , "Ih,fe(mA/cm2)", ,
"Ih,zn (mA/cm2)"
PRINT #1, "_____", , "______", "____________", , "_____________", , "______________",
, "_______________"
PRINT "Ecorr", , "area F", "Ife(mA/cm2)", , "Izn (mA/cm2)", , "Ih,fe(mA/cm2)", , "Ih,zn
(mA/cm2)"
PRINT "_____", , "______", "____________", , "_____________", , "______________", ,
"________________"
IF p = 1 THEN 100
FOR j = .9 TO 0 STEP -.1
100 GOSUB 5000
FOR ecorr# = q TO 0 STEP 9.999999999999999D-11
FOR u = 1 TO p
m = 1
IF u = 2 THEN
A(u) = j
ELSE
A(u) = 1 - j
l# = 1 - j
END IF
ia#(u) = i0(u) * A(u) * EXP((f * m / (R * t)) * (ecorr# - eeq#(u)))
ic#(u) = ih2(u) * A(u) * EXP((-.5 * f / (R * t)) * (ecorr# - eh2#))
NEXT u
w# = ia#(1) + ia#(2) - ic#(1) - ic#(2)
q = ecorr#
IF p = 2 THEN
IF eeq(1) > q THEN ia#(1) = 0
ELSE
END IF
IF p = 1 THEN
IF ABS(w#) <= .001# THEN 200
ELSE
IF ABS(w#) <= .01# THEN 200
END IF
NEXT
200 PRINT "ECORR="; ecorr#; "At Area ="; l; q1$
PRINT ecorr#, l#, ia#(1), ia#(2), ic#(1), ic#(2), w#
PRINT
PRINT #1,
PRINT #1, ecorr#, l#, ia#(1), ia#(2), ic#(1), ic#(2), w#
PRINT #1,
IF p = 1 THEN 300
```

```
NEXT
300 NEXT ph
NEXT t
REM ***********************************************
REM ************* Mass Transfer Control ***********
REM ***********************************************
FOR u = 1 TO 5
IF u = 1 THEN p1 = .5
IF u = 2 THEN p1 = .75
IF u = 3 THEN p1 = 1
IF u = 4 THEN p1 = 3
IF u = 5 THEN p1 = 5
FOR Temp = 25 TO 60 STEP 15
IF Temp = 25 THEN
PP = 996.45: MM = .0009055: dd = 2.405E-09 * (1 / p1) * (((Temp + 273) / 298)) ^ 1.75:
pv = 3.169 / 101.325: cc = (7.8 / 32) * ((p1 - pv) / (1 - pv))
ELSE
END IF
IF Temp = 40 THEN
PP = 992.04: MM = .0006556: dd = 2.405E-09 * (1 / p1) * (((Temp + 273) / 298)) ^ 1.75:
pv = 7.384 / 101.325: cc = (6 / 32) * ((p1 - pv) / (1 - pv))
ELSE
END IF
IF Temp = 55 THEN Temp = Temp + 5
IF Temp = 60 THEN
PP = 983.3: MM = .000471: dd = 2.405E-09 * (1 / p1) * (((Temp + 273) / 298)) ^ 1.75:
pv = 19.94 / 101.325: cc = (3.1 / 32) * ((p1 - pv) / (1 - pv))
ELSE
END IF
PRINT Temp, p1, dd, cc, MM, PP
sc = MM / (PP * dd)
PRINT #2, "T="; Temp, "P="; p1
PRINT #3, "T="; Temp, "P="; p1
PRINT #2, "Re", "Ife(gmd)karman", "Ife(gmd)colburn", "Ife(gmd)palson",
"Ife(mpy)karman", "Ife(mpy)colburn", "Ife(mpy)pauson"
PRINT #3, "Re", "IZn(gmd)karman", "Izn(gmd)colburn", "Izn(gmd)palson",
"Izn(mpy)karman", "Izn(mpy)colburn", "Izn(mpy)pauson"
PRINT #8, "T="; Temp, "P="; p1
PRINT "T="; Temp, "P="; p1
FOR re = 5000 TO 50000 STEP 5000
s#(v) = re * MM / (PP * .05)
f# = .079 * re ^ (-1 / 4)
sh1(v) = ((f# / 2) * re * sc) / (1 + 5 * (f# / 2) ^ .5 * (sc - 1 + LOG(1 + (5 * (sc - 1) / 6))))
sh2(v) = f# * re * sc ^ (1 / 3) / 2
sh3(v) = .026 * re ^ .82 * sc ^ .35
k1(v) = dd * sh1(v) / .05
k2(v) = dd * sh2(v) / .05
```

```
k3(v) = dd * sh3(v) / .05
i1#(v) = 4 * 96487 * k1(v) * cc * 100
i2#(v) = 4 * 96487 * k2(v) * cc * 100
i3#(v) = 4 * 96487 * k3(v) * cc * 100
fe1#(v) = i1#(v) * 25.0728077# / 100
fe2#(v) = i2#(v) * 25.0728077# / 100
fe3#(v) = i3#(v) * 25.0728077# / 100
fe1M#(v) = fe1#(v) * 1.8345562#
fe2m#(v) = fe2#(v) * 1.8345562#
fe3m#(v) = fe3#(v) * 1.8345562#
zn1#(v) = i1#(v) * 29.10236612# / 100
zn2#(v) = i2#(v) * 29.10236612# / 100
zn3#(v) = i3#(v) * 29.10236612# / 100
zn1m#(v) = zn1#(v) * 2.0114891#
zn2m#(v) = zn2#(v) * 2.0114891#
zn3m#(v) = zn3#(v) * 2.0114891#
IF re = 5000 THEN
PRINT #8, "Renold number", "friction factor", "velocity", , "karman MA/cm2", ,
"culbren MA/cm2", , "pulson MA/cm2 "
PRINT #8, "-------------", "---------------", "--------", , "-------------", , "--------------", , "-----
---------"
ELSE
END IF
PRINT
PRINT #8, re, f#, s#(v), i1#(v), i2#(v), i3#(v)
PRINT #2, re, fe1#(v), fe2#(v), fe3#(v), fe1M#(v), fe2m#(v), fe3m#(v)
PRINT #3, re, zn1#(v), zn2#(v), zn3#(v), zn1m#(v), zn2m#(v), zn3m#(v)
PRINT
PRINT #1, re, i3#(v), fe3#(v), fe3m#(v), zn3#(v), zn3m#(v)
'PRINT #2, fe1#(v), fe2#(v), fe3#(v), fe1M#(v), fe2m#(v), fe3m#(v)
'PRINT #3, zn1#(v), zn2#(v), zn3#(v), zn1m#(v), zn2m#(v), zn3m#(v)
IF re = 5000 THEN
PRINT "Re", "f", "u", "karman", "colburn", "paulson-rob."
PRINT "--", "-", "-", "------", "-------", "------------"
ELSE
END IF
PRINT #6, "T="; Temp, , "p="; p1, , "Re="; re
PRINT #6, " ecorr", , " Afe", , " IL", , " Izn", , " Ife"
GOSUB 5200
FOR a1# = .1 TO 1 STEP .1
FOR ecorr1# = ecr TO -.5 STEP .0000001
a2# = 1 - a1#
E1 = -.44: z = 2: i01# = .000001 * EXP(2825 * ((1 / 298) - (1 / (Temp + 273))))
E2 = -.76: z = 2: i02# = .001 * EXP(13609.009# * (1 / 298 - 1 / (Temp + 273)))
eeq1# = E1 - ((8.314 * (Temp + 273) / (z * 96487)) * LOG(1 / .000001))
eeq2# = E2 - ((8.314 * (Temp + 273) / (z * 96487)) * LOG(1 / .000001))
i1a# = i01# * a1# * EXP((96487 / (8.314 * (Temp + 273))) * (ecorr1# - eeq1#))
```

```
i2a# = i02# * a2# * EXP((96487 / (8.314 * (Temp + 273))) * (ecorr1# - eeq2#))
mag = i1a# + i2a# - i3#(v)
IF ABS(mag) <= .01 THEN 910
NEXT ecorr1#
910 PRINT mag
IF ecorr1# >= eeq1# THEN i1a# = 0
PRINT #6, ecorr1#, a1#, i3#(v), i2a#, i1a#
NEXT a1#
PRINT #6,
NEXT re
PRINT
PRINT #2,
PRINT #3,
NEXT Temp
NEXT u
REM ***********************************************
REM ***** Activation & Mass Transfer Control ******
REM ***********************************************
IF p = 2 THEN
PRINT #7, "Eg", "Ife", , "Izn", , "Ihfe", , "Ihzn", , "IL", "Diff"
FOR tempr = 25 TO 60 STEP 15
FOR u = 1 TO 3
FOR re = 10000 TO 50000 STEP 20000
FOR ph = 1 TO 4
IF ph = 1 THEN c = .1: eh = 1: iife = .01: iizn = 30: iihfe = .1: iihzn = .0000016
IF ph = 2 THEN c = .01: eh = 2: iife = .01: iizn = 30: iihfe = .1: iihzn = .0000016
IF ph = 3 THEN c = .0001: eh = 4: iife = .01: iizn = 30: iihfe = .1: iihzn = .0000016
IF ph = 4 THEN c = .0000001: eh = 7: iife = .000001: iizn = .001: iihfe = 1: iihzn =
.00001
IF u = 1 THEN p1 = .5
IF u = 2 THEN p1 = 1
IF u = 3 THEN p1 = 5
IF tempr = 25 THEN
PP = 996.45: MM = .0009055: dd = 2.405E-09 * (1 / p1) * (((tempr + 273) / 298)) ^ 1.75:
pv = 3.169 / 101.325: cc = (7.8 / 32) * ((p1 - pv) / (1 - pv))
ELSE
END IF
IF tempr = 40 THEN
PP = 992.04: MM = .0006556: dd = 2.405E-09 * (1 / p1) * (((tempr + 273) / 298)) ^ 1.75:
pv = 7.384 / 101.325: cc = (6 / 32) * ((p1 - pv) / (1 - pv))
ELSE
END IF
IF tempr = 55 THEN tempr = tempr + 5
IF tempr = 60 THEN
PP = 983.3: MM = .000471: dd = 2.405E-09 * (1 / p1) * (((tempr + 273) / 298)) ^ 1.75:
pv = 19.94 / 101.325: cc = (3.1 / 32) * ((p1 - pv) / (1 - pv))
ELSE
```

```
END IF
PRINT tempr, p1, re, ph
E1 = -.44: z = 2: i01# = iife * EXP(2825 * ((1 / 298) - (1 / (tempr + 273)))): ihfe = iihfe * EXP(2825 * (1 / 298 - 1 / (tempr + 273)))
E2 = -.76: z = 2: i02# = iizn * EXP(13609.009# * (1 / 298 - 1 / (tempr + 273))): ihzn = iihzn * EXP(13609.009# * (1 / 298 - 1 / (tempr + 273)))
eeq1# = E1 - ((8.314 * (tempr + 273) / (z * 96487)) * LOG(1 / .000001))
eeq2# = E2 - ((8.314 * (tempr + 273) / (z * 96487)) * LOG(1 / .000001))
eh2# = -((tempr + 273) * 8.314 / 96487) * LOG(1 / c)
PRINT eeq1#, eeq2#, eh2#
sc = MM / (PP * dd)
sh3 = .026 * re ^ .82 * sc ^ .35
k3 = dd * sh3 / .05
i3# = 4 * 96487 * k3 * cc * 100
PRINT #7, "temp", "press", "Re", "pH"
PRINT #7, tempr, p1, re, eh
PRINT #7, "Eg", , "Ife", , "Izn", , "Ihfe", , "Ihzn", , "IL", , "Diff"
FOR a1# = .1 TO 1 STEP .1
GOSUB 6100
FOR ecorr1# = k TO -.2 STEP .0000000001#
a2# = 1 - a1#
i1a# = i01# * a1# * EXP((96487 / (8.314 * (tempr + 273))) * (ecorr1# - eeq1#))
i2a# = i02# * a2# * EXP((96487 / (8.314 * (tempr + 273))) * (ecorr1# - eeq2#))
ic1# = (ihfe * a1#) * EXP((-.5 * 96487 / (8.314 * (tempr + 273))) * (ecorr1# - eh2#))
ic2# = (ihzn * a2#) * EXP((-.5 * 96487 / (8.314 * (tempr + 273))) * (ecorr1# - eh2#))
if ecorr1# < eeq1# then i1a# = 0
m# = (i1a# + i2a#) - (i3# + ic1# + ic2#)
IF ABS(m#) <= .01 THEN 1000
NEXT ecorr1#
1000 PRINT ecorr1#; i1a#; i2a#; ic1#; ic2#; i3#; m#; a1#
PRINT #7, ecorr1#, i1a#, i2a#, ic1#, ic2#, i3#, m#, a1#
NEXT a1#
NEXT ph
NEXT re
NEXT u
NEXT tempr
ELSE
PRINT #7, "Eg", "Ife", "Izn", "Ihfe", "Ihzn", "IL", "Diff"
FOR tempr = 25 TO 60 STEP 15
FOR u = 1 TO 3
FOR re = 10000 TO 50000 STEP 20000
PRINT #7, "T="; tempr, "P="; p1, "Re="; re; i01#; i02#; ihfe; ihzn
FOR ph = 1 TO 4
IF ph = 1 THEN c = .1: eh = 1: iife = .01: iizn = 30: iihfe = .1: iihzn = .0000016
IF ph = 2 THEN c = .01: eh = 2: iife = .01: iizn = 30: iihfe = .1: iihzn = .0000016
IF ph = 3 THEN c = .0001: eh = 4: iife = .01: iizn = 30: iihfe = .1: iihzn = .0000016
```

```
IF ph = 4 THEN c = .0000001: eh = 7: iife = .000001: iizn = .001: iihfe = 1: iihzn =
.00001
IF u = 1 THEN p1 = .5
IF u = 2 THEN p1 = 1
IF u = 3 THEN p1 = 5
IF tempr = 25 THEN
PP = 996.45: MM = .0009055: dd = 2.405E-09 * (1 / p1) * (((tempr + 273) / 298)) ^ 1.75:
pv = 3.169 / 101.325: cc = (7.8 / 32) * ((p1 - pv) / (1 - pv))
ELSE
END IF
IF tempr = 40 THEN
PP = 992.04: MM = .0006556: dd = 2.405E-09 * (1 / p1) * (((tempr + 273) / 298)) ^ 1.75:
pv = 7.384 / 101.325: cc = (6 / 32) * ((p1 - pv) / (1 - pv))
ELSE
END IF
IF tempr = 55 THEN tempr = tempr + 5
IF tempr = 60 THEN
PP = 983.3: MM = .000471: dd = 2.405E-09 * (1 / p1) * (((tempr + 273) / 298)) ^ 1.75:
pv = 19.94 / 101.325: cc = (3.1 / 32) * ((p1 - pv) / (1 - pv))
ELSE
END IF
IF x$ = "FE" OR x$ = "fe" OR x$ = "Fe" THEN E1 = -.44: z1 = 1: z = 2: i01# = iife *
EXP(2825 * ((1 / 298) - (1 / (tempr + 273)))): ihfe = iihfe * EXP(2825 * (1 / 298 - 1 /
(tempr + 273)))
IF x$ = "ZN" OR x$ = "Zn" OR x$ = "zn" THEN E2 = -.76: z2 = 1: z = 2: i02# = iizn *
EXP(13609.009# * (1 / 298 - 1 / (tempr + 273))): ihzn = iihzn * EXP(13609.009# * (1 /
298 - 1 / (tempr + 273)))
eeq1# = E1 - ((8.314 * (tempr + 273) / (z * 96487)) * LOG(1 / .000001)) * z1
eeq2# = E2 - ((8.314 * (tempr + 273) / (z * 96487)) * LOG(1 / .000001)) * z2
eh2# = -((tempr + 273) * 8.314 / 96487) * LOG(1 / c)
PRINT eeq1#, eeq2#, eh2#
sc = MM / (PP * dd)
sh3 = .026 * re ^ .82 * sc ^ .35
k3 = dd * sh3 / .05
i3# = 4 * 96487 * k3 * cc * 100
PRINT #7, " Ecorr", , "Ia1", , "Ia2", , "Ic1", , "Ic2", "IL", "diff", "pH"
GOSUB 6200
FOR ecorr1# = k TO -.2 STEP .0000000001#
i1a# = i01# * EXP((96487 / (8.314 * (tempr + 273))) * (ecorr1# - eeq1#))
i2a# = i02# * EXP((96487 / (8.314 * (tempr + 273))) * (ecorr1# - eeq2#))
ic1# = ihfe * EXP((-.5 * 96487 / (8.314 * (tempr + 273))) * (ecorr1# - eh2#))
ic2# = ihzn * EXP((-.5 * 96487 / (8.314 * (tempr + 273))) * (ecorr1# - eh2#))
m# = -((i3# + ic1# + ic2#)) + (i1a# + i2a#)
IF ABS(m#) <= .01 THEN 2000
NEXT ecorr1#
2000 PRINT ecorr1#; i1a#; i2a#; ic1#; ic2#; i3#; m#; ph
PRINT #7, ecorr1#, i1a#, i2a#, ic1#, ic2#, i3#, m#; eh
```

```
NEXT ph
NEXT re
NEXT u
NEXT tempr
END IF
END

5000 FOR ecorr# = -1.2 TO 0 STEP .00001#
FOR u = 1 TO p
m = 1
IF u = 2 THEN
A(u) = j
ELSE
A(u) = 1 - j
l = 1 - j
END IF
ia#(u) = i0(u) * A(u) * EXP((f * m / (R * t)) * (ecorr# - eeq#(u)))
ic#(u) = ih2(u) * A(u) * EXP((-.5 * f / (R * t)) * (ecorr# - eh2#))
NEXT u
w = ia#(1) + ia#(2) - ic#(1) - ic#(2)
q = ecorr#
IF p = 1 THEN
IF ph = 1 THEN
IF ABS(w) <= 5 THEN
IF w = ABS(w) THEN q = q - .000001
GOTO 5100
ELSE
END IF
ELSE
IF ph = 2 THEN
IF ABS(w) <= 1 THEN
IF w = ABS(w) THEN q = q - .000001
GOTO 5100
ELSE
END IF
ELSE
IF ABS(w) <= 1 THEN
IF w = ABS(w) THEN q = q - .00001
GOTO 5100
ELSE
END IF
END IF
END IF
ELSE
IF ph = 1 THEN
IF ABS(w) <= 100 THEN 5100
ELSE
```

```
IF ph = 2 THEN
IF ABS(w) <= 50 THEN 5100
ELSE
IF ABS(w) <= 50 THEN 5100
END IF
END IF
END IF
NEXT
IF w# = ABS(w#) THEN q = q + .000001
5100
RETURN
5200 FOR a1 = .9 TO .1 STEP -.1
FOR ecorr1# = -1.2 TO -.2 STEP .001
a2 = 1 - a1
E1 = -.44: z = 2: i01 = .000001 * EXP(2825 * (1 / 298 - 1 / (Temp + 273)))
E2 = -.76: z = 2: i02 = .001 * EXP(13609.009# * (1 / 298 - 1 / (Temp + 273)))
eeq1# = E1 - ((8.314 * (Temp + 273) / (z * 96487)) * LOG(1 / .00001))
eeq2# = E2 - ((8.314 * (Temp + 273) / (z * 96487)) * LOG(1 / .00001))
i1a# = i01 * a1 * EXP((96487 / (8.314 * (Temp + 273))) * (ecorr1# - eeq1#))
i2a# = i02 * a2 * EXP((96487 / (8.314 * (Temp + 273))) * (ecorr1# - eeq2#))
mag# = i1a# + i2a# - i3#(v)
IF ABS(mag#) <= 10 THEN 900
GOTO 6000
900 ecr = ecorr1# - .1
RETURN
6000 NEXT ecorr1#
NEXT a1
6100
i = i + 1
FOR ecorr1# = -1.5 TO -.2 STEP .000001
a2# = 1 - a1#
i1a# = i01# * a1# * EXP((96487 / (8.314 * (tempr + 273))) * (ecorr1# - eeq1#))
i2a# = i02# * a2# * EXP((96487 / (8.314 * (tempr + 273))) * (ecorr1# - eeq2#))
ic1# = (ihfe * a1#) * EXP((-.5 * 96487 / (8.314 * (tempr + 273))) * (ecorr1# - eh2#))
ic2# = (ihzn * a2#) * EXP((-.5 * 96487 / (8.314 * (tempr + 273))) * (ecorr1# - eh2#))
mag1 = (i1a# + i2a#) - (i3# + ic1# + ic2#)
IF ph = 2 THEN
IF ABS(mag1) <= 10 THEN 7000
ELSE
END IF
IF ph = 3 THEN
IF ABS(mag1) <= 10 THEN 7000
ELSE
END IF
IF ph = 1 THEN
IF ABS(mag1) <= 100 THEN 7000
ELSE
```

```
END IF
IF ph = 4 THEN
IF ABS(mag1) <= 1 THEN 7000
ELSE
END IF
NEXT ecorr1#
7000
k = ecorr1# - .000001
RETURN
6200
i = i + 1
IF x$ = "FE" OR x$ = "fe" OR x$ = "Fe" THEN y = -.4
IF x$ = "ZN" OR x$ = "Zn" OR x$ = "zn" THEN y = -1.3
FOR ecorr1# = y TO -.05 STEP .00000001#
i1a# = i01# * EXP((96487 / (8.314 * (tempr + 273))) * (ecorr1# - eeq1#))
i2a# = i02# * EXP((96487 / (8.314 * (tempr + 273))) * (ecorr1# - eeq2#))
ic1# = ihfe * EXP((-.5 * 96487 / (8.314 * (tempr + 273))) * (ecorr1# - eh2#))
ic2# = ihzn * EXP((-.5 * 96487 / (8.314 * (tempr + 273))) * (ecorr1# - eh2#))
IF ecorr1# > eh2# THEN ic1# = 0
IF ecorr1# > eh2# THEN ic2# = 0
mag1 = -((i3# + ic1# + ic2#)) + (i1a# + i2a#)
IF ph = 2 THEN
IF ABS(mag1) <= 1 THEN 8000
ELSE
END IF
IF ph = 3 THEN
IF ABS(mag1) <= .1 THEN 8000
ELSE
END IF
IF ph = 1 THEN
IF ABS(mag1) <= .1 THEN 8000
ELSE
END IF
IF ph = 4 THEN
IF ABS(mag1) <= .01 THEN 8000
ELSE
END IF
NEXT ecorr1#
8000 'PRINT ecorr1#; mag1; i1a#; i2a#; ic1#; ic2#; i3#
k = ecorr1# - .00001
RETURN
```

Appendix B

B.1 Physical and kinetic Properties:

Table B-1: Atomic Weight of Metal [48]

Metal	Atomic Weight of Metal
Fe	55.847
Zn	65.36

Table B-2: Density of Metal [48]

Metal	Density of Metal (Kg/m^3)
Fe	7833
Zn	7144

Table B-3: Exchange Current Density and Standard Potential at 25 ^{0}C [9, 44]

Metal	Standard Potential (V)	Exchange Current Density (A/cm^2)	
		pH < 4	pH=7
Fe	-0.44	10^{-8}	10^{-12}
Zn	-0.76	$3*10^{-5}$	10^{-9}

Table B-4: Exchange Current Density for the Hydrogen Reaction on Metals at 25 ^{0}C. [9, 44]

Metal	Exchange Current Density (A/cm^2)	
	pH < 4	pH=7
Fe	10^{-7}	10^{-6}
Zn	$1.6*10^{-11}$	10^{-11}

Table B-5: Physical Properties of Water at Atmospheric Pressure [2].

T (^oC)	ρ (Kg/m^3)	$\mu \times 10^4$ (Kg/m.sec)
0.00	999.8	17.9
4.44	999.8	15.5
10.0	999.2	13.1
15.56	998.6	11.2
21.11	997.4	9.80
26.67	995.8	8.60
32.22	994.9	7.65
37.78	993.0	6.82
43.33	990.6	6.16
54.44	985.7	5.13
60.0	983.3	4.71
65.55	980.3	4.30
71.11	977.3	4.01
82.22	970.2	3.47
93.33	963.2	3.06

Table B.6: Values of oxygen Diffusivity [2].

T(^oC)	$D_o \times 10^9$ (m^2/sec) (pure water)	$D_o \times 10^9$ (m^2/sec) (0.1 N NaCl solution)
10.0	1.54	1.306
15.0	1.66	1.408
16.0	1.87	1.586
20.0	2.01	1.705
22.0	2.24	1.899
25.0	2.41	2.044
29.6	2.49	2.112
30.0	2.80	2.374
37.0	3.0	2.544
40.0	3.55	3.010
50.0	4.20	3.562
55.0	4.50	3.816
60.0	5.70	4.834

Table B-7: Vapor Pressure of Freshwater in mm Hg as a Function of Temperature[47]

Temp.C	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.700	0.8	0.9
0	4.58	4.62	4.65	4.68	4.72	4.75	4.79	4.82	4.86	4.89
1	4.93	4.96	5.00	5.04	5.07	5.11	5.14	5.18	5.22	5.26
2	5.29	5.33	5.37	5.41	5.45	5.49	5.53	5.57	5.60	5.64
3	5.68	5.73	5.77	5.81	5.85	5.89	5.93	5.97	6.02	6.06
4	6.10	6.14	6.19	6.23	6.27	6.32	6.36	6.41	6.45	6.50
5	6.54	6.59	6.64	6.68	6.73	6.78	6.82	6.87	6.92	6.97
6	7.01	7.06	7.11	7.16	7.21	7.26	7.31	7.36	7.41	7.46
7	7.51	7.57	7.62	7.67	7.72	7.78	7.83	7.88	7.94	7.99
8	8.05	8.10	8.16	8.21	8.27	8.32	8.38	8.44	8.49	8.55
9	8.61	8.67	8.73	8.79	8.85	8.91	8.97	9.03	9.09	9.15
10	9.21	9.27	9.33	9.40	9.46	9.52	9.59	9.65	9.72	9.78
11	9.85	9.91	9.98	10.04	10.11	10.18	10.24	10.31	10.38	10.45
12	10.52	10.59	10.66	10.73	10.80	10.87	10.94	11.01	11.09	11.16
13	11.23	11.31	11.38	11.46	11.53	11.61	11.68	11.76	11.83	11.91
14	11.99	12.07	12.15	12.23	12.30	12.38	12.46	12.55	12.63	12.71
15	12.79	12.87	12.96	13.04	13.12	13.21	13.29	13.38	13.46	13.55
16	13.64	13.73	13.81	13.90	13.99	14.08	14.17	14.26	14.35	14.44
17	14.53	14.63	14.72	14.81	14.91	15.00	15.10	15.19	15.29	15.38
18	15.48	15.58	15.68	15.78	15.88	15.97	16.08	16.18	16.28	16.38
19	16.48	16.59	16.69	16.79	16.90	17.00	17.11	17.22	17.32	17.43
20	17.54	17.65	17.76	17.87	17.98	18.09	18.20	18.31	18.43	18.54
21	18.66	18.77	18.89	19.00	19.12	19.24	19.36	19.47	19.59	19.71
22	19.83	19.96	20.08	20.20	20.32	20.45	20.57	20.70	20.82	20.95
23	21.08	21.20	21.33	21.46	21.59	21.72	21.85	21.99	22.12	22.25
24	22.39	22.52	22.66	22.79	22.93	23.07	23.21	23.34	23.48	23.63
25	23.77	23.91	24.05	24.19	24.34	24.48	24.63	24.78	24.962	25.07
26	25.22	25.37	25.52	25.67	25.82	25.98	25.13	26.28	26.44	26.59
27	26.75	26.91	27.07	27.23	27.39	27.55	27.71	27.87	28.03	28.20
28	28.36	28.53	28.69	28.86	29.03	29.20	29.37	29.54	29.71	29.88

29	**30.06**	**30.23**	**30.41**	**30.58**	**30.76**	**30.94**	**31.12**	**31.30**	**31.48**	**31.66**
30	**34.84**	**32.02**	**32.21**	**32.39**	**32.58**	**32.77**	**32.95**	**33.14**	**33.33**	**33.52**
31	**33.71**	**33.91**	**34.10**	**34.29**	**34.49**	**34.69**	**34.88**	**35.08**	**35.28**	**35.48**
32	**35.68**	**35.89**	**36.09**	**36.29**	**36.50**	**36.70**	**36.991**	**37.12**	**37.33**	**37.54**
33	**37.75**	**37.96**	**38.18**	**38.39**	**38.61**	**38.82**	**39.04**	**39.26**	**39.48**	**39.70**
34	**39.92**	**40.14**	**40.37**	**40.59**	**40.82**	**41.05**	**41.28**	**41.51**	**41.74**	**41.97**
35	**42.20**	**42.43**	**42.67**	**42.91**	**43.14**	**43.38**	**43.62**	**43.86**	**44.10**	**44.35**
36	**44.59**	**44.84**	**45.08**	**45.33**	**45.58**	**45.83**	**46.08**	**46.33**	**46.59**	**46.84**
37	**47.10**	**47.35**	**47.61**	**47.87**	**48.13**	**48.40**	**48.66**	**48.92**	**49.19**	**49.46**
38	**49.72**	**49.99**	**50.27**	**50.54**	**50.81**	**51.09**	**51.36**	**51.64**	**51.92**	**52.20**
39	**52.48**	**52.76**	**53.04**	**53.33**	**53.62**	**53.90**	**54.19**	**54.48**	**54.78**	**55.07**
40	**55.36**	**55.66**	**55.96**	**56.25**	**56.55**	**56.86**	**57.16**	**57.46**	**57.77**	**58.07**

Table B-8: Activation Energy of Metals[50]

Metal	Activation energy (J/mol)
Fe	**2825**
Zn	**13609**

B.2 Sample of Calculation:

For Activation Control

From Table (5.7), the result of galvanic corrosion of Fe/Zn couple at 25 ^{0}C, pH=1, C of [Fe^{++}] = [Zn^{++}] = 10^{-6}, f_{FE}=0.1, f_{Zn}=0.9 and α of Zn=H^+=Fe=0.5, $i_{0Fe}=10^{-8}$ A/cm^2, $i_{0Fe/H2}=10^{-7}$ A/cm^2,$i_{0Zn}=3*10^{-5}$ A/cm^2, $i_{0Zn/H2}=1.6*10^{-11}$ A/cm^2

from Nernest Eq.(4.1)

$$E = E_0 - \frac{RT}{nF} Ln \frac{a_{red}}{a_{oxid}}$$

$$E_{Eq,Fe} = -0.44 - \frac{8.314*298}{2*96487} \ln \frac{1}{10^{-6}} = -0.617375823 \text{ V}$$

$$E_{Eq,Zn} = -0.76 - \frac{8.314*298}{2*96487} \ln \frac{1}{10^{-6}} = -0.937375823 \text{ V}$$

$E_{Eq,H2}$ =0- $\frac{8.314*298}{96487}\ln\frac{1}{0.1}$ = -0.0591252 V

from Eq.(4.39), de-aerated system , i.e. oxygen-free

$i_{Fe}\, f_{Fe} + i_{ZN}\, f_{Zn} = |i_{H/Fe}\, f_{Fe}| + |i_{H/Zn}\, f_{Zn}|$

$I_{Fe} + I_{Zn} = |I_{H/Fe}| + |I_{H/Zn}|$

$I_a = i_{0,a}\, f_a \exp[\frac{\alpha_a n_a F}{RT}(E_a - E_{e,a})]$

$I_{Fe} = 0.01*0.1*\exp[\frac{0.5*2*96487}{298*8.314}(E_g + 0.617375823)]$

$I_{Zn} = 30*0.9*\exp[\frac{0.5*2*96487}{298*8.314}(E_g + 0.937375823)]$

$I_c = i_{0,c}\, f_c \exp[-\frac{\alpha_c n_c F}{RT}(E_g - E_{e,c})]$

$I_{H/Fe} = 0.1*0.1*\exp[-\frac{0.5*96487}{8.314*298}(E_g + 0.0591252)]$

$I_{H/Zn} = 1.6*10^{-5}*0.9*\exp[-\frac{0.5*96487}{298*8.314}(E_g + 0.0591252)]$

by trial and error Eg=-0.7798546 v

$I_{Fe} = 0$, because Eg < $E_{Eq,Fe}$

I_{Zn} = 12461.14 μ A

$I_{H/Fe}$=12443.26 μ A

$I_{H/Zn}$=17.918 μ A

For Mass Transfer Control

From Table (5.25), the results of limiting current at T=25 ^{0}C, P=1 atm, D=$2.405*10^{-9}$ m^2/sec, C_b =7.8 g/m^3, ρ=996.45 Kg/m^3, μ=$9.005*10^{-4}$ Kg/m.s, Re=5000

Sc=μ/ρ.D= $\frac{9.055*10^{-4}}{996.45*2.405*10^{-9}}$=377.8486

by Poulson and robinson Eq.

Sh=.026 $Re^{0.82}$ $Sc^{0.35}$

Sh=0.026 $*(5000)^{0.82}$ $*(377.8486)^{0.35}$=223.97

$Sh=\frac{Kd}{D}$: $K=2.405*10^{-9}*223.97/.05= 1.077296*10^{-5}$ m/s

Limiting current calculated by Eq.(4.46)

$I_L= z_c\ F\ A\ K\ C_b$

$I_L=4*96487*1.077296*10^{-5}*(7.8/32) =1.013464\ A/m^2=101.3464\ \mu A/cm^2$

The results of galvanic corrosion of Fe/Zn couple at 25 ^{0}C, pH=7, C of $[Fe^{++}] = [Zn^{++}] = 10^{-6}$, f_{FE}=0.5, f_{Zn}=0.9 and α of $Zn=H^+=Fe=0.5$

$$\sum I_a = \sum I_L$$

$I_{Fe}\ f_{Fe}+ i_{Zn}\ \ f_{Zn} = i_L\ f_{Fe} +i_L\ f_{Zn}$

$f_{Fe} + f_{Zn} = 1$

$I_{Fe} + I_{Zn} = I_L$

$$I_a = i_{0,a}\ f_a \exp[\frac{\alpha_a n_a F}{RT}(E_a - E_{e,a})]$$

H_2 evolution is assumed negligible

at pH=7

$$I_{Fe} = 10^{-6}*0.1*\exp[\frac{0.5*2*96487}{298*8.314}(E_g + 0.617375823)]$$

$$I_{Zn} = 10^{-3}*0.9*\exp[\frac{0.5*2*96487}{298*8.314}(E_g + 0.937375823)]$$

by trial and error Eg = -0.638703 V

$I_{Fe} = 0$, because $Eg < E_{Eq,Fe}$

$I_{Zn} = 101.336\ \mu\ A/cm^2$

For Activation and Mass Transfer Control

From Table (5.57), the results of galvanic corrosion of Fe/Zn couple at 25 ^{0}C, pH=1, C of $[Fe^{++}] = [Zn^{++}] = 10^{-6}$, f_{FE}=0.5, f_{Zn}=0.5, Re=10000 and α of $Zn=H^+=Fe=0.5$, limiting current was calculated =178.91 μ A/cm^2

$$\sum Ia = \sum Ic + I_L$$

$I_{Fe}+ I_{Zn} = I_{H/Fe}+ I_{H/Zn} + I_L$

$$I_a = i_{0,a}\ f_a \exp[\frac{\alpha_a n_a F}{RT}(E_g - E_{e,a.})]$$

$I_c = i_{0,c}\, f_c \exp[-\frac{\alpha_c n_c F}{RT}(E_g - E_{e,c})]$

I_{Fe}=0.01*0.5* $\exp[\frac{0.5*2*96487}{298*8.314}(E_g + 0.6173758)]$

I_{Zn} = 30*0.5* $\exp[\frac{0.5*2*96487}{298*8.314}(E_g + 0.937375823)]$

$I_{H/Fe}$ = 0.1*0.5* $\exp[-\frac{0.5*96487}{8.314*298}(E_g + 0.0591252)]$

$I_{H/Zn}$ = 1.6*10^{-5}*0.5* $\exp[-\frac{0.5*96487}{298*8.314}(E_g + 0.0591252)]$

by trial and error Eg=-0.74216098 v

I_{Fe} = 0 , because Eg < $E_{Eq,Fe}$

I_{Zn} = 30047.399 μ A

$I_{H/Fe}$= 29863.74 μ A

$I_{H/Zn}$=4.7781 μ A

الخلاصة

ان اهمية التاكل هي اقتصادية فنية بمعنى اخر تقليل من الخسائر المادية الناتجة بسبب التاكل للانابيب ،الخزانات ، القطع المعدنية للمكائن ، السفن ، الجسور ، هياكل الغواصات،.....الخ
بالاضافة الى تحسين الجانب الامني لتشغيل الجهاز حيث عند حدوث عملية التاكل يتدهور الجانب الامني مؤديا الى نتائج سلبية .كذلك يدخل بشكل رئيسي في الحفاظ على مصادر المعادن و على الخسائر في الطاقة المرافقة لها بالاضافة الى تقليل من الجهود البشرية.
بسبب الاهمية العلمية لحماية الاجهزة الصناعية من التاكل الكلفاني فان الحاجة تنشا لتحليل تاثيرات المتغيرة اي ظروف التشغيل مثل درجة الحرارة و الاس الحامضي و عدد رينولد و الضغط و المساحة الجزيئية للمعدن على عملية التاكل الكلفاني في اوساط حامضية عندما تكون فيها المنظومة تحت سيطرة طاقة التنشيط و في ماء البحر عندما يكون تحت سيطرة انتقال الكتلة للمزدوج الكلفاني حديد-خارصين. لهذا السبب تم تطوير برنامج حاسوبي يمكن استخدامة لاعداد و انواع مختلفة من المعادن المزدوجة ولمديات مختلفة من الاس الحامضي ١،٢،٣،٤،٧ و درجة الحرارة ٦٠، ٤٠،٢٥ درجة مئوية والضغط ٠,٥ ، ٠,٧٥، ١، ٣، ٥ جو وعدد رينولد يمتد ما بين ٥٠٠٠-٥٠٠٠٠ والمساحة الجزيئية هي من ٠,١-٠,٩ للحديد. كذلك يمكن استخدام هذا البرنامج لمعدن واحد تحت ظروف التاكل المنتظم٠
ان الحسابات التي اجريت باستخدام برنامج الحاسوب تم بنائها على المعادلات الخاصة بالتاكل الكلفاني وهي:

$$I= i_0 f \exp [(\alpha nF/RT)(E_g- E_{eq})]$$

$$I_L=Z_C\ F\ A\ K\ C_b$$

ولكل حالة عند $(E_{coupling})$

$$\sum I_c=\sum I_a\ ,\ \sum I_g =0$$

ان البرنامج كذلك يستطيع حساب التاكل الكلماني الانودي والكاثودي للمعدن المفرد ولجهد التاكل الكلفاني (E_g)
دلت النتائج في حالة التاكل المنتظم معدل تاكل معدن الحديد والخارصين تحت سيطرة التنشيط ٠ان معدل التاكل تحت سيطرة الانتشار للحديد والخارصين يزداد مع زيادة كل من عدد رينولد والضغط بينما زيادة درجة الحرارة تؤدي الى نقصان معدل التاكل لكلا المعدنين من خلال انخفاض تركيز الاوكسجين كما دلت عليه قيم التيار المحدد.

في حالة التاكل الكلفاني حديد-خارصين دلت النتائج تحت ظروف سيطرة التنشيط ،نقصان الاس الحامضي وزيادة درجة الحرارة تؤدي الى زيادة معدل تاكل الخارصين ،زيادة المساحة الجزئية للمعدن النبيل (الحديد) يؤدي الى زيادة معدل التاكل الكلفاني للمعدن الاكثر فعالية (الخارصين)٠ لم يلاحظ تاثير لعدد رينولد و الضغط على معدل التاكل الكلفاني تحت ضرف سيطرة التنشيط.

عندما تكون المنظومة تحت سيطرة مشتركة (انتقال الكتلة وطاقة التنشيط) اوضحت النتائج عند زيادة الاس الحامضي يؤدي الى نقصان معدل التاكل المنتظم والكلفاني ، في حالة التاكل المنتظم فأن زيادة درجة الحرارة ينتج عنه نقصان قليل لمعدل تاكل الخارصين بينما زيادة عدد رينولد والضغط يؤدي الى زيادة واضحة لمعدل تاكل الخارصين. في حالة التاكل الكلفاني تحت حالة السيطرة المشتركة زيادة درجة الحرارة تؤدي الى زيادة في معدل تاكل المعدن الاكثر فعالية و عند الاس الحامضي اقل من ٤ ، ويقل معدل تاكل الخارصين عند الاس الحامضي ٧.

لم يلاحظ تأثير واضح لعدد رينولد والضغط على معدل تاكل الخارصين الذي يعمل تحت ظروف السيطرة المشتركة عند اس حامضي اقل من ٤ بينما في حالة الاس الحامضي ٧ يزداد معدل التاكل الكلفاني مع زيادة الضغط وعدد رينولد. زيادة المساحة الجزئية للحديد تعمل على زيادة معدل تاكل الخارصين عند اس حامضي اقل من ٤ بينما يؤثر على معدل تاكل الخارصين بشكل اقل عند اس حامضي مقداره ٧.

اوضحت النتائج بشكل عام ان جهد التاكل يزداد باتجاه(الموجب) عند زيادة كل من عدد رينولد والضغط بينما يزداد باتجاه(السالب) عند زيادة كل من درجة الحرارة ةالاس الحامضي . في حالة السيطرة المشتركة يبدي كلا الانحرافين مع زيادة الاس الحامضي.

شكر و تقدير

اودُ أن أعبر عن خالص شكري وتقديري وَ امتناني العميق للمشرف الدكتورقاسم جبار سليمانوالدكتورباسم عبيد حسن لما بذله من جهد كبير و ارشادات سديدة و قيمة طوال فترة اعداد الرسالة.

أودُ أيضاً أن أشكر موظفي قسم الهندسة الكيماوية لإبدائهم المساعدة اللازمة أثناء فترة البحث.

ولا أنسى أن أتقدم بالشكر و الامتنان إلى من لازمني طوال فترة البحث وخلال أصعب الظروف إلى أعز من في الوجود إلى أبي و أمي و جميع أفراد عائلتي فلهم جزيل الشكر و التقدير.

تحليل بمساعدة الحاسوب للتاكل الغلفاني
تحت سيطرة طاقة التنشيط وسيطرة انتقال الكتلة

رسالة
مقدمة الى كلية الهندسة جامعة النهرين وهي جزء من متطلبات
نيل درجة ماجستير علوم في الهندسة الكيمياوية

من قبل
بكر مثنى عبود الزيدي
بكالوريوس في الهندسة الكيمياوية ٢٠٠٢

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