ANALYSIS OF ACTIVATION CONTROLLED GALVANIC CORROSION

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CERTIFICATION

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ABSTRACT

The importance of corrosion studies is threefold. The first area of significance is economic including the objective of reducing material losses resulting from the corrosion of piping, tanks, metal components of machines, ships, bridges, marine structures, etc. The second area is improved safety of operating equipment, which through corrosion may fail with catastrophic consequences.

Because of practical importance of protection of industrial equipments from galvanic corrosion, the need arises to study the effect of variables, such as hydrogen ion concentration, metallic ion concentration, symmetry factor (alpha) and area fraction of metals on galvanic corrosion in de-areated acidic media of several industrially important metals Fe, Zn, Cu. For these reason a computer program is developed. Which can be used for a general number or type of coupled metals with a range for hydrogen ion concentration (0.01-1M), metallic ion concentration (10^{-6}-10^{-2} M), symmetry factor $\alpha=0.3,0.5,0.7$ and area fraction (0.1-0.9) at ambient condition (T=25C and P=1 atm). This program can also be used for free corrosion of metals.

The calculations in the new developed computer program are based on the well known equations of galvanic corrosion which are:-

$$I=i_{0}f\ e^{(Eg - Eeq)/\beta}$$

and for each case at $E_{coulping}$

$$\sum I^{c} = \sum I^{a} , \sum I^{g} = o$$

The program can be used for free corrosion and galvanic corrosion to estimate corrosion rate and potential and galvanic corrosion for any type and number of coupling to find corrosion rate and potential, equilibrium potential, exchange current density and Tafel slopes for metals and hydrogen at different area fractions, symmetry factors, hydrogen ion and metallic ion concentrations. The results obtained from this program agree with most available analysis and experimental data.

From the results corrosion rate increases with increasing in hydrogen ion concentration, metallic ion concentration and symmetry factor for free and galvanic corrosion and also increases with increasing area fraction of active metal .The corrosion potential shifts to more negative because with increasing metallic ion concentration and symmetry factor for free and galvanic corrosion and area fraction of active metal but hydrogen ion concentration shifts the corrosion potential to less negative (i.e. increases).

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Nomenclature

a,b	Tafel constant in Eq.(2.12)	
a_{red}	Activities (concentration) of oxidized species	mol/l
a_{oxid}	Activities (concentration) of reduced species	mol/l
C_b	Bulk concentration of reacting ion	mol/m^3
D	Diffusion coefficient of reacting ion	m^2/s
E_{eq}	Equilibrium potential	V
E^o	The standard electrode potential	V
E_g	Galvanic potential	V
F	Faradays constant (96487 Coulomb/g.eq)	V
f^j	Total area fraction for component j	
f^N	Total area fraction for noble metal	
f^B	Total area fraction for base metal	
f	area fraction	
G	Gibbs free energy	kJ/mol
Ğ	Chemical free energy	kJ/mol
H	Enthalpy	kJ/mol
i	Current density	$\mu A/cm^2$
i_a , i_c	Net anodic and cathodic density current respectively	$\mu A/cm^2$
i_{app}	Applied current density	$\mu A/cm^2$
i_{corr}	Corrosion current	$\mu A/cm^2$
i_{lm}	Maximum rate of a possible reaction for a given system (limiting current density)	$\mu A/cm^2$
i_0	Exchange current density	$\mu A/cm^2$
$\overset{\omega}{i}$, $\overset{\omega}{i}$		
le	Resistance path	
n	Number of electrons transfer	
z	Number of electrons transfer	
q	Electric charge	Coulomb
P	Partial Pressure	atm
R	Gas constant 8.314 J/mol.K	
R_0	Resistance of the electrolyte solution	Ω cm
R_{sol}	The electrical resistance	Ω cm

R_f	Resistance produced by film or coatings	Ω cm
S	Entropy	kJ/mol.K
SHE	Standard hydrogen electrode	
J_a^j	Anodic current from the j^{th} compont	
J_c^j	Cathodic current from the j^{th} compont	
I_a^{system}	Total anodic current	μA
I_c^{system}	Total cathodic current	μA
i_a^B	Anodic current density	$\mu A/cm^2$
i_c^N	Cathodic current density	$\mu A/cm^2$
$\mp$	Anodic or cathodic over potential	mV

Greek Letters

βa	Anodic Tafel slope =[3.202RT/άnF]	mV
βc	Cathodic Tafel slope =[-3.202RT/(1-ά)nF]	mV
α	Symmetry factor in Eq.(2.13)	
σ	Conductivity of the electrolyte solution	$\Omega^{-1}.m^{-1}$
η	Over potential	mV
η_a , η_c	Net anodic and cathodic over potential respectively	mV
η^c	Concentration polarization potential	mV
η^t	Total polarization	mV
η^A	Activation Polarization	mV
δ_m	Thickness of the diffusion layer	
ϕ	Electrical potential	mV

Chapter One

Introduction

1.1CORROSION :

Corrosion is a serious problem because it definitely contributes to the depletion of natural resources , for example, steel is made from iron ore ,that has beendwindled. Another important factor concerns the world's supply of metal resources. The rapid industrialization of many countries indicates that the competition for and the price of metal resources will increase.[1]

There is probably a need for two definitions of corrosion that depend upon these two approaches[2]:

1) Corrosion in the context of corrosion science is the reaction of a solid with its environment .
2) Corrosion in the context of corrosion engineering is the reaction of an engineering construction metal (material) with its environment with consequent deterioration in properties of the metal (material).

The increasing demands being placed on structures and equipments in all industrial activities as well as the daily life (i.e. motor vehicles and house buildings) ,this has led the requirement touse a combination of metals to obtain the desired performance . But this led to an increase in galvanic corrosion between metals and alloys that will secure a high rate of retardation of galvanic corrosion .

Many corrosion products are chemically. similar to the corresponding metallic minerals as shown in the following simple corrosion cycle :[3]

Metallic minerals $\xrightarrow{\text{reduction}}$ Metal $\xrightarrow{\text{oxidation}}$ corrosion product
(Ore) (extraction) (corrosion)

Most corrosion reactions are electrochemical. An example illustrating the electrochemical nature of corrosion is the attack of iron , which is the most commonly used industrial metal , in hydrochloric acid . The reaction is :

$$Fe + 2HCl \longrightarrow Fe\,Cl_2 + H_2 \qquad (1.1)$$

Noting that the chloride ion is not involved in the reaction , this equation can be written in the simplified form : -

$$Fe + 2\,H^{+} \longrightarrow Fe^{2+} + H_2$$
(1.2)

Equation (1. 2) can be conveniently divided into two reaction :

Oxidation (anodic reaction) : $Fe \longrightarrow Fe^{2+} + 2e$

Reduction (cathodic reaction) : $2H^{+} + 2e \longrightarrow H2$

Both the oxidation reaction and the reduction reaction proceed at the same rate during electrochemical corrosion. Any changes in the system, which affect the rate of one, must of necessity affect the other. Thus, attempts at reducing corrosion rate may be directed toward changing either local oxidation or local reduction rate [4].

1.2CORROSION COST :

The people working in the field of corrosion frequently try to point out how much it costs as percentage of a nation economy . The approximate annual cost of corrosion in the United States was first estimated in 1949 to be $ 5 billion, 2.1 % of Gross National Product(GNP) [6] . In the United the estimated cost of corrosion had risen to $70 billion, 2.4 % of GNP [7].

In 1977 it cost, £5,000 perday to take atypical 400 kV transmission line out of service to deal with corrosion damage. A small corroded pipe in a chemical plant may be replaced for just a few pounds, but the loss of product during the time that the process is stopped can run into thousands of pounds an hour . In the worst possible case the whole plant may be taken out and loss of life may occur. The selection of the material or protection system, which optimizes corrosion resistance for a given component life time greatly, reduced the need for costly maintenance during that life time.

In 1971 , a major study of the cost of corrosion in the United Kingdom was carried out by the Government Committee on Corrosion and Protection . The Committee concluded that the total cost to the national economy was a staggering 1, 365 million (1971 prices) , about 3-5 % of the GNP . Of this , it was said that about one – quarter could be saved by better and wider use of well – established corrosion protection techniques .

The survey did not include the agricultural industry ; this was covered in 1981 in a report by the University of Manchester Institute of Science and Technology (UMIST) which reported that corrosion was costing the agricultural industry about 600 million payer and that about half of this could be saved by existing corrosion control technology .

Though the initial cost may be higher, the over all cost is usually much less. The essential factor is the choice of the correct design life time. Problems arise when a time scale chosen at the design stage to fit the various cost parameters is extended later in the life of the component.Al terntively , even though maintenance schedules are laid down , they are not adhered to . Both can have disastrous consequences [7].

Four men died and five were seriously injured at the construction site of a U K power station when the single suspension rope of the hoist cage in which they were travelling broke at a point weakened by corrosion and lack to lubricant [7] .

In other areas of industry , consumer demands for better quality control have increased over all production costs . In general, the heavy – chemical, oil and petrochemical industries have been found to be more corrosion conscious than the pharmaceutical industry . It was suggested that this was because of the former industries experience in the use and storage of highly corrosive substances, and aconsequent tendency to overdesing . A corrosion specialist was employed in less than 10% of the pharmaceutical companies questioned, and in the majority of cases problems were dealt with by a maintenace engineer.The industry was found to be very conscious of product quality, though it suffered higher corrosion costs than were necessary . A medium – sized U K engineering company, believing that it had no problems with corrosion, decided to look deeper into the question. It discovered that corrosion was in fact costing 43, 000 a year. By improving materials hadling and paying greater attention to stock control and records, the company was able to save over £10,000 of this sum.

The industry has certainly had its share of corrosion costs. For boiling water reactors (BWRs) capacity factor losses due to corrosion problems averaged over 6% between 1980 and 1991 , reaching a peak value of 18 % in 1982 . The corresponding numbers for pressurized water reactors (PWRs) are an average capacity loss of 5 % and a peak of 8 % in 1982. It is estimated that corrosion problems have costed the nuclear utility industry more than $ 5 billion since 1980. In addition, repairs and mitigating measures are thought to have cost the average US light water reactor (LWR) more than $ 1 for every megawatt – hour of electricity produced since 1980, i.e. > $ 0.5 billion throughout the industry ; this has also resulted in radiation exposures of about 100 rem per year .

In the 1980,increasing the life time of car bodies became more important for manufacturers than control of exhaust emissions or fule economy .A code for Canada in1981 specified that a body should last aminimum 1.5 years (60, 000 Km) before suffering cosmetic (out side in) corrosion ,5 years (200, 000 Km) for perforation (inside out) corrosion and 6 years (240, 000 Km) for structural corrosion .The code projected for North America in 1990 was to have no cosmetic corrosion in 5 years and no perforation corrosion in 10 years.This resulted in a rise in the use of precoated steel, esecially galvanized steel products which, in 1993,seemed to have satisfied the requirements.Meanwhile, many car owners,in their rightful attemps to own vehicles which remained rust free, had resorted to one of the many rustproofing treatments which could be applied to new vehicles. In 1982 a report by the office of the Attorney General in New York State claimed that consumers were being defrauded of at least $ 11 million annually because of the poor quality of treatments. A remarkable 83% of all cars inspected failed to meet acceptable standards. Most of the manufactures, rustproofing warranties were said to contain limitation or conditions that rendered them essentially worthless.

The Department of Transport (USA) insisted that while there may have been some fatigue failure of wires in the suspension / hanger system, the Problem had been caused by unexpectedly high traffic loading, aggravated by corrosion, as a result of inadequate protection against the salt-laden atmosphere of the Severn Estuary. Estimates of the cost of repair spiraled upwards and in 1983 reached £ 30 million.

In December 1979 the city of Westminster, London reported that it had a problem with falling lampposts. It was suggested that the main culprits for the corrosion that had occurred at the base of the posts were dogs. The city's Pets were daily depositing about 2,000 liters of urine, mostly at the base of the city lampposts and this caused a great increase in the rate of corrosion. One of many problems experienced with the Charing Cross railway bridge in central London was also attributable to this surpassing cause. Repeated visits from dogs had caused severe crevice corrosion in a part of the structure that was impossible to maintain [7].

In fact the economy would be drastically charged if there were no corrosion. For example, automobiles,ships,underground Pipelines, and household appliances would not require coating. The stainless steel industry would essentially disappear and copper would be used only for electrical purposes. Most metallic plants, as well as consumer products, would be made of steel or cast iron. Corrosion touches all-inside and outside the home,on the road, on the sea, in the plant, and in aerospace vehicles.[1]

While corrosion is inevitable, Its cost can be considerably reduced. For example,an inexpensive magnesium anode could double the life of a domestic hot water tank. Washing a car to remove road deicing salts is helpful. Proper selection of materials and good design reduce costs of corrosion. A good maintenance Painting program pays for itself many times over. Here is where the corrosion engineer enters the picture and is effective – his primary function is to combat corrosion[1].

1.3: FORM 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].

Galvanic corrosion:

The classic two dissimilar metal connection with a water electrolyte bridge is the most basic of corrosion problems . [9] The less noble metal (anode) suffers accelerated attack and the more noble metal (cathode) is cathodically protected by the galvanic current parially or totally.The tendency of a metal to corrode in a galvanic cell is determined by its position in the “ galvanic series “ of metals and alloys . [8]

1.4THE SCOPE OF PRENSENT WORK :

This work aims to perform theoreteical study to investigate the influence of area fraction ,hydrogen ion concentration,Tafel slopes (ßa ,ßc) and concentration of metals ion on the corrosion rate of Fe and Zn galvanic corrosion rate (or galvanic corrosion current) (i_{gcorr}) and corrosion potential (E_{corr})$_{Cop}$ of galvanic coupling of Fe , Cu and Zn in deareated acidic environment of hydrogen ion concentration range from 0.01– 1M and metallic ion concentration of $10^{-6} - 10^{-2}$ M under isothermal T = 25˚C and pressure of hydrogen 1atm stationary conditions.

Chapter Two
The scope of Corrosion

2.1 INTRODUCTION:

There are two main reasons for concerning about the study of corrosion economics and conservation, of these two the economics have primarily promoted study and research into the mechanisms of corrosion and means of preventing or reducing its rate [6, 10]. Many engineering projects have developed a new component or processes with out standing only to have it fail prematurely because of corrosion.[11]

2.2 FACTORS THAT INFLUENCE CORROSION:

2.2.1 Solution pH:

An electrode reaction which involves the production or consumption of hydrogen ions will exhibit a reversible single potential which varies with hydrogen ion concentration, and so with pH. Thus, applying Nernst equation (2.1) to the hydrogen electrode yields [4]:

$$E_{H/H^+} = E^o_{H/H^+} - \frac{RT}{2F} \ln \frac{p_{H_2}}{[H^+]^2} \tag{2.1}$$

The accepted method of defining acidity is by means of a term called pH. It is measured as a scale from 0 to 14 and is defined as follows: [7]

$$pH = -\log[H^+] \tag{2.2}$$

so that:

$$E_{H/H^+} = -0.059\ \text{pH} + 0.029\ \log p_{H2} \tag{2.3}$$

$$E_{H/H^+} = -0.059\ \text{pH} \tag{2.4}$$

for p_{H2} = 1 atmosphere at 25 °C.

The relationship between pH and corrosion rates tends to follow one of three general patterns [12]:

1. Acid-soluble metals such as iron have a relationship as shown in Figure 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. Iron is weakly amphoteric. At very high temperature such as those encountered in boilers, the corrosion rate increases with increasing basicity as shown by the dashed line.

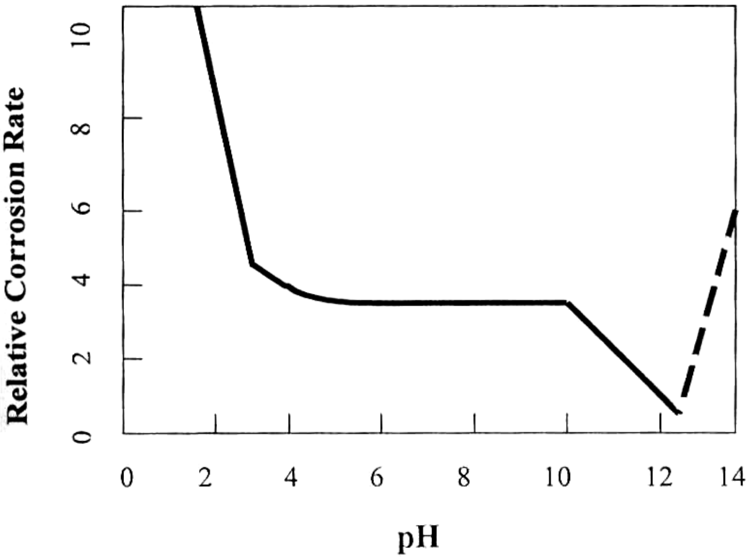

Figure2.1: Effect of pH on corrosion rate of iron[12].

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.

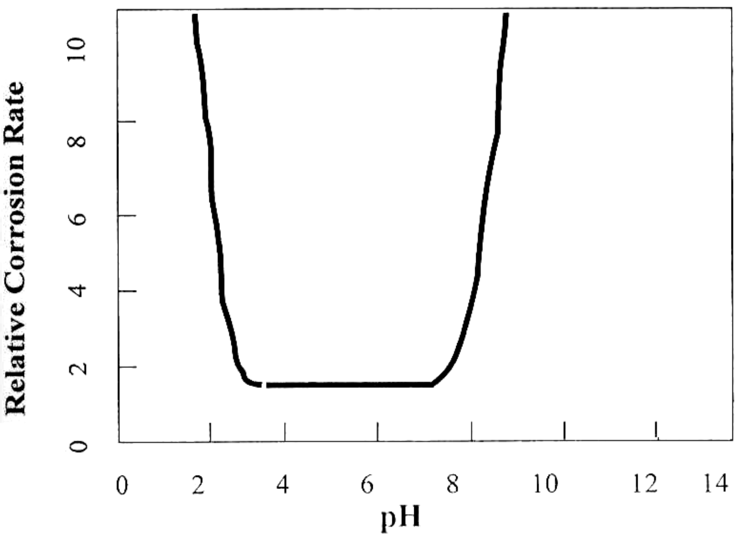

Figure2.2: Effect of pH on the corrosion rate of amphoteric metals (aluminum and zinc) [12].

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

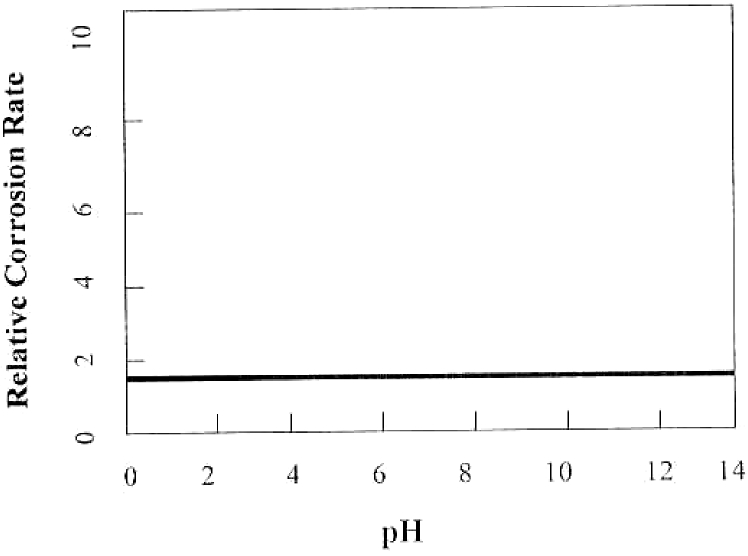

Figure 2.3: Effect of pH on the corrosion rate of noble metals [12].

2.2.2 Oxidizing Agents:

In some corrosion processes [11, 12], 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 its most important single property in so far as corrosion is concerned.

If an active-passive metal is initially passive in a corrosive medium, the addition of further oxidizing agents has only a negligible effect on corrosion rate. This condition frequently occurs when an active-passive metal is immersed in an oxidizing medium such as nitric acid or ferric chloride. Initially, in the passive state, is exposed to very powerful oxidizers and makes a transition into the trnaspassive region. This kind of behaviour is frequently observed with stainless steel when very powerful oxidizing agents such as chromates are added to the corrosive medium. In hot nitrating mixtures containing concentrated sulfuric and nitric acids, the entire active-passive transpassive transition can be observed with the increased ratios of nitric to sulfuric acid [1].

2.2.3 Temperature:

Temperature increases the rate of almost all chemical reactions. When the rate-determining step is the activation process, the temperature change have the greatest effect. In general, if diffusion rates are doubled for a certain increase in temperature, activation process may be increased by 10-100 times, depending on the magnitude of the activation energy.

In solutions when the process is under activation control the main effect of increasing the temperature is to increase the exchange current.

Conway, Beatty and Maine [14] found that for nickel, the exchange current increased by 100 times when the temperature changed from 10 to 75 ^{o}C while for concentration polarization, the diffusion coefficient for hydrogen ions would increase only twice over the same temperature range.

The corrosion process governed by the cathodic reduction of dissolved oxygen might be expected to be wholly controlled by concentration polarization because of low solubility of oxygen, especially in concentrated salt solutions. Temperature is complex in that the diffusivity of oxygen increases, but solubility decreases with temperature increase. Data are scarce for these effects.

2.2.4 Salt Content and Chloride Ion:

Chlorides have probably received most consideration in relation to their effect on corrosion. The effect of sodium chloride concentration on the corrosion of iron in air saturated water at room temperature was found to increase the corrosion rate. The corrosion rate in air saturated water at room temperature was found to increase with increase of sodium chloride concentration reaching maximum at about 3% NaCl (sea water concentration) and then decreases, the value falling below that of distilled water when saturation is reached (26% NaCl). To understand this behaviour, oxygen solubility in water decreases continuously with sodium chloride concentration explaining the falling off of corrosion rate at higher sodium chloride concentration. The initial rise appears to be related to a change in the protective nature of the barrier rust film that forms on the corroding metal. On the other hand, chlorides increase the electrical conductivily of the water so that the flow of corrosion currents will be facilitated [2, 6].

Later, Kolman et al. [16] found the corrosion potential becomes more negative with increasing NaCl concentration. Buhar [17] showed that, in stationary aerated water, the limiting current density increases with increases in NaCl concentration up to 3.5% and the corrosion potential becomes more negative.

2.3 THERMODYNAMIC ASPECTS:

The first problem is what reactions can occur. The application of thermodynamics can help solve this problem, i.e., one determines which of the possible reactions is most favored on the basis of energy considerations.

Even before the discussion of thermodynamics, one very strong caution must be stated about its application to corrosion. Thermodynamic considerations determine whether or not a reaction occur; they do not set the rate at which the reactions occur. However, in spite of this limitation, thermodynamics is very important to an understanding of the electrochemistry of corrosion [15].

The tendency for any chemical reaction to go is measured by the Gibbs free energy change (ΔG). The more negative the value of ΔG, the greater is the tendency for the reaction to go. The relationship at constant pressure and temperature between the total heat content and its various parts is [18]:

$$G = H - TS \qquad (2.5)$$

If some or all of the constituents of a chemical system are electrically charged (i.e., they are ions or electrons, the total energy possessed by a charged chemical entity will be:

$$G^o = G + q\phi \qquad (2.6)$$

The quantity G^o is called the electrochemical free energy, q is the electronic charge and ϕ is the electrical potential. Thus if the chemical reaction leads to the production or elimination of ions or electrons, the driving force becomes the electrochemical free energy. Reaction will proceed in such a direction that ΔG^o is negative [4] Fig.(2.4). At equilibrium, there is no net driving force and ΔG^o is zero.

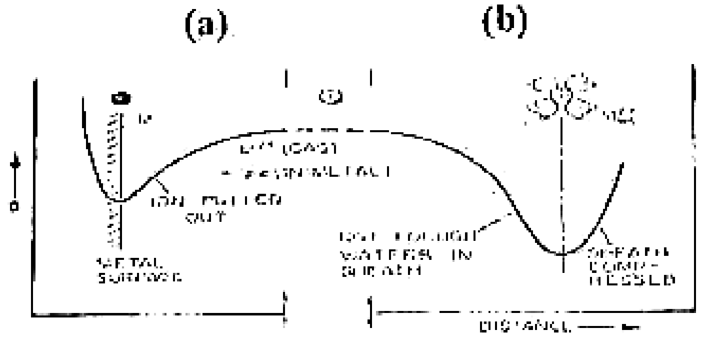

Figure 2.4: The chemical free energy of a family of metals ions. (a) Pulled out of the metal surface and (b) Subsequently solvated[4].

As the metal M dissolved to form aquoions M^{+Z}, there occurs an increasing separation of electric charge, the metal having a net negative charge and the aqueous solution adjacent to it a positive one. Any such system is called an electrode. At equilibrium, when the net change in electrochemical free energy accompanying either dissolution or deposition will be zero [17],

$$\Delta G = -zFE \qquad (2.7)$$

Equation (2.7) is known as Faraday's law. The symbol F represents the charge transported by one mole of electrons and has the value of 96,494 coulombs per mole of electron. The potential, E is measured in volts, and z is the number of electrons transferred in the corrosion reaction. A negative sign is necessary to indicate the conventional assignment of negative charge to electrons, and since z and F are positive constants, this leads to a positive measured potential when the reaction is spontaneous. The equation shows that free energy change directly measurable with electrochemical potential.

Again using the superscript (o) to represent standard condition, we can rewrite equation (2.7) as [7]:

$$\Delta G^0 = -zFE_0 \tag{2.8}$$

To determine the potential of a system in which the reactions are not at unit activity, the familiar Nernst equation can be employed:

$$E = E^0 - \frac{RT}{ZF}\ln\frac{[a_{red}]}{[a_{ox}]} \tag{2.9}$$

Where E is the half-cell electrode potential, E_0 is the standard half-cell potential, a_{oxid} and a_{red} are the activities (concentration) of oxidized and reduced species. As indicated in the above equation, half-cell potential becomes as more positive the amount of oxidized species increases. For each tenfold increase in oxidized reactant, the half-cell potential increases by 59 mV for a single electron reaction [1].

2.4 KINETIC ASPECTS:

Since metals can react with their environments, the important question is how fast they react. This question is the basis for the study of the kinetics of corrosion reactions [20].

One of the keystones of electrochemistry is Faraday’s law which relates chemical charge and electrical energy. For every equivalent of chemical reaction 96487 coulombs must pass through the cell. This equivalence between reaction and electrical charge makes it possible to write the rates for electrochemical reactions in terms of electrical currents [15].

Corrosion system [20] is not at equilibrium, and therefore thermodynamic calculations cannot be applied. Essentially, it’s a matter of interest in what is happening when the cell illustrated in Fig.2.5 is short-circuited. In this instance, a vigorous reaction occurs, the zinc electrode rapidly dissolves in the solution and simultaneously a rapid evolution of hydrogen is observed at the platinum electrode. Electrons released from the dissolution reaction are transferred through the connecting wire to the platinum electrode where they are consumed in the hydrogen reduction. The process, which occurs in Fig.2.5, is exactly the same process that occurs when zinc metal is immersed in a hydrogen saturated acid solution containing zinc ions as shown in Fig.2.6. In both instance, the overall reaction is the dissolution of zinc and the evolution of hydrogen. In the divided cell shown in Fig.2.5, the reactions occur on separate electrodes, while in Fig.2.6 these reactions occur on the same metal surface. In both instance, the free-energy change for the reaction is exactly the same, since the platinum metal does no precipitate in the reaction.

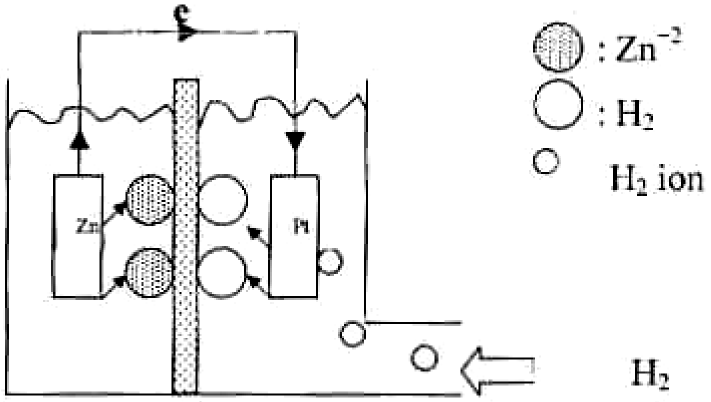

Figure 2.5: Short-circuited cell containing zinc and hydrogen electrodes [21].

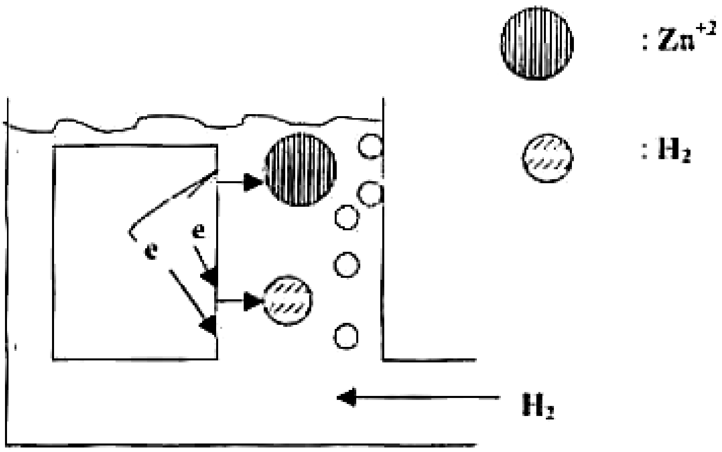

Figure2.6: Corroding zinc [21].

2.5 POLARIZATION:

An electrode is at equilibrium when a net current flows to/or from surface is zero. Equilibrium is a dynamic situation. Reactants and products jump back and forth at a very real rate, but since there is no accumulation of product, direct measurement of this rate is difficult. For an electrochemical reaction this equilibrium exchange rate is called the exchange current density (i_0) [4, 15, 21].

When a metal is not in equilibrium with a solution of its ions, the electrode potential differs from the equilibrium potential by amount known as the polarization. Other terms having equivalent meaning are overvoltage and over potential. The symbol commonly used is η [7]. The amount of potential change is the overvoltage defined as [6]:

$$\eta = E_i - E_{eq} \tag{2.10}$$

where η is the overpotential, E_{eq} is the equilibrium potential, and E_i is the polarized (current flowing) potential.

The current applied to cause the departure from equilibrium is the net reaction of electron, thus:

$$i_{app} = \Sigma \overrightarrow{i} - \Sigma \overleftarrow{i} \tag{2.11}$$

where $\overrightarrow{i}$, $\overleftarrow{i}$ and $i_{app.}$ are the anodic, cathodic and applied current density respectively. An anodic current density ($i_{app.} > 0$) causes a positive anodic overpotential and a cathodic current density ($i_{app.} < 0$) causes a negative cathodic overpotential.

The assumption applied to the reversible system is also useful for a corroding system. The zero-net current point for a reversible system is the equilibrium potential. In a corroding system, the no-current point is the corrosion potential. Although no current flows from a corroding electrode, the two (or more) reactions that occur on the electrode surface are not simply the same reaction going in opposite directions. The electrons generated by the dissolution of the metal are used by the reduction of the other reactant on the metal surface (e.g., hydrogen ions) as reaction proceeds at steady state. Graphically this is shown in Fig.2.7 [18].

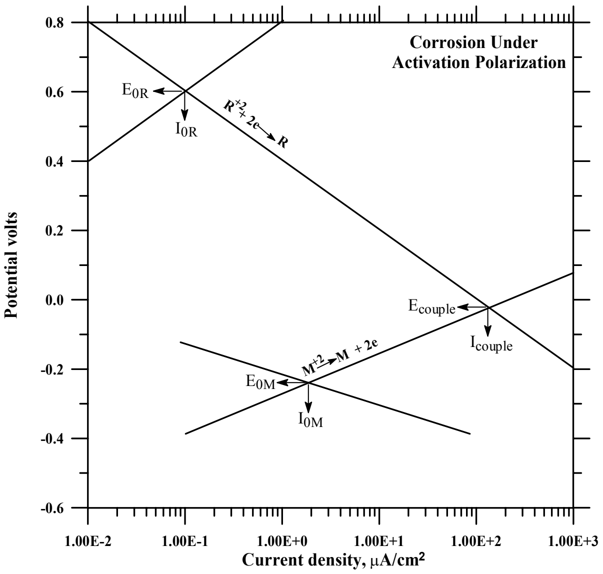

Figure 2.7: Corrosion under activation control [23].

2.5.1 Activation Polarization:

Polarization refers to an electrochemical process, which is controlled by the reaction sequence at the metal-electrolyte interface or stated in another way the reaction at the electrode requires activation energy in order to go. Activation polarization is usually the controlling factor during corrosion in strong acids. This is easily illustrated by considering hydrogen evolution reaction on zinc during corrosion in acid solution; Fig.2.8 shows some of the possible steps in hydrogen reduction on a zinc surface as [1]:

1. It occurs rapidly and the species must be adsorbed or attached to the surface before the reaction.
2. Electron transfer (resulting in a reduction of the species) to H^+ discharge.
3. Two hydrogen atoms then combine to form hydrogen molecule.
4. Hydrogen bubbles are formed.

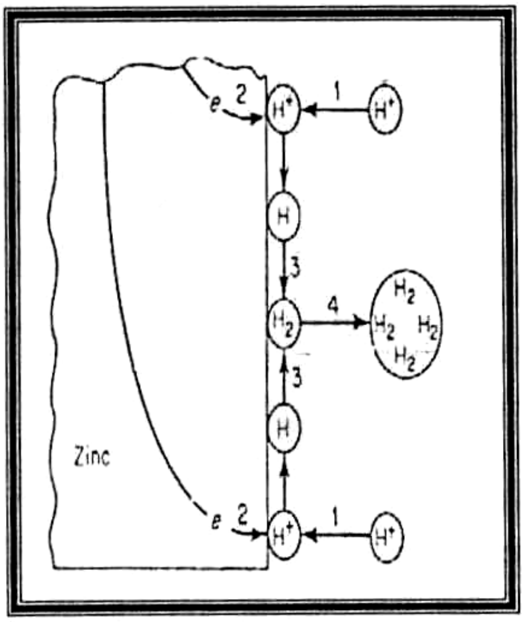

Figure2.8: Hydrogen-Reduction Reaction under Activation Control [1].

The controlling slow step of H^+ discharge is not always the same, but varies with metal, current density, and environment [6].

Activation polarization is function of the nature and concentration of the species being reduced, surface roughness, composition and temperature. In addition it is sensitive to traces of reducible impurities in the system [11]. The activation-over potential, and hence the activation energy varies exponentially with the rate of charge transfer per unit area of electrode surface, as defined by Tafel equation [2]:

$$\eta_A = a \pm b \log i \tag{2.12}$$

where:

i : current density.

a, b : Tafel constants

± : Anodic and cathodic area overpotential respectively.

The activation polarization η_A of any kind increases with anodic and cathodic current density in according with the Tafel equation [7]:

$$\eta_A = \frac{2.303\,RT}{\alpha zF}\log\left[\frac{i_a}{i_0}\right] \text{ for anodic reaction} \tag{2.13}$$

$$\eta_A = \frac{2.303\,RT}{\alpha zF}\log\left[\frac{i_c}{i_0}\right] \text{ for cathodic reaction} \tag{2.14}$$

These equations may be simplified to:

$$\eta_A = \beta_A \log\left[\frac{i_a}{i_0}\right] \tag{2.15}$$

$$\eta_A = \beta_C \log\left[\frac{i_c}{i_0}\right] \tag{2.16}$$

where β_A, β_C, and i_0 are constants of a given metal and environment and are both dependent on temperature. The exchange current density i_0 represents the current density equivalent to the equal forward and reverse reactions at the electrode at equilibrium. The larger the value of i_0 and the smaller value of β_A and β_C, the smaller is the corresponding overvoltage. Figure 2.7 shows typically the positions of Tafel slopes, i_{corr} and E_{corr}. At the equilibrium potential for the hydrogen electrode (–0.059 pH), for example, overpotential is zero.At the applied current density, it is given by η, the difference between measured and equilibrium potentials [1].

2.5.2 Concentration Polarization:

It refers to electrochemical reaction, which is controlled by a mass transfer process, such that a drop in the concentration of the electrochemically active species on the electrode surface may result in causing a change in potential. The relationship between the reaction rate and concentration polarization is [4]:

$$i = i_{lm}\,[1 - \exp(\frac{-nF}{RT}\eta^{c})] \tag{2.15}$$

where i_{lm} is the maximum rate of a possible reaction for a given system, under which all the transferred species to the electrode react very soon, η^{c} concentration polarization. The maximum rate is known as the limiting current and can be defined mathematically by the following equation [1]:

$$i_{lm} = \frac{DnFC_b}{\delta_m} \tag{2.16}$$

where:

D : Diffusion coefficient of reacting ion (m^2/sec.).

C_b : Bulk concentration of reacting ion (moles/m^3).

δ_m : Thickness of the diffusion layer (m).

Equation (2.15) can be expressed in terms of η^c as:

$$\eta^c = \frac{-2.303}{nF}\log\left(1-\frac{i}{i_{1m}}\right) \tag{2.16}$$

The value of the concentration polarization depends on the concentration, temperature, and diffusion boundary layer thickness. For a particular electrode in any system, the diffusion layer thickness is dependent on the velocity of the solution past the electrode surface. As this velocity increases, δ_m decreases and the limiting current increases [15]. It has been observed that concentration polarization is the controlling factor during reduction processes where the supply of reducible species is limited as shown in Fig.2.9 [1].

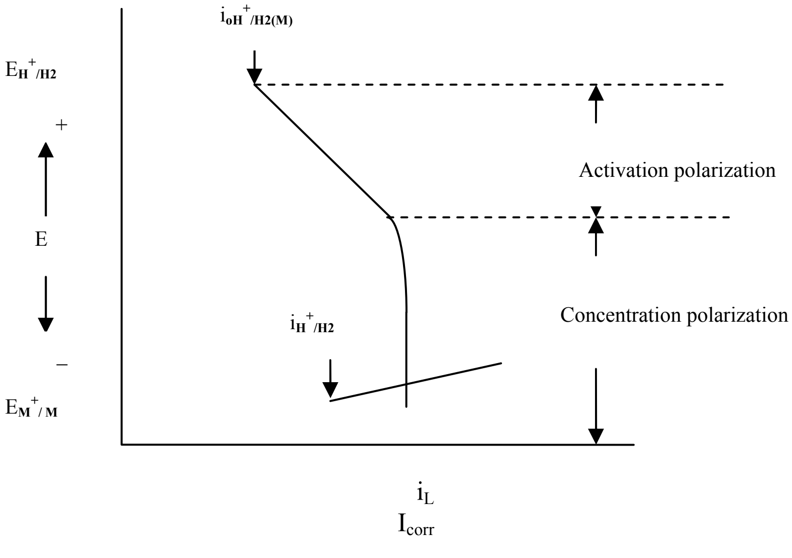

Figure2.9: Corrosion of metal M under reduction diffusion control [1].

2.5.3 Resistance Polarization:

It refers to electrochemical reaction, which is working under conditions would result in potential drop through a portion of the electrolyte surrounding the electrode, or through the reaction product. This is usually called the ohmic potential drop, which contributes to polarization as [6]:

$$\text{Ohmic potential drop [IR drop)} = IR_0 = \frac{1_e I}{\sigma A_e} \qquad (2.17)$$

Where:

i : Reaction rate expressed as current density (i = I/Ae).

R_0 : Resistance of the electrolyte solution.

σ : Conductivity of the electrolyte solution.

λ_e : Resistance path (i.e., separation distance between electrodes).

A_e : Cross sectional area of electrode (cm^2).

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 [6, 15, 24]:

$$\eta^R = I(R_{solu.} + R_f) \qquad (2.20)$$

where:

$R_{solu.}$is the electrical resistance which is a function of electrical resistivity (Ω cm) of the solution and the geometry of the corroding system, ad 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 value of the ohmic potential drop is influenced by the conductivity of the electrolyte; the latter is usually a strong function of temperature and composition. This term of polarization is usually neglected in highly conductive solutions [18].

2.5.4 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 [6]. The total polarization of an electrode is the contribution of activation polarization and concentration polarization [1]:

$$\eta_t = \eta_A + \eta_C \tag{2.18}$$

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 cathodic overpotential for activation process is given by [1]:

$$\eta_t = \eta_A + \eta_C$$

$$\eta^{real} = -\beta_C \log\frac{i}{i_0} + \frac{2.303\,RT}{nF}\log\left(1-\frac{i}{i_L}\right) \tag{2.19}$$

This case is shown in Fig.2.9.

The total polarization at a metal electrode then becomes as the algebraic sum of the three types described above [11]:

$$\eta = \eta_A + \eta_C + \eta_R \qquad (2.21)$$

Chapter Three

Galvanic Corrosion

3.1 INTRODUCTION:

Galvanic corrosion occurs when two different metals are connected in the presence of an electrolyte [23]. Because corrosion is an electrochemical process involving the flow of electric current, corrosion can be generated by a galvanic effect, which arises from the contact of dissimilar metals in an electrolyte (an electrolyte is an electrically conductive liquid). In fact, three conditions are required for galvanic corrosion to proceed, the two metals must be widely separated in the galvanic series, and they must be in electrical contact and their surfaces bridged by an electrically conducting fluid. Removal of any of these three conditions will prevent galvanic corrosion.[26]

Galvanic corrosion greatly contributes to stress corrosion cracking, pitting corrosion, crevice corrosion, and hydrogen absorption, etc. [25].

In complex process streams and piping arrangement different metals and alloys are frequently in contact with each other and the corrosion media. Most galvanic corrosion is unwanted and often unexpected, for example a yacht with amonel hull and steel rivets became un-sea worthy because of rapid corrosion of the rivets. Several attack occurred on aluminum tubing connected to brass return bends. Domestic hot water tanks made of steel fail, where copper tubing is connected to the tank. Pumps, shafts, an valve stems made of steel or more corrosion resistance materials fail because of contact with graphite packing [5].

A filtration unit in a platform seawater injection system handling fully aerated sea water is constructed of 316 stainless steel, The attached piping upstream of each filter is heavy wall carbon steel to provide galvanic protection, preventing crevice corrosion of 316 stainless steel. Inside each filter bolts are used to retain the non-metallic filter elements. In several instances 303 stainless steel bolts were substituted for 316 stainless steel. After six months operation, crevice corrosion had virtually destroyed the 303 stainless steel. The substitution of 303 stainless steel for 316 stainless steel is a very common problem that is particularly prevalent with small parts such as compression tube fittings and small valves [26].

When trying to prevent galvanic corrosion designers employ a number of tactics. One is to choose fasteners, which provide the least galvanic activity such as aluminum instead of steel. Another prevention tactic is to help prevent moisture from being present by proving adequate drainage where dissimilar metals are in contact. A commonly used method in the aerospace industry is to apply a very thin layer of paint to bolts prior to inserting them into or through the magnesium part and then additional paint over the top of the bolts. This is often referred to as wet assembly. The paint helps prevent intimate contact between the magnesium and steel, thus reducing conductivity between the two metals. The paint on top of the bolt head prevents moisture from connecting the base of the bolt head with the magnesium. When steel must be used, cadmium plating helps reduce potential galvanic activity [27]. A beneficial act of galvanic corrosion is the catholic protection provided. Most sacrificial anodes in use in the United States are of magnesium construction. Approximately 10 millions pounds of magnesium is used annually for this purpose [6, 8, and 28].

3.2 FUNDAMENTALS OF GALVANIC CORROSION:

The more active metal (base metal) anode is corroded more rapidly than it would if it were uncoupled in the same medium. The less active (noble metals), a cathode, generally corrodes less than would be the case if it were uncoupled in the same medium or it could be made resistant to corrosion. This effect is refered to as galvanic cathodic protection [31].

3.3 THEORY OF GALVANIC CORROSION:

The galvanic couple between dissimilar metals can be treated by application of mixed potential theory [1]. Consider a galvanic couple between a corroding and an inert metal. If a piece of platinum is coupled to zinc a corroding in an air-free acid solution, vigorous hydrogen evolution occurs on the platinum surface and the rate of hydrogen evolution on the zinc sample is decreased. Also, the corrosion rate of zinc is greater when coupled to platinum. The electrochemical characteristics of this system are schematically illustrated in Fig. 3.1 [4].

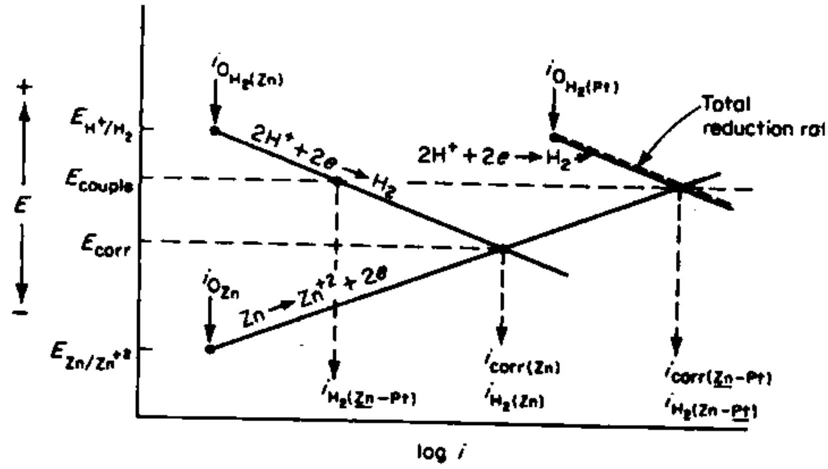

Figure 3.1: Effect of galvnically zinc to platinum.

The corrosion rate of zinc in an air-free acid is determined by the interaction between the polarization curves corresponding to the hydrogen evolution and zinc-dissolution reaction, yielding a corrosion rate equal to $i_{coor.(Zn)}$. When equal areas of platinum and zinc are coupled, the total rate of hydrogen evolution is equal to the sum of the rates of this reaction on both the zinc and platinum surfaces. Since the hydrogen-hydrogen ion exchange current density is very high on platinum and very low on zinc, the total rate of hydrogen evolution is effectively equal to the rate of hydrogen evolution on the platinum surface, as shown in Fig.3.1. Figure 3.1 shows that coupling zinc to platinum shifts the mixed potential from $E_{corr.}$ to E_{couple}, increases corrosion rate from $(i)_{corr(Zn)}$ to $i_{corr(Zn-pt)}$ and increases the rate of hydrogen evolution on the zinc from $i_{H_2(Zn)}$ to $i_{H_2(Zn-pt)}$. The rate of hydrogen ion reduction on the platinum is $i_{H_2(Zn-pt)}$. As mentioned above, the increase in corrosion rate of zinc observed when this metal is coupled to platinum is the result of the higher exchange current density for hydrogen evolution on platinum surface. It is not due to the noble reversible potential of the platinum-platinum-ion electrode, as frequently stated in the literature. To illustrate this point, consider the relative positions of platinum and gold in the emf and galvanic series. The reversible potential of the gold electrode is more positive than that of platinum in the emf series, where as in most galvanic seriestabulations the position of the platinum is below gold as shown galvanic series(3.1). The effect of coupling zinc to gold and to platinum is compared. As mentioned before, the exchange current density for the rate of hydrogen reaction on the zinc metal surface is very low, and as a consequence the rate of hydrogen evolved in a galvanic couple can be assumed to be almost equal to the rate of hydrogen evolution on either gold or platinum .

If equal areas of gold and zinc are coupled, the corrosion rate increase is less than that observed if equal areas of platinum and zinc are coupled. The reason why gold produces a less severe galvanic effect is not related to its revisable potential but rather to the fact that it has a lower hydrogen exchange current density than platinum[13].

A couple between a corroding and an inert material represents the simplest example of galvanic corrosion. A couple between two corroding metals may also be examined by application of mixed potential principles, as shown in Fig.3.2.

Figure 3.2: Galvanic couple between two corroding metals.**[13]**

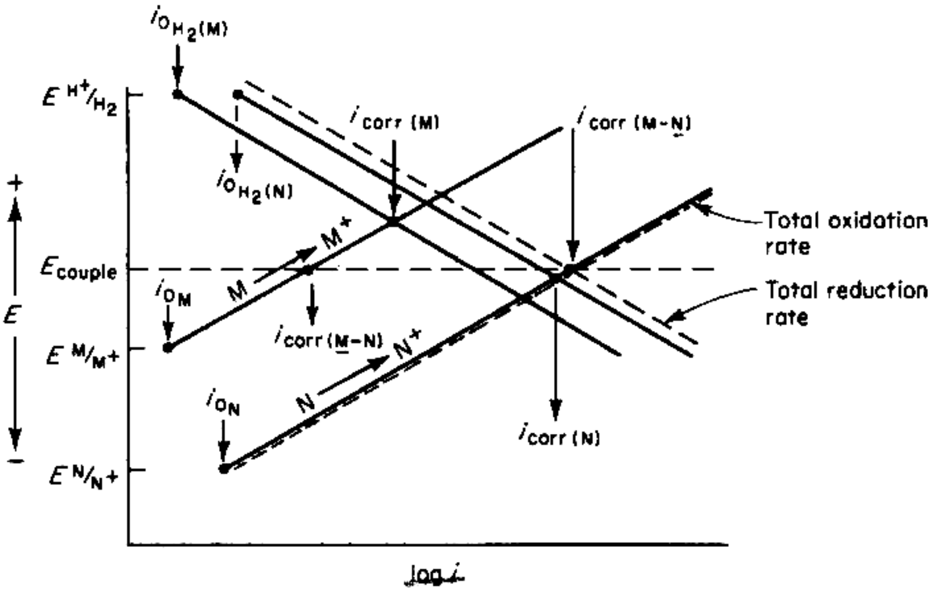

Figure 3.2: Galvanic couple between two corroding metals. [13]

The Figure shows the corrosion rate of two metals before and after coupling. Metal M has a relatively noble corrosion potential and a low corrosion rate $i_{corr(M)}$, while metal N corrodes at a high rate $i_{corr(N)}$ at an active corrosion potential. If equal areas of these two metals are coupled, the resultant mixed potential of this system occurs at the point where the total oxidation rate equals total reduction rate. The rates of the individual partial processes are determined by the mixed potential. As shown in Fig.(3.2), coupling equal areas of these two metals decreases the corrosion rate of metal M to $i_{corr(\underline{M}-N)}$ and increases the corrosion rate of metal N to $i_{corr(M-\underline{N})}$ [13].

The relative areas of the two electrodes in a galvanic couple also influence galvanic behavior. Figure 3.3 illustrates the effect of cathode area on the behavior of a galvanic couple of zinc and platinum.

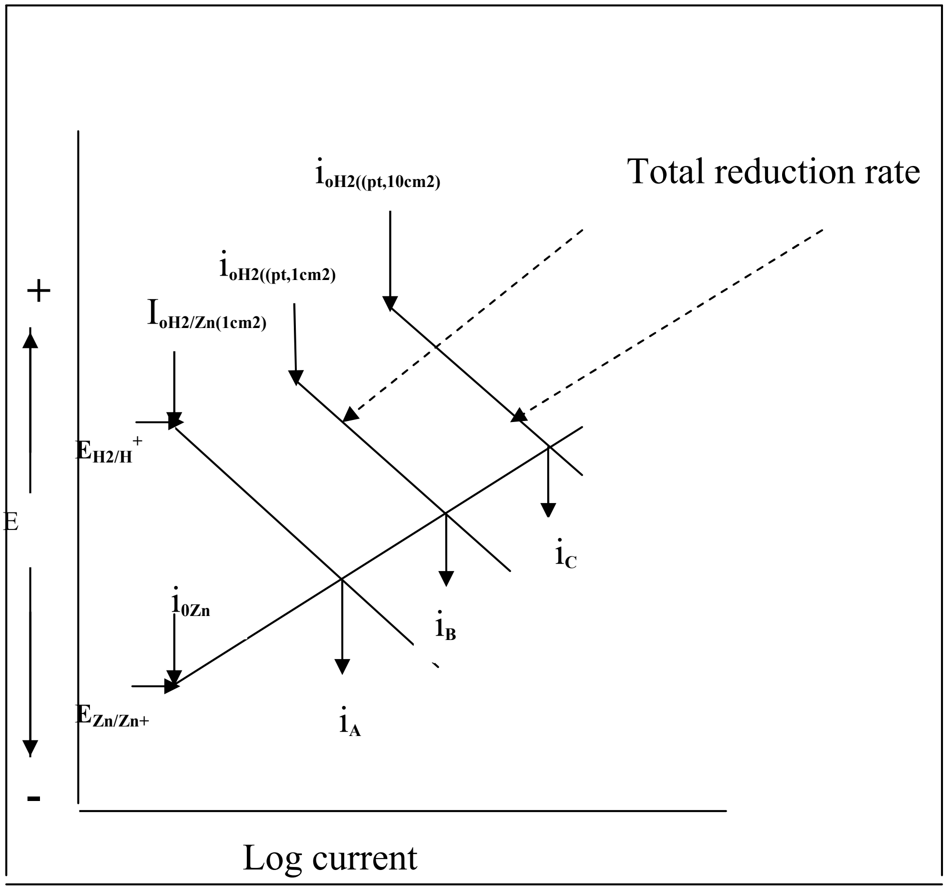

Figure 3.3:Effect of Cathode - Anode Ratio on Galvanic Corrosion of Zinc-Platinum Couple.[13]

Current rather than current density is used in this figure. If a piece of zinc 1 cm^2 in area is exposed to the acid solution, it will corrode with a rate equal to i_A. Note that since 1 cm^2 of zinc is considered, current and current density i_A are equal. If this zinc specimen is coupled to a platinum electrode of 1 cm^2 area, the zinc corrosion rate is equal to i_B. Again, since electrodes with 1 cm^2 areas are used, current and current density are equal. However, if a platinum electrode with an area 10 cm^2 and plot its behavior in terms of current, it has an exchange current i_0^*, which is 10 times greater than 1 cm^2 of an electrode. Thus, increasing the area of an electrode increases its exchange current density, which is directly proportional to specimen area. This is illustrated in Figure 3.4. As shown the corrosion rate is of the couple is increased as the area of platinum is increased. As the size of the cathode in a galvanic couple is increased, the corrosion rate of the anode is increased. If the relative area of the anode electrode in a galvanic couple is increased, its overall corrosion rate is reduced [13].

So the situation often arises where: (a) components of several different metals are in electrical contact and/or(b) more than one cathodic reactant is present. In these circumstances, several anodic and/or cathodic processes may take place simultaneously: the corroding system is then called a polyelectrode.

Because the current density i, and hence the current I, at any given electrode is a function of the potential it follows that, for a given potential, the total anodic current of polyelectrode system is the sum of the corresponding anodic currents of the individual electrodes. If the total area of the system is S, made up of fractions f^A, f^B, …etc for the various components A, B, …, then the anodic current from the j^{th} component is [4]:

$$I_a^{system} = \sum_j J_a^j = S\sum_j f^j i_a^j \tag{3.1}$$

Similarly, the total cathodic current is:

$$I_c^{system} = \sum_j J_c^j = S\sum_j f^j i_c^j \tag{3.2}$$

At the corrosion potential adopted by the polyelectrode, the total anodic and cathodic currents are equal, so that:

$$I_{corr.}^{system} = I_{a}^{system} = \left| I_{c}^{system} \right| \tag{3.3}$$

And:

$$\sum_{j} f^{j} i_{a}^{j} = \sum_{j} f^{j} \left| i_{c}^{j} \right| \tag{3.4}$$

where the current densities on the various components are those corresponding to E = $E_{corr.}$. It should be noted that the anodic and cathodic current densities on any particular component might be very different. That is, attack of a component is intensified if it is connected to large cathode. The combination of large cathode/small anode is all too frequently encountered in corrosion process. This conclusion regarding the intensifying effect of large cathode/small anode upon corrosion rate is a general one that is elegantly formulated by equation (3.5) [4]:

$$\frac{i_{a}^{B}}{i_{c}^{N}} = \frac{f^{N}}{f^{B}} \left[\frac{\left| i_{c}^{N} \right|}{i_{a}^{N}} - 1 \right] + \left[\frac{\left| i_{c}^{N} \right|}{i_{a}^{N}} \right] \tag{3.5}$$

For instance [8] if a metal is placed in a aqueous solution containing cations of a more noble metal, i.e. one which is above it in the electrochemical series, then it will displace the more noble ions from solution and itself dissolves. Such a spontaneous reaction is called galvanic displacement and is presented by Fig 3.4. Displacement continues until the baser metal is with a “flash” porous coating of the more noble one, possibly 1 μm or so in thickness, where upon further reaction substantially ceases. Iron dipped into a copper solution rapidly develops a flash coating of copper, whilst copper dipped into silver nitrate acquires a black deposit of finely divided silver within seconds. The structures of these coatings correspond closely to these obtained at high i/i_L values. They are therefore frequently non-adherent or only loosely so. In these instances the reaction is soon over but, when two different solid metals are in contact with one another, the consequences can be more disastrous. For a noble [11] metal N and abase metal B immersed in a corrodent, the corrosion of the resulting polyelectrode can be represented by equation (3.5) given previously. If the cathodic process takes place readily on the noble metal, i.e. the term in brackets is positive, a small area of B connected to a large one of N($f^B << f^N$)results in an intense attack of B such might occur, for example, if a small area of steel or cast iron, in electrical contact with a much larger area of bronze, were immersed in seawater, the cathodic reactant being dissolved oxygen. Or again, if aluminum rivets were used in a steel structure exposed to weather, the rivets would corrode preferentially whenever the structure got wet. These are both examples of galvanic of attack (bimetallic corrosion). The intensification of attack of the baser metal depends on:

a. The relative area (f^N/f^B) and

b. The relative electrochemical activities of the metals concerned.

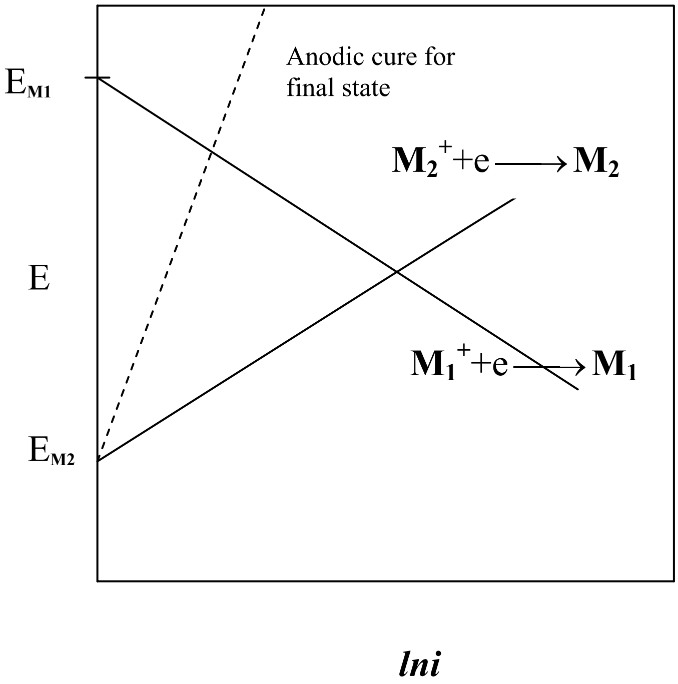

Figure3.5: Galvanic Displacement [1].

3.4 GALVANIC SERIES:

The galvanic series tell that the more negative metal will corrode quickly when electrical coupled in seawater, but not how fast. Two metals far a part in series will not necessarily experience more corrosion than two metals close together. Finding the rate of corrosion in galvanic couples requires knowledge of polarization, the ability of metal to change voltage while accepting or giving a certain amount of electron[10].

Table 3.1: Galvanic series in Seawater.

Anodic **(Least Noble, Corroded)**	Magnesium
	Magnesium Alloys
	Zinc
	Beryllium
	Aluminum 1100, 3003, 3004, 5052, 6053
	Cadmium
	Aluminum 2017, 2024, 2117
	Mild Steel 1018, Wrought Iron
	HSLA Steel, Cast Iron
	Chrome Iron (Active)
	430 Stainless (Active)
	302, 303, 321, 347, 410, 416 Stainless Steel (active)
	Ni-Resist
	316, 317 Stainless Steel (active)
	Carpenter 20cb-3 Stainless (Active)
	Aluminum Bronze (CA687)
	Hastelloy C (Active) Inconel
	625 (Active) Titanium (Active)
	Lead/Tin solder
	Lead
	Tin
	Inconel 600 (active)
	60 % Ni 15 % Cr (Active)
	80 % Ni 20 % Cr (active)
	Hastelloy B (active)
	Navel Brass (CA464, Yellow)
	Brass (CA230)
	Red brass (CA268)
	Admiralty brass (CA443)
	Copper (CA102)
Direction of Attack	Manganese bronze (CA675)
	Tin bronze (CA903, 905)
	410, 416 stainless (passive)
	Phosphor bronze
	Nickel silver
	Cupro nickel 90-10
	Cupro nickel 80-20
	Monel 400, k500
	Chrome iron (passive)
	302, 303, 321, 347, 410, 416 Stainless Steel (passive)
	316, 317 Stainless Steel (passive)
	Silver
Cathodic	Titanium
	Graphite
	Zirconium
(Most Noble, Protcted)	Gold
	Platinum

3.5. FACTORS AFFECTING GALVANIC CORROSION [28]

Many factors including the electrochemical ones determine whether or not galvanic corrosion will occur, as follows:

I. Electrode Potentials [26]:

The standard electrode potential of a metal in a solution of its ions gives a rough guide to the position of the metal in a galvanic series. In practice however usually concerned with alloys rather than pure metals and in environments that does 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 consideration.

II. Reaction kinetics [11]:

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 overpotentials 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.

III. Alloy Composition [26]:

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.

IV. Protective film characteristics [26]:

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, and resistance to various solution constituents are important.

V. Mass Transport [11]:

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.

VI. Bulk Solution Environment [26]:

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

VII. Bulk Solution properties [26]:

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

VIII. Total Geometry [30, 31]:

One of the most important parameters in galvanic corrosion is the "area ratio" a high cathode to a rode ratio usually resulting in rapid corrosion or high anode (Base) to cathode noble ratio giving lower no corrosion [28]. If the area of the less noble material is large compared to that of more noble (cathodic) the corrosive effect is greatly reduced, and may in fact become negligible. Conversely a large area of noble (base) metal in contact with a small area of less noble (base) will accelerate the galvanic corrosion rate [30]. 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 [26].

3.6 LITERRATURE REVIEW ON GALVANIC CORROSION

The galvanic action as a phenomenon has been investigated by several authors in the field of corrosion during the last 50 years.

Copson [30] 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.

Alemany [32] studied the cementation with the Cd (11)/Zn and Ag (1)/Cu systems, and on corrosion with the Ce (iv) / Zn and Cr (vi)/Zn couples, were carried out on a rotating disc electrode immersed in relatively concentrated solutions. Time variation of the concentration of the reacting species and SEM observations showed that the change in reaction kinetics was due to the roughness of the changing surface of the electrode, depending on the chemical system considered. For corrosion, the average roughness was shown to exceed the thickness of the Nernst diffusion layer, and the rougher surface created allows local flow disruption and mass transfer enhancement. Besides, corrosion by Cr (vi) species results in greater roughness of the metal surface with more significant flow disruption than with Ce (iv) at the same concentration.

Pryor [33] investigated the galvanic corrosion of Al/steel couple in chloride containing solution and found that aluminum completely protects steel catholically 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.

Pohlmn [34] studied the corrosion and electrochemical behaviour of Boron / Al composites and found that galvanic corrosion would be expected between the aluminum boride intermetallic and the aluminum matrix causing preferential attack of the aluminum.

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

Shalaby [36] studied the effect of galvanic coupling of T_i with admiralty brass. Al-brass, Cu-Ni and Al-Mg alloys in 32.7 gl/NaCl solution at ambient temperature and 90 ^oC under flowing (O_2) and (Ar) atmospheres. The results showed that T_i was highly resistant material in the corrosive medium and its behavior was not affected by coupling with these alloys which were slightly attacked. However, when Cu-Al alloy was coupled to a relatively large area of T_i (1:10) it showed a pitting corrosion.

Kim [31] carried out electrochemical tests conducted to study the external corrosion of a steel pipeline beneath the disbonded insulation with a holiday in synthetic groundwater. The corrosion rate of pipeline steel under the insulated condition was much lower than that under the uninsulated condition. The better corrosion property of the insulated steel was attribute to the formation of a protective rust layer under the insulation. This is mainly because the mass transfer or the thickness loss rate through the insulation was small compared to the connective mass transfer directly to the electrolyte without insulation. Breaks or holidays in insulation exposed the pipeline steel to possible galvanic corrosion. Galvanic corrosion occurred on the insulted and uninsulated steel.Galvanic corrosion at the cracked insulation developed because the uninsulated steel (cracked) was active to the insulated steel (crack-free) and galvanic attack is concentrated in a small cracked area by a large cathode (crack free)/anode (cracked) area ratio. Pipeline-insulation crevices resulting from insulation disbondments on the pipeline did not induce crevice corrosion because the solution and oxygen could permeate through the insulation. Thus, corrosion at the pipeline insulation interfact was anodic dissolution rather than crevice corrosion.

Klassen [37] investigated the galvanic corrosion by studied design factors such as proximity to a source of pollution, degree of wind exposure and an object's size affect the rate of pollution deposition to an object. In certain regimes of atmospheric corrosion, the corrosion rate is limited not by electrochemical reactions but by the rate of mass transfer of pollutions. In these cases, a mass transfer model that accounts for the transport of pollutants, such as a marine salt aerosol, provides a theoretical and predictive framework for assessing corrosively severity. A limited, but fairly realistic, model was developed that accounts for a steady source of marine aerosol particles and their transport near the ground,well whith in the planetary bounding layer. The predicted aerosol concentration as a function of distance for 1500 m from a steady source was consistent with published data on steel corrosion and salinity rates near an ocean. Implications for outdoor design are: (i) smaller objects can be expected to corrode faster because of a greater capture efficiency of salt aerosols; (ii) objects exposed to faster wind speeds and aerosols will corrode faster; and (iii) objects in the lee of prevailing winds from an aerosol source will corrode faster than objects upwind of an aerosol source.

Morris [38] studied galvanic currents and potentials which have been calculated on heterogeneous electrode surfaces compared to random configurations of coplanar anodes and cathodes. For the purpose of investigating system behaviour on different electrode geometrices. 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 current and potentials so calculated were investigated for similarities linking bahaviour on different electrode gemoetries. 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 accuate prediction of galvanic current for an arbitrarily complex electrode surface geometry.

Leumer [39] studied the effects of hydrodynamic variables and fluid properties on corrosion of 90/10 Cu-Ni (CDA 706) in single metal exposures and in galvanic couples with platinum were studied in synthetic seawater. An apparatus utilizing circuling foils as the specimen holder was redesigned as an experimental apparatus for this study. Various methods were applied to develope corrosion rate data for different flow situation. Particular emphasis was placed on the determined corrosion rates. Also, the corrosion morphology was studied macroscopically and microscopically for different velocities. A transfer and corrosion in a flowing medium concluded this study.

Mansfeld [40] investigated the effect of variations of area ratio of two metals in a galvanic couple. In case 1, it is assumed that the galvanic potential will be in a region where only a significant process on the more active metal A is dissolution, while the only significant process on the more noble metal C is reduction of oxidizer. In this case, a measurement of the galvanic current density will give an exact value or the dissolution rate of the anode.

In case 2, it is assumed that coupling of metal A to metal C causes only such a small shift of the potential of metal A that a cathodic C as well as an anodic process takes place with significant rates on metal A and Tafel behaviour is therefore not observed,. In this case, the galvanic current density is always smaller than the dissolutio current density of the anode, It is assumed that the corrosion rate metal of A is controlled by the diffusion rate of the oxidizer (O_2) to the surface of metal (A), and metal of (C) is acting as an oxygen electrode.

Mansfeld [41] followed the galvanic corrosion behaviour of Al alloys couples to coated pH13-8MO stainless steel in aerated 3.5% NaCl by continuous monitoring of the galvanic current and by weight loss data and found that results from galvanic current and by weight loss data how a decrease indissolution rate when Al alloy coupled to coated stainless steel and there is appreciable difference in the absolute values of dissolution rate and this difference between weight and galvanic current data is not due to experimental errors but to be expected and can readily be explained based on mixed potential theory.

Mansfeld [42] investigated the relationship between galvanic current and dissolution rates in aerated 3.% NaCl, found that the galvanic current can not be accurate measure of dissolution rates, since dissolution rates from the galvanic current are smaller than the true dissolution rates.

Mansfeld et al. [43] studied the galvanic corrosion of Al alloys in air saturated 3.5% NaCl coupled to using dissimilar metal and found that the measurements of dissolution rates of Al alloy coupled to a variety of dissimilar metals showedthat the difference of corrosion potential of uncoupled materials is a poor indicator of the extent of galvanic corrosion of coupled dissimilar materials.

Mansfeld [44] worked on the galvanic interaction between active and passive titanium in aqueous CH_3OH-1 NHCl and found that if the area ratio (A^C/A^A) is increased to higher value, the anodic will be polarized to more noble potentials and only an oxidation process (dissolution) will occur.

Mansfeld et al. [45] studied the galvanic action of Al alloys 7075, 6061, 2024, bare or coated with chemical conversion coating alodine 600, coupled to stainless steel 304 immersed in aerated 3.5% NaCl solution. Differences between dissolution rates and calculations from galvanic current data and weight loss data were explained based on theoretical consideration.

Mansfled [46] studied the instrumentation for measurement of galvanic current as a function of velocity of metal/electrolyte and found that the relationship between galvanic current density and velocity is:

$$i_g = \text{Const.} + \text{Const} (\sqrt{V})$$

Mansfeld et al. [47] investigated also the effect of area ratio on the galvanic corrosion and found the galvanic current density i_g^A with respect to the anode is directly proportional to the area ratio, $i_g^A = K_1A^C/A^A$, while the dissolution rate of the anode is related to the area ratio by $r_A = K_2(1 + A^C/A^A)$.

Mansfeld et al. [48] worked on the galvanic corrosion of Al alloys and the effect of solution composition when coupled to Cu, stainless steel 3041, Ti-6Al-4V, 4130 steel or zinc in 3.5% NaCl, found that the galvanic effect decreases in the order Cu > 4130 steel > Ti-6Al-4V for Al alloys coupled to one of these metals. Zinc although being the anode in all galvanic couples, can sometimes accelerate corrosion rates of Al alloys.

Mansfeld [49] investigated the galvanic corrosion of Cu/Al 6061 in water containing hydrous salts of sodium sulfate, sodium chloride and sodium bicarbonate, and found that Al(6061) to be the anode initially and becomes the cathode later in the test and concluded this is due to the low chloride concentration of the solution which leads to a more noble pitting potential of Al 6061.

Song [50] provided an overview of the corrosion mechanisms of magnesium alloys based on recent research and the literatures. Magnesium is a very reactive metal. Thus galvanic corrosion is very important. Galvanic corrosion is associated with (1) impurities, particularly Fe, Ni and Cu (2) second phases, eg., beta and (3) coupling with a less active metal. Magnesium alloys exposed without galvanic coupling have a corrosion resistance that, in general, is not as good as that of aluminum alloys. When magnesium is passive, then the corrosion rates are low. But the range of environmental conditions for passivity of magnesium is less than for aluminum; i.e. passive films are not very stable. Corrosion is typically important as localized corrosion such as pitting and stress corrosion cracking (SCC). There is the exception that SCC failures will increase with increased use of Mg alloys in load bearing applications. Corrosion of AZ91 is by “pitting” in 1N NaCl. The corrosion potential is above the “pitting” potential. Corrosion of cast AZ91 has the following morphologies, (1) preferential attack of primary alpha, (2) preferential attack of eutectic alpha and undermining of beta. The beta phase is more stable than alpha, and beta is a better cathode. There is corrosion protection and low corrosion rates if there is a significant fraction of finely divided continuous beta.Other wise beta accelerates corrosion. Corrosion acceleration is significant if there are large blocks of interconnected beta. Corrosion acceleration may be small if beta is small and finally divided.

Lee [51] studied the corrosion behavior of an as-cast magnesium alloy 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 details. The corrosion rate of an as-cast alloy increased abruptly to 9 wt% Al, the corrosion reveals a different tendency than the alloy system. The beta phase that is a typically 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 behaviour 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.

Han [52] studied the measures how to impede the galvanic occurring between Pd outer layer and Alloy 42 lead frame matrix and at the same time the formation of microcrocks by hydrogen absorption into Pd layer electrodeposited on the Alloy 42 lead frame. For this purpose, charge- transfer resistance, surface morphology, surface chemical composition and electrochemical characteristics of various electrodeposited layers were investigated by using a.c.- impedance spectroscopy, and cyclic voltammetry, respectively. From the analysis of a.c.- impedance spectra, it is found that introduction of the intermediate electrodepsited layers between Pd outer layer and Alloy 42 lead frame improves the galvanic corrosion resistance and Alloy 42/Cu/Ni/Pd- Ni/Pd structure shows the highest corrosion resistance of all structures. As the hydrogen- charging potential decreases below the beta- Pd H formation potential, the formation rate of microcrocrack on the surface of the electrodeposited outer layer remarkably increases. This is attributed to the molar volume expansion by 10% developed due to the formation of the beta-

PdH phase. It is suggested that the formation of microcracksin the electrodeposited pd outer layer is hindered by empolying the Pd-Ni or Pd-Au alloy as outer layer instead of the pure Pd outer layer and /or by introducing the Cu/Ni intermediate electrodeposited layer between the Alloy 42 lead frame substrate and Pd outer layer.

Scully [53] investigated the electrochemical behaviors of Pi- Al_2 Cu Phase, Beta- Al_3 Ta and, to a lesser extent, Al_3 Zr compared to high purity Al in ambient temperature inert buffer solutions and, in certain cases, dilute halide solutions. The aim of this work is to develop a better understanding of electrochemical characteristics of these intermetallic phases. In particular, information sought concerning (a) their galvanic couple relationship with respect to Al and (b) the relationship between the passive films formed on each phase and its ability to support both cathodic and anodic electron transfer reaction. The open circuit potentials of all three intermetallic phases were more positive than that of Al in inert solutions ranging from PH_2 to 12. The Al_2 Cu phase supports the reduction of water reaction at en hanced rates relative to pure Al due to the presence of metallic CuO in an Al_2O_3 rich oxide but supports oxygen evolution due to a combination of this effect as well as formation of more electrically conductive copper oxides. A similar effect is observed for Al_3Ta and is attributed mainly to the formation of a more conductive mixed oxide containing Ta_2O_3.

Wilhelm [54] studied galvanic corrosion between dissimilar materials using laboratory simulation of oil/gas production environments. Galvanic corrosion of materials used in production equipment (4130,9Cr, 13Cr, 2205, 718, 825, N/C42, SM2550, Beta- CTi, C-276, 925) was studied in corrosive environments, which included sweet well produced fluids, sour well produced fluids, heavy brine packer fluids, and acid zing fluids. Corrosion coupons of various geometries were used to measure corrosion rates and morphologies. Electrochemical measurements were performed to determine potentials and current densities. The experimental study found that the severity of galvanic attack is a strong function of the type of corrosion products that from an metal surface. Galvanic interactions are mitigated in produced fluids where carbonate and/or sulfide scales dominate morphology. Carboneate scales tend to block long-range galvanic currents and sulfide scales tend to short-circuit them. As a result, coupling of dissimilar martial in produced fluids may be less of a problem than suspected. In more aggress fluids, such as acid zing or packer fluids where protective scales do no form, the severity of galvanic corrosion is much more pronounced. In these situations, however, many chromium-containing materials activity corrode, and their galvanic chromium contents provides short-range galvanic assistance to dissolution, thus reducing long-range effects provided by coupling to dissimilar materials. A galvanic series was constructed based on coupon data and electrochemical measurements for each of the four environments examined.

Aung [55] studied galvanic corrosion by studying an AZ91o ingot in the as-cast condition as homogenized solution treatment and then aged for various periods of time. The microstructures produced were studied in detail and the beta phase volume fraction was measured quantitatively. The corrosion resistance of all the different microstructures was studied in 3.5%. NaCl solution through weight loss measurement in constant immersion conditions and potentiodynamic polarization experiments. The corroded surfaces were analyzed using SEM and XRD. The volume fraction of the beta phase was found to have a significant influence on the corrosion behaviour. The T_4 condition improved the corrosion resistance of AZ91D alloy compared to the T_6 heat treatment. The results support the idea of microgalvanic coupling between cathodic beta phase and anodic alpha matrix.

Wei [56] studied galvanic corrosion by using Manganese to remove iron from molten magnesium alloys in order to produce high purity alloys. A study of manganese. containing particales in the magnesium alloys is therefor of technological significance with regard to the corrosion properties of Mg-Al-based alloys. TEM/SEM investigations of the as-cast microstructure and the corrosion morphologies revealed that the corrosion resistance of the alloys studied is dependent on (1) the distribution and types of small Mn-containing particles where corrosion pits can form to initiate corrosion fissures, and (2) the barrier effects for the propagation of fissures the alloys. Two effects for the propagation of the fissures in the alloys. Type l is a flower-shaped phase, and Type ll is of equiaxed or short-bar morphologies. The type 11 particles have particles have a lower Al/Mn ratio and a much higher cathodic reaction rate than the Type l phase. The Typel 11 particles may provide sites to form pits and initiate corrosion fissures. The seqregated regions of higher Al content adjacent to the grain boundaries and the beta-Al sub12Mg sub17 particles may act as barriers to the propagation of corrosion fissures. Alloys include AM50L. AM50H, AM20, AM60, and AZ91.

Sakamoto [57], studied galvanic corrosion by following the changes in mechanical properties and corrosion resistance of Al-Mg alloys with the addition 10 mass% Ni by the electron beam welding process were investigated by the tensile test and the immersed corrosion test of the specimens with or without improved treatment in 1×101 K.mol bullet m sup-3HC10 sub 4 solution at 303 K. The X-ray diffraction or EDAX analysis of the precipitates and the observations of scanning electron micrographs of the specimens and the surfaces of the corroded specimens were also performed. The main results obtained are summarized as follows:

1. The needle structure of Al sub3 Ni (beta) intermetallic compound and Al (alpha) + Al sub3 Ni (beta) eutectic structure was precipitated by the improved treatment of Al-Mg alloys.

Furthermore, the small size of teritectic structure of Al sub3Ni (beta) and Al sub 3 Ni sub 2 (gamma) intermetallic compounds was also detected.

2. The mechanical properties such as 0.2% proof stress and Vickers hardness of Al-Mg alloys were increased by the improved treatment. On the contrary, the values of U.T.S. and elongation of the improvd specimens were reduced in comparison with the untreated speciments regardless of the Al-Mg alloys.

3. The corrosion resistance of the improved specimens decreased slightly compared with that of the untreated specimens. The deterioration of the corrosion resistance was caused by an electrochemical interaction of galvanic coupling produced between the grains of Al (alpha) phase in the eutectic structure and the Al sub3 Ni (beta) intermetallic compound

Conrad [58] studied fasteners for top-side applications on navalships have historically been steel fasteners. These fasteners when exposed to marine environments suffer extensive corrosion. Alternatives such as high strength stainless steel, Ni alloy and Ti alloy fasteners are being considered. While these alternative materials offer better corrosion resistance than steel, they can suffer from treated galling when use in the uncoated and/or unlubricated condition. Solid film lubricantions such as molybendum disulfide impregnated epoxy polyamide have shown anti-galling properties. Additionally, anti seizes compounds such as Cu loaded grease have also shown anti-galling properties. In a paper on Ti as alternative fasteners, Faller compares Ti fasteners to steel and high strength alternative materials, In this study, Beta-CTi fasteners are investigated as an alternative fastener for Naval use. Galvanic interactions and thread galling are evaluated to identify candidate coatings or lubricantes so that Beta-CTi fasteners can be utilized for top-side applications.

Kostic [59] decribed the effects of cold work and galvanic coupling on corrosion of chromium-nickel stainless steel in nitric acid solutions during nitric acid production, found that the corrosion potential ofstrained chromium-nickel stailess steel in nitric acid solution are nobler than the corrosion potentials of unstrained samples and are in the transpassive region on the anodic polarization curves.

Yau et al. [60] investigated the effect on corrosion composition and microstructure in a series of FeCr-10% Ni alloys with increasing chromium content in reducing acids, found that in reducing acids (H_2SO_4 and HCl), preferential attack occurs on the ferrite phases. However, the rate of attack on ferrite is considering greater than expected on the basic of its chromium and nickel content.

Pollock et al. [61] studied the hydrogen embattlement of the plated high-strength (4340 steel) by galvanic corrosion in aqueous sodium chloride environments, and found that anodic protection of high strength steels by the use of aluminum and cadmium coating can lead to severe embattlement of the steel during exposure to aqueous NaCl environments.

Micka Louis [62] investigated the corrosion inhibition of steel by lead pigments through the steel-lead galvanic couple in acetate solution is a function of pH, and also found that steel is anodic to steel in an alkaline solution, so this polarity reversal is attributed to the breakdown of the oxide on steel in the low pH solution. The corrosion process is under activation control in the alkaline solution.

Symniotis [63] investigated the effects on the active dissolution of duplex stainless steel in different acidic solutions, and found that a galvanic action between the α' and γ' phases is found to arise at the corrosion potential of aduplex steel (SAF2205) acid solution. The results of this galvanic action are an accelerated selective dissolution of α-phase in the case of low Cl^- and sulfuric acid solution. On the contrary in the high Cl^- containing solutions was the galvanic action to more even distribution of the dissolution rates over the α' and γ' phases, this latter being strongly protected by the pressure of α' phase, compared to its uncoupled corrosion rates.

CHAPTER FOUR

Equation for Analysis Galvanic Corrosion

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 [64]. This chapter summarizes these equations as utilized in the present analysis.

4.2 ACTIVATION CONTROL:

When the slowest step in an electrochemical reaction is an electron transfer across the metal/solution interface, it is said that the reaction is under activation (charge transfer) control. The activation kinetics is not affected by fluid flow. [64]

4.3 THE CORROSION REACTION:

A corrosion reaction is the combination of two (or more) electrochemical reactions, e.g.,

(a) $Fe \longrightarrow Fe^{+2} + 2e$ (anode).

(b) $2H^+ + 2e \longrightarrow H_2$ (cathode).

Overall:

$Fe + 2H^+ \longrightarrow Fe^{+2} + H_2$.

4.4 EQUILIBRIUM POTENTIAL:

To determine the potential of a system, in which the reductions are not at unit activity, Nernest equation can be employed [1]:

$$E = E_0 - \frac{RT}{nF} \ln \frac{a_{red}}{a_{oxid}} \qquad (2.10)$$

Or:

$$E = E_0 - 2.303 \frac{RT}{nF} \log \frac{a_{red}}{a_{oxid}} \qquad (4.1)$$

where E is the equilibrium half cell potential, E_0 the standard equilibrium half-cell potential, R is the gas constant (8.314 J/deg.mol), T absolute temperature (K), n is the number of electrons transferred, F is the faraday constant(96487 coulomb/equiv.)[6], a_{red} and a_{oxid} are activities or (concentrations) of oxidized and reduced species.

4.5 EXCHANGE CURRENT DENSITY:

Exchange current density is the rate of oxidation and reduction reaction at an equilibrium electrode and it may be calculated for various concentrations by [4]:

$$\log\frac{i_0}{i'_0} = \frac{\beta}{\nu}\log\frac{C_s}{C'_s} \qquad (4.2a)$$

and simplified to:

$$i_0 = i'_0\left(\frac{C_s}{C'_s}\right)^{\beta/\nu} \qquad (4.2b)$$

for most reactions $\frac{\beta}{\nu} \cong 1.0$.

4.6 TAFEL EQUATION:

Tafel slopes (Tafel constants) are determined from the following equations [1]:

$$\beta_a = 2.303\ \frac{RT}{\alpha nF} \qquad (4.3a)$$

$$\beta_c = -2.303\frac{RT}{(1-\alpha)nF} \qquad (4.3b)$$

or using natural logarithm:

$$b_a = \frac{RT}{\alpha nF} \text{ (for anode reaction)}$$

$$b_c = -\frac{RT}{(1-\alpha)nF} \text{ (for cathode reaction)}$$

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 [1]:

$$\eta_a = \pm\beta \log \frac{i}{i_0} \tag{4.4}$$

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 [63]:

$$i_a = i_{0,a} e^{(E - E_{e,a} / \beta_a)} \tag{4.5}$$

and:

$$|i_c| = i_{0,c} e^{(E - E_{e,c} / \beta_c)} \tag{4.6}$$

where E is the electrode potential relative to the standard hydrogen electrode (SHE); and E_e is the equilibrium potential, V.

4.7 CORROSION POTENTIAL AND CURRENT:

Anodic reaction rate is:

$$i_a = i_{0,a} A_a e^{(E - E_{e,a} / \beta_a)} \tag{4.7a}$$

and as fraction of total:

$$I_a = i_{0,a} F_a e^{(E - E_{e,a} / \beta_a)} \tag{4.7b}$$

and the cathodic one:

$$|i_c| = i_{0,c} A_c e^{(E - E_{e,c} / \beta_c)} \tag{4.8a}$$

$$|i_c| = i_{0,c} F_c e^{(E-E_{e,c}/\beta_c)} \qquad (4.8b)$$

where A_a and A_c are the anodic and cathodic electrode areas respectively and F_a and F_c are the anodic and cathodic electrode area fractions.

When corrosion takes place,

$i_a = |i_c| = i_{corr}$ [Provided $A_{\mathbf{a}}=A_{\mathbf{c}}$]

or:

$I_a = |I_c| = I_{corr}$

and $E_a = E_c = E_{corr}$.

4.8GALVANIC CORROSION:

When two different metals are in corrosive environment, they corrode at different rates, according to their specific corrosion resistances to that environment. However, if the two metals are in contact in the same environment, 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 i_c heavily dependent on the relative surface area of the metals and electrochemical parameters in galvanic corrosion.

If the total area of the system S, made of fractions f^A, f^B, …, etc., for the various components A, B, …, then the anodic current from the j-th component is given by [4]:

$$I_a^{system} = S\sum f_j i_a^j \tag{4.9}$$

similarly, for the cathodic i_c currents of polyelctrode:

$$I_c^{system} = S\sum f_j i_c^j \tag{4.10}$$

At the corrosion potential ($E_{coupling}$) adopted by the polyelectrode, the total anodic and cathodic currents are equal so that:

$$I_{corr}^{system} = I_a^{system} = |\, I_c^{system} \,| \tag{4.11}$$

For example, for two metals:

$$I_{a,1} + I_{a,2} = |I_{c,1}| + |I_{c,2}| \tag{4.12}$$

Or, in terms of current densities and areas:

$$i_{a,1}\, A_1 + i_{a,2}\, A_2 = |i_{c,1}A_1| + |i_{c,2}A_2| \tag{4.13}$$

If $I_{a,1} >> I_{a,2}$, that means metal (2) have only cathode current, equation (4.13) reduces to:

$$i_{a,1}\, A_1 = |i_{c,1}A_1| + |i_{c,2}A_2| \tag{4.14}$$

4.9 A NUMERICAL METHOD:

In some cases, simplifications leading to analytic solutions of the above equations are not possible, so numerical solutions must be attempted. As an example, anumerical method implemented on a microcomputer. The sweeping method is as follows:

(a) After input data takes from appendix B equilibrium potentials for metals and for hydrogen evolution are estimated on these metals from equation (4.1).

(b) Tafel slopes for anodic and cathodic reactions are established from equations (4.3a) and (4.3b) for three values of α (0.3, 0.5 and 0.7).

(c) The exchange current density is calculated from equation (4.2) for twenty values of ionic metal concentrations in the range (10^{-2} to 10^{-6} M) and twenty values of hydrogen ion concentrations in the range (0.01-1 M).

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

(e) The values of E_{eq}, β, i_0,and assumed E_g are substituted in eqs.(4.5) and (4.6) to determine anodic and cathodic currents.

(f) The summation of the anodic and cathodic current are calculated and compared to determine the absolute value of their difference.

(g) A new value of E_g is assumed as in (d) and the program is executed again showing the difference between the values obtained in (e) and (f) should decrease.

(h) Step (g) is repeated until a minimum difference at accuracy 10^{-12} 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.

(i) A program written in Quick Basic (see appendix A) containing (140) statements for the galvanic corrosion of multi-metals in deatreted acid media implementing the present analysis under activation control.

Assuming that all the relevant cathodic reactions are taken into account and that no undetected galvanic effects or stray currents are present. The results provided by the equations given in this work represent the upper limits to the true corrosion rates. This is because often found phenomena such as the formation of protective surface layers of corrosion products or the presence in the environment of species which may act as corrosion inhibitors (i.e., substances which slow down the corrosion process) can, in practice, only reduce the rate.

CHAPTER FIVE

Results

5.1 Introduction:

As mentioned in ch.1,that the aim the present work is to study the influence of hydrogen and metal ion concentration and symmetry factor on the corrosion rate and potential of free corrosion of Fe and Zn. Also studding the same variables in addition to area fraction on galvanic corrosion for Fe,Zn and Cu couples in de-areated acid environment.

5.2 Free corrosion:

Corrosion is the destructive attack of a metal by chemical or electrochemical reaction with its environmet.Both the scientific and engineering viewpoint supplements each other in the diagnosis of corrosion damage and in the prescription of proper remedies.

5.2.1 Effect of hydrogen ion concentration:

5.2.1.1 Iron:

Hydrogen ion concentration an important role in increasing the corrosion rate of metals.This is clear in the results of Tables 5.1 to5.6,in which the increasing in hydrogen ion concentration leads to increase corrosion rate of this metal and shifts corrosion rate to less negative values.

Table 5.1: Corrosion of iron versus hydrogen ion concentration under the following conditions: $[Fe^{++}]=10^{-6}$ M, Alpha of H2=0.5, Alpha of Fe=0.5,T=25°C,P=1atm in de-areated acid solutions.

$[H^+]$	Ecorr(mV)* vs. SHE	i_{Fe}(A/cm^2)
0.01	-332.75	6.5154E-7
0.062105	-285.856	4.04641 E-6
0.114211	-270.213	7.44129 E-5
0.166316	-260.562	1.083616
0.218421	-253.564	1.423103 E-5
0.270526	-248.07	1.762591 E-5
0.322632	-243.547	2.102078 E-5
0.374737	-239.703	2.441565 E-5
0.426842	-236.36	2.781052 E-5
0.478947	-233.403	3.12054 E-5
0.531053	-230.751	3.460027 E-5
0.583158	-228.348	37.99514 E-5
0.635263	-226.15	4.139002 E-5
0.687368	-224.126	4.478489 E-5
0.739474	-222.25	4.817976 E-5
0.791579	-220.501	5.157463 E-5
0.843684	-218.864	5.496951 E-5
0.895789	-217.325	5.836438 E-5
0.947895	-215.874	6.175925 E-5
1	-214.5	6.515413 E-5

Table 5.2: Corrosion of iron versus hydrogen ion concentration under the following conditions: $[Fe^{++}]=10^{-6}$ M, Alpha of H2=0.5, Alpha of Fe=0.3,T=25°C,P=1atm in de-areated acid solutions.

$[H^+]$	Ecorr(mV) vs. SHE	i_{Fe}(A/cm^2)
0.01	-229.25	8.68E-08
0.062105	-165.304	3.87E-07
0.114211	-143.972	6.37E-07
0.166316	-130.812	8.66E-07
0.218421	-121.269	1.08E-06

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[*] To obtain summation equal zero, the computer program sensitive for at least 3 decimals for corrosion potential.

0.270526	-113.778	1.29E-06
0.322632	-107.61	1.49E-06
0.374737	-102.368	1.68E-06
0.426842	-97.8093	1.87E-06
0.478947	-93.7764	2.06E-06
0.531053	-90.1604	2.24E-06
0.583158	-86.8831	2.42E-06
0.635263	-83.8864	2.59E-06
0.687368	-81.1261	2.77E-06
0.739474	-78.5676	2.94E-06
0.791579	-76.1834	3.1E-06
0.843684	-73.9513	3.27E-06
0.895789	-71.8529	3.44E-06
0.947895	-69.8732	3.6E-06
1	-67.9995	3.76E-06

Table 5.3: Corrosion of iron versus hydrogen ion concentration under the following conditions: [Fe^{++}]=0.01 M, Alpha of H2=0.5, Alpha of Fe=0.5,T=25˚C,P=1atm in de-areated acid solutions.

[H$^+$]	Ecorr(mV) vs. SHE	iFe(A/cm^2)
0.01	-332.751	6.52E-07
0.062105	-285.857	4.05E-06
0.114211	-270.214	7.44E-06
0.166316	-260.563	1.08E-05
0.218421	-253.565	1.42E-05
0.270526	-248.071	1.76E-05
0.322632	-243.548	2.1E-05
0.374737	-239.704	2.44E-05
0.426842	-236.361	2.78E-05
0.478947	-233.403	3.12E-05
0.531053	-230.752	3.46E-05
0.583158	-228.348	3.8E-05
0.635263	-226.151	4.14E-05
0.687368	-224.126	4.48E-05
0.739474	-222.25	4.82E-05
0.791579	-220.502	5.16E-05
0.843684	-218.865	5.5E-05
0.895789	-217.326	5.84E-05
0.947895	-215.874	6.18E-05
1	-214.5	6.52E-05

5.2.1.2 Znic:

Table 5.4: Corrosion of iron versus hydrogen ion concentration under the following conditions: $[Zn^{++}]=10^{-6}$ M, Alpha of Zn=0.5, Alpha of H_2=0.5,T=25°C,P=1atm in de-areated acid solutions.

$[H^+]$	Ecorr(mV) vs. SHE	i_{Zn}(A/cm^2)
0.01	-742.063	6.03E-08
0.062105	-695.169	3.75E-07
0.114211	-679.526	6.89E-07
0.166316	-669.875	1E-06
0.218421	-662.877	1.32E-06
0.270526	-657.383	1.63E-06
0.322632	-652.86	1.95E-06
0.374737	-649.016	2.26E-06
0.426842	-645.673	2.57E-06
0.478947	-642.715	2.89E-06
0.531053	-640.064	3.2E-06
0.583158	-637.66	3.52E-06
0.635263	-635.463	3.83E-06
0.687368	-633.439	4.15E-06
0.739474	-631.562	4.46E-06
0.791579	-629.814	4.78E-06
0.843684	-628.177	5.09E-06
0.895789	-626.638	5.4E-06
0.947895	-625.186	5.72E-06
1	-623.812	6.03E-06

Table 5.5: Corrosion of iron versus hydrogen ion concentration under the following conditions: $[Zn^{++}]=10^{-6}$ M, Alpha of Zn=0.3, Alpha of H_2=0.5,T=25°C,P=1atm in de-areated acid solutions.

$[H^+]$	Ecorr(mV) vs. SHE	i_{Zn}(A/cm^2)
0.01	-671.04	1.51E-08
0.062105	-607.094	6.74E-08
0.114211	-585.762	1.11E-07
0.166316	-572.602	1.51E-07
0.218421	-563.059	1.89E-07
0.270526	-555.568	2.25E-07
0.322632	-549.4	2.6E-07

0.374737	-544.158	2.93E-07
0.426842	-539.599	3.26E-07
0.478947	-535.566	3.59E-07
0.531053	-531.95	3.9E-07
0.583158	-528.673	4.21E-07
0.635263	-525.676	4.52E-07
0.687368	-522.916	4.82E-07
0.739474	-520.358	5.12E-07
0.791579	-517.973	5.41E-07
0.843684	-515.741	5.7E-07
0.895789	-513.643	5.99E-07
0.947895	-511.663	6.27E-07
1	-509.79	6.55E-07

Table 5.6: Corrosion of iron versus hydrogen ion concentration under the following conditions: [Zn^{++}]=0.01M, Alpha of Zn=0.5, Alpha of H_2=0.5,T=25˚C,P=1atm in de-areated acid solutions.

$[H^+]$	Ecorr(mV) vs. SHE	I_{Zn}(A/cm^2)
0.01	-819.125	3E-07
0.062105	-774.005	1.74E-06
0.114211	-758.361	3.2E-06
0.166316	-748.711	4.66E-06
0.218421	-741.712	6.12E-06
0.270526	-736.219	7.57E-06
0.322632	-731.696	9.03E-06
0.374737	-727.852	1.05E-05
0.426842	-724.509	1.2E-05
0.478947	-721.551	1.34E-05
0.531053	-718.899	1.49E-05
0.583158	-716.496	1.63E-05
0.635263	-714.299	1.78E-05
0.687368	-712.274	1.92E-05
0.739474	-710.398	2.07E-05
0.791579	-708.65	2.22E-05
0.843684	-707.013	2.36E-05
0.895789	-705.474	2.51E-05
0.947895	-704.022	2.65E-05
1	-702.648	2.8E-05

5.2.2 Effect of symmetry factor:

5.2.2.1 Iron:

In this section the effect of increasing symmetry factor of the dissolved metal and its effect on corrosion has been studied. Tables 5.7 and 5.8 show that increasing symmetry factor of metal (Fe and Zn) and shifts corrosion potential to more negative.

Table 5.7: Corrosion of iron versus symmetry factor (alpha) under the following conditions: $[Fe^{++}]=10^{-6}$ M, $[H^{+}]=10^{-2}$ M, alpha of H2=0.5,T=25˚C,P=1atm in de-areated acid solutions.

Alpha	Ecorr(mV) vs. SHE	i_{Fe}(A/cm^2)
0.3	-229.25	8.68E-08
0.5	-332.751	6.52E-07
0.7	-392.672	2.09E-06

5.2.2.2 Znic:

Table 5.8:Corrosion potential and corrosion rate with symmetry factor of Zn at $[Zn^{++}]=10^{-6}$M, $[H^{+}]=10^{-2}$ M,alpha of H2=0.5,T=25˚C,P=1atm inde-areated acid solution.

Alpha	Ecorr(mV) vs. SHE	i_{Zn}(A/cm^2)
0.3	-671.042	1.51E-08
0.5	-742.065	6.03E-08
0.7	-783.183	1.34E-07

5.1.3 Effect of metallic ion concentration:

Increasing metallic ion concentration has no effect on corrosion rate and corrosion potential of Fe,but increases corrosion rate of Zn and shifts corrosion potential to more negative direction.

Table 5.9: Corrosion of iron versus metallic ion concentration under the following conditions: [H$^+$]=10^{-2} M,alpha of H$_2$=0.5, alpha of Fe=0.5,T=25˚C,P=1atm in de-areated acid solutions.

[Fe^{++}]	Ecorr(mV) vs. SHE	$i_{Fe(A/cm^2)}$
0.000001	-332.751	6.52E-07
0.000527	-332.751	6.52E-07
0.001054	-332.751	6.52E-07
0.00158	-332.751	6.52E-07
0.002106	-332.751	6.52E-07
0.002632	-332.751	6.52E-07
0.003159	-332.751	6.52E-07
0.003685	-332.751	6.52E-07
0.004211	-332.751	6.52E-07
0.004737	-332.751	6.52E-07
0.005264	-332.751	6.52E-07
0.00579	-332.751	6.52E-07
0.006316	-332.751	6.52E-07
0.006842	-332.751	6.52E-07
0.007369	-332.751	6.52E-07
0.007895	-332.751	6.52E-07
0.008421	-332.751	6.52E-07
0.008947	-332.751	6.52E-07
0.009474	-332.751	6.52E-07
0.01	-332.751	6.52E-07

Table 5.10: Corrosion potential and corrosion rate with hydrogen ion concentration of Zn at [H$^+$]=10^{-6}M, alpha of H$_2$=0.5, alpha of Zn=0.5,T=25˚C,P=1atm inde-areated acid solution**.**

[Zn^{++}]	Ecorr(mV) vs. SHE	i_{Zn}
0.000001	-742.065	6.03E-08
0.000527	-795.712	1.71E-07
0.001054	-801.636	1.92E-07
0.00158	-805.104	2.06E-07
0.002106	-807.565	2.16E-07
0.002632	-809.474	2.24E-07

0.003159	-811.034	2.31E-07
0.003685	-812.353	2.37E-07
0.004211	-813.496	2.42E-07
0.004737	-814.504	2.47E-07
0.005264	-815.406	2.52E-07
0.00579	-816.221	2.56E-07
0.006316	-816.966	2.59E-07
0.006842	-817.651	2.63E-07
0.007369	-818.285	2.66E-07
0.007895	-818.876	2.69E-07
0.008421	-819.428	2.72E-07
0.008947	-819.947	2.75E-07
0.009474	-819.819	2.84E-07
0.01	-819.125	3E-07

5.3 Galvanic coupling:

Study of free corrosion (i.e. single corrosion) has been performed as aback ground for studding the galvanic corrosion of these metals in de-aerared acid solution. These studies are carried out under the influence of the variables mentioned above and illustrated in the following Tables.

5.3.1 Effect of hydrogen ion concentration:

5.3.1.1 Zn/Cu couple:

Table 5.11: Galvanic corrosion of Zn/Cu couple versus hydrogen ion concentration under the following conditions: $[Zn^{++}]=10^{-6}$M, Alpha of H_2=0.5,alpha of Zn=0.5,f_{Zn}=0.9, f_{Cu}=0.1, T=25°C, P=1atm in de-areated acid solution .

$[H^+]$	Eg(mV)	$i_{Zn(A/cm^2)}$	$i_{H2/Zn(A/cm^2)}$	$i_{H2/Cu(A/cm^2)}$
0.01	-590.635	1.97638E-5	2.846 E-8	1.976095 E-5
0.062105	-543.741	1.2274361.97638E-4	1.7673 E-8	1.227259 E-4
0.114211	-528.098	2.2572341.97638E-4	3.2499 E-8	2.256909 E-4
0.166316	-518.447	3.2870321.97638E-4	4.7326 E-8	3.286559 E-4
0.218421	-511.449	4.316831.97638E-4	6.2153 E-8	4.316209 E-4
0.270526	-505.955	5.346628E-4	7.698 E-8	5.345858 E-4

0.322632	-501.433	6.376426E-4	9.1807 E-8	6375508 E-4
0.374737	-497.588	7.406224E-4	1.06634 E-8	7.405158 E-4
0.426842	-494.245	8.436022E-4	1.21461 E-8	8.434808 E-4
0.478947	-491.288	9.46582E-3	1.36288 E-8	9.464458 E-4
0.531053	-488.636	1.049562E-3	1.51115 E-8	1049411 E-3
0.583158	-486.233	1.152542E-3	1.65942 E-7	1.152376 E-3
0.635263	-484.035	1.25552E-3	1.80769 E-7	1.255341 E-3
0.687368	-482.011	1.358501 E-3	1.95596 E-7	1.358306 E-3
0.739474	-480.135	1.461481 E-3	2.10423 E-7	1.461271 E-3
0.791579	-478.386	1.564461 E-3	2.2525 E-7	1.564236 E-3
0.843684	-476.749	1.667441 E-3	2.40077 E-7	1.667201 E-3
0.895789	-475.211	1.77042 E-3	2.54904 E-7	1.770166 E-3
0.947895	-473.759	1.8734 E-3	2.69731 E-7	1.873131 E-3
1	-472.385	1.97638 E-3	2.84558 E-7	1.976096 E-3

Table 5.12: Galvanic corrosion of Zn/Cu couple versus hydrogen ion concentration under the following conditions: [Zn^{++}]=10^{-6}M, Alpha of H$_2$=0.5,alpha of Zn=0.3,f$_{Zn}$=0.9, f$_{Cu}$=0.1, T=25˚C, P=1atm in de-areated acid solution.

[H+]	Eg(mV)	i_{Zn}(A/cm^2)	$i_{H2/Zn}$(A/cm^2)	$i_{H2/Cu}$(A/cm^2)
0.01	-464.549	1.7E-06	2.4E-10	1.7E-06
0.062105	-400.603	7.56E-06	1.09E-09	7.56E-06
0.114211	-379.271	1.24E-05	1.79E-09	1.24E-05
0.166316	-366.111	1.69E-05	2.44E-09	1.69E-05
0.218421	-356.568	2.12E-05	3.05E-09	2.11E-05
0.270526	-349.077	2.52E-05	3.63E-09	2.52E-05
0.322632	-342.909	2.91E-05	4.19E-09	2.91E-05
0.374737	-337.667	3.29E-05	4.74E-09	3.29E-05
0.426842	-333.108	3.66E-05	5.27E-09	3.66E-05
0.478947	-329.075	4.02E-05	5.79E-09	4.02E-05
0.531053	-325.459	4.38E-05	6.3E-09	4.38E-05
0.583158	-322.182	4.72E-05	6.8E-09	4.72E-05
0.635263	-319.185	5.07E-05	7.3E-09	5.07E-05
0.687368	-316.425	5.4E-05	7.78E-09	5.4E-05
0.739474	-313.866	5.74E-05	8.26E-09	5.74E-05
0.791579	-311.482	6.07E-05	8.73E-09	6.07E-05
0.843684	-309.25	6.39E-05	9.2E-09	6.39E-05
0.895789	-307.152	6.71E-05	9.66E-09	6.71E-05
0.947895	-305.172	7.03E-05	1.01E-08	7.03E-05
1	-303.298	7.34E-05	1.06E-08	7.34E-05

Table 5.13: Galvanic corrosion of Zn/Cu couple versus hydrogen ion concentration under the following conditions:[Zn^{++}]=10^{-6}M, Alpha of H$_2$=0.5,alpha of Zn=0.5,f$_{Zn}$=0.1, f$_{Cu}$=0.9, T=25°C, P=1atm in de-areated acid solution.

[H+]	Eg(mV)	i_{Zn}(A/cm^2)	$i_{H2/Zn}$(A/cm^2)	$i_{H2/Cu}$ (A/cm^2)
0.01	-515.412	4.11E-05	7E-11	4.11E-05
0.062105	-468.518	0.000255	4.5E-10	0.000255
0.114211	-452.875	0.000469	8.3E-10	0.000469
0.166316	-443.224	0.000684	1.22E-09	0.000684
0.218421	-436.226	0.000898	1.6E-09	0.000898
0.270526	-430.733	0.001112	1.98E-09	0.001112
0.322632	-426.21	0.001326	2.36E-09	0.001326
0.374737	-422.365	0.00154	2.74E-09	0.00154
0.426842	-419.022	0.001755	3.12E-09	0.001755
0.478947	-416.065	0.001969	3.5E-09	0.001969
0.531053	-413.413	0.002183	3.88E-09	0.002183
0.583158	-411.01	0.002397	4.26E-09	0.002397
0.635263	-408.812	0.002611	4.64E-09	0.002611
0.687368	-406.788	0.002825	5.02E-09	0.002825
0.739474	-404.912	0.00304	5.4E-09	0.00304
0.791579	-403.163	0.003254	5.78E-09	0.003254
0.843684	-401.526	0.003468	6.17E-09	0.003468
0.895789	-399.988	0.003682	6.55E-09	0.003682
0.947895	-398.536	0.003896	6.93E-09	0.003896
1	-397.162	0.00411	7.31E-09	0.00411

5.2.1.2 Fe/Cu couple:

Table 5.14: Galvanic corrosion of Fe/Cu couple versus hydrogen ion concentration under the following conditions: [Fe^{++}]=10^{-6} M, f$_{Fe=}$0.9, f$_{Cu}$=0.1, Alpha of H$_2$=0.5,alpha of Fe=0.5,T=25°C,P=1atm in de-areated acid solutions.

[H$^+$]	Eg(mV)	i_{Fe} (A/cm^2)	$i_{H2/Fe}$ (A/cm^2)	$i_{H2/Cu}$ (A/cm^2)
0.01	-421.925	3.8215 E-7	3.1266E-7	6.948E-8
0.062105	-386.065	2.69987 E-6	2.20899E-6	4.9089E-7
0.114211	-374.103	5.18319 E-6	4.24079E-6	9.424E-7
0.166316	-366.723	7.75079E-6	6.34156E-6	1.40923E-6
0.218421	-361.371	1.037676E-5	8.49008E-6	1.88668E-6

0.270526	-357.17	1.304775E-5	1.067543E-5	2.37232E-6
0.322632	-353.711	1.575552E-5	1.289088E-5	2.86464E-6
0.374737	-350.772	1.849447E-5	1.513184E-5	3.36263E-6
0.426842	-348.215	2.126053E-5	1.739497E-5	3.86555E-6
0.478947	-345.954	2.405057E-5	1.967774E-5	4.37283E-6
0.531053	-343.926	2.686217E-5	2.197814E-5	4.88403E-6
0.583158	-342.088	2.969333E-5	2.429454E-5	5.39879E-6
0.635263	-340.407	3.254243E-5	2.662563E-5	5.91681E-6
0.687368	-338.859	3.5.4081E-5	2.897026E-5	6.43784E-6
0.739474	-337.425	3.828915E-5	3.132749E-5	6.96166E-6
0.791579	-336.088	4.118458E-5	3.369647E-5	7.48811E-6
0.843684	-334.836	4.40935E-5	3.60765E-5	8.017E-6
0.895789	-333.659	4.701514E-5	3.846694E-5	8.54821E-6
0.947895	-332.549	4.994881E-5	4.086721E-5	9.0816E-6
1	-331.498	5.289389E-5	4.327682E-5	9.61707E-6

Table 5.15: Galvanic corrosion of Fe/Cu couple versus hydrogen ion concentration under the following conditions: $[Fe^{++}]=10^{-6}$ M, $f_{Fe=}0.9$, $f_{Cu}=0.1$, Alpha of $H_2=0.5$,alpha of Fe=0.3,T=25˚C,P=1atm in de-areated acid solutions.

$[H^+]$	Eg(mV)	i_{Fe} (A/cm^2)	$i_{H2/Fe}$ (A/cm^2)	$i_{H2/Cu}$ (A/cm^2)
0.01	-224.566	8.72E-08	7.13E-08	1.59E-08
0.062105	-160.62	3.88E-07	3.18E-07	7.06E-08
0.114211	-139.288	6.4E-07	5.23E-07	1.16E-07
0.166316	-126.128	8.7E-07	7.12E-07	1.58E-07
0.218421	-116.585	1.09E-06	8.89E-07	1.98E-07
0.270526	-109.093	1.29E-06	1.06E-06	2.35E-07
0.322632	-102.926	1.5E-06	1.22E-06	2.72E-07
0.374737	-97.6836	1.69E-06	1.38E-06	3.07E-07
0.426842	-93.125	1.88E-06	1.54E-06	3.42E-07
0.478947	-89.0921	2.07E-06	1.69E-06	3.76E-07
0.531053	-85.476	2.25E-06	1.84E-06	4.09E-07
0.583158	-82.1987	2.43E-06	1.99E-06	4.41E-07
0.635263	-79.2021	2.6E-06	2.13E-06	4.73E-07
0.687368	-76.4418	2.78E-06	2.27E-06	5.05E-07
0.739474	-73.8833	2.95E-06	2.41E-06	5.36E-07
0.791579	-71.4991	3.12E-06	2.55E-06	5.67E-07
0.843684	-69.2669	3.28E-06	2.69E-06	5.97E-07
0.895789	-67.1685	3.45E-06	2.82E-06	6.27E-07
0.947895	-65.1888	3.61E-06	2.96E-06	6.57E-07
1	-63.3151	3.77E-06	3.09E-06	6.86E-07

Table 5.16: Galvanic corrosion of Fe/Cu couple versus hydrogen ion concentration under the following conditions: $[Fe^{++}]=10^{-6}$ M, f_{Fe}=0.1, f_{Cu}=0.9, Alpha of H_2=0.5,alpha of Fe=0.5,T=25˚C,P=1atm in de-areated acid solutions.

$[H^+]$	Eg(mV)	i_{Fe} (A/cm^2)	$i_{H2/Fe}$ (A/cm^2)	$i_{H2/Cu}$ (A/cm^2)
0.01	-282.346	4.64E-07	2.44E-08	4.4E-07
0.062105	-235.452	2.88E-06	1.52E-07	2.73E-06
0.114211	-219.809	5.3E-06	2.79E-07	5.02E-06
0.166316	-210.158	7.72E-06	4.06E-07	7.31E-06
0.218421	-203.16	1.01E-05	5.33E-07	9.6E-06
0.270526	-197.666	1.26E-05	6.61E-07	1.19E-05
0.322632	-193.143	1.5E-05	7.88E-07	1.42E-05
0.374737	-189.299	1.74E-05	9.15E-07	1.65E-05
0.426842	-185.956	1.98E-05	1.04E-06	1.88E-05
0.478947	-182.999	2.22E-05	1.17E-06	2.1E-05
0.531053	-180.347	2.46E-05	1.3E-06	2.33E-05
0.583158	-177.944	2.71E-05	1.42E-06	2.56E-05
0.635263	-175.746	2.95E-05	1.55E-06	2.79E-05
0.687368	-173.722	3.19E-05	1.68E-06	3.02E-05
0.739474	-171.846	3.43E-05	1.81E-06	3.25E-05
0.791579	-170.097	3.67E-05	1.93E-06	3.48E-05
0.843684	-168.46	3.91E-05	2.06E-06	3.71E-05
0.895789	-166.921	4.16E-05	2.19E-06	3.94E-05
0.947895	-165.47	4.4E-05	2.31E-06	4.17E-05
1	-164.096	4.64E-05	2.44E-06	4.39E-05

5.2.1.3 Fe/Zn couple:

Table 5.17: Galvanic corrosion of Fe/Zn couple versus hydrogen ion concentration 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=0.5,alpha of Fe=0.5,T=25˚C,P=1atm in de-areated acid solutions.

$[H^+]$	Eg(mV)	i_{Fe} (A/cm^2)	$i_{H2/Fe}$ (A/cm^2)	i_{Zn} (A/cm^2)	$i_{H2/Zn}$ (A/cm^2)
0.01	-527.277	0.0003	25.89549	25.89528	0.00009
0.062105	-480.383	0.00187	160.8246	160.8233	0.00057

0.114211	-464.74	0.00343	295.7537	295.7514	0.00105
0.166316	-455.089	0.005	430.6829	430.6794	0.00153
0.218421	-448.091	0.00657	565.612	565.6074	0.00201
0.270526	-442.597	0.00813	700.5411	700.5355	0.00249
0.322632	-438.074	0.0097	835.4702	835.4635	0.00297
0.374737	-434.23	0.01127	970.3994	970.3916	0.00345
0.426842	-430.887	0.01283	1105.329	1105.32	0.00393
0.478947	-427.93	0.0144	1240.258	1240.248	0.00441
0.531053	-425.278	0.01597	1375.187	1375.176	0.00489
0.583158	-422.874	0.01753	1510.116	1510.104	0.00537
0.635263	-420.677	0.0191	1645.045	1645.032	0.00585
0.687368	-418.653	0.02067	1779.974	1779.96	0.00633
0.739474	-416.776	0.02223	1914.903	1914.888	0.00681
0.791579	-415.028	0.0238	2049.832	2049.816	0.00729
0.843684	-413.391	0.02537	2184.762	2184.744	0.00777
0.895789	-411.852	0.02693	2319.691	2319.672	0.00825
0.947895	-410.401	0.0285	2454.62	2454.6	0.00873
1	-409.026	0.03007	2589.549	2589.528	0.00921

Table 5.18: Galvanic corrosion of Fe/Zn couple versus hydrogen ion concentration 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=0.7,alpha of Fe=0.3,T=25°C,P=1atm in de-areated acid solutions.

$[H^+]$	Eg(mV)	i_{Fe} (A/cm^2)	$i_{H2/Fe}$ (A/cm^2)	i_{Zn} (A/cm^2)	$i_{H2/Zn}$ (A/cm^2)
0.01	-613.615	1E-11	0.000139	0.000139	4.9E-10
0.062105	-576.593	8E-11	0.001047	0.001047	3.72E-09
0.114211	-564.243	1.6E-10	0.002053	0.002053	7.3E-09
0.166316	-556.624	2.5E-10	0.00311	0.00311	1.11E-08
0.218421	-551.099	3.3E-10	0.004203	0.004203	1.49E-08
0.270526	-546.762	4.2E-10	0.005325	0.005325	1.89E-08
0.322632	-543.191	5.1E-10	0.006469	0.006469	2.3E-08
0.374737	-540.156	6.1E-10	0.007633	0.007633	2.71E-08
0.426842	-537.517	7E-10	0.008814	0.008814	3.13E-08
0.478947	-535.182	8E-10	0.010011	0.010011	3.56E-08
0.531053	-533.089	8.9E-10	0.011221	0.011221	3.99E-08
0.583158	-531.192	9.9E-10	0.012444	0.012444	4.43E-08

0.635263	-529.457	1.09E-09	0.013679	0.013679	4.86E-08
0.687368	-527.859	1.19E-09	0.014924	0.014924	5.31E-08
0.739474	-526.377	1.29E-09	0.016179	0.016179	5.75E-08
0.791579	-524.997	1.39E-09	0.017444	0.017444	6.2E-08
0.843684	-523.705	1.49E-09	0.018717	0.018718	6.66E-08
0.895789	-522.49	1.59E-09	0.019999	0.019999	7.11E-08
0.947895	-521.344	1.69E-09	0.021289	0.021289	7.57E-08
1	-520.259	1.79E-09	0.022586	0.022586	8.03E-08

Table 5.19: Galvanic corrosion of Fe/Zn couple versus hydrogen ion concentration 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=0.5,alpha of Fe=0.5,T=25°C,P=1atm in de-areated acid solutions.

$[H^+]$	Eg(mV)	i_{Fe} (A/cm²)	$i_{H2/Fe}$ (A/cm²)	i_{Zn} (A/cm²)	$il_{H2/Zn}$ (A/cm²)
0.01	-602.5	0	1.24E-05	1.25E-05	3.58E-09
0.062105	-555.606	1E-11	7.73E-05	7.73E-05	2.23E-08
0.114211	-539.963	2E-11	0.000142	0.000142	4.09E-08
0.166316	-530.312	3E-11	0.000207	0.000207	5.96E-08
0.218421	-523.314	4E-11	0.000272	0.000272	7.83E-08
0.270526	-517.82	5E-11	0.000337	0.000337	9.7E-08
0.322632	-513.297	6E-11	0.000402	0.000402	1.16E-07
0.374737	-509.453	7E-11	0.000466	0.000467	1.34E-07
0.426842	-506.11	8E-11	0.000531	0.000531	1.53E-07
0.478947	-503.152	9E-11	0.000596	0.000596	1.72E-07
0.531053	-500.501	9E-11	0.000661	0.000661	1.9E-07
0.583158	-498.097	1E-10	0.000726	0.000726	2.09E-07
0.635263	-495.9	1.1E-10	0.000791	0.000791	2.28E-07
0.687368	-493.875	1.2E-10	0.000856	0.000856	2.46E-07
0.739474	-491.999	1.3E-10	0.00092	0.000921	2.65E-07
0.791579	-490.251	1.4E-10	0.000985	0.000986	2.84E-07
0.843684	-488.614	1.5E-10	0.00105	0.00105	3.02E-07
0.895789	-487.075	1.6E-10	0.001115	0.001115	3.21E-07
0.947895	-485.623	1.7E-10	0.00118	0.00118	3.4E-07
1	-484.249	1.8E-10	0.001245	0.001245	3.58E-07

5.3.2 Effect of symmetry factor:

5.3.2.1 Fe/Cu couple:

Table 5.20: Galvanic corrosion of Fe/Cu couple versus symmetry factor under the following conditions: $[Fe^{++}]=10^{-6}$ M, $[H^{+}]=0.01$M, alpha of $H_2=0.5$, $f_{Fe}=0.1$, $f_{Cu}=0.9$,T=25˚C, P=1atm in de-areated acid solutions.

Alpha	Eg(mV)	i_{Fe} (A/cm^2)	$i_{H2/Fe}$ (A/cm^2)	$i_{H2/Cu}$ (A/cm^2)
0.3	-224.566	8.72E-08	7.13E-08	1.59E-08
0.5	-329.316	6.7E-07	5.48E-07	1.22E-07
0.7	-389.96	2.18E-06	1.79E-06	3.97E-07

5.3.2.2 Zn/Cu couple:

Table 5.21: Galvanic corrosion of Zn/Cu couple versus symmetry factor under the following conditions: $[Zn^{++}]=10^{-6}$ M, $[H^{+}]=0.01$M, $f_{Zn}=0.9$, $f_{Cu}=0.1$,alpha of $H_2=0.5$,T=25˚C, P=1atm in de-areated acid solutions.

Alpha	Eg(mV)	i_{Zn}(A/cm^2)	$i_{H2/Zn}$(A/cm^2)	$i_{H2/Cu}$(A/cm^2)
0.3	-464.549	1.7E-06	2.4E-10	1.7E-06
0.5	-590.637	1.98E-05	2.85E-09	1.98E-05
0.7	-663.634	8.19E-05	1.18E-08	8.19E-05

5.3.2.3 Fe/Zn coupled:

Table 5.22: Galvanic corrosion of Fe/Zn couple versus symmetry factor under the following conditions: $[Fe^{++}]= [Zn^{++}]=10^{-6}$ M, $[H^{+}]=0.01$M, alpha of $H_2=0.5$,alpha of Fe=0.5,$f_{Zn}=0.9$, $f_{Cu}=0.1$,T=25˚C, P=1atm in de-areated acid solutions.

Alpha	Eg(mV)	i_{Fe}(A/cm^2)	i_{Zn}(A/cm^2)	$i_{H2/Fe}$(A/cm^2)	$i_{H2/Zn}$(A/cm^2)
0.3	-378.191	2.41E-09	1.42E-06	1.42E-06	1E-11
0.5	-527.278	3E-10	2.59E-05	2.59E-05	9E-11
0.7	-613.615	1E-11	0.000139	0.000139	4.9E-10

Table 5.23: Galvanic corrosion of Fe/Zn couple versus symmetry factor under the following conditions: [Fe^{++}]= [Zn^{++}]=0.01M, [H$^+$]=0.01M, alpha of H_2=0.5,alpha of Fe =0.5,f_{Zn}=0.9, f_{Cu}=0.1,T=25°C, P=1atm in de-areated acid solutions.

Alpha	Eg(mV)	i_{Fe}(A/cm^2)	i_{Zn}(A/cm^2)	$i_{H2/Fe}$(A/cm^2)	$i_{H2/Zn}$(A/cm^2)
0.3	-528.653	4.5E-10	2.66E-05	2.66E-05	9E-11
0.5	-606.112	1E-11	0.00012	0.00012	4.3E-10
0.7	-650.957	0	0.000288	0.000288	1.02E-09

5.3.3 Effect of area fraction:

5.3.3.1 Fe/Cu couple:

Table 5.24: Galvanic corrosion of Fe/Cu couple versus area fraction under the following conditions: [Fe^{++}]=10^{-6} M, [H$^+$]=0.01M, alpha of Fe=0.5, alpha of H_2=0.5,T=25°C, P=1atm in de-areated acid solution.

f_{Fe}	f_{Cu}	Eg(mV)	i_{Fe} (A/cm^2)	$i_{H2/Fe}$ (A/cm^2)	$i_{H2/Cu}$ (A/cm^2)
0.9	0.1	-329.315	6.7032 E-7	5.4845 E-7	1.2188E-7
0.8	0.2	-325.809	6.8301 E-7	4.5534 E-7	2.2767 E-7
0.7	0.3	-322.153	6.8908 E-7	3.7104 E-7	3.1804 E-7
0.6	0.4	-318.246	6.8772 E-7	2.9474 E-7	3.9298 E-7
0.5	0.5	-313.944	6.7763 E-7	2.2588 E-7	4.5175 E-7
0.4	0.6	-309.019	6.5671 E-7	1.6418 E-7	4.9253 E-7
0.3	0.7	-303.056	6.2127 E-7	1.0964 E-7	5.1164 E-7
0.2	0.8	-295.137	5.6381 E-7	0.6265 E-8	5.0117 E-7
0.1	0.9	-282.346	4.6392 E-7	0.2442 E-8	4.395 E-7

Table 5.25: Galvanic corrosion of Fe/Cu couple versus area fraction under the following conditions: [Fe^{++}]=10^{-6} M, [H^{+}]=0.01M, alpha of Fe=0.3, alpha of H_2=0.5,T=25˚C, P=1atm in de-areated acid solution.

f_{Fe}	f_{Cu}	Eg(mV)	i_{Fe} (A/cm^2)	$i_{H2/Fe}$ (A/cm^2)	$i_{H2/Cu}$ (A/cm^2)
0.9	0.1	-208.209	1.28E-07	1.05E-07	2.32E-08
0.8	0.2	-204.164	1.25E-07	8.32E-08	4.16E-08
0.7	0.3	-199.946	1.21E-07	6.49E-08	5.56E-08
0.6	0.4	-195.437	1.15E-07	4.92E-08	6.56E-08
0.5	0.5	-190.473	1.07E-07	3.58E-08	7.16E-08
0.4	0.6	-184.791	9.82E-08	2.45E-08	7.36E-08
0.3	0.7	-177.911	8.65E-08	1.53E-08	7.12E-08
0.2	0.8	-168.773	7.14E-08	7.93E-09	6.34E-08
0.1	0.9	-154.014	5.04E-08	2.65E-09	4.77E-08

5.3.3.2 Zn/Cu couple:

Table 5.26: Galvanic corrosion potential and galvanic corrosion rate with area fraction of Zn/Cu couple at [Zn^{++}]=10^{-6} M, [H^{+}]=0.01M, alpha of H_2=0.5,alpha of Zn=0.5,T=25˚C, P=1atm in de-areated acid solution.

f_{Fe}	f_{Zn}	Eg(mV)	i_{Zn}(A/cm^2)	$i_{H2/Zn}$(A/cm^2)	$i_{H2/Cu}$(A/cm^2)
0.9	0.1	-590.635	1.98E-05	2.85E-09	1.98E-05
0.8	0.2	-576.755	3.02E-05	1.93E-09	3.02E-05
0.7	0.3	-567.528	3.78E-05	1.41E-09	3.78E-05
0.6	0.4	-559.965	4.35E-05	1.04E-09	4.35E-05
0.5	0.5	-553.024	4.75E-05	7.6E-10	4.75E-05
0.4	0.6	-546.083	4.98E-05	5.3E-10	4.98E-05
0.3	0.7	-538.52	5.01E-05	3.4E-10	5.01E-05
0.2	0.8	-529.293	4.79E-05	1.9E-10	4.79E-05
0.1	0.9	-515.411	4.11E-05	7E-11	4.11E-05

Table 5.27: Galvanic corrosion potential and galvanic corrosion rate with area fraction of Zn/Cu couple at $[Zn^{++}]=10^{-6}$ M, $[H^{+}]=0.01$M, alpha of $H_2=0.5$,alpha of Zn=0.3,T=25˚C, P=1atm in de-areated acid solution.

f_{Fe}	f_{Zn}	Eg(mV)	$i_{Zn(\ A/cm^2)}$	$i_{H2/Zn(\ A/cm^2)}$	$i_{H2/Cu(\ A/cm^2)}$
0.9	0.1	-464.548	1.7E-06	2.4E-10	1.7E-06
0.8	0.2	-445.62	2.35E-06	1.5E-10	2.35E-06
0.7	0.3	-433.038	2.76E-06	1E-10	2.76E-06
0.6	0.4	-422.725	3.01E-06	7E-11	3.01E-06
0.5	0.5	-413.26	3.12E-06	5E-11	3.12E-06
0.4	0.6	-403.795	3.12E-06	3E-11	3.12E-06
0.3	0.7	-393.481	2.98E-06	2E-11	2.98E-06
0.2	0.8	-380.899	2.66E-06	1E-11	2.66E-06
0.1	0.9	-361.97	2.07E-06	0	2.07E-06

5.3.3.3 Fe/Zn couple:

Table 5.28: Galvanic corrosion potential and galvanic corrosion rate with area fraction of Fe/Zn couple at $[Zn^{++}]=10^{-6}$ M, $[H^{+}]=0.01$M, alpha of $H_2=0.5$,alpha of Zn=0.5, alpha of Fe=0.5,T=25˚C, P=1atm in de-areated acid solution.

f_{Fe}	f_{Zn}	Eg(mV)	$i_{Fe(\ A/cm^2)}$	$i_{H2/Fe(\ A/cm^2)}$	$i_{Zn\ (\ A/cm^2)}$	$i_{H2/Zn\ (\ A/cm^2)}$
0.9	0.1	-527.277	3E-10	2.59E-05	2.59E-05	9E-11
0.8	0.2	-541.159	1.6E-10	3.02E-05	3.02E-05	2.4E-10
0.7	0.3	-550.385	1E-10	3.16E-05	3.16E-05	4.3E-10
0.6	0.4	-557.949	6E-11	3.14E-05	3.14E-05	6.7E-10
0.5	0.5	-564.89	4E-11	2.99E-05	2.99E-05	9.6E-10
0.4	0.6	-571.83	2E-11	2.74E-05	2.74E-05	1.32E-09
0.3	0.7	-579.393	1E-11	2.38E-05	2.38E-05	1.78E-09
0.2	0.8	-588.619	1E-11	1.9E-05	1.9E-05	2.43E-09
0.1	0.9	-602.498	0	1.24E-05	1.25E-05	3.59E-09

Table 5.29: Galvanic corrosion potential and galvanic corrosion rate with area fraction of Fe/Zn couple at $[Zn^{++}]=10^{-6}$ M, $[H^{+}]=0.01$M, alpha of $H_2=0.5$,alpha of Zn=0.7, alpha of Fe=0.3,T=25˚C, P=1atm in de-areated acid solution.

f_{Fe}	f_{Zn}	Eg(mV)	i_{Fe}(A/cm^2)	$i_{H2/Fe}$(A/cm^2)	i_{Zn} (A/cm^2)	$i_{H2/Zn}$ (A/cm^2)
0.9	0.1	-510.414	3.07E-09	0.038632	0.038632	1.37E-07
0.8	0.2	-519.09	1.7E-09	0.048143	0.048143	3.85E-07
0.7	0.3	-524.857	1.09E-09	0.052732	0.052733	7.23E-07
0.6	0.4	-529.584	7.2E-10	0.054335	0.054336	1.16E-06
0.5	0.5	-533.922	4.7E-10	0.053613	0.053614	1.72E-06
0.4	0.6	-538.26	3E-10	0.050784	0.050786	2.44E-06
0.3	0.7	-542.987	1.7E-10	0.045786	0.045789	3.42E-06
0.2	0.8	-548.753	8E-11	0.038209	0.038214	4.89E-06
0.1	0.9	-557.428	3E-11	0.026782	0.02679	7.71E-06

5.3.4 Effect of metallic ion concentration:

5.3.4.1 Fe/Cu couple:

Table 5.30: Corrosion of Fe/Cu couple versus metallic ion concentration under the following conditions: $[H^{+}]=10^{-2}$ M,alpha of $H_2=0.5$,alpha of Fe=0.5, $f_{Fe}=0.9$, $f_{Cu}=0.1$,T=25˚C,P=1atm in de-areated acid solutions.

$[Fe^{++}]$	Eg(mV)	i_{Fe} (A/cm^2)	$i_{H2/Fe}$ (A/cm^2)	$i_{H2/Cu}$ (A/cm^2)
0.000001	-329.316	6.7E-07	5.48E-07	1.22E-07
0.000527	-329.316	6.7E-07	5.48E-07	1.22E-07
0.001054	-329.316	6.7E-07	5.48E-07	1.22E-07
0.00158	-329.316	6.7E-07	5.48E-07	1.22E-07
0.002106	-329.316	6.7E-07	5.48E-07	1.22E-07
0.002632	-329.316	6.7E-07	5.48E-07	1.22E-07
0.003159	-329.316	6.7E-07	5.48E-07	1.22E-07
0.003685	-329.316	6.7E-07	5.48E-07	1.22E-07
0.004211	-329.316	6.7E-07	5.48E-07	1.22E-07
0.004737	-329.316	6.7E-07	5.48E-07	1.22E-07
0.005264	-329.316	6.7E-07	5.48E-07	1.22E-07
0.00579	-329.316	6.7E-07	5.48E-07	1.22E-07
0.006316	-329.316	6.7E-07	5.48E-07	1.22E-07
0.006842	-329.316	6.7E-07	5.48E-07	1.22E-07
0.007369	-329.316	6.7E-07	5.48E-07	1.22E-07

0.007895	-329.316	6.7E-07	5.48E-07	1.22E-07
0.008421	-329.316	6.7E-07	5.48E-07	1.22E-07
0.008947	-329.316	6.7E-07	5.48E-07	1.22E-07
0.009474	-329.316	6.7E-07	5.48E-07	1.22E-07
0.01	-329.316	6.7E-07	5.48E-07	1.22E-07

5.3.4.2 Zn/Cu couple:

Table 5.31: Corrosion of Zn/Cu couple versus metallic ion concentration under the following conditions: $[H^+]=10^{-2}$ M,alpha of H_2=0.5,alpha of Zn=0.5, f_{Zn}=0.9, f_{Cu}=0.1,T=25°C,P=1atm in de-areated acid solutions.

$[Zn^{++}]$	Eg(mV)	i_{Zn} (A/cm^2)	$i_{H2/Zn}$ (A/cm^2)	$i_{H2/Cu}$ (A/cm^2)
0.000001	-590.637	1.98E-05	2.85E-09	1.98E-05
0.000527	-644.284	5.62E-05	8.09E-09	5.62E-05
0.001054	-650.208	6.3E-05	9.08E-09	6.3E-05
0.00158	-653.676	6.74E-05	9.71E-09	6.74E-05
0.002106	-656.137	7.08E-05	1.02E-08	7.07E-05
0.002632	-658.046	7.34E-05	1.06E-08	7.34E-05
0.003159	-659.606	7.57E-05	1.09E-08	7.57E-05
0.003685	-660.925	7.77E-05	1.12E-08	7.77E-05
0.004211	-662.068	7.94E-05	1.14E-08	7.94E-05
0.004737	-663.076	8.1E-05	1.17E-08	8.1E-05
0.005264	-663.977	8.24E-05	1.19E-08	8.24E-05
0.00579	-664.793	8.37E-05	1.21E-08	8.37E-05
0.006316	-665.538	8.5E-05	1.22E-08	8.5E-05
0.006842	-666.223	8.61E-05	1.24E-08	8.61E-05
0.007369	-666.857	8.72E-05	1.26E-08	8.72E-05
0.007895	-667.447	8.82E-05	1.27E-08	8.82E-05
0.008421	-668	8.91E-05	1.28E-08	8.91E-05
0.008947	-668.519	9E-05	1.3E-08	9E-05
0.009474	-669.008	9.09E-05	1.31E-08	9.09E-05
0.01	-669.471	9.17E-05	1.32E-08	9.17E-05
0.000001	-590.637	1.98E-05	2.85E-09	1.98E-05

5.3.4.2 Fe/Zn couple:

Table 5.32: Corrosion of Fe/Zn couple versus metallic ion concentration under the following conditions: $[H^+]=10^{-2}$ M,alpha of H_2=0.5, alpha of Fe=0.5,alpha of Zn=0.5, f_{Zn}=0.9, f_{Cu}=0.1,T=25˚C,P=1atm in de-areated acid solutions.

$[Fe^{++}]=[Zn^{++}]$	Eg(mV)	i_{Fe} (A/cm^2)	$i_{H2/Fe}$ (A/cm^2)	i_{Zn} (μ A/cm^2)	$i_{H2/Zn}$ (A/cm^2)
0.000001	-527.278	3E-10	2.59E-05	2.59E-05	9E-11
0.000527	-580.925	4E-11	7.36E-05	7.36E-05	2.6E-10
0.001054	-586.85	3E-11	8.26E-05	8.26E-05	2.9E-10
0.00158	-590.318	3E-11	8.84E-05	8.84E-05	3.1E-10
0.002106	-592.779	2E-11	9.27E-05	9.27E-05	3.3E-10
0.002632	-594.688	2E-11	9.62E-05	9.62E-05	3.4E-10
0.003159	-596.248	2E-11	9.92E-05	9.92E-05	3.5E-10
0.003685	-597.567	2E-11	0.000102	0.000102	3.6E-10
0.004211	-598.709	2E-11	0.000104	0.000104	3.7E-10
0.004737	-599.717	2E-11	0.000106	0.000106	3.8E-10
0.005264	-600.619	2E-11	0.000108	0.000108	3.8E-10
0.00579	-601.435	2E-11	0.00011	0.00011	3.9E-10
0.006316	-602.179	2E-11	0.000111	0.000111	4E-10
0.006842	-602.864	2E-11	0.000113	0.000113	4E-10
0.007369	-603.498	2E-11	0.000114	0.000114	4.1E-10
0.007895	-604.089	2E-11	0.000116	0.000116	4.1E-10
0.008421	-604.641	1E-11	0.000117	0.000117	4.2E-10
0.008947	-605.16	1E-11	0.000118	0.000118	4.2E-10
0.009474	-605.649	1E-11	0.000119	0.000119	4.2E-10
0.01	-606.112	1E-11	0.00012	0.00012	4.3E-10

CHAPTER SIX

DISCUSSION, CONCULSSIONAND FTURE WORK

DISCUSSION:

6.1 Introduction

Chapter five introduced the analysis of results. This is because of the number of variables involved, i.e., metallic ion concentration, hydrogen ion concentration, symmetry factor (alpha), area fraction and their interactions. The influence of these variables on the analysis needs to be interpreted.

In discussing the results, the following manner is followed: section 6.2 deals with free corrosion and section 6.3 deals with galvanic coupling and the effect of metallic ion concentration, hydrogen ion concentration, symmetry factor (alpha) and area fraction.

6.2: Free corrosion:

Investigation of mechanisms involved in corrosion processes and the development on the basis of these mechanisms of new effective methods for the protection of metals against corrosion is of paramount importance to the national economy of any country.

In view of the complex problems facing modern technology it is not possible to wage a successful battle against corrosion simply by an experimental choice of new stable materials and methods of protection. Only by a thorough study of the basic principles involved in corrosion processes generalization of the many complex cases of corrosion can be explained, predictions of the corrosion behavior of the metallic system subjected to actual service conditions be made and effective methods for protection against corrosion deterioration developed.

6.2.1: Effect of hydrogen ion concentration:

Since the equilibrium potential of the metal electrode (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) .

In chapter two, it was mentioned that pH (or hydrogen ion concentration) as a factor plays an important role in increasing the corrosion rate of metals. This is clear in results from chapter five in Tables 5.1 to 5.6 are plotted in Fig. 6.1 to Fig. 6.6, in which the current density increases and corrosion potential shifts to less negative by altering the hydrogen ion concentration from (0.01 - 1 M) for all values of symmetry factor (alpha) and metallic ion concentration. This fact is shown in these figures, which is attributed to the fact that increasing hydrogen ion concentration (H^+) at the interface between metal and solution leads to increased rate of reaction for metal dissolution:-

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

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

Therefore the higher the concentration of hydrogen ion is the higher the corrosion rate of metal.

It is to be noticed from the above figures, (E_{corr} vs. hydrogen ion concentration) that as hydrogen ion concentration increases corrosion potential (E_{corr}) decreases (become less negative).This behavior can be understood by noting Figure 6.7 From this figure initially the corrosion current (i_{corr}) is (i_{corr1}) and corrosion potential (E_{corr}) is (E_{corr1}) as the dissolution of metal increases the cathodic (hydrogen reduction) and anodic (metal dissolution) currents increases to (i_{corr2}) leading to shift the interaction potential between the two curves to less negative (E_{corr2}) for all values of symmetry factor (alpha) and metallic ion concentration .This is in agreement with previous experimental studies (12 , 22, 65 and 66) .

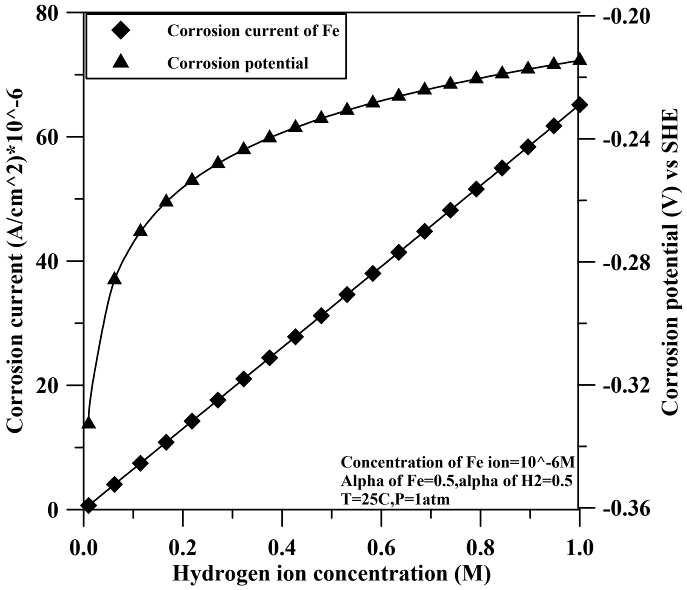

Figure 6.1: Free corrosion of Fe as function of hydrogen ion concentration in de-aerated acid solutions.

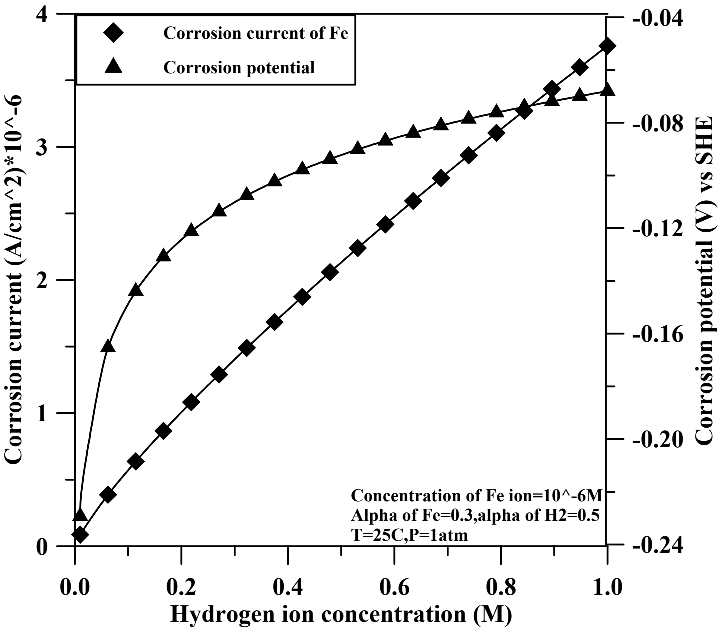

Figure 6.2: Free corrosion of Fe as function of hydrogen ion concentration in de-aerated acid solutions.

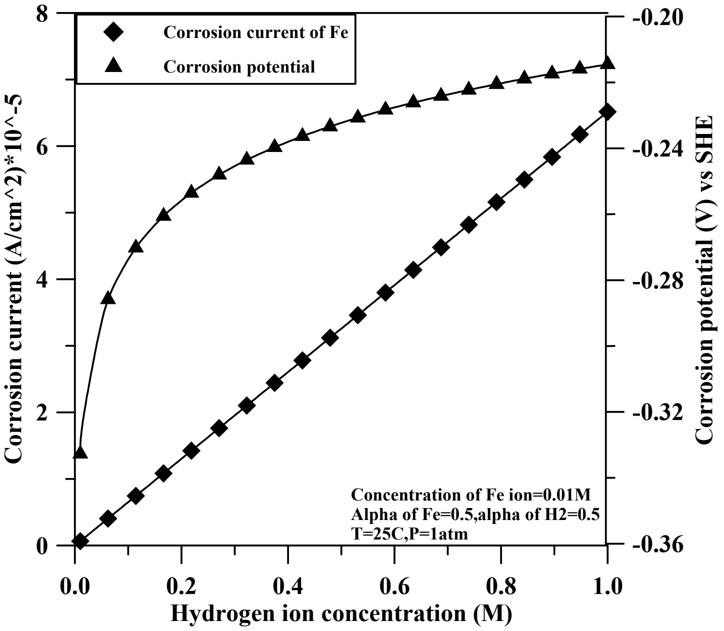

Figure 6.3: Free corrosion of Fe as function of hydrogen ion concentration in de-aerated acid solutions.

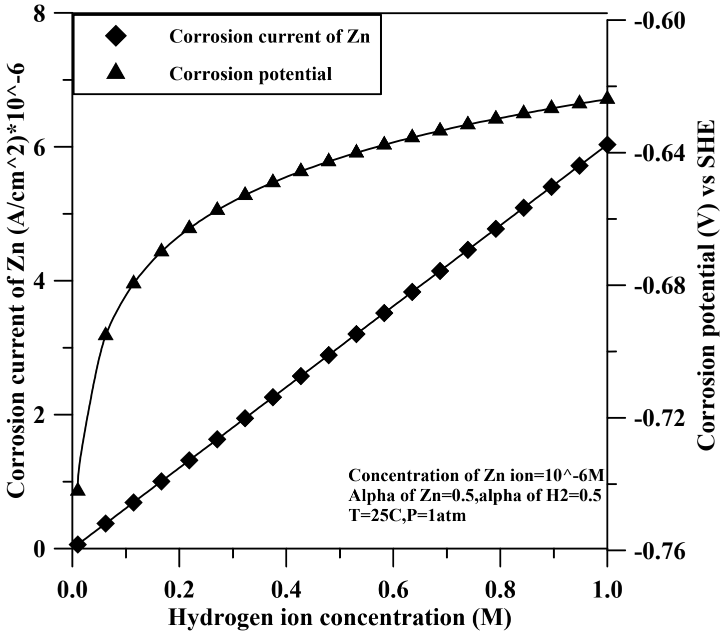

Figure 6.4: Free corrosion of Zn as function of hydrogen ion concentration in de-aerated acid solutions.

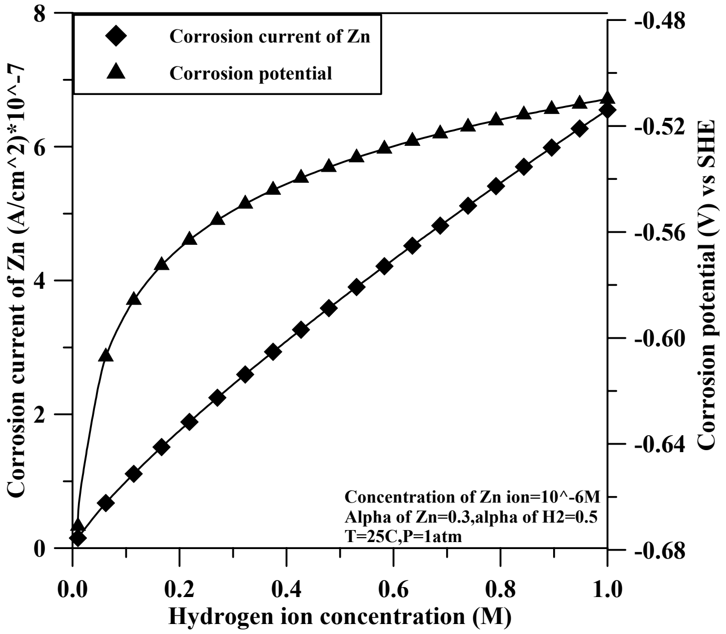

Figure 6.5: Free corrosion of Zn as function of hydrogen ion concentration in de-aerated acid solutions.

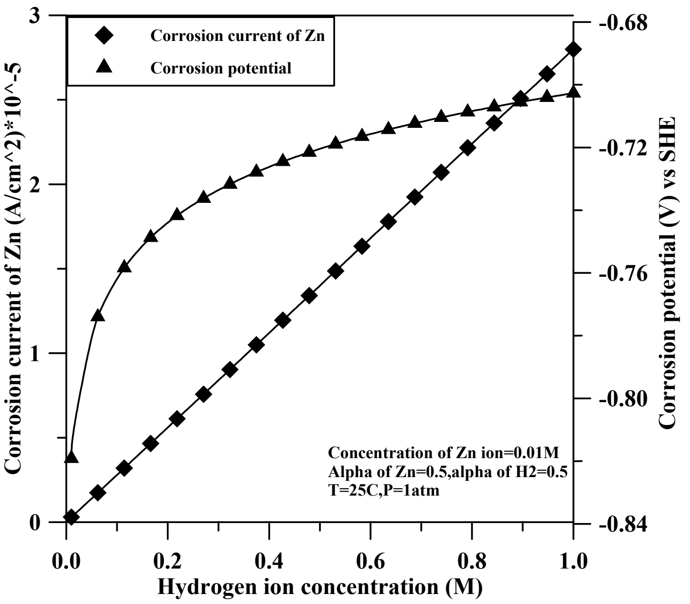

Figure 6.6: Free corrosion of Zn as function of hydrogen ion concentration in de-aerated acid solutions.

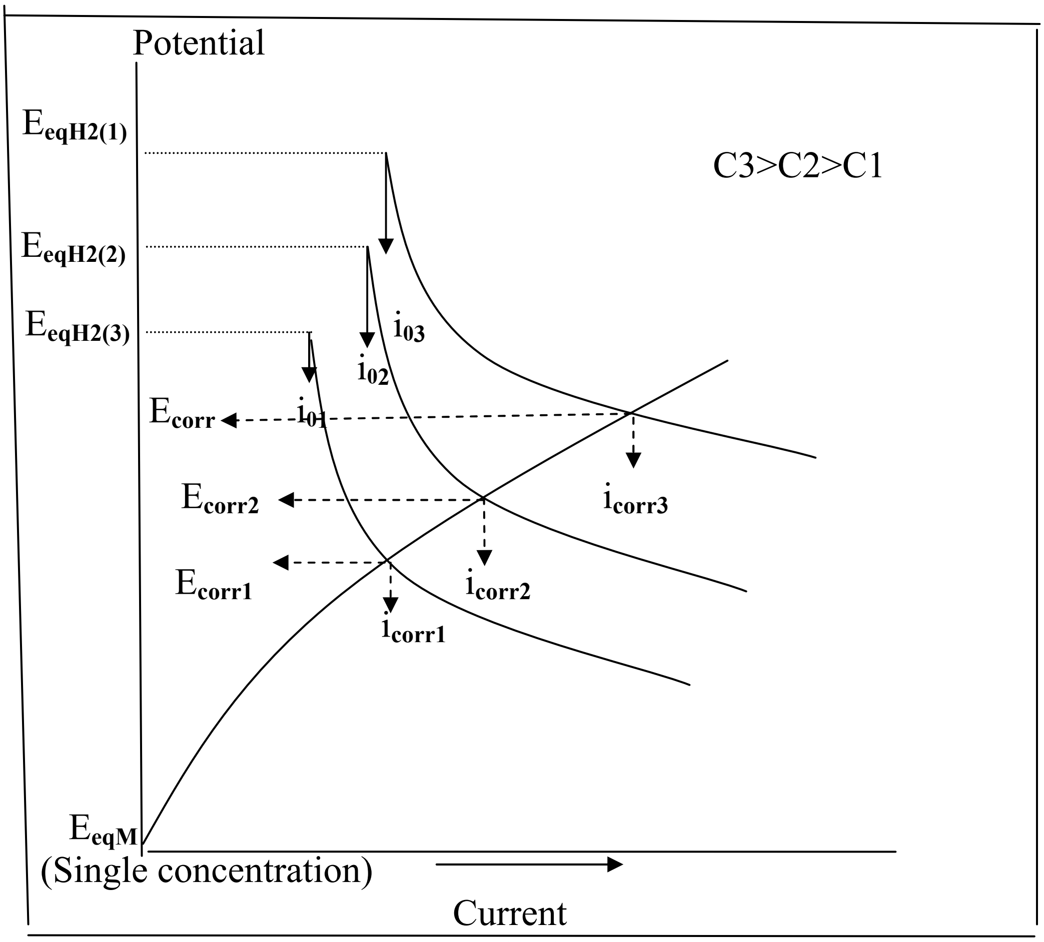

Figure 6.7: Effect of increasing of hydrogen ion concentration on corrosion rate and corrosion potential. (22)[Schematic]

6.2.2 Effect of symmetry factor (alpha):

From Figs. 6.8 to 6.9 plotted from Tables 5.7 to 5.8 it can be noted that increasing symmetry factor (alpha) of corroded metal leads to increase corrosion current ($I_{\mathbf{corr}}$) of each metal (Zn and Fe) and shifted corrosion potential to more negative direction. This is because increasing symmetry factor (alpha) decreases Tafel slope (β), which increases the exponential term (in eq. (4.4)), therefore increases corrosion current according to the following equation:

$$\eta=\pm\beta\ \log i/i_{\circ}=\pm 2.303RT/\alpha nF\ \log i/i_{\mathbf{a,c}}=\pm RT/\alpha nF\ \exp i/i_{\mathbf{a,c}} \qquad (4.4)$$

In all these theoretical analysis, alpha of H_2 evolution is kept constant at 0.5.

Also these figures indicate that increasing symmetry factor shifts the corrosion potential to more negative direction for all values of hydrogen ion and metallic ion concentration. This behavior is shown (in Fig. 6.10), when symmetry factor increases corrosion current of metal increases, which leads to shift corrosion potential to more negative value. These facts were also studied by many investigators (67, 68).

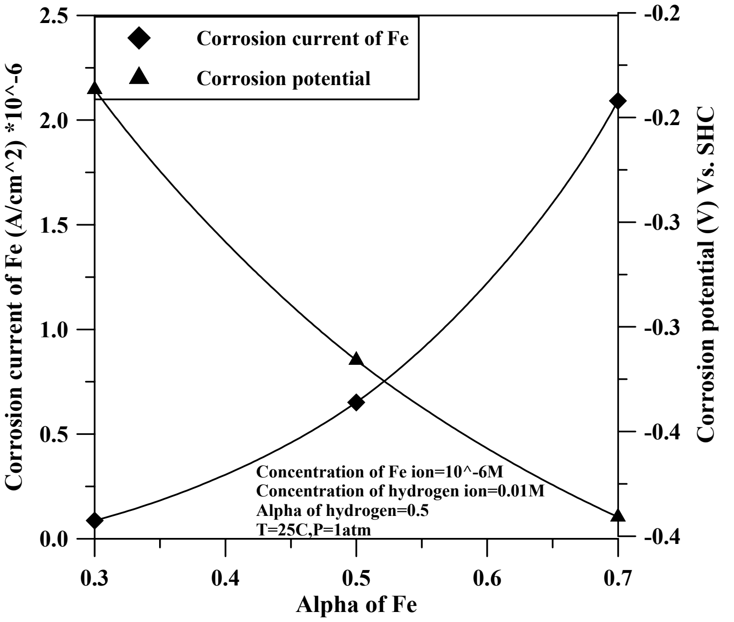

Figure 6.8: Free corrosion of Fe as function of symmetry factor (alpha) in de-aerated acid solutions.

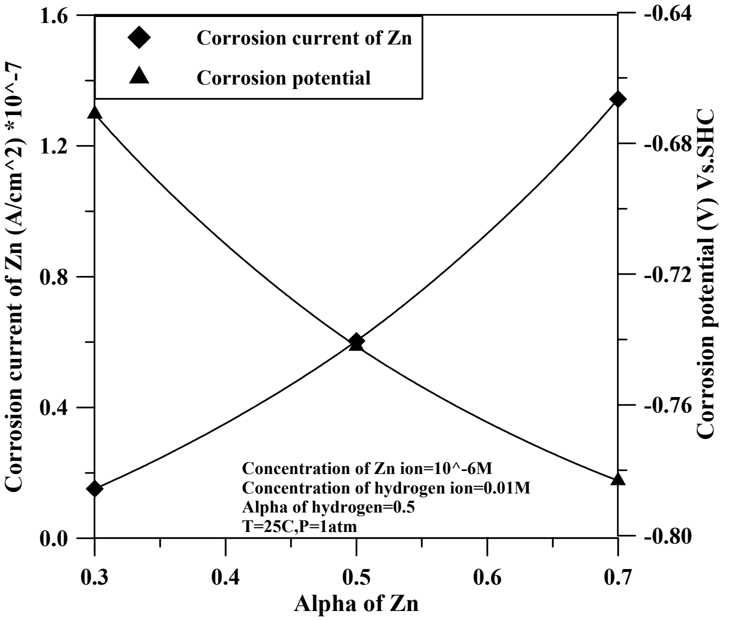

Figure 6.9: Free corrosion of Zn as function of symmetry factor (alpha) in de-aerated acid solutions.

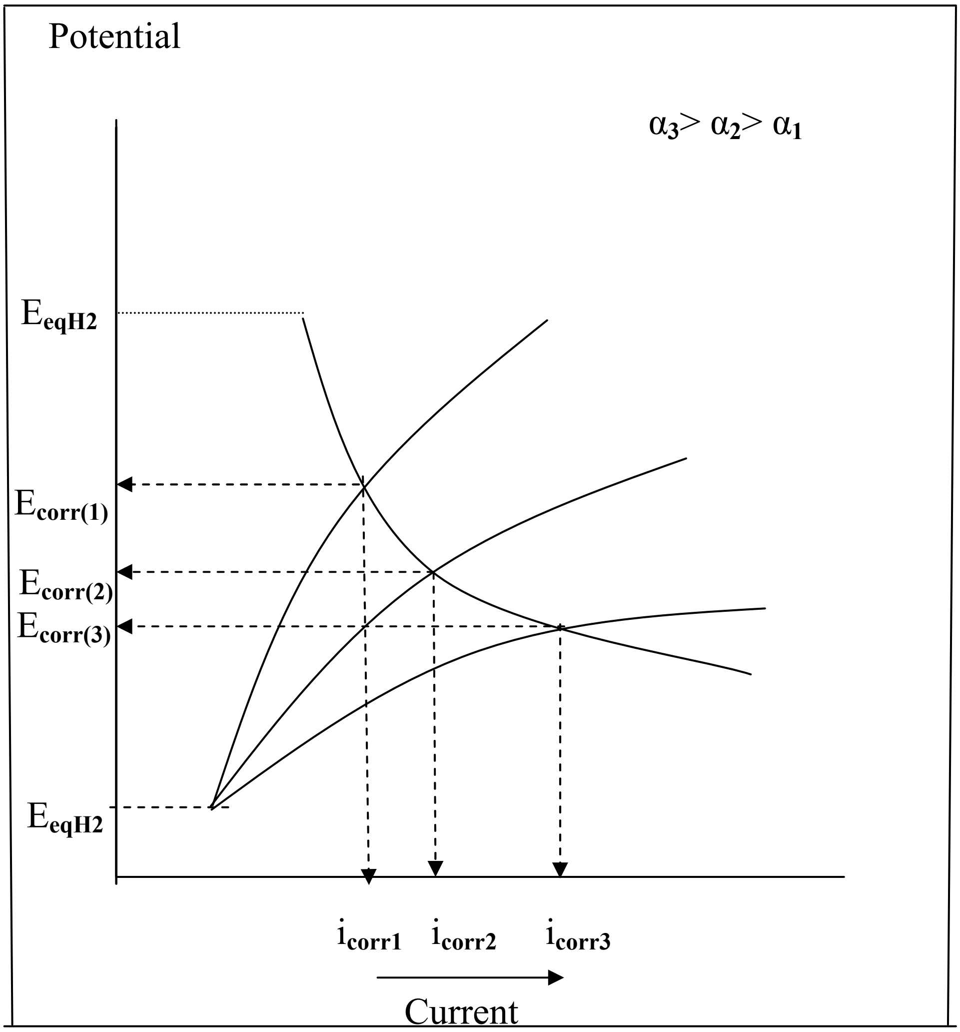

Figure 6.10: Effect of increasing symmetry factor on corrosion rate and corrosion potential.

6.2.3: Effect of metallic ion concentration:

The corrosion rate and corrosion potential of Fe as shown in Table 5.9 and plotted in Fig.6.11 are not effected by metal ion concentration increase. The reason are explained in the following Fig. (6.10b) based on the following data for Fe/Fe^{++} system: $i_0=10^{-11}$A/cm^2 at $C_{Fe}{}^{++}=10^{-6}$ M and $i_0=10^{-9}$ A/cm^2 at $C_{Fe}{}^{++}=10^{-2}$ M using Tafel eq. As following:

$$I_{Fe}=i_0 \exp (Ei-Eeq/\beta a)$$

Or $I_{Fe}=10^{-11}\ \exp((-0.49913+o.6174)/0.02568)$

$=9.99*10^{-10}$

$=10^{-9}\ A/cm^{2} = i_{0}$ of Fe^{++} at $(C_{Fe}^{++}=0.01M)$

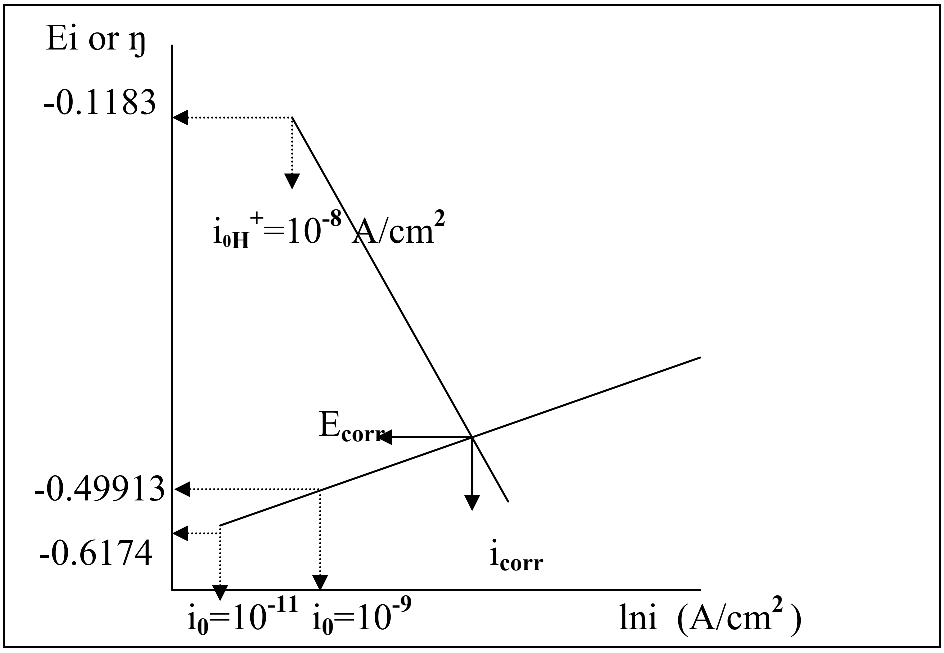

Figure 6.10b: Sehematic, illustration Fig.6.11.

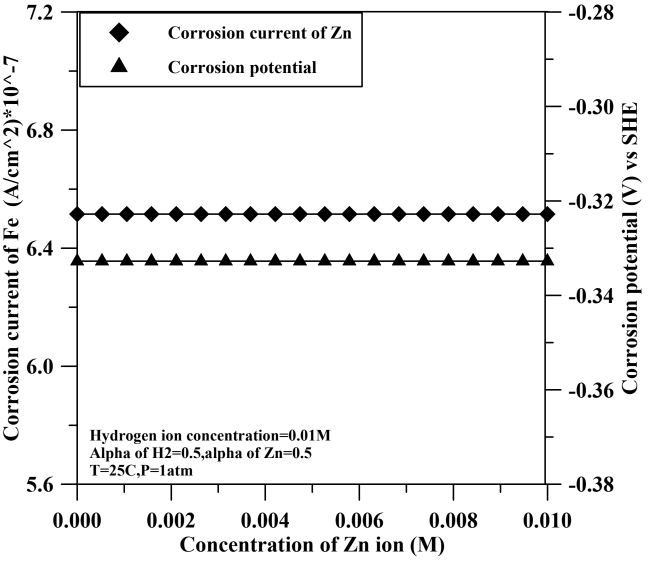

Figure 6.11: Free corrosion of Fe as function of metallic ion concentration in de-aerated acid solutions.

It can be shown from Table 5.10 for Zn in chapter five plotted in Fig. 6.12 that increasing metallic ion concentration will increase corrosion current and shifts corrosion potential to more negative direction because increase metallic ion concentration leads to increasing equilibrium potential (equation (2.10)) and exchange current (i_{0m}) (equation (4.2b)) and that causes an increase in corrosion current of the metal.

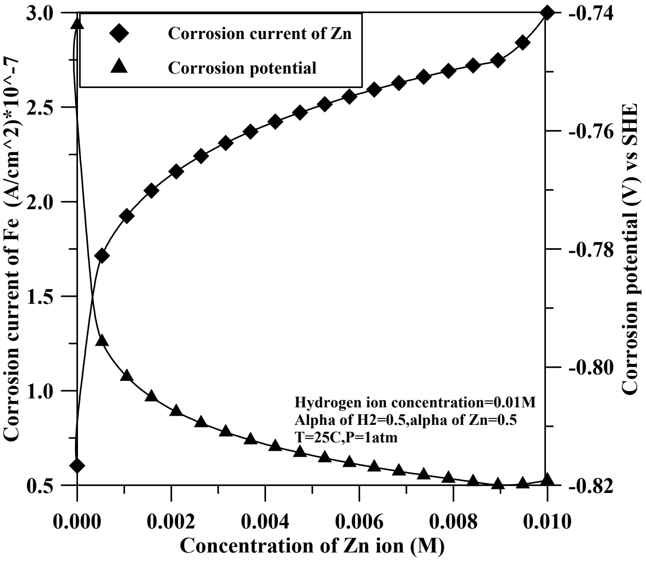

Figure 6.12: Free corrosion of Zn as function of metallic ions concentration in de-aerated acid solutions.

The increasing in corrosion current of metal leads to shift the corrosion potential to more negative direction for all values of symmetry factor and hydrogen ion concentration. It is clear that increasing corrosion current of metal accompanied by shifting the decreases corrosion potential to more negative values as shown in Fig. 6.13.

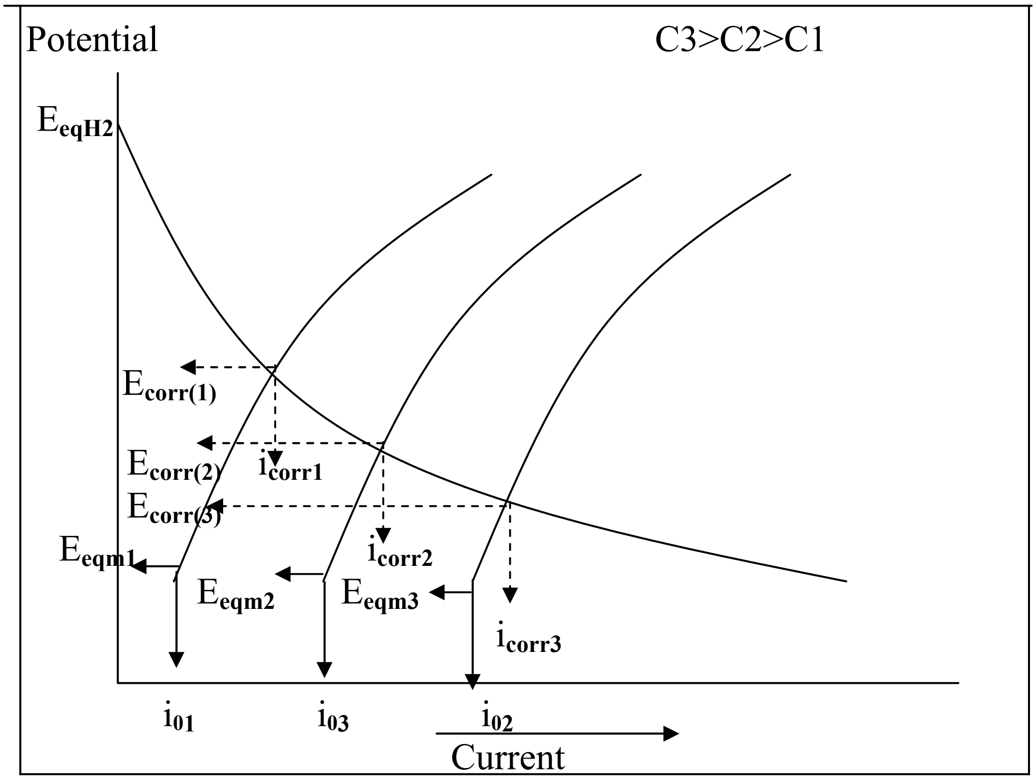

Figure 6.13: Effect of increasing metallic ion concentration of Zn on corrosion rate and corrosion potential.

As stated previously of investigation single metals as function of hydrogen and metallic ion concentration and symmetry factor is to furnish a background for studying the galvanic corrosion and its applications whether beneficial or damaging.

6.3: Galvanic Coupling :

As shown in chapter three that for a given potential, the total anodic current of polyelectrode systems is the sum of the corresponding anodic currents of individual electrodes. If the total area of the system S , made of fractions f^A , f^B . . . . for the various components A , B , …, then the anodic current from the jth component is given by :

$$I_{a}^{system} = S \, \Sigma \, f^{j} \, i_{a}^{j} \qquad (4.1)$$

Similarly for the cathodic currents of polyelectrode :

$$I_{c}^{system} = S \, \Sigma \, f^{j} \, i_{c}^{j} \qquad \mathbf{(4.2\,)}$$

At the corrosion potential ($E_{\mathbf{coupling}}$) adopted by the polyelectrode , the total anodic and cathodic currents are equal so that :

$$I_{corr}^{system} = I_{a}^{system} = I_{c}^{system} \qquad (4.3)$$

6.3.1:Effect of hydrogen ion concentration:

When two different metals are coupled in galvanic corrosion, the rate of electrons consumption is increased and hence the rate of metal dissolution increases.**[1]**

When coupled metals exposed to de-aerated solutions for which corrosion is accompanied by hydrogen evaluation, corrosion rate will increase when hydrogen ion concentration increases.

6.3.1.1:Galvanic corrosion rate:

6.3.1.1.1: Zn – Cu couple :

According to Tables 5.11 to 5.13 shown graphically in Figs. 6.14 to 6.16.itcan be seen that the galvanic corrosion current of Zn and hydrogen evolution currents on Cu increase with increasing hydrogen ion concentration. Increasing hydrogen ion concentration leads to increase the rate of dissolution of Zn because it is more active metal than copper. In this medium copper is inert, it tends to increase the surface at which hydrogen evolution occurs much more readily than zinc **[1]**. These factors increase rate of the cathodic reaction and consequently increase corrosion rate of the zinc, but hydrogen evolution current on Zn is negligible, because i_0 of hydrogen evolution on zinc is exceedingly small (10^{-6} A/cm^2) in (1M). Increasing hydrogen ion at interface between metal and solution leads to increase rate of reaction for zinc dissolution which leads to increase hydrogen evolution current on copper, because this increase in Zn dissolution is due to increasing transfer of electrons on coupling to (Cu).

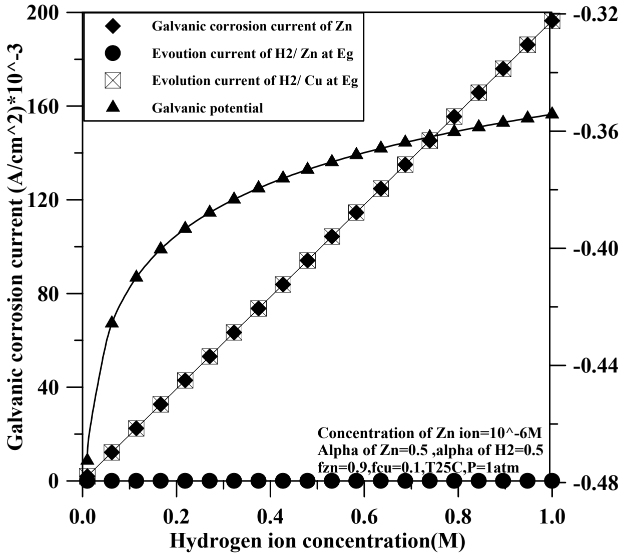

Figure 6.14: Galvanic corrosion of Zn/Cu coupling as function of hydrogen ion concentration in de-aerated acid solutions.

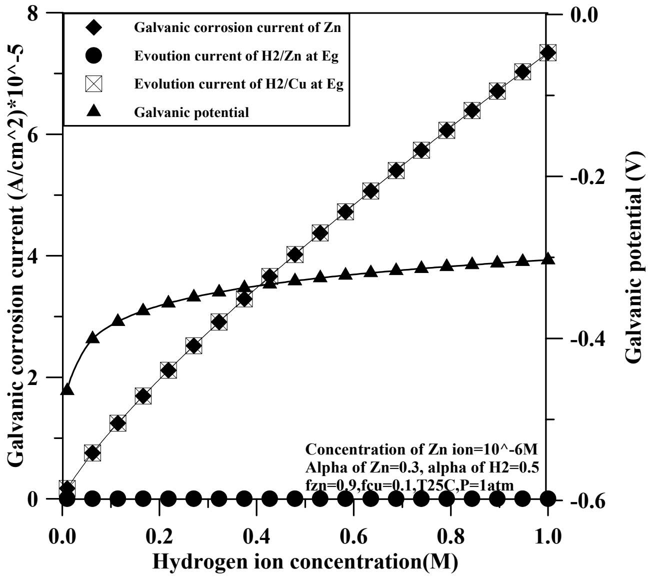

Figure 6.15: Galvanic corrosion of Zn/Cu coupling as function of hydrogen ion concentration in de-aerated acid solutions.

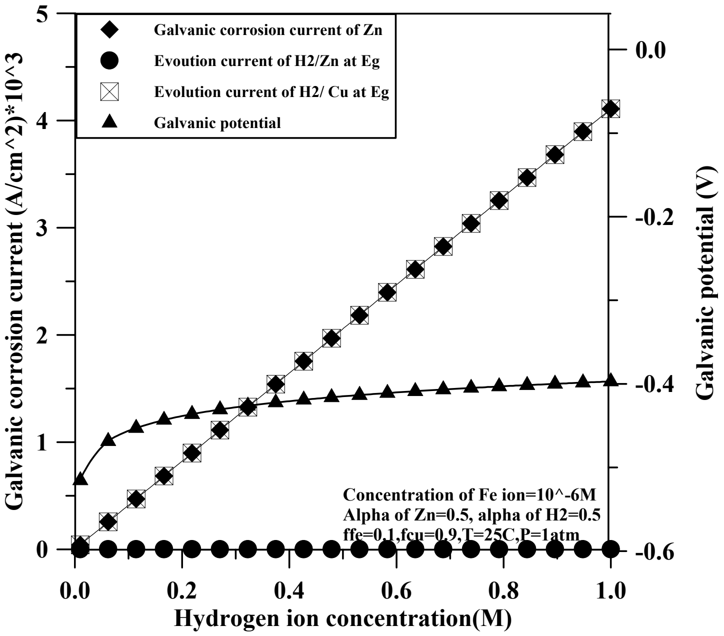

Figure 6.16: Galvanic corrosion of Zn/Cu coupling as function of hydrogen ion concentration in de-aerated acid solutions.

6.3.1.1.2:Fe – Cu couple:

Since iron electrode (Fe) is more active than copper electrode (Cu) , therefore copper will not dissolve , but it behaves as a surface for hydrogen evolution (like Zn-Cu coupled) .

The results presented in Tables 5.14 to 5.16,are plotted in Figs. 6.17 to 6.19, in which the galvanic corrosion current of iron and evolution current of hydrogen on iron and copper increase with hydrogen ion concentration increasing.The corrosion rate of iron is higher than the evolution currents of hydrogen, because iron dissolution current is the anodic current which is equal to the summation of two cathodic currents (H_2/Fe & H_2/Cu).Also the hydrogen evolution current on Fe is higher than the hydrogen evolution current on Cu , because reaction of iron is more active and exchange current density(i_0)of H_2 on Fe is higher than on Cu.In Fe/Cu coupling it is clear that hydrogen evolution current on copper is the lowest current in this system because iron electrode is more active than copper electrode, therefore iron electrode gives electrons to other electrode and both attract the positive ions (H^+).In Figs. section (6.3.1.1.1) for Zn/Cu couple evolution current of hydrogen on copper is equal to galvanic corrosion current of Zn while evolution current of hydrogen on Zn is nearly zero. Although Zn is more active than iron electrode, it doesn't tend to give electrons (likes iron electrode) to other electrode, and that leads for evolution of hydrogen on iron to be higher than on Zn. The second reason is the exchange current density (i_0) of H_2 on Zn ($3.2*10^{-11}$ A/cm^2) in (1M) is smaller than exchange current density (i_0) of H_2 on Fe (10^{-6} A/cm^2) in (1M) therefore evolution of hydrogen on iron is higher than on Zn [4].

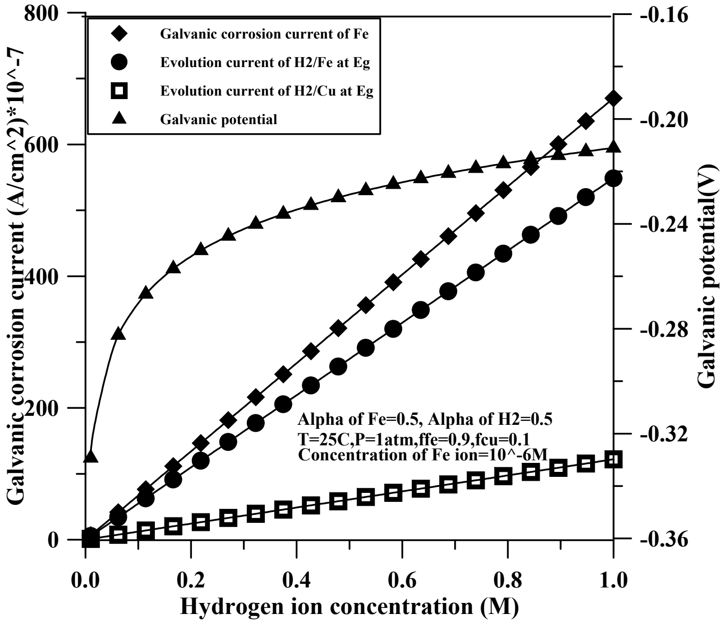

Figure 6.17: Galvanic corrosion of Fe/Cu coupling as function of hydrogen ion concentration in de-aerated acid solutions.

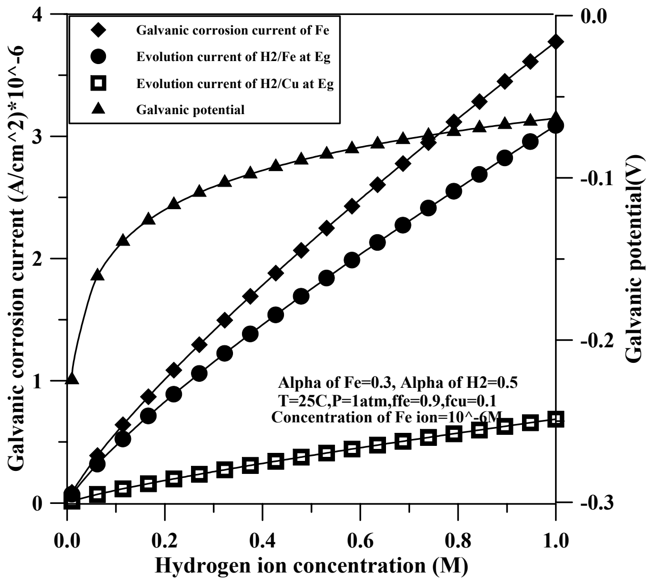

Figure 6.18: Galvanic corrosion of Fe/Cu coupling as function of hydrogen ion concentration in de-aerated acid solutions.

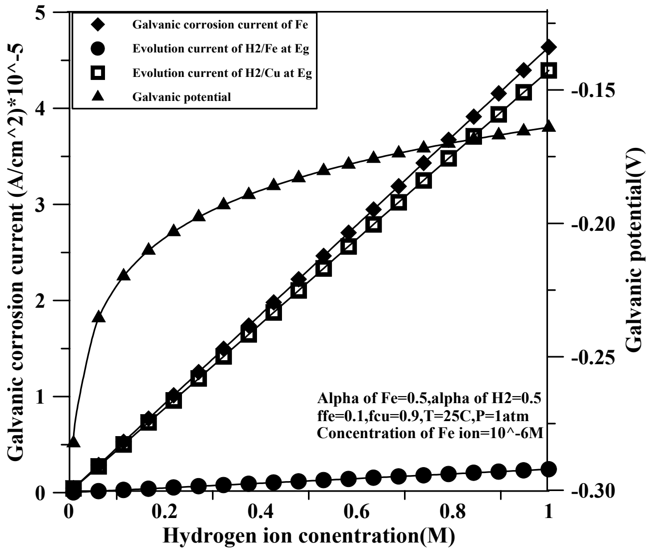

Figure 6.19: Galvanic corrosion of Fe/Cu coupling as function of hydrogen ion concentration in de-aerated acid solutions.

6.3.1.1.3:Fe – Zn couple:

In this couple both metals are active, therefore both of them worked as anode and as surface for hydrogen evolution. Because of Zn electrode is more active than Fe electrode, it is clear in Tables 5.17 to 5.19 and Figs. 6.20 to 6.22 that the galvanic corrosion current of Zn and hydrogen evolution current on Fe are equal but the galvanic corrosion current of Fe and hydrogen evolution current on Zn are equal and nearly zero. All the currents increase with hydrogen ion concentration increase for the same reason explained in section (6.3.1.1.2). Zn electrode is more active than Fe electrode, therefore Zn electrode attracts positive ions (H^+) more than Fe making hydrogen evolution current on Fe large and equal to galvanic corrosion current of Zn. Hydrogen evolution current on Zn and galvanic corrosion current of Fe are almost equal and negligible, because of the difference between exchange current density (i_0) of H_2 on Fe (10^{-6} A/cm^2) in (1M) and Zn ($3.2*10^{-11}$ A/cm^2) in (1M) which leads to increased hydrogen evolution on Fe more than on Zn.

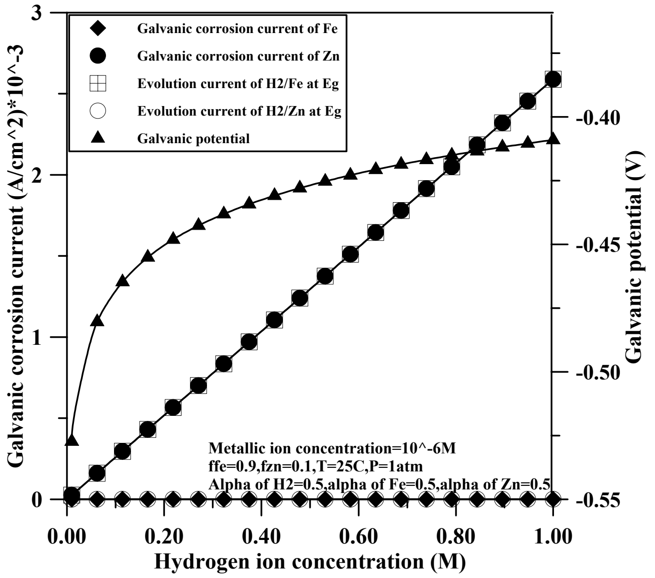

Figure 6.20: Galvanic corrosion of Fe/Zn coupling as function of hydrogen ion concentration in de-aerated acid solutions.

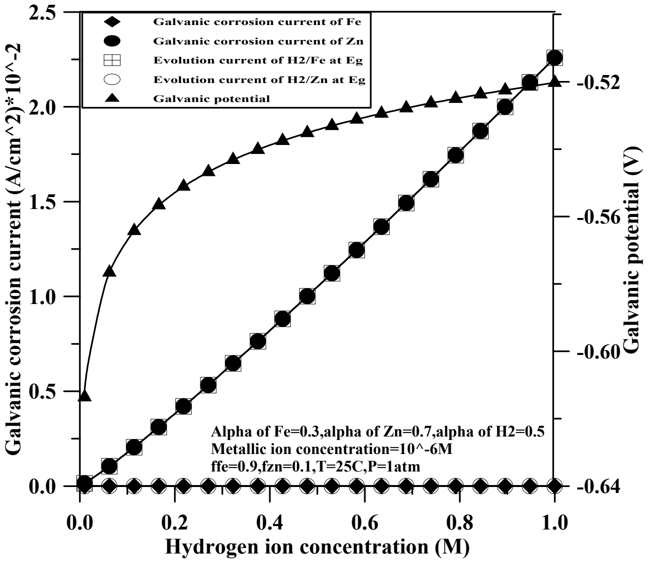

Figure 6.21: Galvanic corrosion of Fe/Zn coupling as function of hydrogen ion concentration in de-aerated acid solutions.

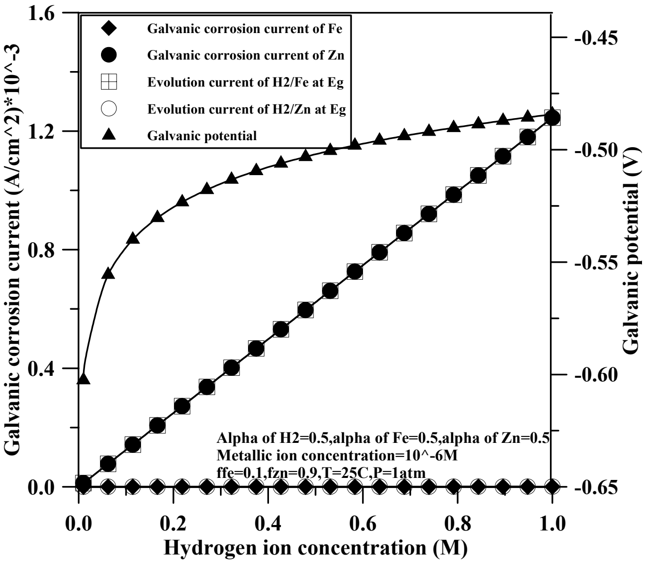

Figure 6.22: Galvanic corrosion of Fe/Zn coupling as function of hydrogen ion concentration in de-aerated acid solutions.

6.3.1.2:Galvanic corrosion potential:

Figs.6.14 to 6.22 indicate that increasing hydrogen ion concentration shifts the galvanic corrosion potential (E_g) to less negative direction for all values of symmetry factor (alpha), area fraction and metallic ion concentration which can be understood by reasons discussed in Fig. 6.7 for free corrosion. From this Fig. initially the galvanic corrosion current (I_g) is (I_{g1}) and corrosion potential (E_g) is (E_{g1}) as the dissolution of metal increases the cathodic (hydrogen reduction) and anodic (metal dissolution) currents increase leading to shift the interaction potential between the two curves to less negative E_g for all values of symmetry factor (alpha) and metallic ion concentration ,because increasing hydrogen ion concentration make the galvanic potential be approximately near the equilibrium potential of hydrogen (E_{eqH2}) and the increase in corrosion rate with an increase in hydrogen ion concentration is due to increase in galvanic potential (E_g) .

6.3.2:Effect of symmetry factor (alpha):

6.3.2.1:Galvanic corrosion rate :

6.3.2.1.1:Fe – Cu couple:

It can be noted in Figs. 6.23 that increasing symmetry factor (alpha) increases galvanic corrosion current of Fe and hydrogen evolution currents on Fe and Cu, because increasing alpha leads to increase the exponent in eq.(4.4) ,therefore corrosion rate increases. The above behaviour this system was explained in Fig. 6.10 for free corrosion,which shows that increasing alpha leads to increasing corrosion current.

It is clear that galvanic corrosion current of Fe is higher than the other H_2 evolution currents that because galvanic corrosion current of Fe is equal to the summation of other H_2 evolution current on Fe and Cu.But H_2 evolution current on Fe is higher than Cu, because exchange current density of H_2 on Fe (10^{-6}A/cm^2) in (1M) is higher than on Cu ($2*10^{-8}$A/cm^2) in (1M) [4].

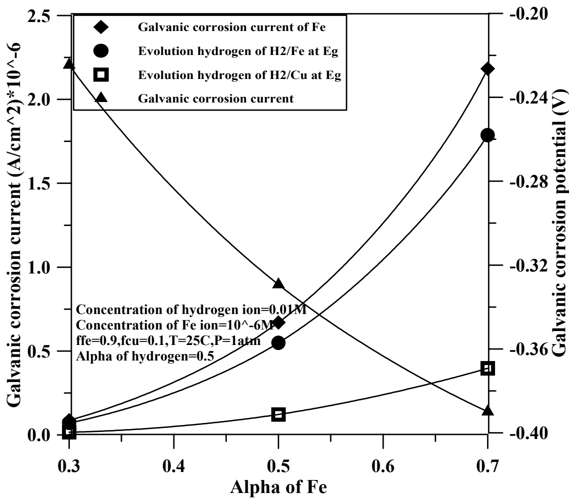

Figure 6.23: Galvanic corrosion of Fe/Cu as function of symmetry factor (alpha) in de-aerated acid solutions.

6.3.2.1.2:Zn – Cu couple :

The behavior of galvanic corrosion current of Zn (in Tables 5.21 and Figures 6.24 is like the galvanic corrosion current of Fe in (section 6.3.2.1.1) for Fe – Cu couple, because increasing alpha leads to increase the exponent in eq. (4.5 and 6). The galvanic corrosion current of Zn is equal to hydrogen evolution current on Cu, because of increasing corrosion rate of Zn leads to increase the electrons transfer to second electrode (Cu). Hydrogen evolution current on Zn is negligible, because the exchange current density of hydrogen evolution on Zn is very small ($3.2*10^{-11}$ A/cm^2) in (1M).

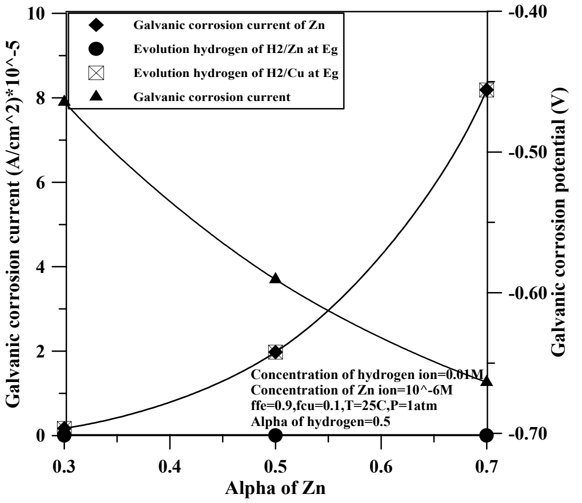

Figure 6.24: Galvanic corrosion of Zn/Cu as function of symmetry factor (alpha) in de-aerated acid solutions.

6.3.2.1.3:Fe – Zn couple:

Tables 5.22 to 5.23 are plotted in Figs.6.25 to 6.26. The galvanic corrosion current of Zn is equal to hydrogen evolution current on Fe because of increasing corrosion rate of Zn leads to increase electrons transfer to Fe electrode. Galvanic corrosion current of Fe is close to zero, because Fe electrode is protected by Zn dissolution. Also hydrogen evolution current on Zn is closely equal to zero, because of hydrogen evolution current on Zn have small exchange current density due to weak adsorption on Zn as compared with such adsorption on Fe and Cu [4].

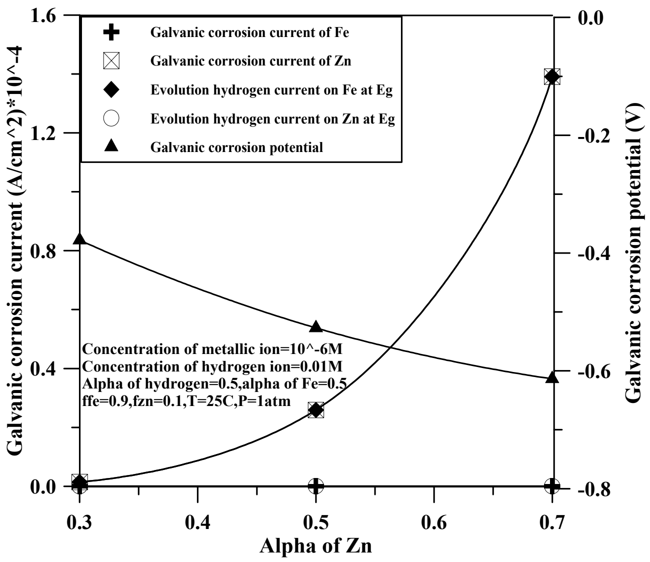

Figure 6.25: Galvanic corrosion of Fe/ Zn as function of symmetry factor (alpha) in de-aerated acid solutions.

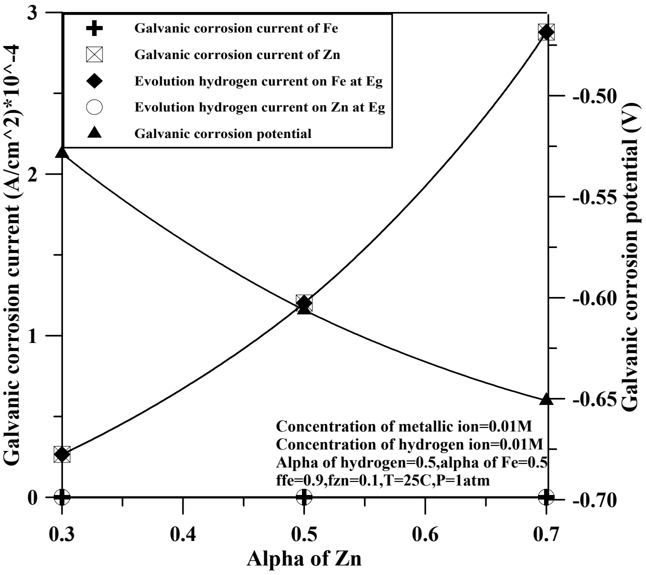

Figure 6.26: Galvanic corrosion of Fe/Zn as function of symmetry factor (alpha) in de-aerated acid solutions.

6.3.2.2:Corrosion potential:

The same Figs. (above) indicate that increasing symmetry factor shifts the corrosion potential to more negative direction, because increasing symmetry factor (alpha) leads to increase corrosion rate (as discussed in Fig.6.10) and that leads to decreased E_g.

6.3.3:Effect of area fraction:

6.3.3.1:Galvanic corrosion rate:

6.3.3.1.1:Fe – Cu couple:

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 Tables 5.24-5.25 and in Figs.6.27–6.28 that show that increasing area fraction of Fe increases galvanic corrosion of Fe. This effect can be interpreted as follows:

Increasing area fraction leads to increase the exposed area to corrosive solution. Figure 6.27 indicates that i_{corr} increases as Fe area increases until 0.6 where deceleration of Fe galvanic corrosion will prevail for higher area fraction. This means that area fraction of Fe above 0.6 will not affect corrosion rate of Fe greatly. This behavior of galvanic corrosion current of Fe vs. area fraction leads to increase Fe galvanic corrosion current of this system. Since Fe is more active than Cu, thus increasing Fe area will create anodic currents in the system leading to increase galvanic evolution of hydrogen. Also it can be observed that when area fraction of Fe reached 0.6 galvanic corrosion current of Fe becomes nearly constant associated with a decrease in hydrogen evolution on Cu substituted by an increase on Fe.

Also it can be noted that increasing area fraction of Fe leads to increase hydrogen evolution current on Fe.This is because increasing area fraction of Fe shifts the corrosion potential of the system to more negative values until the hydrogen evolution potential is reached, thus hydrogen evolution will increase.

It is obvious from the same Figures that increasing area fraction of Fe leads to increase hydrogen evolution current on Cu at start and then decreases. This behavior can be explained as follows:
As area fraction of Fe increases the corrosion rate of Fe increases leading to increase hydrogen evolution current on coupled electrode (Cu) due to increasing electron transfer from Fe and Cu, but with further increase of area fraction of Fe, hydrogen evolution current on Cu will decrease because of large reduction in area fraction of Cu.

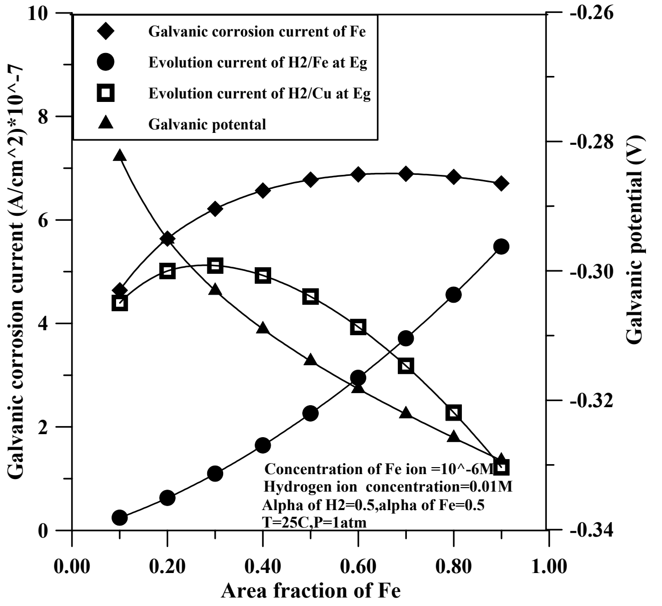

Figure 6.27: Galvanic corrosion of Fe/ Cu as function of area fraction in de-aerated acid solutions.

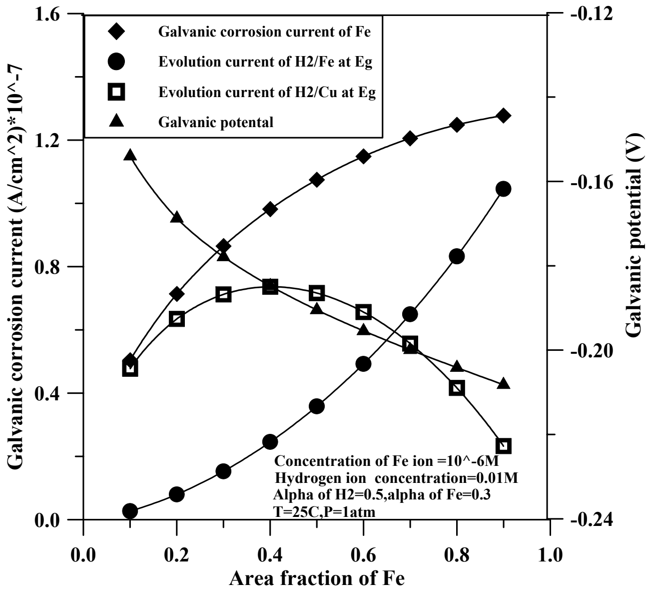

Figure 6.28: Galvanic corrosion of Fe/ Cu as function of area fraction in de-aerated acid solutions.

6.3.3.1.2:Zn – Cu couple :

From Figs. 6.29-6.30 and Tables 5.26-5.27 it can be noted as area fraction of Zn increases the galvanic corrosion current of Zn increases until area fraction of Zn becomes 0.5 the corrosion starts to decrease. This situation is the same as before that increasing area fraction leads to increase exposed area to oxidizer until area fraction be (0.5) then corrosion rate begins to decrease with increasing area fraction. This finding conforms to previous observations where the metal with lower area fraction undergoes higher rate of corrosion. In other word as area fraction increases (greater than >0.5) the corrosion rate decreases.

Hydrogen evolution current on Cu is nearly equal to galvanic corrosion current of Zn because increasing electrons transfer from Zn electrode to Cu electrode which attracks the positive ions (H^+), while hydrogen evolution current on Zn is very small, because of the large potential difference between Zn and Fe, which will increase corrosion of Zn and increase hydrogen evolution current on Cu leading to decrease hydrogen evolution current on Zn. This behaviors is due to the large difference in (i_0) for H_2 evolution on Zn and Cu(also on Fe).H_2 adsorption on Cu(&Fe) is stronger and higher on these metals than on Zn.

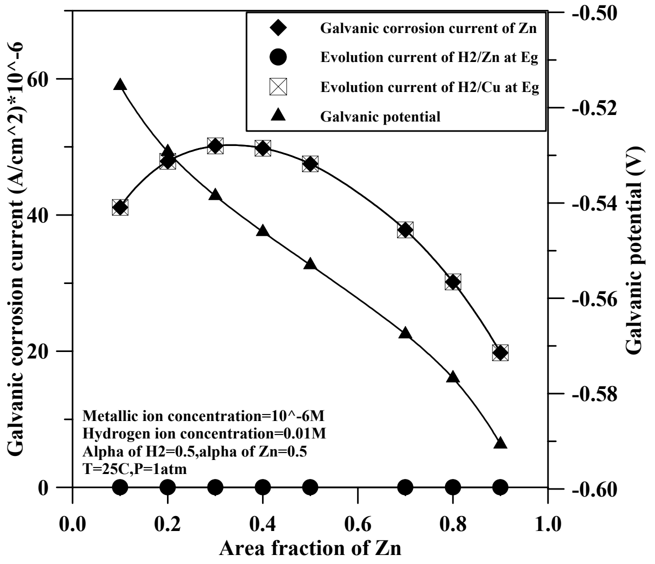

Figure 6.29: Galvanic corrosion of Zn/Cu as function of area fraction in de-aerated acid solutions.

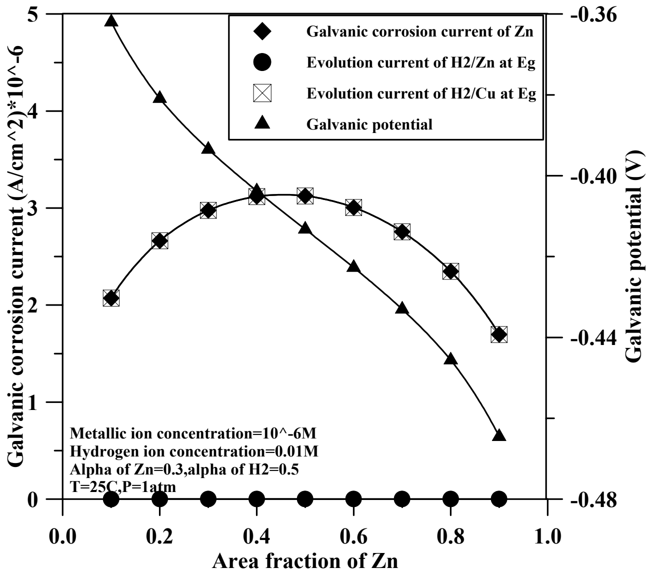

Figure 6.30: Galvanic corrosion of Zn/Cu as function of area fraction in de-aerated acid solutions.

6.3.3.1.3:Fe-Zn couple :

From Tables 5.28-5.29 and Figs. 6.31-6.32 it is evident that the coupling of (Fe/Zn) leads to increase the corrosion of Zn and decrease corrosion of Fe,in other word the more negative electrode will corrode while the less negative electrode will be protected .This fact is true for the whole range of area fraction.

Following the same Figures it is obvious that no nearly hydrogen evolution current on Zn for both coupling system. This phenomenum can be ascribed to the reasons explained above .

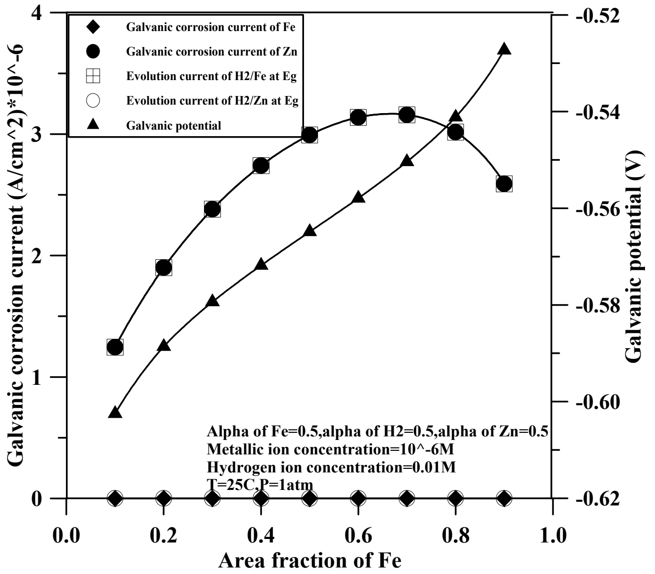

Figure 6.31: Galvanic corrosion of Fe/Zn as function of area fraction in de-aerated acid solutions.

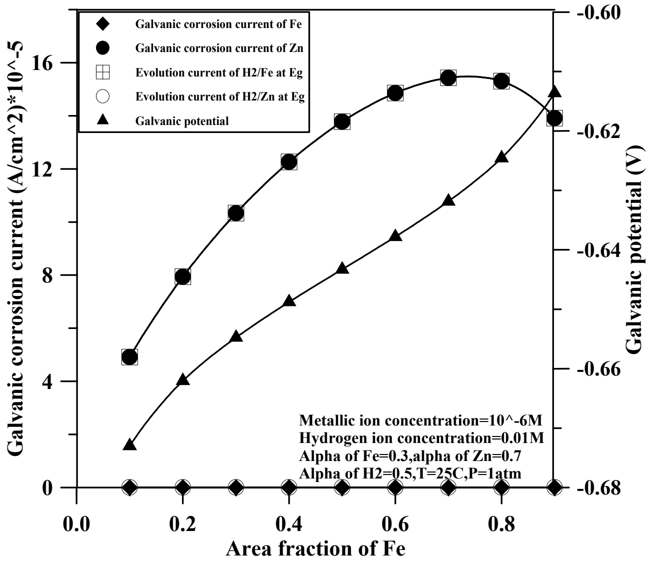

Figure 6.32: Galvanic corrosion of Fe/Zn as function of area fraction in de-aerated acid solutions.

6.3.3.2: Galvanic corrosion potential:

From Figs. 6.27 to 6.32 for three coupling systems, it can be seen that as area fraction of a particular metal increases the galvanic corrosion potential shifts toward the equilibrium potential of this metal.

6.3.3.2.1: Fe – Cu couple:

In Fig.6.27 increasing area fraction of Fe makes the galvanic corrosion potential to shift from (-329.315 mV) to (-325.809 mV) because Fe is negative.

6.3.3.2.2: Zn – Cu coupled:

Increasing area fraction of Zn in Fig. 6.29 leads to shifting galvanic corrosion potential from (-576.755 mV) to (-590.635mV) (i.e. shift to more negative), because Zn is strongly more negative.

6.3.3.2.3: Fe-Zn couple:

In Figs. 6.31 to 6.32 galvanic corrosion potential shift to less negative value with increasing area fraction of Fe, because Fe is less negative from Zn.

6.3.4:Effect of metal ion concentration:

6.3.4.1: Galvanic corrosion rate:

6.3.4.1.1: Fe – Cu couple:

In Fig. 6.33 from Table 5.30, the currents (galvanic corrosion current of Fe, evolution hydrogen current on Fe and Cu) are constant with Fe ion concentration because exchange current density increases with shift of equilibrium potential to less negative direction, therefore corrosion rate and galvanic potential remain also be constant. The reason are as explained previously for case of free corrosion.

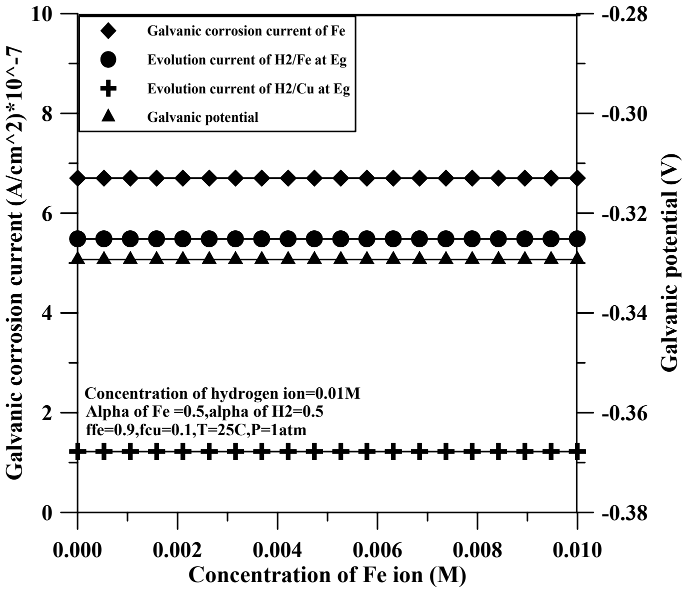

Figure 6.33: Galvanic corrosion of Fe/Cu as function of metallic ion concentration in de-aerated acid solutions.

6.3.4.1.2: Zn – Cu couple:

It is clear that in Fig.6.34 from Table 5.31, that increasing galvanic corrosion current of Zn and evolution hydrogen corrosion on Cu with increasing metallic ion concentration, because increasing metallic ion concentration leads to increase equilibrium potential (in equation (2.10)) and exchange current (i_{0m}) (in equation (4.2b)) which that causes an increase in corrosion current of this metal. Increasing metallic ions concentration leads to increase the rate of dissolution of Zn because it is more active metal than copper .In this medium copper is inert, it tends to increase the surface at which hydrogen evolution occurs much more readily on the surface of copper than zinc[1]. These factors increase the rate of the cathodic reaction and consequently increase the corrosion rate of zinc, while hydrogen evolution current on Zn is almost zero, because of the much lower value of H_2 exchange current on Zn.

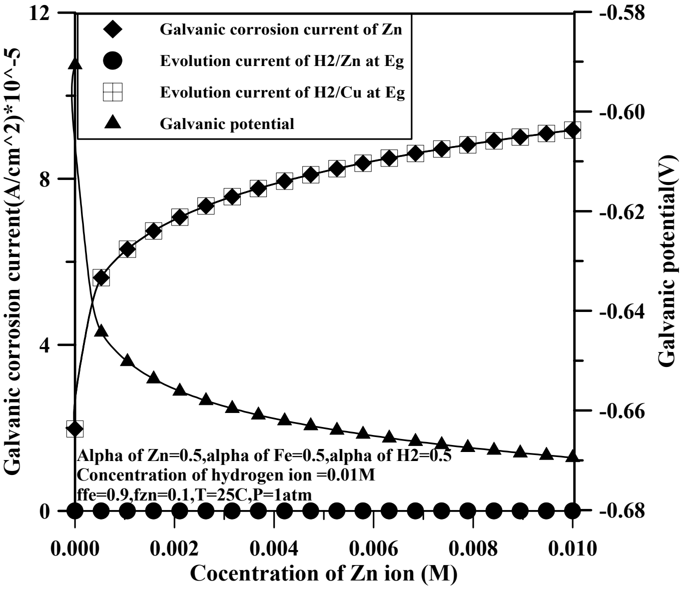

Figure 6.34: Galvanic corrosion of Zn/Cu as function of metallic ion concentration in de-aerated acid solutions.

6.3.4.1.3: Fe-Zn couple:

In Figs. 6.35 plotted from Table 5.32 it can be noted that increasing metallic ion concentration leads to increase galvanic corrosion current of Zn and evolution hydrogen corrosion on Fe, because the same reason in section (6.3.4.1.2) for Zn/Cu coupled, because increasing metal ion concentrations leads to increasing equilibrium potential (in equation (2.10)) and exchange current (i_{0m}) (in equation (4.2b)) and that causes increasing in corrosion current for this metal, Increasing metal ion concentration leads to increase the rate of dissolution of Zn because it is more active metal than Iron .Galvanic corrosion current of Fe and hydrogen evolution current on Zn are almost zero. Indicating scraficial anodic protection of Fe.

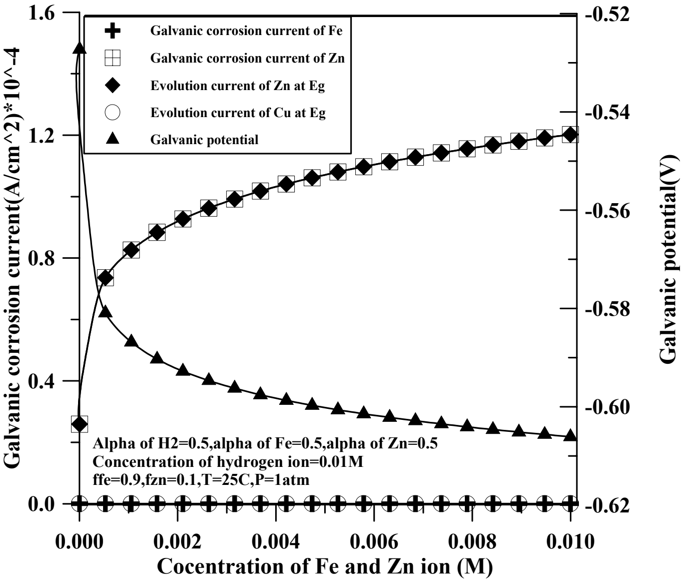

Figure 6.35: Galvanic corrosion of Fe/Zn as function of metallic ion concentration in de-aerated acid solutions.

6.3.4.2:Galvanic corrosion potential:

The same Figs. for Zn/Cu and Fe/Zn couples indicate that increasing metal ion concentration shift galvanic corrosion potential (E_g) to more negative direction, because the increase in corrosion rate with increasing metal ion concentration decreases (E_g) as Fig. 6.13 explained.

CONCLUSIONS:

1. The occurrence of galvanic corrosion is efficiently verified using the following equation:

$$I=i_0 \, f \; e^{(Eg - Eeq / \beta)}$$

and for each case at $E_{coulping}$

$$\sum I^c = \sum I^a , \sum I^g = o \, .$$

2. Zinc and iron work as good anodic metals when coupled to copper, as copper does not dissolve in de-areated acid solutions but only acts as a surface for hydrogen evolution.
3. Fe/Zn couples behave as anodic and cathodic electrodes concurrently, depending on prevailing conditions.
4. Hydrogen ion concentration and metal ion concentration play an important role in increasing the galvanic attack in most of the cases and corrosion rate increases with hydrogen ion concentration in both free and galvanic corrosion, expect Fe and Fe/Cu have no change in corrosion rate with increasing metallic ion concentration.
5. Increasing area fraction leads to increase corrosion rate of active metal to intermediate value of area fraction then begins to decrease with further increase in area fraction of that metal.
6. Galvanic corrosion potential shifts to more negative direction with increasing symmetry factor, area fraction and metal ion concentration for the more negative metal, but with increasing metal ion concentration, galvanic corrosion potential will shift to less negative corrosion potential.

FUTURE WORK:

1. Three electrode couples should be investigated under different conditions of area fraction, metallic and hydrogen ion concentrations.
2. The possibility of adding inhibitor and analyze their effects on galvanic corrosion of metals and alloys.
3. Studying points 1 and 2 in air saturated acid environments, i.e. in presence of two cathodic reactions.
4. Studying the effect of temperature on galvanic corrosion.

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Appendix A

```
CLS
DEFDBL A-Z
' **** Variables definition ****
'r=Gas constant=Temprature,ff=Area fraction,ar=concentration of reduced atm
 r = 8.314: t = 298: ff = 96487: ar = 1: e0h = 0
 h = (.01 - .000001) / 19: k = (1 - .01) / 19
 DIM a0m(21), a0h(21), eqm(20)
 FOR i = 1 TO 20
 a0m(i) = .000001 + (i - 1) * h
 a0h(i) = .01 + (i - 1) * k
 NEXT i
' ******************************
 DIM e0m(10)
 INPUT "number of metals, m=", m
 INPUT "No. of electrons=", n
 FOR i = 1 TO m
 INPUT "Exchange current density (iod)and its concentration(csd)="; i0dm(i), csdm(i)
 INPUT "Exchange current density of hydrogen on metal(i0dh2)and its concentration(csdh2)="; i0dh(i), csdh(i)
 INPUT "am and bm=", aaam(i), bbbm(i)
 INPUT "ah2 and bh2=", aaah(i), bbbh(i)
 INPUT "Stander potential of metal,e0m=", e0m(i)
```

```
 INPUT "Area fraction of metal="; f(i)
 INPUT "symmetry factor of metal=", alfa
 ' Area fraction of hydrogen=area fraction of this metal
 fh(i) = f(i)
 NEXT i
 INPUT "symmetry factor of H2=", alfah
' ********************************

' **** Functions definition **********************************
DEF fneqm (e0m, a0) = e0m - ((r * t) / (n * ff)) * LOG(ar / a0)
DEF fneqh (e0h, a0) = e0h - ((r * t) / (n * ff)) * LOG(ar / a0 ^ 2)
DEF fni0 (a0, csd, i0d, aaa, bbb) = i0d * (a0 / csd) ^ (aaa * bbb)
DEF fnba (alfa) = (r * t) / (alfa * n * ff)
DEF fnbc (alfah) = -(r * t) / ((1 - alfah) * ff)
DEF fni (i0, f, eg, eq, beta) = i0 * f * EXP ((eg - eq) / beta)
' ************************************************************

' ******************************
' ******** Optimization ********
' ******************************
10 n1 = 1
20 H1 = .0001
30 betaa = fnba(alfa)
40 betac = fnbc(alfah)
50 PRINT "symmetry factor(alfa),Tafel constant of anode(betaa),Tafel constant of cathode(betaa)= "; alfa(jj), betaa, betac
60 FOR ii = 1 TO 1
70 a0m = a0m(ii)
```

```
100 FOR kk = 1 TO 20
110 a0h = a0h(kk)
120 PRINT "Metallic ions concentration (a0m), Hydrogen ions concentration (a0h)="; a0m (ii), a0h(kk)
130 x1(1) = fneqh(e0h, a0h) - .001
140 K1 = H1: FE = 0
150 FOR i = 1 TO n1
160 Y1 (i) = x1 (i): P1 (i) = x1 (i): B1 (i) = x1 (i): NEXT i
170 GOSUB 830: FI = Z1
180 PS = 0: BS = 1
190 REM EXPLORE ABOUT BASE POINT
200 J = 1: FB = FI
210 x1 (J) = Y1 (J) + K1
220 GOSUB 830
230 IF Z1 < FI THEN GOTO 290
240 x1 (J) = Y1 (J) - K1
250 GOSUB 810
260 IF Z1 < FI THEN GOTO 290
270 x1(J) = Y1(J)
280 GOTO 300
290 Y1 (J) = x1(J)
300 GOSUB 830
310 FI = Z1
320 IF J = n1 THEN GOTO 350
330 J = J + 1
340 GOTO 210
350  IF FI < FB - 1E-16 THEN GOTO 530
```

```
360  REM AFTER 350 MAKE A PATTERN MOVE IF FUNCTION HAS BEEN REDUCED
370  IF PS = 1 AND BS = 0 THEN GOTO 420
380  REM BUT IF EXPLORATION WAS ABOUT APATTERN PT.
390  REM AND NO REDUCTION WAS MADE CHANGE BASE AT 420
400  REM OTHERWISE REDUSE STEP LENGTHE AT 470
410  GOTO 470
420  FOR i = 1 TO n1: P1(i) = B1(i): Y1(i) = B1(i): x1(i) = B1(i): NEXT i
430  GOSUB 810: BS = 1: PS = 0
440  FI = Z1: FB = Z1
450  REM (FOLLOW ON FROM 395)AND EXPLOR ABOUT NEW BASE POINT
460  J = 1: GOTO 210
470  K1 = K1 / 10
480  IF K1 < 1E-16 THEN GOTO 590
490  REM IF WE HAVE NOT FINISHED MAKE NEW
500  REM EXPLORATION ABOUT LATEST BASE POINT
510  J = 1: GOTO 210
520  REM PATTERN MOVE
530  FOR i = 1 TO n1: P1(i) = 2 * Y1(i) - B1(i)
540  B1(i) = Y1(i): x1(i) = P1(i): Y1(i) = x1(i)
550  NEXT i
560  GOSUB 810: FB = FI: PS = 1: BS = 0: FI = Z1
570  REM THEN EXPLORE ABOUT LATEST PATTERN POINT
580  J = 1: GOTO 210
590  FOR i = 1 TO n1
600  PRINT "Corrosion potential="; P1(i): NEXT i
610  PRINT "Z1="; Z1
```

```
620  FOR i1 = 1 TO m
630  e0m = e0m(i1)
640  csdm = csdm(i1): csdh = csdh(i1)
650  i0dm = i0dm(i1): i0dh = i0dh(i1)
660  aaam = aaam(i1): bbbm = bbbm(i1): aaah = aaah(i1): bbbh = bbbh(i1)
670  i0m = fni0(a0m, csdm(i1), i0dm(i1), aaam(i1), bbbm(i1)): i0h =
fni0(a0h, csdh(i1), i0dh(i1), aaah(i1), bbbh(i1))
680  eqm(i1) = fneqm(e0m(i1), a0m): eqh = fneqh(e0h, a0h)
690  im(i1) = fni(i0m(i1), f(i1), x1(1), eqm(i1), betaa)
700  ih(i1) = fni(i0h(i1), f(i1), x1(1), eqh, betac)
710  PRINT "Corrosion current of metal(im)="; fni(i0m(i1), f(i1), x1(1),
eqm(i1), betaa);
720  PRINT "Evolution current of hydrogen(ih)="; fni(i0h(i1), f(i1), x1(1),
eqh, betac);
730  PRINT "Equlliubrium potential of metal(Eeqm)="; eqm(i1)
740  NEXT i1
750  PRINT "Equlliubrium potential of hydrogen(Eeqh)="; eqh
760 : INPUT ss
770  NEXT kk
780  EXT ii
800  END
810    ' **** Subroutine ****
820  summ = 0: sumh = 0
830  FOR i1 = 1 TO m
840  e0m = e0m(i1)
850  csdm = csdm(i1): csdh = csdh(i1)
860  i0dm = i0dm(i1): i0dh = i0dh(i1)
870  aaam = aaam(i1): bbbm = bbbm(i1): aaah = aaah(i1): bbbh = bbbh(i1)
```

```
880  i0m(i1) = fni0(a0m, csdm(i1), i0dm(i1), aaam(i1), bbbm(i1)): i0h(i1) = fni0(a0h, csdh(i1), i0dh(i1), aaah(i1), bbbh(i1))
890  eqm(i1) = fneqm(e0m(i1), a0m): eqh = fneqh(e0h, a0h)
900  im(i1) = fni(i0m(i1), f(i1), x1(1), eqm(i1), betaa)
910  ih(i1) = fni(i0h(i1), f(i1), x1(1), eqh, betac)
920  IF eqm(i1) > eqh THEN i0m(i1) = 0
930  summ = summ + fni(i0m(i1), f(i1), x1(1), eqm(i1), betaa)
940  sumh = sumh + fni(i0h(i1), f(i1), x1(1), eqh, betac)
950  NEXT i1
960  IF eqm(1) < eqm(2) THEN eqmmin = eqm(1) ELSE eqmmin = eqm(2)
970  eqh = fneqh(e0h, a0h)
980  IF eqmmin < eqh THEN
990  IF x1(1) < eqmmin OR x1(1) > eqh THEN Z1 = 1E+30:  PRINT "%"; : GOTO 1060
1000 END IF
1010 IF eqh < eqmmin THEN
1020 IF x1(1) < eqh OR x1(1) > eqmmin THEN Z1 = 1E+30:  PRINT "$"; : GOTO 1060
1030 END IF
1050 Z1 = ABS(summ - sumh)
1060 FE = FE + 1
1070 RETURN
```

Appendix B

1. The exchange current density of metals:

for Fe :$1*10^{-8}$ A/ cm^2 at 1 M
for Zn :$3*10^{-5}$
for Cu : $4*10^{-5}$ A/ cm^2

2. The exchange current density for hydrogen on metals:
on Fe :$1*10^{-6}$
on Zn :$1*10^{-4}$ at 0.5 m
on cu: $2*10^{-7}$ A/cm^2 at 0.1 m

3. stander potential:
Eo_{Fe}=-0.44 V , Eo_{Zn}=-0.76 V , Eo_{cu}= 0.337 V

4. Tafel constants:
for Fe :β=0.5 ,ν=1
for H_2 on Fe :β=1 ,ν=1
for Zn: β=0.5 , ν=2
for H_2 on Zn :β=1 , ν=1
for Cu :β=1 , ν=1
for H_2 on Cu:β=1 , ν=1

الخلاصة

ان لدراسة التآكل اهمية مضاعفة و ذلك لمالها من تاثير اقتصادي في تقليل حجم خسارة المواد المكونة لكل من الانابيب , الخزانات , اجزاء المكائن , السفن ,الابراج ,هياكل المعدات البحرية ,......الخ . بالاضافة الى العمل على تجنب حدوث كوارث متعاقبة نتيجةتاثير المعدات الصناعية .

بسبب الاهمية العملية لحماية المعدات الصناعية من التآكل الغلفاني ظهرت الحاجة لدراسة المتغيرات المختلفة مثل تركيز ايون الهيدروجين ,تركيز ايون المعدن , معامل التناظر (alpha) ,نسبة مساحة المعدن وتاثيرها على التآكل الغلفاني في وسط حامضي خالي من الاوكسجين ولعدة معادن مهمة صناعيا مثل (الخارصين , الحديد , النحاس)؛ لجميع الاسباب المذكورة اعلاه تم استحداث برنامج هيء ليستخدم مع اي عدد او نوع من المعادن ضمن مدى التركيز لايون الهيدروجين (1-0.01 مولاري) , تركيز ايون المعدن (10^{-6} - 10^{-2} مولاري) ,معامل التناظر (0.7,0.5,0.3) , نسبة مساحة المعدن (0.1-0.9) تحت ظروف الجو الاعتيادي (25 م° ,1 جو) , ويمكن استخدام هذا البرنامج ايضا للتآكل الحر (اي تاكل معدن واحد فقط).

الحسابات التي استتنتجت من البرنامج المستحدث تعتمد على المعادلات المشهورة للتاكل الغلفاني :

$$I=i_0 f\ e^{(Eg-Eeq)/\beta}$$

للكل حالة جهد عند الربط $E_{coulping}$:

$$\sum I^c=\sum I^a\ ,\ \sum I^g=o$$

وهذا البرنامج ممكن ان يستخدم لحساب التآكل الحر والغلفاني لاي عدد ونوع من المعادن المربوطة لحساب سرعة تاكل المعدن (I) وجهد المربوط للمعدن (E_g) ,جهد الاتزان (E_{eq}) ,كثافة التيار التبادلي (i_o) ,الميل (ميل تافل) (β) للمعدن والهيدروجين لمختلف نسب المساحات ,تركيز ايون الهيدروجين والمعدن ,معامل التناظر (alpha).

النتائج المستحصلة من البرنامج تتوافق بشكل ممتاز مع النتائج المستحصلة من التحليل النظري والطرق العملية.

والنتائج المستحصلة من البرنامج اوضحت ان زيادة سرعة التآكل تزداد مع زيادة كل من تركيز ايون الهيدروجين وايون المعدن ومعامل التناظر لكل من التآكل الحر والغلفاني وكذلك مع زيادة نسبة مساحة المعدن(الاكثر فعالية)

إن جهد التآكل يقل (يصبح اكثر سالبية) مع زيادة تركيز ايون المعدن ومعامل التناظر لكل من التآكل الحر والغلفاني وكذلك نسبة مساحة المعدن الفعال لكن زيادة تركيز الهيدروجين يزيد جهد التآكل (يصبح اقل سالبية).

شكر وتقدير

أود أن اعبر عن خالص شكري وتقديري وامتناني العميق للمشرف الدكتور قاسم عبد الجبار سليمان لما قدمه لي من توجيهات قيمة ونصائح سديدة طوال فترة إنجاز البحث.

أود أيضاً أن اشكر الدكتور باسم عبيد حسن وجميع أساتذة وموظفي قسم الهندسة الكيمياوية في جامعة النهرين لأبدائهم المساعدة اللازمة أثناء هذا العمل.

ولا أنسى أن أتقدم بالشكر والامتنان إلى من ساندني طوال فترة البحث بكل الحب والعطف إلى أحب من في الوجود إلى قلبي أبي وأمي وجميع أفراد عائلتي فلهم جزيل الشكر والتقدير.

تحليل السيطرة على التاكل الغلفاني للمعدن

رسالة

مقدمة الى كلية الهندسة في جامعة النهرين كجزء من متطلبات نيل درجة ماجستير

علوم في الهندسة الكيمياوية

من قبل

شيماء كاظم رحيم الشمري

(بكالوريوس في الهندسة الكيمياوية2001)

وذلك في

شهرشعبان 1425 هـ

تشرين الاول 2004م